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STUDIES ON LATE QUATERNARY TEPHRAS IN THE
WAIKATO AND OTHER REGIONS IN NORTHERN NORTH
ISLAND, NEW ZEALAND, BASED ON DISTAL
DEPOSITS IN LAKE SEDIMENTS AND PEATS

A thesis
submitted in fulfilment
of the requirements for the degree
of
Doctor of Philosophy in Earth Sciences
at the
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by

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Frontispiece

Lakes Ngaroto (background), Ngarotoiti, and Rotopiko (foreground) in Waipa County, c.15 km south of Hamilton City. The lakes are c.16 000 years old and were formed during the final stages of alluvial aggradation of the Hinuera Formation by the ancestral Waikato River.

Such lakes, containing soft, fine-grained organic lake sediments, have proved ideal sites for elucidating late Quaternary tephrostratigraphy in the central Waikato area, and record a comprehensive sequence of eruptives derived from six North island volcanic centres. Photograph by D.J. Lowe.



Dedication

This thesis is dedicated to Maria Lowe and to the memory
of the late Margaret Mary Lowe.

ABSTRACT

Aspects of late Quaternary tephrostratigraphy and tephrochronology of the Waikato and other regions in northern North Island, New Zealand, are investigated using distal tephras contained in lake sediments and peats. Such environments are advantageous for tephra studies, particularly in distal localities where tephra identifications have previously been difficult, because the tephras are preserved as discrete layers relatively little affected by postdepositional reworking or weathering processes. Tephras can thus be correlated with confidence much further from source and mapped with a degree of thickness resolution around 10-100 times better than previously possible. Sediment cores from lakes and bogs enable the stratigraphic, chronologic, and compositional relationships of tephras erupted from different sources to be elucidated, and a record of explosive volcanism to be documented.

Forty-one distal tephras of rhyolitic or andesitic composition have been deposited in lakes in the Waikato area over the past c.17 000 years. The tephras originated from six volcanic centres and are identified using their mineralogy (particularly ferromagnesian silicate assemblages) and glass and mineral composition (determined by electron microprobe) in combination with stratigraphic position and ^{14}C chronology. The correlated tephras associated with each source (approximate ages in years B.P., old $T\frac{1}{2}$ basis) are: **Taupo:** Taupo (1800), Mapara (2200), Whakaipo (2800), Hinemaiaia (4500), Opepe (8900); **Okataina:** Whakatane (4800), Mamaku (7000), Rotoma (8500), Waiohau (12 200), Rotorua (13 300), Rerewhakaaitu (14 700), Okareka (17 000); **Maroa:** Puketarata (14 000); **Mayor Island:** Tuhua (6200), uncorrelated (14 500); **Tongariro:** Mangamate (Te Rato Lapilli?) (9950), Okupata (8 informal units Oa-1 to Oa-8: 10 100, 10 500, 10 800, 11 050, 11 200, 11 700, 12 100, 12 700), uncorrelated (13 100), Rotoaira (13 700); **Egmont:** 15 informal (uncorrelated) units Eg-1 to Eg-15 (2500, 3700, 3750, 4100, 4400, 5250, 5850, 5900, 9300, 9600, 10 100, 11 050, 14 500, 15 000, 15 500).

Eleven Holocene tephras, mostly rhyolitic, are identified in bogs in Urewera National Park (Kaipo Lagoon, Te Rangaakapua): Kaharoa (700 years B.P.), Taupo, Mapara, Waimihia (3200 years B.P.), Hinemaiaia, Whakatane, Rotoma. Opepe, Poronui (9900 years B.P.), Karapiti (10 100 years B.P.), and Okupata (10 300 years B.P.). Distal rhyolitic tephras identified in Auckland (Lake Waiatarua) include Tuhua, Mamaku(?), Rotoma, and Opepe(?); in Northland (Lake Omapere), Mamaku and Rotoehu (c.50 000 years B.P.) tephras are identified.

New methods for detecting thin tephra layers in organic sediments are investigated: x-radiography of unopened, small diameter sediment cores, rapid x-ray fluorescence of peat samples, and the application of subsurface interface radar (SIR) to tephra-bearing lake sediments and peats. SIR is fast and precise with depth penetration up to 10 m, and could be very effective in mapping shallow tephra layers in various environments.

Controls on the rates of weathering and the genesis of clay minerals in tephras of acid to intermediate composition are reviewed. A study of controls on weathering and clay mineral genesis in subaerial late Quaternary tephra deposits and soils in the Waikato region is greatly facilitated by the stratigraphic, compositional, and pattern of distribution of the unweathered counterpart tephras preserved in adjacent lakes and bogs. The study demonstrates that rates of weathering and clay mineral transformations in tephra materials are strongly influenced by composition and environmental factors, especially microenvironmental factors, rather than a tephra age-dependent factor.

The dated tephras in c.17 000 year-old lakes in the Waikato region provide time-stratigraphic markers for multidisciplinary palaeoenvironmental studies, many of which are currently in progress, on the lake sediments. The developmental history of Lake Maratoto, near Hamilton, is investigated using tephrochronology and ^{14}C dating, and enables some aspects of postglacial climatic change to be inferred.

ACKNOWLEDGEMENTS

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INTRODUCTION

INTRODUCTION

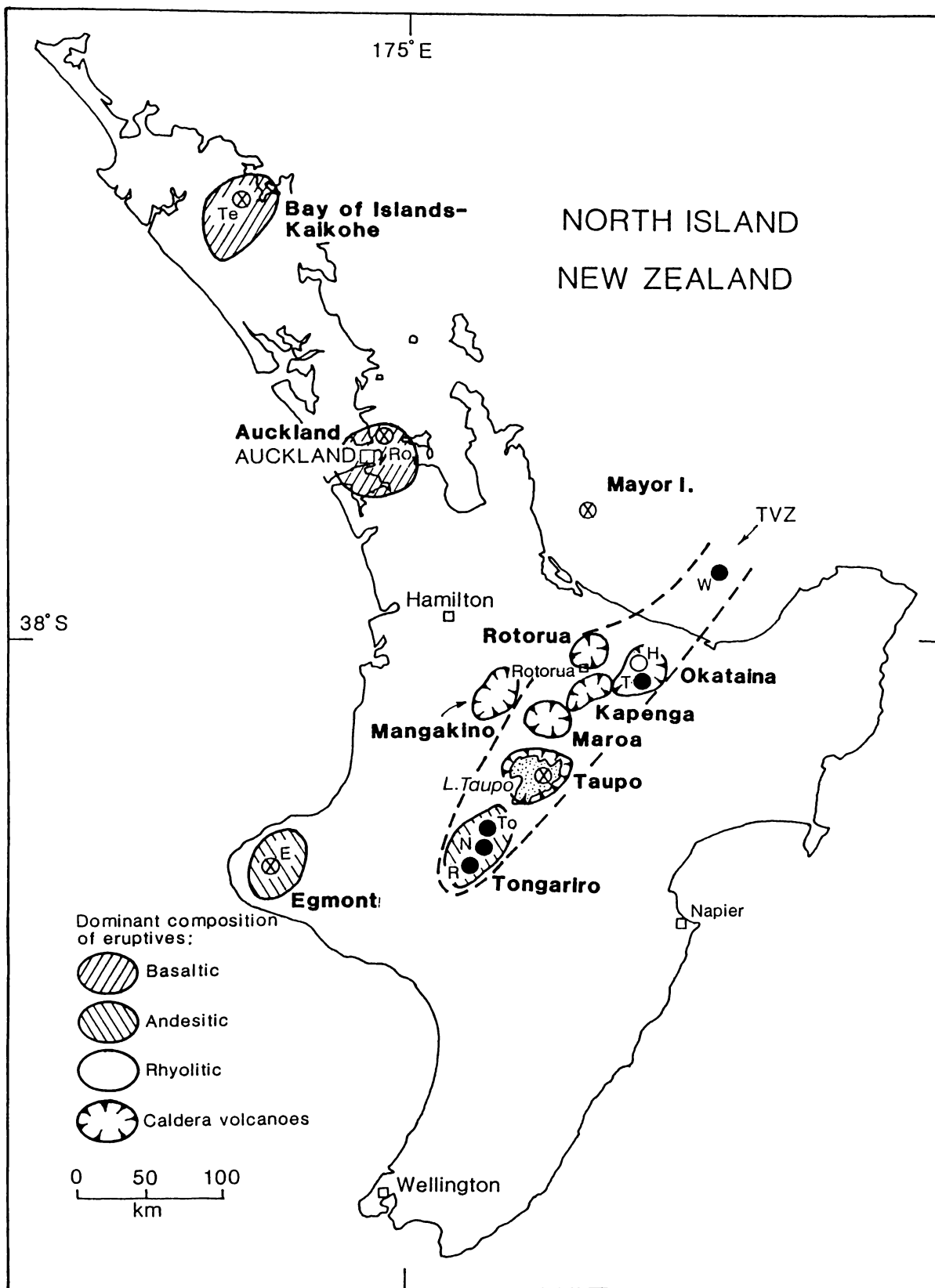
Current plate tectonic models show that the North Island of New Zealand lies on the leading edge of the Australian Plate and is being obliquely underthrust by the subducting oceanic Pacific Plate (e.g., see Hatherton 1978; Walcott 1978, 1984; Kamp 1984, 1986; Cole 1986). Volcanic activity resulting from the interaction of these lithospheric plates has been a feature of the geological development of much of the central North Island in the Quaternary, and large quantities of lava and pyroclastic material, mainly of rhyolitic and andesitic composition, have been erupted from volcanoes in the Taupo Volcanic Zone (TVZ), and from Mt. Egmont and Mayor Island (Fig. 1; Cole and Nairn 1975; Buck et al. 1981; Nairn 1981; Healy 1982; Wilson et al. 1984, 1986; Cole et al. 1986; Neall et al. 1986). These eruptives, especially the lavas, have been the subject of study for around 100 years (e.g., see Suggate et al. 1978), but it is only in the past 50 years or so that the pyroclastic deposits have received any detailed attention. Of particular interest are the airfall pyroclastic deposits or tephra - the principal subject of this thesis - which are widespread and form a more or less continuous mantle over about 20% of the North Island (Pullar et al. 1973; McCraw 1975). To provide a background to the research objectives of the thesis, the development of tephra studies in New Zealand, largely pertaining to rhyolitic and andesitic eruptives, is reviewed.

TEPHRA STUDIES IN NEW ZEALAND - A HISTORICAL PERSPECTIVE

The development of tephra studies and the establishment of tephrochronology (a method of dating past geological events and

Fig. 1. Generalised distribution of volcanic centres or districts (bold names) in North Island active in the last c.0.5 million years. The tephras studied in this thesis were erupted in late Quaternary times (past c.50 000 years) from the Taupo, Maroa, Okataina, and Mayor Island centres (rhyolitic), and the Tongariro and Egmont centres (andesitic). TVZ = Taupo Volcanic Zone (dashed). ● = volcanoes that have erupted since c.A.D. 1850 (recorded history)*; ⊗ = volcanoes that have erupted during the last c.1800 years (mainly dated by ¹⁴C or dendrochronology); ○ = volcanoes that have erupted during the last c.5000 years (dated by ¹⁴C). Named volcanoes are: W, White Island (andesitic-dacitic); H, Haroharo; T, Mt. Tarawera; To, Mt. Tongariro; N, Mt. Ngauruhoe; R, Mt. Ruapehu; E, Mt. Egmont* (also known as Mt. Taranaki); Ro, Rangitoto Island; Te, Te Puke. (After Cole & Nairn 1975; McCraw 1975; Buck et al. 1981; and Wilson et al. 1986).

*There is some evidence to suggest that a small pyroclastic flow may have been erupted from Egmont in the last 100 years or so (V.E. Neall pers. comm. 1986; Neall & Alloway 1986).



landscapes based on the identification, correlation, and dating of tephra layers) as a separate discipline in New Zealand may be traced through four broad periods:

Period 1 : late 19th century to late 1920s

Period 2 : late 1920s to early 1950s

Period 3 : early 1950s to c.1973

Period 4 : c. 1973 to 1980s.

Some of the significant events that characterise each of these periods, and their influences, are described below.

Period 1 (late 19th century - late 1920s)

Geologists undertook reconnaissance and regional mapping, chiefly of hard rocks, but also noted the widespread pyroclastic materials and commented on possible stratigraphic relationships. In the Taupo district, von Hochstetter (1864, translated by Fleming) described some of the pyroclastic deposits as "volcanic fragmental rocks" of rhyolitic composition (p.116). Later writers (e.g., Crawford 1875, Smith 1876, Cussen 1887; see also Froggatt 1981a) described the pumice deposits around Lake Taupo in more detail. Thomas (1888a) used mineralogy and whole rock chemical analyses (p. 349), together with thickness relationships, of Taupo Pumice to demonstrate that it was not derived from Tongariro volcano as earlier writers had believed (Mt. Tauhara was suggested as a possible source). He also described andesitic ash beds and paleosols formed within them on Mt. Tongariro.

The eruption of Mt. Tarawera in June, 1886 resulted in the publication of the first isopach map in New Zealand (Fig. 2; Thomas 1888b), and stimulated an awareness that other volcanoes may have

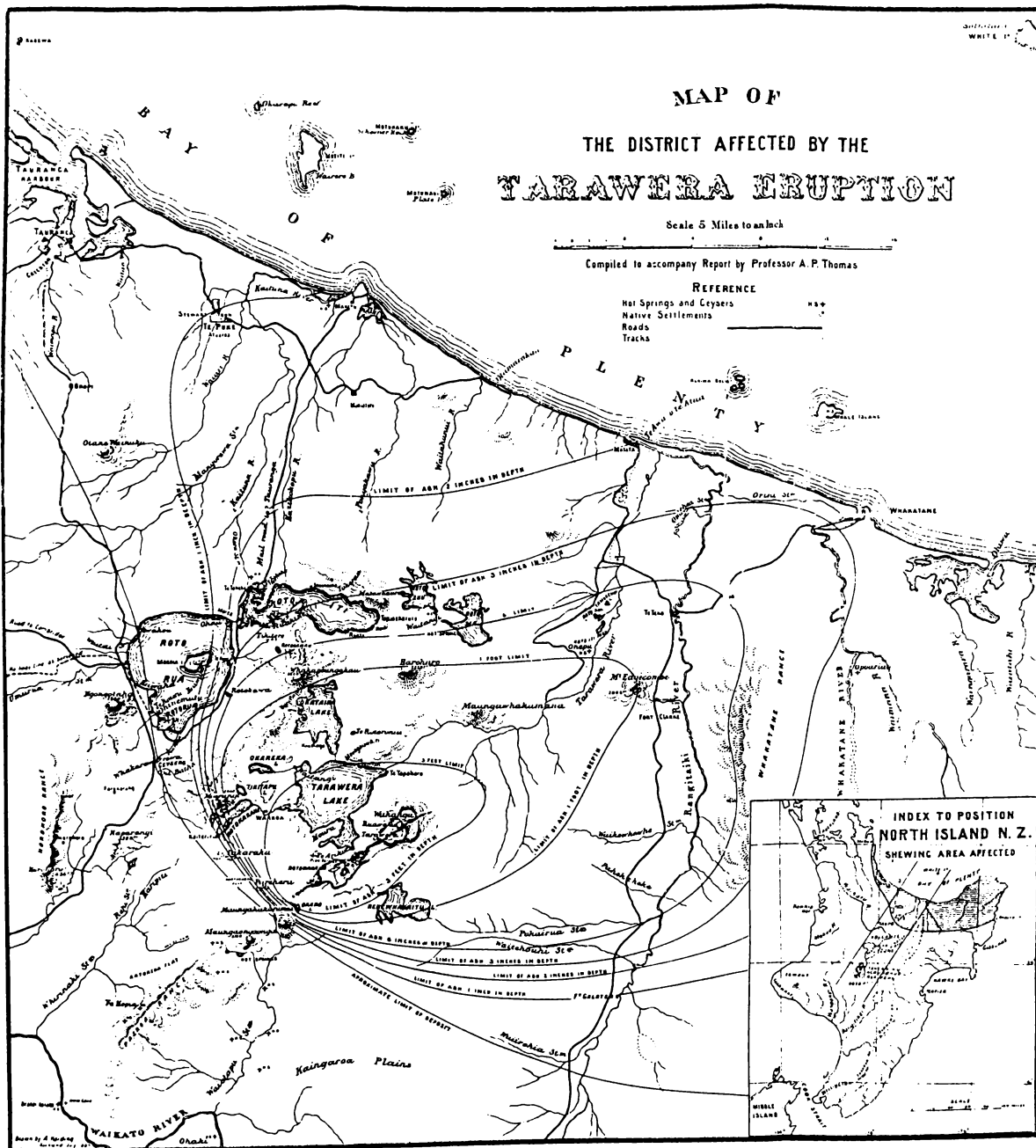


Fig. 2. Isopach map of tephra fallout from the Tarawera eruption of 10 June, 1886, as determined by Thomas (1888b, map I) (cf. maps of Pullar & Birrell 1973b and Walker et al. 1984).

spread showers of ash to distal parts of the North Island in the recent past. Hill (1886) describes how he analysed soil samples from eastern North Island, and reaches the following discerning conclusions (p. 386-7):

"From the results of my experiments I feel convinced that the East Coast District of this island has been subject, at a not very remote date, to dust showers of volcanic ejectamenta. Had the wind been blowing from the north-west at the time of the recent eruptions, it is a matter of certainty that the dust showers which fell in the district extending in a north-easterly direction for about 120 miles from the seat of the volcanic outburst, would have fallen throughout the East Coast District as far as Napier and the Hawke's Bay river system. Within 75 miles of Napier there are many volcanic cones, including the semi-dormant Tongariro and the not-altogether-extinct cone of Ruapehu - the highest point of elevation in the North Island; and although this district is separated by the Ruahine chain of mountains, and other minor ranges, from what may be termed the zone of active volcanic phenomena, as represented by hot springs, solfataras, geysers, and burning mountains, it is certainly not outside the zone of volcanic influences, the effects of which may be seen at any time along the East Coast. A recurrence of activity in and about the district of which Lake Taupo is the natural centre, would undoubtedly bring showers of volcanic dust and debris as far as Napier, should the wind be blowing in this direction at the time; but I cannot agree with those who say that such showers would be detrimental to vegetation. They may cause temporary inconvenience, but of their beneficial effects in the production and formation of soils I think there can be no question for a doubt. To me, volcanic dust showers are blessings in disguise. They may cause loss and inconvenience at the time of their deposition; but they contain within their particles the elements of fertility, and only need, like wine, age to make them valuable adjuncts in the formation of rich soils."

The first absolute date on a pre-historic tephra deposit appears to have been determined in the Taranaki district in 1883 by Mr A.W. Burrell (Oliver 1931; Druce 1966). Burrell used tree-ring counts from a matai tree (*Podocarpus spicatus*), in the forks of which "scoria" (lapilli) was lodged, to obtain an eruption age of c.1430 A.D. for the Burrell tephra (the most recent estimate for the age of the Burrell Formation is c.1655 A.D.: Druce 1966). Oliver's (1931) report on the age of burial of a Maori oven (umu) by the tree-ring dated Burrell Formation may qualify as the first application of tephrochronology (using a prehistoric tephra) in New Zealand.

The eruption of Mount Pelée in 1902 and the ensuing destruction of St. Pierre town awakened memories of the Tarawera eruption and resulted in the visit of an eminent volcanologist, T.A. Jagger, Jr., to New Zealand in 1910. His recommendation to set up a major volcanological observatory in the central volcanic region has not yet been realised¹ but eventually it prompted the initiation of detailed geological mapping in the Rotorua-Taupo area by L.I. Grange in 1926 (published in Grange 1937). At around the same time, B.C. Aston surveyed the soils of the Rotorua area and published, using a newly-developed classification system based on texture, the first soil maps in New Zealand (Aston 1926, 1927). Aston was investigating the serious problem of "bush sickness" (later traced to cobalt deficiency). Grange (1929), following Aston's lead, mapped soil-forming ash showers and soils in the Rotorua district and identified the relationship between ash showers, soil series, and bush sickness.

Thus the first steps towards the development of modern tephrostratigraphy and tephrochronology began as the result of a combination of events: the decision to do geological mapping in the Rotorua-Taupo district, partly because of perceived volcanological hazards; advances in soil classification and soil mapping procedures in New Zealand; and, perhaps most importantly, the urgent need to remedy the problem of bush sickness.

¹ Jagger did manage to establish the Hawaii Volcanological Observatory in 1912.

Period 2 (late 1920s to early 1950s)

The recognition of a relationship between the incidence of bush sickness and soil derived from tephra lead to extended soil surveys in central North Island, chiefly by Grange and N.H. Taylor (Grange 1931; Grange & Taylor 1932; Grange et al. 1939; Taylor 1930, 1933, 1953; Fleming 1953; N.Z. Soil Bureau 1954). These were carried out as part of the "Reconnaissance Soil Survey of the Central North Island Territory", which was instituted by the Department of Scientific and Industrial Research in collaboration with the Cawthron Institute Trust Board in 1930, and directed by T. Rigg (Grange & Taylor 1932). During the course of this work, many important soil-forming tephras were named, described, and mapped (e.g. Fig. 3). Grange and Taylor noted that the ash showers (tephras) mantle the topography, may show shower bedding, and thin away from source. From mineralogical studies, often based on samples separated and examined in the field, they recognised contributions from four volcanic centres: Taupo, Rotorua, Tongariro, and Egmont (e.g., see Table 1). Rhyolitic tephras were generally attributed to paroxysmal, and andesitic tephras to intermittent, eruptions (Taylor 1933).

Table 1. Ferromagnesian mineralogy of tephra beds in the Mairoa district (from Taylor 1933, p.201). Bed 1 is a composite of tephras from more than one volcano. Bed 2 is probably Kawakawa Tephra (Vucetich & Pullar 1969; Vucetich & Howorth 1976a).

	Depth of Sample.	Mairoa.			Five Miles North of Mairoa.			Depth of Sample.	Fifteen Miles East of Mairoa.		
		Horn-blende.	Hypers-thene.	Augite.	Horn-blende.	Hypers-thene.	Augite.		Horn-blende.	Hypers-thene.	Augite.
Bed 1	In.							In.			
	3	35	25	40	2	37	30	33
	6	34	26	40	30	22	48	9	28	47	25
	13	30	32	38
	22	30	47	23	24	30	60	10
Bed 2	29	14	73	13	10	75	15	34	8	77	15

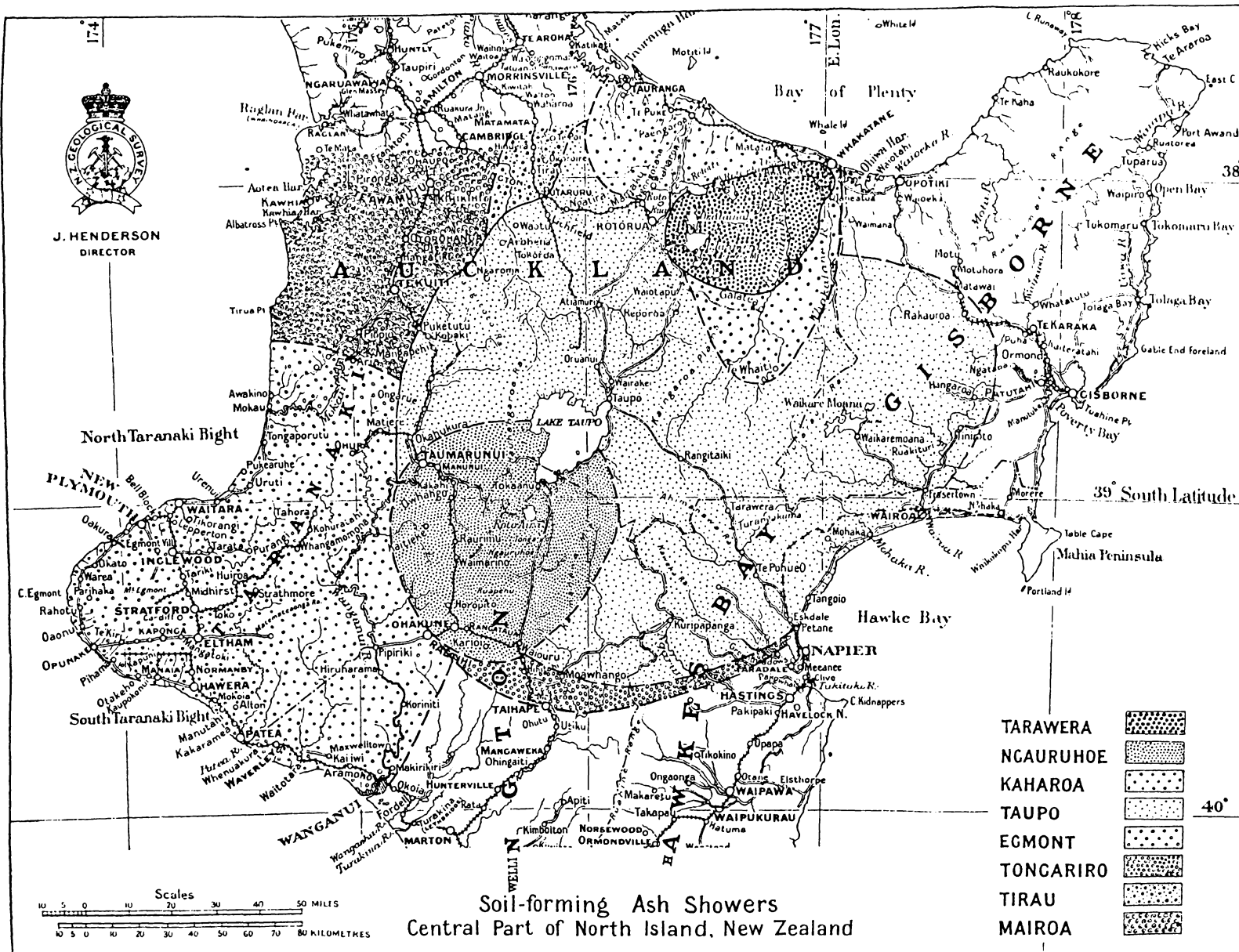


Fig. 3 Soil-forming ash showers in central North Island, New Zealand (thicknesses for each "shower" are generally c.15 cm [6 inches] or more). (From Grange & Taylor 1932, facing p.62).

This period thus marks the beginning of tephra mapping in New Zealand, and might be described as one of "proto-tephrostratigraphy". It is emphasised that this work was initially undertaken to provide a better understanding of soils and their parent materials, and that many subsequent advances in tephrostratigraphy in New Zealand (chiefly in Period 3) were made by pedologists (McCraw 1975).

Studies of tephra layers as a tool for research in various disciplines (i.e., the development of tephrochronology) began in Iceland and other countries also around 1930 (see Thorarinsson 1981). In a paper mainly describing the nature and origin of chalazoidites on Scinde Island, Napier, Berry (1928) also made the following perceptive and highly relevant observations (p.608):

"It seems that a study of volcanic [ash] layers will acquire more importance as knowledge of them increases. In an eruption, for example, in Miocene times, where volcanic material had covered a widespread area of country, it seems extremely probably that much valuable information would be obtained as to the contemporaneity of various deposits, and what effect influences such as climate, depth of water, etc., have had in altering the fauna and flora, if this particular volcanic deposit could be identified by its continuity and its physical and chemical peculiarities."

Period 3 (early 1950s to c.1973)

The advent of radiocarbon dating and the establishment of a radiocarbon dating laboratory in New Zealand in the early 1950s provided the means for obtaining an absolute chronology of tephra eruptions of late Quaternary age. The first ^{14}C date published in New Zealand (NZ1 1820 \pm 150 years B.P.) was on carbonised wood from within the Hatepe Lapilli (Fergusson & Rafter 1953). Baumgart's (1954) paper is a benchmark study for this period because it is the first to focus on the stratigraphy and chronology (based on ^{14}C dating) of a sequence of tephras erupted from a single source. Baumgart used the

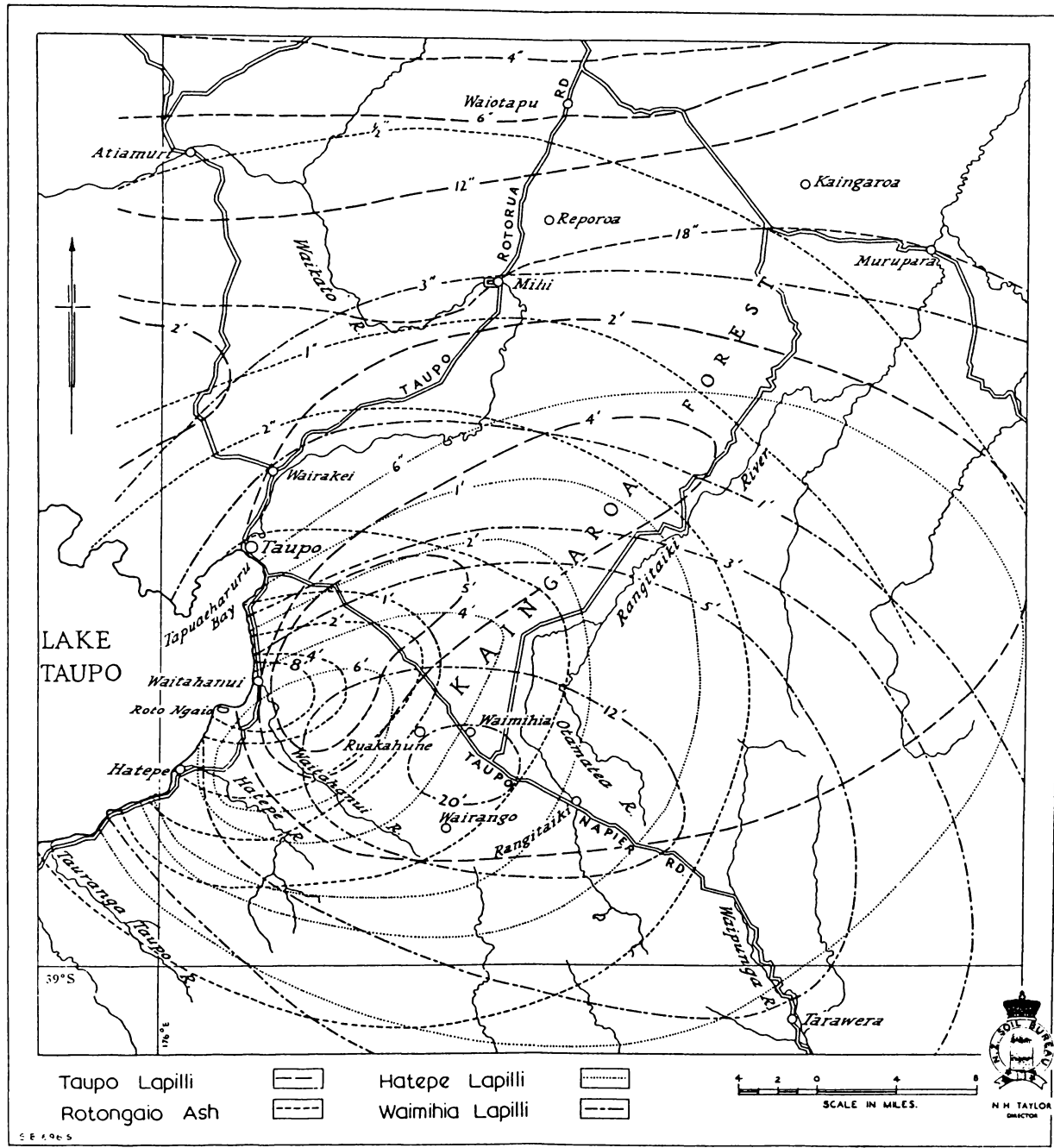


Fig. 4. Isopachs of some ¹⁴C-dated tephras erupted from the Taupo Volcanic Centre. (From Baumgart 1954, facing p.461.)

tephrostratigraphic record to interpret the recent volcanological history of the Taupo volcano. In addition, the paper included the first isopach maps for Taupo Lapilli, Rotongaio Ash, Hatepe Lapilli (members of Taupo Pumice Formation), and Waimihia Lapilli (Fig. 4). from which the locations of possible source vents were inferred (Baumgart 1954).

The framework for a regional stratigraphy of late Quaternary tephras in the central North Island developed from this point, aided considerably by the exposure of many new cuttings during the course of road construction. Tephra were correlated by detailed "hand-over-hand" methods from cutting to cutting using the physical properties of the tephras, marker beds, and principles of stratigraphy; ^{14}C dates were obtained where possible (e.g., Gibbs 1960; Healy 1964; Vucetich & Pullar 1963, 1964, 1969, 1973; Pullar 1967a; Pullar & Heine 1971; Nairn 1972; Pullar & Birrell 1973a, b; Topping 1973). These studies established stratigraphic procedures and nomenclature, and made wide use of isopach maps and "picket fence" correlation diagrams to document tephra distribution patterns, tephrostratigraphic relationships, and to estimate tephra volumes. The outermost margins of isopach maps were generally restricted to about 10-20 cm, the minimum thickness for tephra identification based on field procedures. Mapping in areas outside the central volcanic region was also undertaken (e.g., Druce 1966; Topping 1972; Neall 1972), and some of the older tephra deposits examined (e.g., Te Punga 1963; Ward 1967; Ninkovich 1968; Tonkin 1970).

Although mineralogical and chemical studies on tephras were comparatively sparse during this period (e.g., Ewart 1963, 1966, 1971;

Cole 1970). they were to lead to the start of the development of laboratory-based tephra "fingerprinting" methods, particularly as new analytical techniques (including dating methods) became available in the late 1960s and 1970s. An important contribution here was made by B.P. Kohn who used the trace element chemistry of bulk Fe-Ti oxides (titanomagnetites) to characterise and distinguish a range of late Quaternary tephras (e.g., Fig. 5; Kohn 1970, 1973; Kohn & Neall, 1973). This fingerprinting method was used in conjunction with diagnostic ferromagnesian mineral assemblages (e.g., Lewis & Kohn 1973; Topping & Kohn 1973). Rankin (1973) attempted tephra correlations using micro-element concentrations in bulk glass separates.

Tephrochronological applications were made in a wide range of earth sciences and related disciplines, including geomorphology, archaeology, sea level and coastal studies, loess stratigraphy, palaeopedology and tephra weathering studies, and volcanology (e.g., Fieldes 1955, 1966; Wellman 1962; Cowie 1964; Pullar 1967b, 1970, 1973; Pain & Pullar 1968; Gibbs 1968; Vucetich 1968; Pullar & Selby 1971; Pullar & Warren 1968; Selby et al. 1971; Birrell & Pullar 1973; Kohn & Neall 1973; see also bibliographies in Kohn 1973, Westgate & Gold 1974, and McCraw 1975).

This period culminated in the 1973 International Union for Quaternary Research (INQUA) Congress held in Christchurch, New Zealand. A number of papers dealing with tephrostratigraphy and tephrochronology were published in a special issue of the *New Zealand journal of geology and geophysics* (Volume 16, Issue 3) (most have been referred to above). Valuable summary papers were given by Pullar &

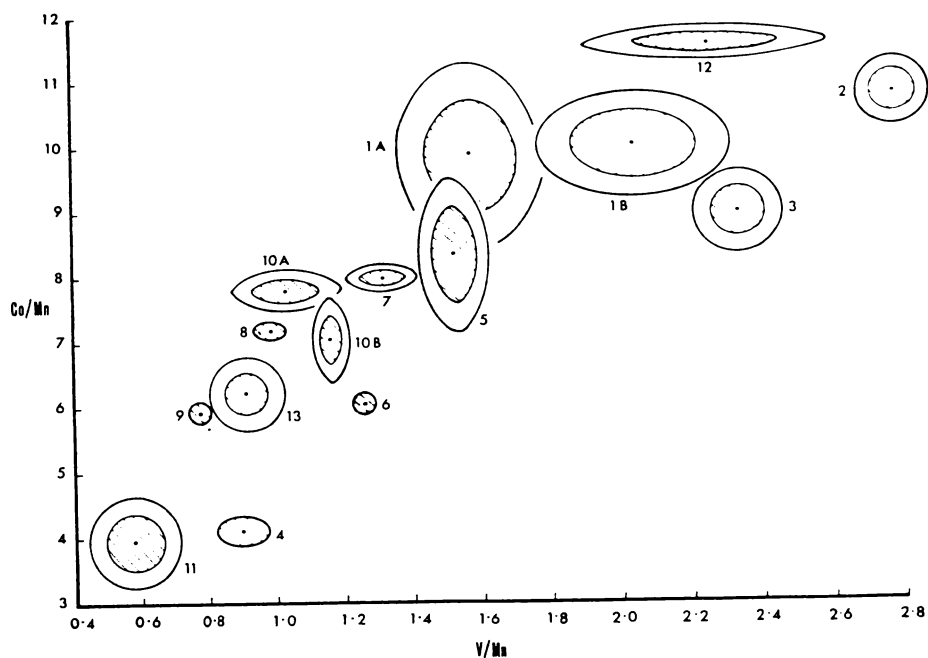


Fig. 5. X' values of titanomagnetites from fifteen numbered New Zealand tephras showing Co/Mn ratios plotted against V/Mn ratios (based on analysis of bulk samples). X' is the antilog of an X ratio. Each tephra is represented by a dot showing its mean value, by a shaded area that includes 68% (1 s.d.) of its plotted points, and by an outer line that includes 90% (1.645 s.d.) of its plotted points. Only two samples were taken for tephras 4, 6, 8, and 9, and for these the shaded area gives the mean deviation and not the 68% value (1 s.d.). (From Kohn 1970, p.365.)

1A = Kaharoa northern lobe. 1B = Kaharoa south-eastern lobe. 2 = Taupo Lapilli. 3 = Waimihia, 4 = Rotokawau. 5 = Whakatane. 6 = Mamaku. 7 = Rotoma, 8 = Waiohau. 9 = Rotorua. 10A = Rerewhakaaitu phenocryst-rich, 10B = Rerewhakaaitu phenocryst-poor, 11 = Oruanui, 12 = Mangaone. 13 = Rotoehu.

Birrell (1973b), Pullar et al. (1973), and McCraw (1975; see Table 2), and reflect the major advances made in the two decades since the early 1950s. A generally sound framework of late Quaternary tephrostratigraphy and tephra distribution had been established for central North Island volcanoes in particular, and wide applications of tephrochronology were being made. At the same time, laboratory methods to help correlate tephras over wide distances were beginning to be developed and applied.

Period 4 (c.1973 to 1980s)

This period saw a new generation of university-trained graduates building on the advances made in Period 3, with a number of more specific studies, commonly involving laboratory work, aimed at revising or refining the tephrostratigraphy associated with particular volcanic centres (e.g., Howorth 1975; Vucetich & Howorth 1976a, b; Buck 1978; Hogg 1979; Froggatt 1981a, b, c; Nairn 1981; Neall & Geddes 1981; Franks 1984). Relatively few new ^{14}C dates on late Quaternary tephras were obtained, however, usually because of scarcity of suitable datable material. Mapping was generally restricted to revisions of the distributions of deposits near source (e.g., Howorth 1975; Froggatt 1981b; Geddes & Neall 1982), but occurrences of some more distal deposits, including the newly-identified and petrographically distinctive Mayor Island-derived Tuhua Tephra, were reported (Pullar et al. 1977; Howorth & Topping 1979; Howorth et al. 1980; Lowe et al. 1980; Lowe 1981; Geddes et al. 1981; Kohn et al. 1981; Hogg & McCraw 1983). Some of these latter papers (as had a few earlier ones including Tonkin 1967, Pullar 1970, and Topping & Kohn 1973), showed how useful organic sediments could be in recording

Table 2. Summary of named tephra formations and published radiocarbon dates from North Island volcanic centres, as known at the end of Period 3. (From McCraw 1975, p.38.)

Years before Present	OKATAINA CENTRE	MAROA -TAUPO CENTRE	TONGARIRO CENTRE	EGMONT CENTRE	OTHER or UNKNOWN CENTRES	Years before Present
250	Tarawera Formation (64 B.P.) (3 members)			Tahurangi Formation (250 B.P.)		250
500				Burrell Form. (315 B.P.) (4 mem.) Newall Form. (450 B.P.) (4 mem.)		500
750					Rangitoto Ash (750 B.P.) (Auckland Centre)	750
1,000	Kaharoa Ash (930 B.P.)					1,000
1,500						1,500
2,000		Taupo Pumice Formation (1,850 B.P.) (7 members)	Ngauruhoe Tephra Formation (0-1,819 B.P.)			2,000
2,500		Mapara Pumice (2,270 B.P.)	Mangatawai Tephra Formation (2,500 B.P.)			2,500
3,000		Whakaipo Tephra (2,800 B.P.)				3,000
4,000	Rotokawau Ash (no date)	Waimihia Formation (3,150 B.P.) (2 members)	Papakai Tephra (3,420 B.P.)	Inglewood Tephra (c3,000 B.P.)		4,000
5,000					Whangamata Ash (no date) (2 members) (Waihi Centre)	5,000
6,000	Whakatane Ash (5,180 B.P.)	Hinemaiaia Ash (5,085 B.P.)		Korito Tephra (no date)		6,000
7,000				Oakura Tephra (6,900 B.P.)		7,000
8,000	Mamaku Ash (7,050 B.P.) Rotoma Ash (7,330 B.P.)			Stent Ash		8,000
9,000		Opepe Tephra (8,850 B.P.)				9,000
10,000		Poronui Tephra (9,780 B.P.)	Mangamate Tephra (9,700 BP) (5 mem) Okupata Tephra (9,790 B.P.)	Okato Tephra (no date) (2 members)		10,000
15,000	Waiohau Ash (11,250 B.P.) Rotorua Ash (13,450 B.P.) Rerewhakaaitu Ash (14,700 B.P.)	Puketarata Ash (no date)	Rotoaira Lapilli (13,800 B.P.)			15,000
20,000		Oruanui Formation (19,850 B.P.) (2 members)		Saunders Ash (16,000 B.P.) Carrington Tephra		20,000
30,000	Okareka Ash (20,700 B.P.) Te Rere Ash (no date)	Aokautere Ash (20,500 B.P.)		Koru Tephra (no date) (2 members)		30,000
40,000	Mangaoni Lapilli Formation (30,100 B.P.)			Pukeiti Tephra (no date)		40,000
	Rotoiti Breccia Formation (41,000 B.P.) (3 members)			Weld Tephra (no date)		
				New Plymouth Ashes (more than 70,000 y)	Upper Hamilton Ash Formation (? less than 220,000 years) Lower Hamilton Ash Formation (? more than 330,000 years) Kauroa Ash Formation	

tephra deposits in distal localities where the tephrostratigraphy of subaerial exposures is often equivocal.

Subsurface loess deposits associated with tephra beds, and first described in late Period 3 surveys (Vucetich & Pullar 1969), received increased attention (Stewart et al. 1977; Lowe 1980, 1981; Benny 1982; Kennedy 1982).

Analyses of titanomagnetites for long distance tephra correlation continued (Pullar et al. 1977; Kohn & Glasby 1978; Kohn 1979), but was essentially based on earlier data of Kohn (1973). The only new work published on Fe-Ti oxides was by Hogg & McCraw (1983) (described below; also see Franks 1984). Apart from those by Howorth & Rankin (1975), no studies on glass analyses for correlation purposes were published until 1983 (Froggatt 1983; see also Froggatt & Gosson 1982). Froggatt was the first to systematically document the basis of electron microprobe analysis of glass shards for correlating tephras and ignimbrites in New Zealand. Some representative glass analyses of New Zealand tephras are listed in Table 3.

This relative dearth of detailed fingerprinting studies involving chemical analyses of various minerals in tephras in New Zealand contrasts with the rapid rate of development and application in overseas countries (e.g., Smith & Westgate 1969; Borchardt et al. 1971; Izett et al. 1972; Sarna-Wojcicki 1976; Westgate & Evans 1978; Kittleman 1979; Federman & Carey 1980; Westgate & Gorton 1981; King et al. 1982; Smith & Leeman 1982; Fisher & Schmincke 1984), and probably relates in part to the limited availability of analytical facilities in New Zealand. Nevertheless, Hodder & Wilson (1976) made an

Table 3. Representative glass analyses of some New Zealand tephras as determined by electron microprobe. (From Froggatt 1983, p.194.)

	1		2		3		4		5			
SiO ₂	77.25	(0.24)	79.04	(0.31)	78.22	(0.27)	77.16	(0.48)	77.99	(0.27)		
Al ₂ O ₃	13.35	(0.13)	12.49	(0.18)	12.36	(0.22)	13.07	(0.37)	12.17	(0.11)		
TiO ₂	0.24	(0.03)	0.11	(0.02)	0.09	(0.04)	0.21	(0.05)	0.15	(0.02)		
FeO ^a	1.96	(0.08)	1.16	(0.09)	1.08	(0.14)	1.23	(0.11)	1.07	(0.07)		
MnO	0.07	(0.03)	0.06	(0.05)	0.07	(0.03)	0.04	(0.04)	0.03	(0.03)		
MgO	0.27	(0.03)	0.12	(0.04)	0.09	(0.01)	0.24	(0.09)	0.11	(0.03)		
CaO	1.18	(0.03)	1.03	(0.07)	0.76	(0.09)	1.32	(0.18)	0.78	(0.02)		
Na ₂ O	3.22	(0.17)	2.99	(0.16)	3.71	(0.25)	3.62	(0.29)	3.28	(0.15)		
K ₂ O	2.46	(0.05)	3.01	(0.11)	3.61	(0.17)	3.11	(0.28)	4.43	(0.17)		
Water	0.23	(0.79)	6.72	(0.93)	5.50	(1.35)	5.75	(1.14)	3.23	(0.50)		
<i>N</i>	11		14		11		11		10			
Na/K	1.31		0.99		1.03		1.16		0.74			
	6		7		8		9		10		11	
SiO ₂	77.55	(0.15)	77.98	(0.32)	78.16	(0.36)	77.81	(0.42)	77.65	(0.34)	78.06	(0.72)
Al ₂ O ₃	12.64	(0.15)	12.55	(0.23)	12.41	(0.20)	12.57	(0.28)	12.63	(0.32)	12.48	(0.35)
TiO ₂	0.15	(0.02)	0.10	(0.02)	0.14	(0.04)	0.13	(0.03)	0.13	(0.03)	0.11	
FeO ^a	1.41	(0.09)	1.08	(0.03)	0.97	(0.10)	1.10	(0.09)	1.13	(0.09)	1.11	(0.08)
MnO	0.04	(0.04)	—		0.03	(0.03)	0.03	(0.03)	0.05	(0.04)	0.03	
MgO	0.11	(0.03)	0.11	(0.04)	0.12	(0.03)	0.10	(0.04)	0.11	(0.03)	0.12	(0.08)
CaO	1.01	(0.05)	0.87	(0.15)	0.80	(0.06)	0.78	(0.04)	0.80	(0.04)	0.75	(0.04)
Na ₂ O	3.65	(0.06)	3.81	(0.14)	3.21	(0.30)	3.50	(0.09)	3.53	(0.16)	3.34	(0.39)
K ₂ O	3.45	(0.09)	3.46	(0.16)	4.22	(0.14)	4.00	(0.20)	3.98	(0.16)	3.96	(0.22)
Water	6.73	(0.35)	5.22	(0.83)	4.83	(0.99)	6.06	(1.11)	6.02	(1.18)	6.22	(1.35)
	7		9		20		10		10		10	
	1.06		1.10		0.76		0.88		0.89		0.84	

Note. (1) Taupo Ignimbrite; (2) Kawakawa Tephra; (3) Matahina Ignimbrite; (4) Griffin Rd 2; (5) Whakamaru Ignimbrite; (6) Marshall Ignimbrite; (7) Potaka Pumice. Mt. Curl Tephra Correlatives: (8) Mt. Curl; (9) Ohariu; (10) Pahiatua; (11) Rewa Hill. *N* = number of analyses in mean. Numbers in parentheses are 1 standard deviation.

^a All Fe calculated as FeO.

important contribution to the study of mixed tephra assemblages. They suggested ways of circumventing problems associated with multiple tephra populations, and showed how such populations may be effectively separated using single particle methods (Hodder 1978). The study by Hogg & McCraw (1983) on mixed calcalkaline and peralkaline tephra of the Coromandel Peninsula, based partly on electron microprobe analysis, demonstrates some of the advantages of single particle (grain discrete) methods over multi-particle methods (Fig. 6). However, it also exemplifies the effort and detail that may be required to identify thinly bedded tephra deposits in distal environments where many of the diagnostic field properties are lost and laboratory methods made difficult by postdepositional mixing and weathering processes.

With the increasing availability of new dating and analytical methods, more attention was given to older tephra, both on and offshore, and their possible relationship to ignimbrite deposits considered (e.g., Milne 1973; Seward 1974, 1975, 1976, 1979; Pain 1975; Watkins & Huang 1977; Vucetich et al. 1978, 1981; Naeser et al. 1980; Pillans & Kohn 1981; Froggatt 1983; Kyle & Seward 1984; Froggatt et al. 1986). Wide-ranging tephrochronological applications are recorded, with a notable increase in the number of palynological applications and in new studies on clay mineralogy and the weathering of tephra (e.g., Kirkman 1975, 1976, 1980; Birrell et al. 1977; Neall 1977; Kennedy et al. 1978; McGlone 1978, 1981, 1983; McGlone & Topping 1977, 1983; McGlone et al. 1984; McFadgen 1981; Froggatt & Howorth 1980; Pullar 1981; Parfitt & Henmi 1980; Parfitt et al. 1980, 1982, 1983; Theng 1981; Palmer 1982; Pillans et al. 1982; Pillans 1983; Stevens & Vucetich 1984). Although palynological studies using

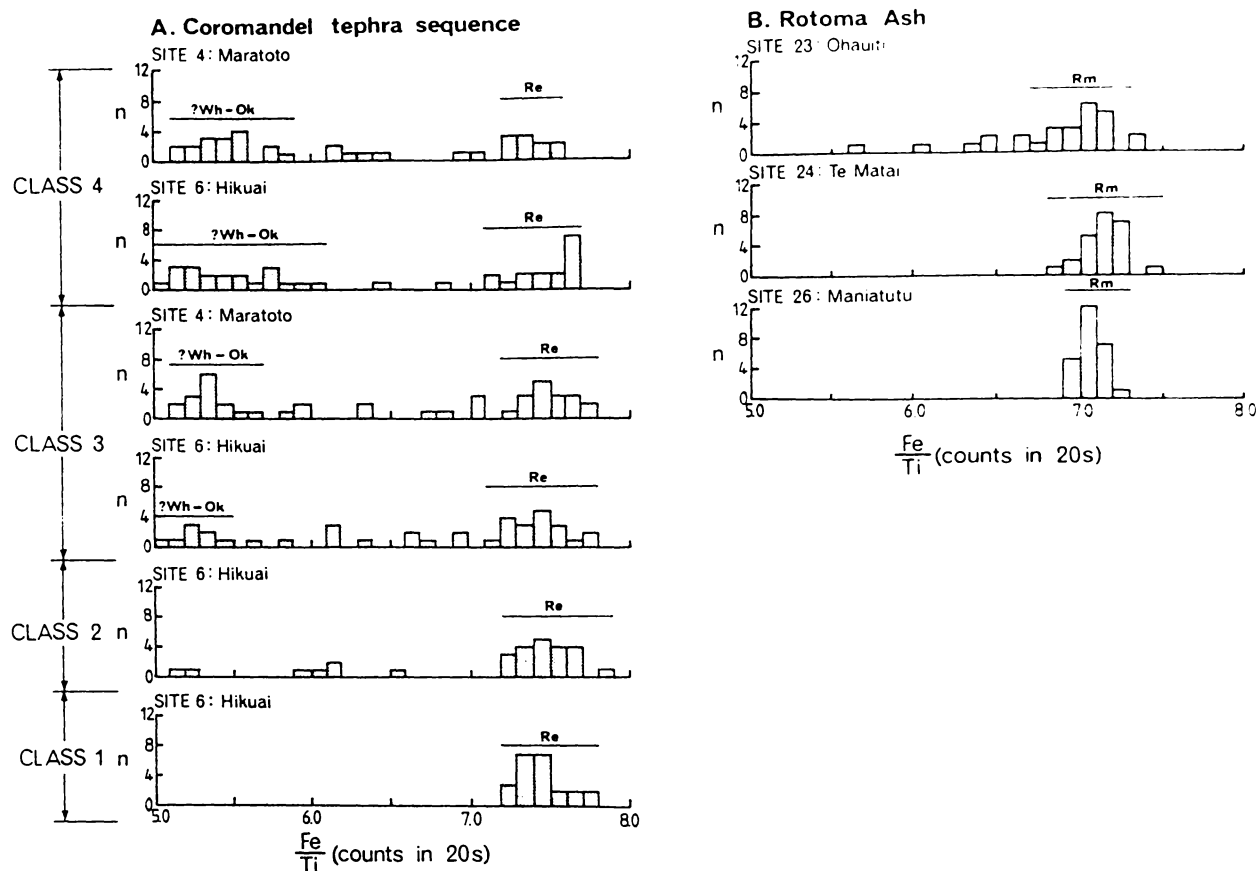


Fig. 6. Fe/Ti ratios of titanomagnetites extracted from calcalkaline tephtras of Coromandel Peninsula (A), and from Rotoma Ash in western Bay of Plenty (B) (based on analysis of single grains). n = the number of titanomagnetite grains in any particular 0.1 Fe-Ti ratio-interval; dominant modes are indicated by lines overlying the data points. The graphs illustrate that the Coromandel tephtra sequence, except class 1 (Rotoehu Ash), is a mixed deposit. Rotoma Ash is probably absent or only sparsely represented in the Coromandel tephtra sequence. Rm = Rotoma Ash; ?Wh-Ok = the Waiohau, Rotorua, Okareka tephtras; Re = Rotoehu Ash. (From Hogg & McCraw 1983, p.173.)

tephrochronology have increased. McGlone & Topping (1977) note that their efficacy is governed by the time control available.

Perhaps the most significant development in tephra research since about 1980 has been its increased application to the fields of physical volcanology and petrology, both in New Zealand (e.g.. Nairn & Self 1978; Kohn & Topping 1978; Nairn 1980; Hodder 1981; Froggatt 1982; Self 1983; Blake et al. 1986; Wallace et al. 1986) and overseas (see Self & Sparks 1981; Fisher & Schmincke 1984). In New Zealand, this trend may be attributed in large part to the influence of G.P.L. Walker. Walker's dynamism, wide international experience, and simple yet highly effective approach has resulted in many conceptual advances in physical volcanology (e.g., Walker 1979, 1980, 1981a, b, c, d; Walker et al. 1984; Wilson & Walker 1985; Wilson et al. 1984, 1986). Another major stimulus in this field was the eruption of Mt. Saint Helens in 1980, the products of which have been intensively studied (e.g.. Lipman & Mullineaux 1981).

Thus Period 4 is characterised by more specialised studies, which have built on and refined the stratigraphic framework established previously (see also Editorial in Howorth et al. 1981). Most of these studies have been located in areas relatively near to the tephra source volcanoes. Limited studies aimed at identifying distal tephras have been carried out, but have been only partly successful. Most tephra fingerprinting methods have progressed relatively slowly, but recent work using the electron microprobe has established a basis necessary for further development. Generally, fundamental mineralogical and chemical data for many tephras, particularly those derived from andesitic sources, are sparse. Late Quaternary tephras

have been used extensively as time stratigraphic markers in a wide range of projects; older tephras are being used increasingly in this role as new dates are obtained for them. Studies on tephra weathering and clay mineral formation and transformations are also important areas of research, particularly in pedology and palaeopedology.

It might be argued that tepthrostratigraphy and tepthrochronology "came of age" as disciplines in their own right at around the start of the 1980 decade. A workshop devoted solely to tephra studies was held at Victoria University of Wellington in late June - early July 1980, the first such conference of its kind in New Zealand (Smalley 1980; Howorth et al. 1981). In the same year, the first international conference on tephras was held at Reykjavík, Iceland (Self & Sparks 1981). Since then, significant advances in physical volcanology in New Zealand have been based largely on studies of tephras and pyroclastic flow deposits.

DEVELOPMENT OF THESIS RESEARCH PROGRAMME

The preceding review, whilst emphasising important advances in tephra studies in New Zealand, also indicates that there are many gaps in our knowledge. Some inadequacies, relating specifically to late Quaternary tephras, are identified as follows.

- (1) The tepthrostratigraphy of distal areas is poorly known. How far from the eruptive centres have tephras been deposited in New Zealand, and what is their pattern of distribution? What volcanological inferences can be made from the occurrence and

distribution of distal tephra fallout? What effects have distal tephras had on soil genesis?

- (2) Many tephras have been dated, but commonly only by one or two dates. Other tephras, particularly from andesitic sources, are undated. The effective use of tephras as isochronous stratigraphic markers requires that their ages are reliably known, as do studies of volcanological history. How reliable are the present dates and inferred ages? Where might sites containing material suitable for improving the ^{14}C -based chronology be obtained?
- (3) Methods of tephra fingerprinting, particularly those involving use of the electron microprobe, have not been developed to their potential. Only very recently have systematic studies using electron microprobe analysis of glass shards for correlation purposes been attempted. How useful is the electron microprobe, and glass chemistry in particular, for correlating tephras? Are other minerals also suitable? How best are the volcanic centres characterised in terms of the composition of the associated tephras? Can individual tephras be fingerprinted without stratigraphic control?

A potential means for answering these and other questions was discovered when a sediment core was taken from Lake Maratoto, a small peaty lake near Hamilton (Lowe et al. 1980). The core contained a sequence of ash layers, which were provisionally identified as distal airfall tephra deposits derived from volcanoes in the TVZ, Mayor Island, and possibly Mt. Egmont sources. Consequently, a thesis

research programme investigating distal tephras from such occurrences in lake sediments and peats in northern North Island has been developed. The Waikato region has been the main focus of study, but sites in Auckland, Northland, and eastern North Island have also been investigated (Fig. 7). The aim and scope of the project are outlined below.

THESIS OBJECTIVES AND SCOPE OF STUDY

The broad aim of the thesis is to advance our knowledge of the distribution, stratigraphy, chronology, and composition of late Quaternary tephras in northern New Zealand using distal occurrences in lake sediments and peats, and thereby to contribute to the greater understanding and application of tephrostratigraphy and tephrochronology in New Zealand.

More specific objectives of the thesis are:

- (1) to determine the occurrence, stratigraphy, chronology, and origin of distal late Quaternary tephras in the Waikato and other regions in northern North Island, and, where possible, to map and account for their distribution;
- (2) to help establish compositional criteria, particularly using the electron microprobe, for identifying and correlating late Quaternary rhyolitic and andesitic tephras in New Zealand;
- (3) to investigate new methods for detecting thin tephra layers in lake sediments and peats;
- (4) to improve the chronology of late Quaternary rhyolitic and andesitic tephras in New Zealand;

- (5) to investigate the developmental history of Lake Maratoto using tephrochronology to help our understanding of palaeoenvironmental changes in the Waikato region;
- (6) to critically review the various controls of clay mineral genesis in tephras, and to develop a new model of tephra weathering and clay mineral formation and transformation based partly on tephra compositional and distributional data from (1) and (2) above;
- (7) to demonstrate the value of lake sediments and peats as recorders of volcanism, and to assess the comprehensiveness of the record obtained for late Quaternary eruptions in New Zealand.

These objectives are broad in scope but all hinge on distal tephras preserved in lake sediments and peats. The objectives are approached in a series of studies written as papers. The papers are arranged into two broad sections. The first section, comprising Papers 1 to 8, deals chiefly with the stratigraphy, chronology, composition, and distribution of late Quaternary tephras in the Waikato and other regions, i.e., addresses objectives 1 - 4. The second section, comprising Papers 9 - 12, looks at applications of the tephrostratigraphy to palaeolimnology, to clay mineral genesis in tephras, and to volcanic history, i.e., addresses objectives 5 - 7. The aims, scope, and findings of each study are documented in detail in the individual papers. The study areas are shown in Fig. 7.

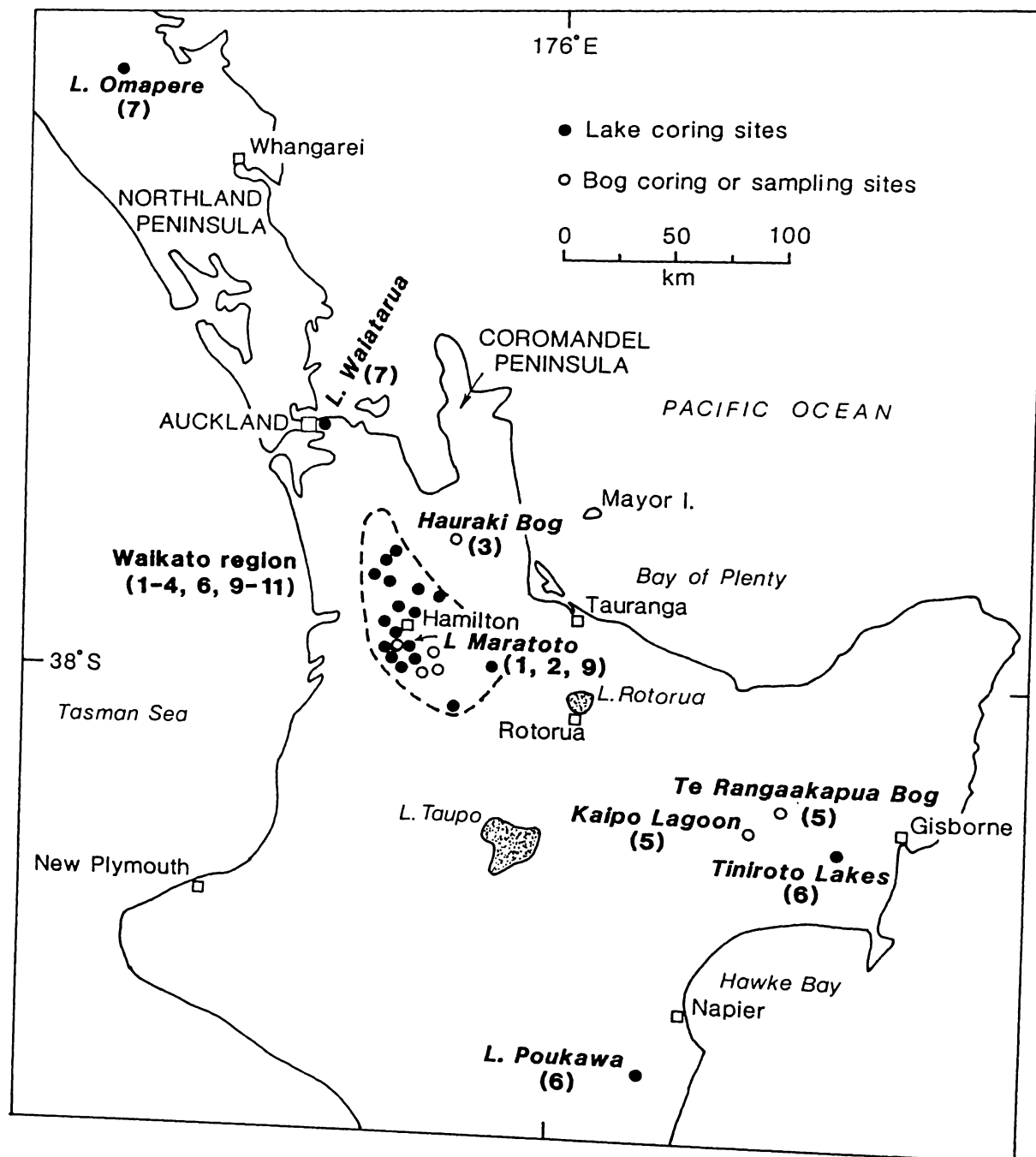


Fig. 7. Study sites in northern North Island, New Zealand. The numbers in parentheses refer to the thesis Papers that relate to the named site or sites. Papers 8 and 12 cover almost all of the sites.

ORGANISATION OF THE THESIS

As noted above, the thesis is organised and presented as a series of 12 papers. At the time of binding, 9 of these were published, one had been submitted for publication, and two were still undergoing peer review. Because of the different requirements of the different scientific journals to which they have been submitted, some papers have different formats. A small degree of duplication, particularly of references, is one consequence of organising the thesis as a series of papers. The duplication arises because each paper is a discrete article.

Referencing in the papers is done in the normal way, with references cited in the text of a particular paper appearing in a reference list at the end of that paper. For the reader's convenience, the thesis paper numbers have been cross-referenced with their counterpart references in a supplement following each reference list.

Two appendices are included at the end of the thesis.

COMMENTS ON NOMENCLATURE

"Tephra" (a Greek word meaning "ash") is a collective term for material that has been explosively ejected from a volcano and transported through the air. "Tephrochronology" is a dating method based on the identification, correlation, and dating of tephra layers. These terms were first introduced by Sigurdur Thorarinsson in his

doctoral thesis, "Tefrokronologiska studier på Island", published in 1944 (Thorarinsson 1981). He chose "tephra" as a succinct collective term for all pyroclasts transported through the air because (a) it fitted phonetically and linguistically with magma and lava (also derived from Greek), and (b) it had been used by Aristotle for volcanic ash in an account of an eruption on the island of Hieria (probably the oldest description of a tephra fall and transport in European literature) (Thorarinsson 1981). Also the term "volcano" is derived from the Roman name of that island, Vulcano, and the term tephra is thus closely related to classical volcanology.

Although Thorarinsson (1954 *in* Pullar et al. 1973, p.497) defined tephra as "all the clastic volcanic materials which during an eruption are transported from the crater through the air", the problem arose as to whether the term included both fall and flow deposits. It was suggested that predominantly unconsolidated pyroclastic materials be designated "tephra" (and, if known, as "tephra-fall" or "tephra-flow") (see Cole & Kohn 1972). However, difficulties of origin and separation persisted, hence the INQUA Commission on Tephrochronology (1973 meeting in New Zealand) broadened the term to include both airfall and pyroclastic flow material resulting from a volcanic eruption (Westgate & Gold 1974; McCraw 1975 and pers. comm. 1987). Although this usage is widely used (e.g., Self & Sparks 1981; Schmid 1981; Fisher & Schmincke 1984), a recent trend in New Zealand has been to loosely equate tephra with pyroclastic fall deposits, and to use "ignimbrite" (welded or unwelded) for pyroclastic flow deposits. (Pyroclastic surge deposits are usually described separately: Wright et al. 1980.) This usage is generally adopted in this thesis, the deposits studied being demonstrably airfall in origin. Some of the

deposits may include a "co-ignimbrite ash" component, however (Sparks & Walker 1977; see Paper 4). I also refer to "lacustrine tephras" which, although having settled through water, may still be regarded as tephra deposits because they are essentially fallout deposits (Fisher & Schmincke 1984).

The term "tephra" when used to describe unconsolidated pyroclastic material is a collective noun and therefore no "s" should normally be appended. However, when used for a series of stratigraphic units, it is common practice (e.g., Pullar et al. 1973) to refer to them collectively as "tephras" (as in "the rhyolitic tephras from Mt. Tarawera") (Cole 1981).

The term "late Quaternary" in New Zealand is commonly applied to all tephras aged \leq c.50 000 years B.P., i.e., younger than and including Rotoehu Ash, as used by Pullar (1967a), Topping (1973), Pain (1975), and Hogg & McCraw (1983), for example.

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PAPER 1

Stratigraphy and chronology of late Quaternary tephras in Lake Maratoto, Hamilton Basin, New Zealand.

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Stratigraphy and chronology of late Quaternary tephras in Lake Maratoto, Hamilton, New Zealand

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Abstract A 3 m piston core from Lake Maratoto (37°53'S 175°18'E) near Hamilton shows at least 12 thin, well-preserved distal airfall tephras intercalated with humic copropel (dy) deposits. Most of the tephras have been identified by their dominant ferromagnesian mineralogy, their stratigraphic position, and 5 radiocarbon dates. The majority of the tephras are derived from the Taupo and Okataina Volcanic Centres, while others originate from Mayor Island, Tongariro, and possibly Mount Egmont sources. The tephras dated (Libby ages) are: Taupo Pumice (Wk215) 1730 ± 60 years B.P., Tuhua Tephra (Wk214) 6210 ± 70 years B.P., Mangamate Tephra (Wk213) 10 120 ± 100 years B.P., and Rerewhakaaitu Ash (2 dates) (Wk237) 14 700 ± 220 years B.P. and (Wk238) 14 700 ± 180 years B.P.

The identification of the tephras in Lake Maratoto extends the previously mapped distribution of North Island post-glacial (Holocene) tephras, and complements studies of soil genesis and weathering in the Waikato region. The core also provides a geochronological basis for further multidisciplinary studies of the paleolimnology, paleoclimate, and sedimentological history of the region.

Keywords pyroclastics; carbon dating; paleolimnology; late Quaternary; tephrochronology; Hamilton Basin; Lake Maratoto

INTRODUCTION

As part of an investigation of the paleolimnology of the small lakes in the Hamilton (or Middle Waikato) Basin a sediment core has been taken from Lake Maratoto near Hamilton (Fig. 1). The core reveals a succession of distal, well-preserved, discrete tephra

layers separated by organic lake sediment. In this paper the tephras are identified on the basis of their stratigraphic relationships and dominant ferromagnesian mineralogy. New radiocarbon dates are reported for 4 of them.

LAKE MARATOTO SAMPLE SITE

Lake Maratoto is one of a number of small lakes in the Hamilton Basin formed by aggradation of the ancestral Waikato River system (McCraw 1967). It occupies an embayment in low Pleistocene hills dammed by alluvium of Hinuera Formation (Hinuera-2) deposited mainly between 20 000 and 17 000 years ago (McGlone et al. 1978). The lake lies on the perimeter of the Rukuhia peat bog (Fig. 1) and is dystrophic. Its paleolimnology has been described by Green (in press).

The core was taken in 4 m of water from the northern end of the lake (N65/813353*) using a hand operated piston corer with 4 m of 60 mm I.D. PVC tubing. It was transported to the laboratory in the tube, split longitudinally, and sampled immediately.

DESCRIPTION AND STRATIGRAPHY OF THE CORE

The core, which was not compressed during sampling, comprises about 3 m of very fine grained brownish-black organic lake sediment (known as humic copropel, or dy) intercalated with at least 12 thin (2-40 mm) distinct layers overlying basal greenish-grey muds (Fig. 2). Most of the layers are pumiceous and highly vitric, occasionally finely bedded, and range from fine ash to very fine lapilli. Their total thickness is 20-25 cm. The layers, exceptionally well preserved and clearly distinguished from the dy by their contrasting colour and lithology, are unweathered and unmixed, and hence are considered as primary airfall tephra deposits.

The stratigraphy and dominant ferromagnesian mineralogy of the tephras, and their probable identification, are given in Fig. 2. The tephras can be readily related to volcanic source areas from their stratigraphy and mineralogical assemblages (as in

* Grid reference based on national thousand-yard grid of the 1:63 360 topographical map series (NZMS 1).

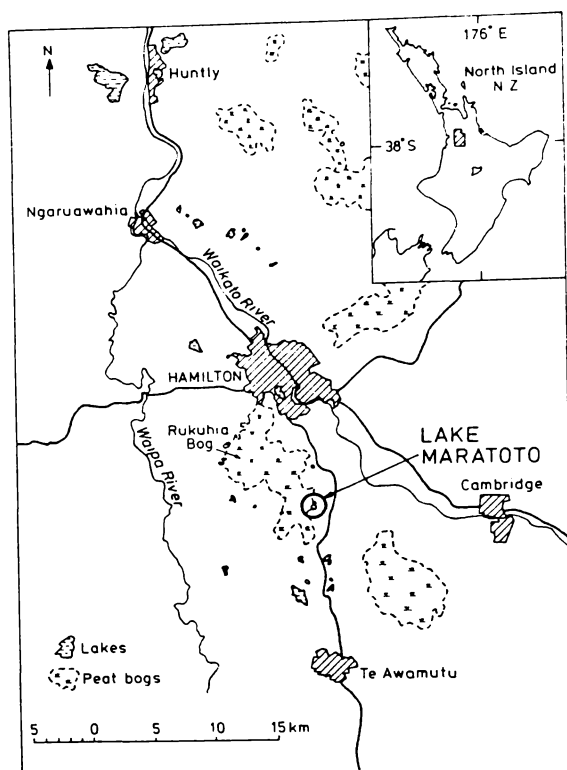


Fig. 1 Location of Lake Maratoto in the Hamilton (Middle Waikato) Basin.

Fieldes & Weatherhead 1968; Ewart 1971; Kohn 1973; Kohn & Neall 1973; Topping & Kohn 1973; Ewart et al. 1975; Kohn & Glasby 1978). Most of the tephrae originate from the Taupo and Okataina Volcanic Centres, and others are derived from Mayor Island, Tongariro, and possibly Mount Egmont sources. Further work to identify the unnamed deposits in Fig. 2 is proceeding.

When considered in conjunction with stratigraphic position, aegirine, cummingtonite, olivine, and biotite are useful as marker minerals for 4 of the tephrae. Aegirine is diagnostic of a peralkaline eruptive from Mayor Island (Hogg 1979) named Tuhua Tephra (Hogg & McCraw in prep. "Late Quaternary tephrae of Coromandel Peninsula, New Zealand: the Whangamata Ash"). Cummingtonite, which originates from the Haroharo Complex in the Okataina Volcanic Centre (Ewart 1971; Ewart et al. 1971; Kohn 1973; Ewart et al. 1975), occurs in moderate amounts (15%)* in 1 tephra which is

* Relative abundances (by point-count) expressed as a percentage of the total ferromagnesian silicate mineral assemblage in the 2-4 ϕ fraction.

tentatively identified as ?Rotoma Ash. Olivine, recognised in some eruptives in the Tongariro Volcanic Centre (Clark 1960; Ewart 1965; Wood 1976; Cole 1978), is abundant (34%) in the dark greyish-black tephra below Opepe Tephra (Fig. 2). This tephra is therefore considered to represent the Mangamate Tephra Formation of Topping (1973). The dark colour suggests that the Te Rato Lapilli Member is represented, but the ferromagnesian mineralogy also resembles that of the Poutu Lapilli Member. Consequently the actual member correlative for this tephra is still uncertain. Biotite is the dominant (38%) ferromagnesian mineral in the lowest tephra of the core and hence is correlated with Rerewhakaitu Ash (Cole 1970; Topping & Kohn 1973; Kohn & Glasby 1978).

CHRONOLOGY

To confirm the identifications of 4 of the tephrae, and to determine accurate rates of sedimentation in the lake, samples of dy were ^{14}C dated (Table 1). Slices 1 cm thick were extracted from immediately beneath Taupo Pumice (Wk215+), Tuhua Tephra (Wk214), and Mangamate Tephra (Wk213), and give maximum ages; 2 samples, one taken above (Wk237) and the other below (Wk238) Rerewhakaitu Ash, give identical minimum and maximum ages for this tephra (Table 1). Further radiocarbon dates are being determined.

Table 1 Radiocarbon ages of 4 tephra formations identified in the core from Lake Maratoto.

Tephra	^{14}C Age * Years B.P.	University of Waikato Radiocarbon Dating Laboratory No.
Taupo Pumice	1730 \pm 60	Wk215
Tuhua Tephra	6210 \pm 70	Wk214
Mangamate Tephra (?Te Rato Lapilli Mb.)	10 120 \pm 170	Wk213
Rerewhakaitu Ash	14 700 \pm 220 14 700 \pm 180	Wk217 Wk218

* Libby age based on mean life of 8033 years.

The youngest tephra in the core is Taupo Pumice, and the age determined (Table 1) is consistent with many other dates derived for this tephra elsewhere (Healy 1964). Similarly, a previous date on Tuhua Tephra of 6280 \pm 70 years B.P. (Wk106 from Hauraki Peat Bog, Hogg 1979) closely matches the date determined for this tephra in Lake Maratoto (Table 1).

† Numbers prefixed Wk refer to the University of Waikato radiocarbon dating laboratory number.

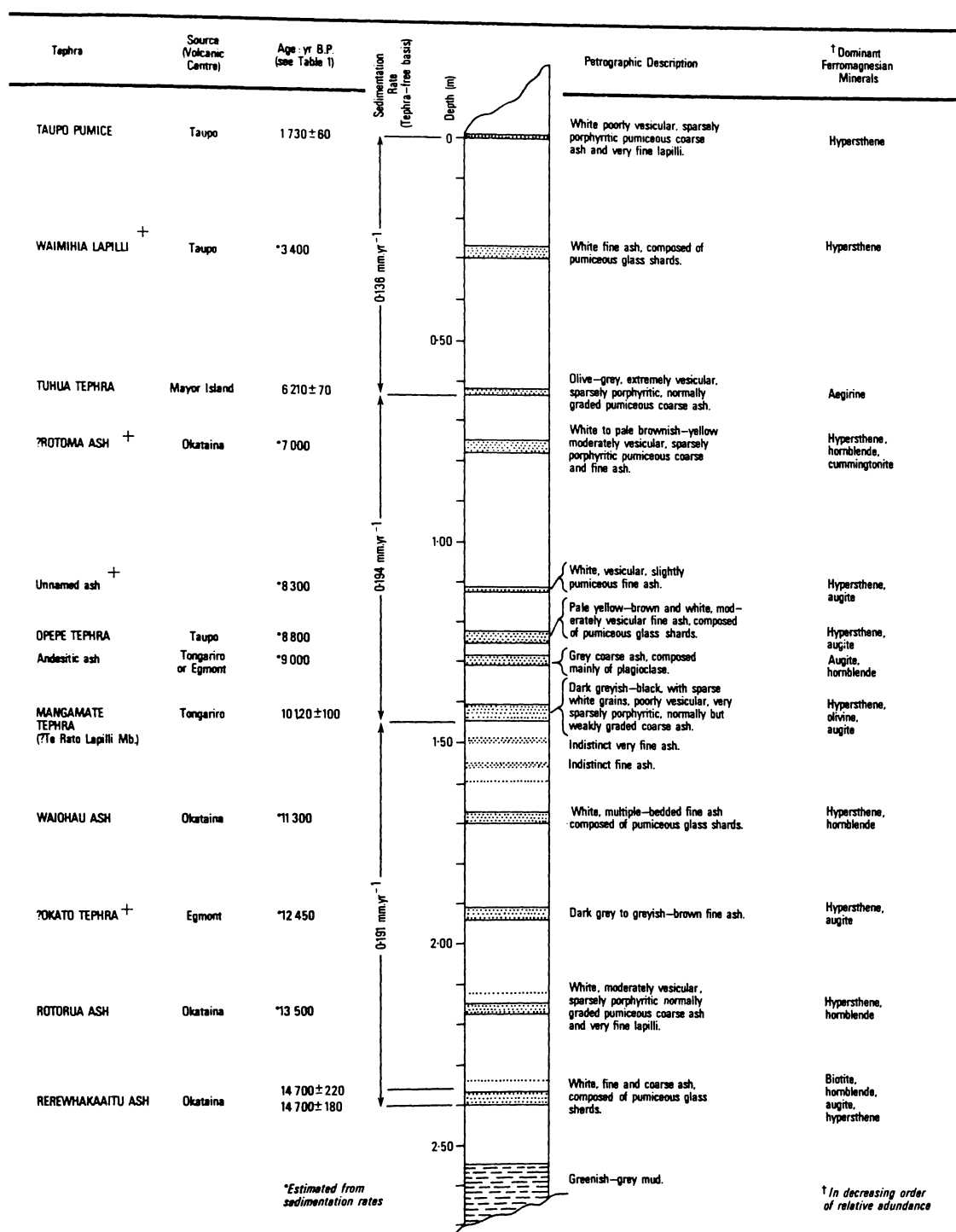


Fig. 2 Stratigraphy and chronology of late Quaternary tephtras in the Lake Maratoto core. Tephra layers shown in stipple.

+ See Postscript p.57

The date (Wk213) of $10\,120 \pm 100$ years B.P. for Mangamate Tephra Formation (?Te Rato Lapilli) in the Lake Maratoto core is only slightly older than an age (NZ1372) of 9780 ± 170 years B.P. given by Topping (1973) for the near-source Mangamate Tephra.

The only published date for Rerewhakaaitu Ash is (NZ716) $14\,700 \pm 200$ years B.P. (Pullar et al. 1973), identical to those (Wk237 and Wk238) from Lake Maratoto (Table 1).

Estimates of ages of other tephras are interpolated from sedimentation rates (assumed to be constant) between the dated sections of the core (Fig. 2). The identification of ?Rotoma Ash cannot be confirmed from the estimated age (near 7000 years B.P.) because previously published dates (Grant-Taylor & Rafter 1971; Pullar & Heine 1971; Pullar et al. 1973; Vucetich & Pullar 1973) on this tephra and the younger Mamaku Ash are ambiguous. The tentative identification of ?Okato Tephra is based mainly on an estimated age of about 12 450 years B.P. (Fig. 2) which matches a previously published date for this tephra of (NZ1143) $12\,550 \pm 150$ years B.P. (Neall 1975).

IMPLICATIONS AND FURTHER WORK

Identification of the tephras in Lake Maratoto enables tephra distribution to be extended beyond that mapped previously for the Waikato region (e.g., Pullar 1967; Vucetich & Pullar 1969; Pullar & Birrell 1973a; Pullar et al. 1973). Their occurrence also provides new information for pedological studies of soil genesis and weathering (Jessen 1977; Lowe 1979). The component tephric units of the Tirau and Mairoa Ashes, whose composite nature is well established (Gibbs 1968; Vucetich & Pullar 1969; Pullar & Birrell 1973b; Hodder & Wilson 1976; Pullar 1978) but only partly resolved at a few sites (Pullar & Birrell 1973b), are difficult to identify because of post-depositional mixing and weathering in the soil-forming environment. These problems, which tend to increase as the deposits thin with distance from source, do not occur in the Lake Maratoto environment where the tephras are remarkably preserved as unweathered and discrete units.

In addition, the tephrostratigraphy provides a geochronological framework for paleolimnological and palynological studies currently in progress on the post-glacial sedimentology, and climatic and biological history, of the Hamilton Basin.

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Postscript to Paper 1.

This paper was written early in the course of the research leading to the thesis, and several of the tephra identifications were provisional. Subsequent work has resulted in four modifications to the tephrostratigraphy reported in Paper 1: "Waimihia Lapilli" is re-identified as Whakaipo Tephra (Paper 4); "? Rotoma Ash" and "Unnamed ash" are re-identified as Mamaku Ash and Rotoma Ash, respectively (Paper 9); "? Okato Tephra" is re-identified as the basal lapilli unit(?) of the Okupata Tephra Formation (Paper 4).

PAPER 2

Application of impulse radar to continuous profiling of tephra-bearing lake sediments and peats: an initial evaluation.

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Application of impulse radar to continuous profiling of tephra-bearing lake sediments and peats: an initial evaluation

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Abstract Subsurface interface radar (SIR), or impulse radar, uses electromagnetic pulses for continuous stratigraphic profiling. It has been applied to lake sediments (dy-gyttja) and peat deposits containing a sequence of thin, late Quaternary, ash-grade tephra at Lake Maratoto, North Island, New Zealand. The SIR system is very rapid, precise, and reasonably accurate compared with conventional coring and probing methods, but still requires good stratigraphic control for reliable interpretation. Radar penetration depths of up to 10 m were attained. Interfaces between lake bottom and lake sediments and underlying volcanogenic materials of varying lithologies could be readily discerned, as could many of the tephra layers preserved within the lake sediments. Peat depths and positions of stumps or logs on the surface of the subpeat materials could also be determined. Given adequate calibration by drilling, the SIR system appears useful for various shallow subsurface exploration studies, particularly those involving tephrostratigraphy and paleoenvironmental reconstructions from limnic and peat deposits, and in projects on buried wood.

Keywords subsurface interface radar; radar methods; electromagnetic logging; pyroclastics; stratigraphy; lake sediments; peat; limnology; paleolimnology; Lake Maratoto; Rukuhia; bogs; organic materials

INTRODUCTION

This paper briefly describes and evaluates the first application in New Zealand of impulse radar to stratigraphic profiling of tephra-bearing lake sediments, peat, and some associated volcanogenic deposits. Impulse radar, known also as subsurface interface radar (SIR) or electromagnetic subsurface profiling (ESP), has only recently become available

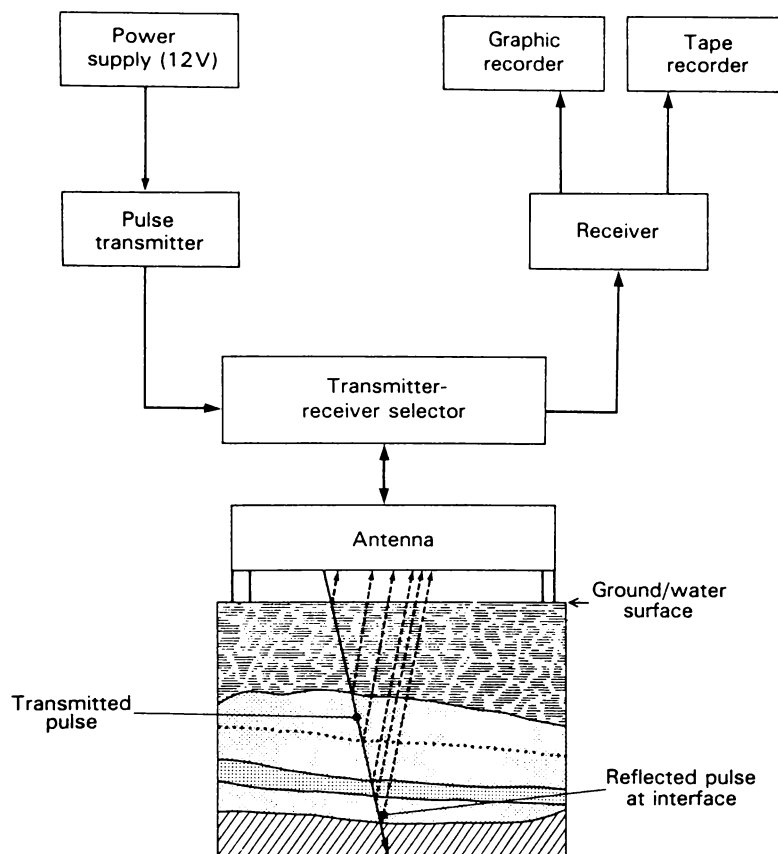
in New Zealand. It has, however, been used elsewhere since 1970 (Morey 1974), initially for civil engineering purposes but lately for other geoscience applications such as permafrost and ice thickness measurement, alluvial stratigraphy, lake and peat profiling, and subsurface erosion studies (e.g., Campbell & Orange 1974; Kovacs & Gow 1975; Davis et al. 1976; Kovacs 1977; Rossiter & Gustajtis 1978; Bjelm 1980; Ulriksen 1980, 1983; Leggo 1983; Arcone & Delaney 1984).

Conventional studies on peat and lake sediment stratigraphy and subsurface topography are done by laborious and costly drilling, coring, and probing methods (e.g., Davoren 1978; Green & Lowe 1985, this issue), or seismic profiling. Alternative methods such as peat penetrometer and electrical resistivity soundings have also been tried in New Zealand but with little success (Risk 1974). The SIR system, which functions like an echo-sounder but utilises electromagnetic pulses rather than sound waves, has been acclaimed as being extremely rapid and also accurate in shallow subsurface exploration studies (Bjelm 1980), and highly advantageous in providing a continuous subsurface profile. Consequently, it was seen as a potentially valuable tool for investigating the geomorphology of the shallow lakes and peat bogs in the Waikato region as part of the University of Waikato's programme of paleolimnological studies in northern North Island, New Zealand. In addition, the ability of SIR to detect the thin tephra layers preserved within the lake sediments and the peats was of particular interest because a series of profiles, with suitable stratigraphic and chronologic control, would possibly enable developmental stages of the lakes and peats to be accurately and rapidly mapped in both space and time. Thus, Lake Maratoto and the adjacent Rukuhia peat bog (Fig. 1), with a known subsurface geomorphology and tephrostratigraphy (Lowe et al. 1980; Green & Lowe 1985), were selected for a trial investigation of the capabilities of SIR. This study is necessarily only a preliminary evaluation because of limitations posed by the availability of the SIR equipment.

PRINCIPLES OF THE SIR METHOD

The SIR system can be considered the electromagnetic equivalent of single-trace acoustic profiling systems (Morey 1974). It radiates repetitive short-duration (1-6 ns) electromagnetic pulses (voltage

Fig. 2 Schematic block diagram of the impulse radar system (after Morey 1974).



which is usual, or from a knowledge of the electromagnetic parameters of the materials being investigated. The effective (average) propagation velocity through the material overlying a subsurface interface is derived from the relationship

$$v_m = \frac{2D}{t}$$

where D = measured depth to reflecting interface, t = elapsed time between transmitted and received pulse and, once known at one or more sites along a profile of similar deposits, can be used to determine D for other sites along that profile (Morey 1974). (For example, the average velocity through peat is about 0.4×10^8 m/s; Ulriksen 1980.) Another way of estimating v_m without drill calibration is the common point depth method (e.g., see Taner & Koehler 1969; Ulriksen 1980). The effective relative dielectric constant of the penetrated material can be derived from the relationship

$$\epsilon_r = \left(\frac{c}{v_m} \right)^2$$

where c = propagation velocity in free space (3×10^8 m/s). This is useful for getting an idea of the type of materials being probed and, because ϵ_r is affected by water, their moisture content (Morey 1974; Ulriksen 1980).

In peat bog studies, volumes of peat can be calculated from the areas of a series of profiles, with accuracies only slightly below those obtained by drilling methods (Ulriksen 1980).

The graphic recorder instrumentation, through an overlapping scale expansion facility, allows any desired ratio of vertical to horizontal scale (the vertical scale is typically greatly exaggerated). In practice, continuous profiling is done by towing the antenna on a sled over the ground surface, or floating it behind a boat on water, at a speed of about 5 km/h.

APPLICATION OF SIR AT LAKE MARATOTO

Investigation site and methods

Lake Maratoto (37°53'S 175°18'E) is a small peat lake up to 7.1 m deep lying on the eastern border of the Rukuhia peat bog near Hamilton (Fig. 1). Its stratigraphy and developmental history has recently been described in detail by Green & Lowe (1985). The lake was formed c. 17 000 years ago when alluvium (Hinuera Formation) deposited by the ancestral Waikato River dammed a southwest-draining embayment in low Pleistocene hills. The lake was initially shallow but for the past 11 000 years or so has been greatly affected by the growth of the Rukuhia bog, becoming deeper and dystrophic but probably maintaining a fairly constant area. The peat is now 8 m deep on the southwestern edge of the lake and up to 10 m deep in a narrow paleovalley to the north of the lake (Fig. 1B).

Between 2 and 3 m of fine-grained, organic-rich lake sediment (gyttja or dy-gyttja) has been deposited in the lake, the uppermost metre or so being peaty in character, and it contains numerous (c. 20) thin, distal, well-preserved tephra layers of 2–40 mm thickness and of mainly fine to coarse ash (Lowe et al. 1980). The 10 or so thickest tephrae are compact and clearly distinguished from the soft lake sediment by their contrasting colour and lithology (Fig. 3). The lake sediment is underlain by clays or muds or gravelly sands of the Hinuera Formation, or weathered gritty muds (mainly colluvium) derived from late Pleistocene tephrae overlying strongly weathered middle Pleistocene tephrae and volcanogenic deposits (Fig. 3; Green & Lowe 1985). Three or four diffuse tephra layers (each about 20 mm thick) can usually be detected, together with occasional woody fragments, in the peat column near the lake.

Four transects were made (Fig. 1B), two across Lake Maratoto (A–A', B–B') and two across the peat (C–C', D–D'). The detailed stratigraphy of the subsurface materials along these transects has been determined by intensive coring and probing as recorded in Green & Lowe (1985). An SIR System 4*, with a 3130 transducer, an antenna centre frequency of 120 MHz, and a pulse time of 3 ns, was used in each of the radar transects.

Lake transects

Sections of the radar profiles (radargrams) as obtained in the field are reproduced in Fig. 4. No subsequent processing has been done. The SIR system was able to clearly show: (1) the lake bottom

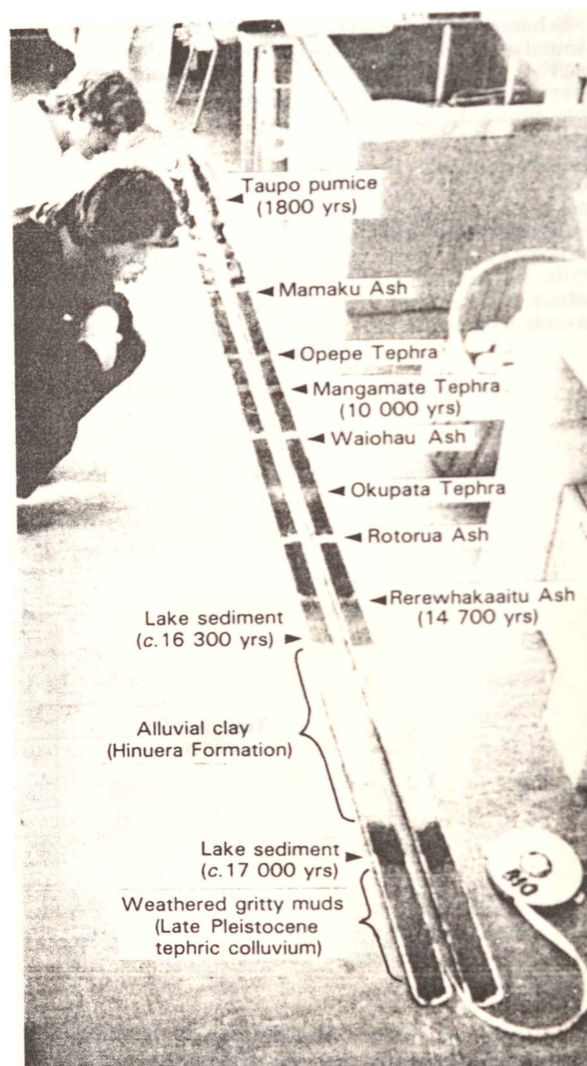


Fig. 3 A 3.3 m long longitudinally sliced core taken from the northern part of Lake Maratoto (Fig. 1B) using a modified Livingstone piston corer. Interfaces between the gross stratigraphic units were identified on the radar profiles along A–A' (Fig. 4). The stratigraphy and chronology of the core is after Lowe et al. (1980) and Green & Lowe (1985).

(Photo: R. R. Julian)

(i.e., the lake water – lake sediment interface); (2) the boundary between the lake sediments and the underlying materials; (3) multiple interfaces, assumed to correspond to some of the thicker, more compact tephra layers within the lake sediments; and (4) differences in the sublake sediment materials which, from prior knowledge through coring, could be appropriately designated as alluvial muds or clays ("smooth" or linear reflections in Fig. 4) (Hinuera Formation), or gritty muds ("blotchy"

*Geophysical Survey Systems, Inc., Hudson, U.S.A.

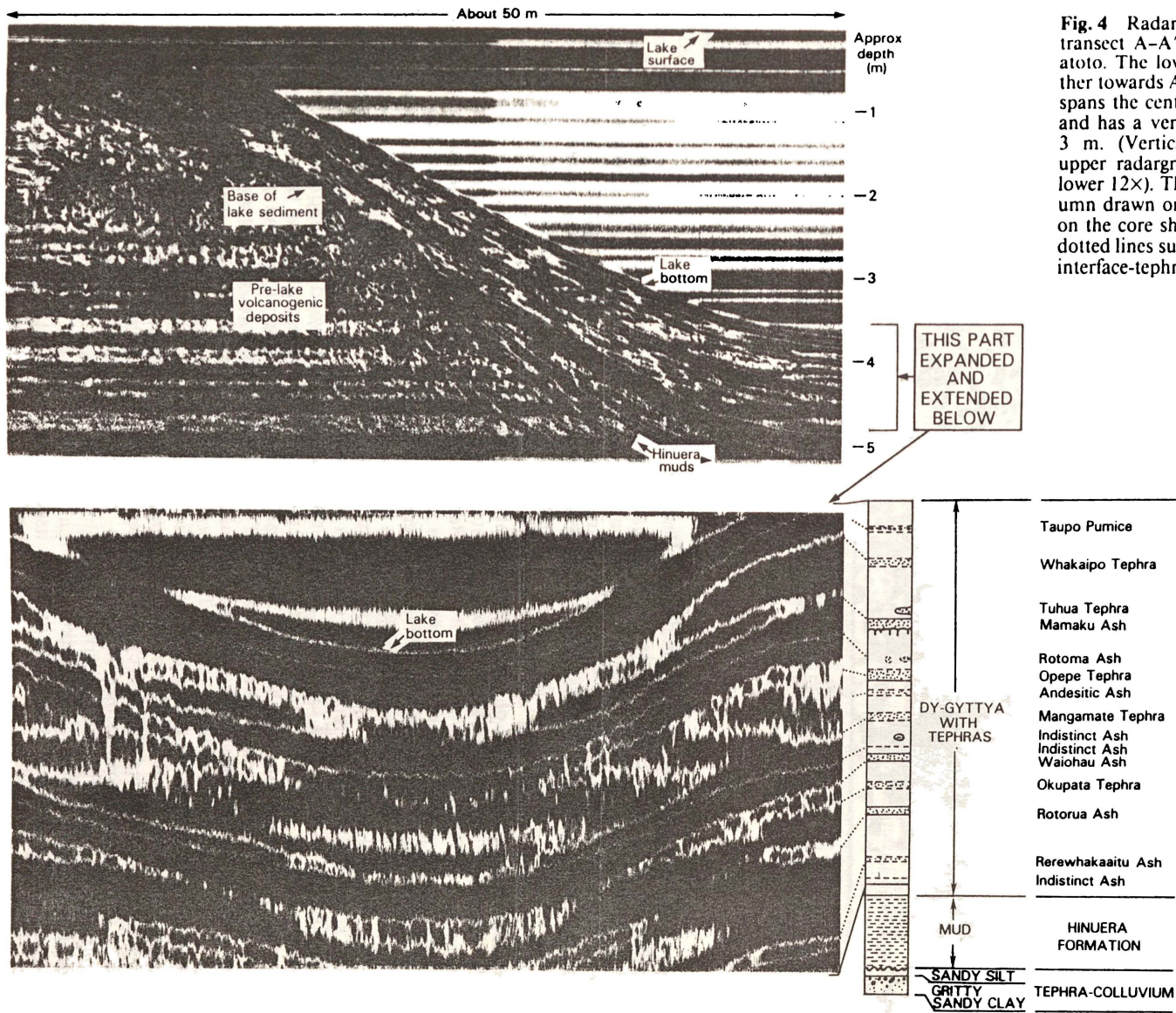


Fig. 4 Radar profiles of part of transect A-A' across Lake Maratoto. The lower radargram (further towards A along the transect) spans the central axis of the lake and has a vertical scale of about 3 m. (Vertical exaggeration of upper radargram is approx. 5X, lower 12X). The stratigraphic column drawn on the right is based on the core shown in Fig. 3. The dotted lines suggest some possible interface-tephra correlations.

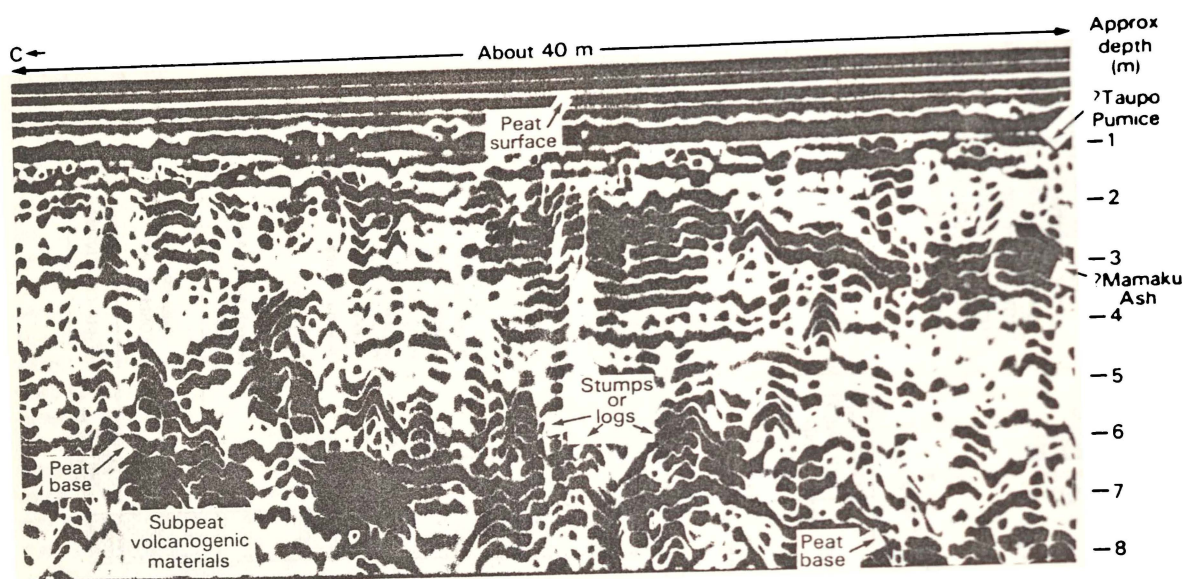


Fig. 5 Radar profile of part of transect C-C' about midway across an arm of the Rukuhia peat bog at Lake Maratoto (vertical exaggeration approx. 2×). The interface-tephra correlations are tentative suggestions only. Taupo Pumice occurs just below the water table.

reflections in Fig. 4) (weathered tephric colluvium and volcanogenic materials). Each of these different units is visible in the sediment core, shown in Fig. 3, which was taken from the centre of the lake along transect A-A' (core 4,1b of Green & Lowe 1985).

The total depth of penetration achieved was about 10 m (including up to 7 m of water plus 3 m of lake sediment); the depths closely matched those determined by Green & Lowe (1985). It was evident from scale expansion of the lake sediment parts of the profiles (as in the lower part of Fig. 4) that the tephra layers are often uneven in thickness but generally follow the shape of the basin topography. Not all of the tephra are represented right across the lake basin (cf. fig. 8 of Green & Lowe 1985). This is because the lake area contracted to about half its present size at c. 13 000 years ago due to marginal peat development (Green & Lowe 1985). Also, the depth of water in the lake (hence thickness of lake sediment) remained low (c. 2 m in the deepest part) until the Rukuhia bog began expanding rapidly from about 11 000 years ago. A series of accurately positioned SIR surveys would enable such features as paleoshorelines of the lake to be rapidly plotted using the spatial distributions of the identified tephra as chronologic markers (as achieved to a certain extent, but with far greater effort, by Green & Lowe 1985).

Peat transects

Peat profiles obtained by SIR (Fig. 5) were less clear than the lake ones, but enabled the peat-substratum interface to be readily mapped. Some gross stratification within the subpeat materials (i.e., tephric colluvium and older volcanogenic deposits) was also evident in the radargrams. The hyperbolic-shaped reflections on the subpeat surface are interpreted as stumps (possibly *in situ*) or logs. (Because of their form they are evidently exposed to the radar beam for a relatively long time and hence look bigger on the radargrams than they are in reality—Bjelm 1980; Ulriksen 1980.) Emergent stumps and logs are abundant on the Rukuhia bog in areas that have been drained and developed (cf. Cranwell 1939), and wood was frequently encountered at the base of the peat during the probing and coring around Lake Maratoto. One such large piece of wood, embedded in the uppermost subpeat materials at c. 6 m depth in a drillhole close to point C (Fig. 1B; Green & Lowe 1985), has been identified as rimu root wood, *Dacrydium cupressinum* (L. Donaldson, Forest Research Institute, pers. comm. 1983). It has an age of (Wk508) $12\,550 \pm 110$ years B.P. (old half-life), determined by the University of Waikato Radiocarbon Dating Laboratory (Hogg 1982). Within the peat column itself are several broad interfaces (spaced at 2 m or so depth intervals) that may correspond to changes

in the degree of peat humification (cf. Bjelm 1980) and/or water content. The diffuse tephra layers in the peat were not able to be made out with certainty, apart from two possible layers as indicated in Fig. 5. This may be due in part to considerable noise on the radargrams because of the coarse, occasionally fibrous and woody nature of the peat. Also, the tephra in the peat are more disseminated and have greater depth variability than their counterparts preserved in the fine lake sediments. Evidently, computer processing techniques that improve the signal-to-noise ratio and help in data interpretation have been developed by the SIR manufacturer (Morey 1974), but they were not available for this study.

The total depth of penetration achieved on the peat transects was about 8 m (including up to 8 m of peat) and corresponded closely with the depths obtained by probing. Repetitive profiling along the same transects gave consistent results.

CONCLUSIONS

This pilot study at Lake Maratoto, the first of its kind in New Zealand, was limited in scope, and the interpretations should properly be viewed cautiously. Nevertheless, the results confirmed many of the previously claimed attributes of the SIR system. SIR is very fast and precise, is reasonably accurate when compared with conventional techniques, and provides an instant, continuous subsurface profile. At Lake Maratoto, a total depth penetration of 10 m was achieved through a variety of materials including fresh water, peat, lake sediments, tephra, and water-saturated sediments ranging in texture from clays to gravelly sands. Apart from the clays, these materials are apparently well suited to SIR because their low conductivities cause minimal attenuation of the electromagnetic pulses; other materials may be less amenable to investigation by SIR (Morey 1974; Arcone & Delaney 1984).

Resolution of the SIR system was good enough to identify several different units making up the subsurface materials. It was particularly easy to map the lake bottom and to distinguish between the lake sediments and the coarser underlying materials. The depth of peat and the positions of stumps or logs on the subpeat surface were also readily determined. The apparent delineation by SIR of thin ash-grade tephra layers, of only a few centimetres thickness, in the fine-grained lake sediment is particularly impressive. The system could thus be very effective in various studies involving tephrostratigraphy, especially in mapping limnic and peat deposits for paleoenvironmental reconstructions, and in studies on buried wood.

As with most geophysical tools, data interpretation of SIR requires experience and at least some knowledge of the subsurface terrain under investigation. Hence, confident interpretations of the radargrams need good stratigraphic control, as was available in this study. With further refinements, such as the incorporation of computer processors (noise filters) and in-line 3-D block diagram plotters, the SIR system appears to offer considerable potential as a valuable tool for shallow subsurface exploration in New Zealand.

ACKNOWLEDGMENTS

I thank Dr J. D. Green, Mr K. Thompson, and Professor J. D. McCraw (University of Waikato) for their useful discussions and support in this study, and an anonymous reviewer for helpful comments on the manuscript. Mr L. Donaldson (Forest Research Institute, Rotorua) and Dr A. G. Hogg (Waikato Radiocarbon Dating Laboratory) are thanked for respectively identifying and dating wood sample Wk508. I acknowledge also the assistance of Strata Geophysics Ltd (Wellington) in obtaining the SIR profiles, and am especially grateful to Mr B. Davies for providing access to Lake Maratoto.

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Cross referencing to thesis papers

Green, J.D.; Lowe, D.J. 1985 = Paper 9

Lowe, D.J. *et al.* 1980 = Paper 1

PAPER 3

Detection of thin tephra deposits in peat and organic lake sediments by rapid x-radiography and x-ray fluorescence techniques.

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Workshop, June 30th - July 1st 1980, Victoria
University of Wellington. *Geology Department,
Victoria University of Wellington publication no. 20
74-77 (1981).*

R. Howorth, P. Froggatt, C. G. Vucetich,
J. D. Collen (Editors)

DETECTION OF THIN TEPHRA DEPOSITS
IN PEAT AND ORGANIC LAKE SEDIMENTS BY
RAPID X-RADIOGRAPHY AND X-RAY FLUORESCENCE TECHNIQUES

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ABSTRACT

This paper reports the application of the X-ray image process of X-radiography to unopened, small diameter organic sediment cores containing thin tephra deposits. Second, a rapid technique for detecting tephra layers in peat samples by X-ray fluorescence (XRF) analysis is described.

X-RADIOGRAPHY

X-radiography has been widely used in sedimentary petrology as an effective technique in the study of textural, structural, fabric and compositional differences in sediment cores and rocks (e.g., Baker & Friedman, 1969; Hamblin, 1971; Scott & Lewis, 1979; Stow, 1979). The method records on photographic film differences in absorption of radiation by various constituents when X-rays are transmitted through a sample, and has been recently applied to piston cores taken from shallow, peaty lakes in the Waikato region (Green, 1979; Lowe, *et al.*, 1980). Unopened cores encased in 60mm internal diameter PVC tubing were X-rayed in 50cm sections with a medical X-ray unit operated at 35 kV and 300 mA. Exposure time was 0.6 s with a focus-film distance of 90cm.

The X-radiographs reveal thin (<10mm), distinct and discrete, often finely-laminated tephra layers set in an essentially homogeneous matrix of very fine grained organic (humic copropel) lake sediments (Fig. 1). In positive prints, the tephtras show as dark layers in contrast to a pale greyish-white background representative of the organic deposits. Resolution is such that wavy, very fine (<0.5mm thick) silt laminae intercalated with organic material are clearly seen. Some of these thinly bedded layers are not apparent from visual inspection of the freshly opened, split core. Further, only part of each of the thicker or coarser tephtras is visible in the opened core. Both the lower and, particularly, upper portions of the deposit tend to be partly disseminated in the dark brownish-black organic sediments. Upon dehydration, the organic material cracks and shrinks away from the tephra layers which consequently become more clearly visible (Fig. 1b, c).

The X-radiographs thus provide rapid and accurate determination of tephra occurrence, stratigraphic position, and thickness. Similarly, the sedimentation rates of the organic material can be readily measured, and the fresh, unaltered organic deposits subsequently sampled accurately with respect to the tephra layers. The X-radiograph method is also advantageous in that it requires minimal sample preparation, it is non-destructive, and it provides a detailed visual record.

Future work will include assessment of a new X-ray image process, Xeroradiography (McMullin & van de Poll, 1979), which utilises a re-usable photo receptor plate instead of conventional X-ray film, and is claimed to improve further upon standard X-radiograph image definition, resolution and contrast.

XRF ANALYSIS

A rapid XRF technique has been devised and applied to studies on thin tephra deposits dispersed among organic material in peat cores from the Hauraki peat bog (Hogg, 1979; Hogg & McCraw, 1983). An air-dried core was sliced into 4cm-long sections which were crushed and then analysed by an energy dispersive ORTEC XRF unit for Fe and Si. The elemental count rates are shown in Fig. 2.

The peaks define the presence of inorganic material set in a background of organic deposits. The high Fe count rate for the Tuhua Tephra, as a solitary peak at 6m depth, is indicative of its peralkaline composition (Hogg & McCraw, 1983). In contrast, the high Si count rates at 1.5m and 2.3m depth, with negligible Fe peaks, correspond to deposits of calc-alkaline Kaharoa Ash and Taupo Pumice respectively. The high Si counts occurring at depths greater than 6m indicate thin layers of very fine and well sorted pure volcanic glass, and represent either overbank silt deposits from nearby rivers or very thin distal airfall tephtras.

The XRF method described is thus valuable for detecting thinly bedded tephric deposits disseminated in peaty or organic material, and, in this instance, for also distinguishing between the calc-alkaline and per-alkaline deposits.

ACKNOWLEDGEMENTS

Mr. A.O. Vallinga and the Waikato X-ray Clinic are gratefully thanked for X-raying the cores and processing the X-ray film negatives. Mr. R.R. Julian and colleagues (University of Waikato) are thanked for producing high quality positive X-radiograph prints.

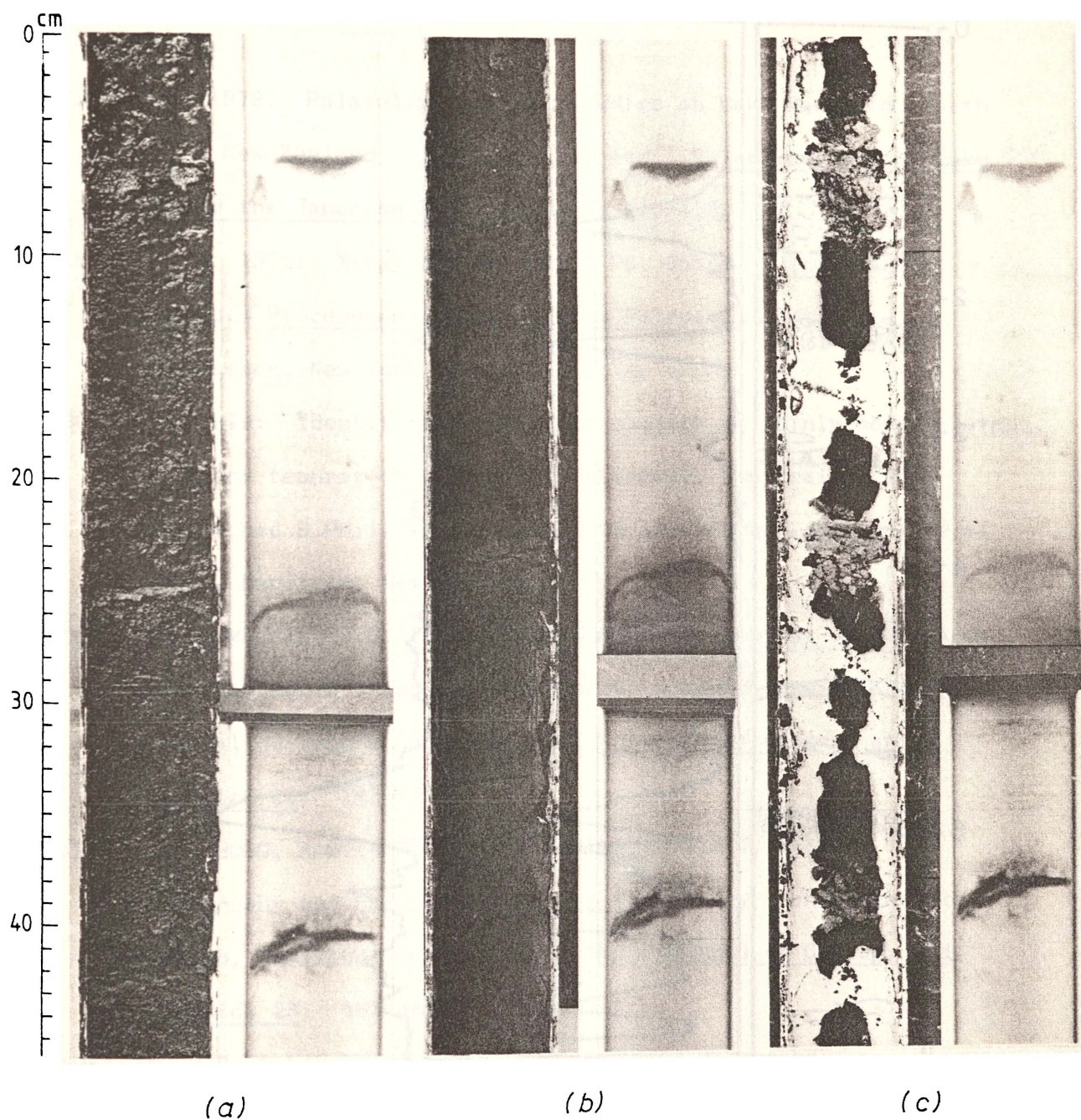


FIG. 1 - Photographs of opened small diameter (60 mm I.D.) organic sediment core (left) and matching X-radiograph (right) - (a) core freshly opened; (b) core dried 48 hours; (c) core dried two weeks. The X-radiographs reveal five possible tephra layers, three distinct (at 6, 25 and 40 cm depth) and two indistinct (at 32 and 36 cm depth). These become more evident in the core itself as the organic material dehydrates and contracts away from the tephtras.

The core is from Lake Mangahia, located ~10 km SW of Hamilton City. The top tephra layer is Taupo Pumice.

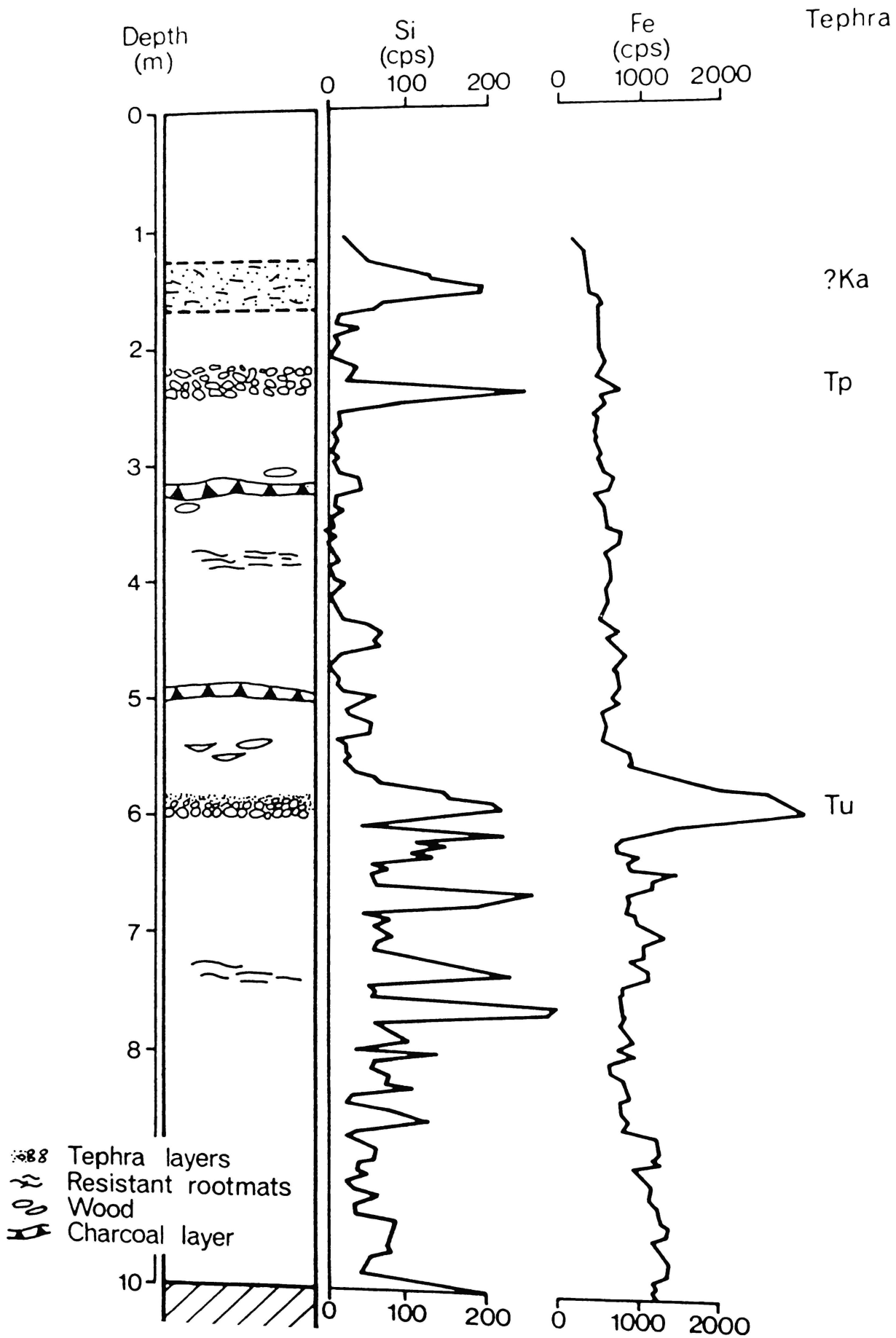


FIG. 2 - Schematic representation of a peat core from the Hauraki Peat Bog showing positions of ?Kaharoa Ash (Ka), Taupo Pumice (Tp) and Tuhua Tephra (Tu), and elemental count rates for Si and Fe from XRF analysis (after Hogg and McCraw, 1983).

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Cross referencing to thesis paper

Lowe, D.J. *et al.* 1980 = Paper 1

Footnote to Paper 3

Dr C.H. Hendy had the idea to try x-raying unopened cores using medical laboratory facilities. Dr A.G. Hogg devised the XRF method for detecting tephra occurrences in peaty sediments.

PAPER 4

Stratigraphy, age, composition, and correlation of late Quaternary tephra interbedded with organic sediments in Waikato lakes, North Island, New Zealand.

To be submitted to: *New Zealand journal of geology and geophysics.*

Stratigraphy, age, composition, and correlation of late Quaternary tephras interbedded with organic sediments in Waikato lakes, North Island, New Zealand

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Abstract

Cores from 14 peaty lakes in the central Waikato region, northern North Island, contain a sequence of 41 well-preserved, mainly macroscopic, occasionally bedded, ash and lapilli layers ranging in thickness from c.2-110 mm and interbedded with fine-grained organic lake sediment. The layers, whose field properties are described in detail, are distal airfall tephras that were erupted between c.17 000 and c.1800 ¹⁴C years ago from six rhyolitic and andesitic volcanic centres located c.70-200 km from the Waikato sites: Taupo (5 tephras), Okataina (7), Maroa (1) (rhyolitic); Mayor Island (2) (peralkaline); Tongariro (11), Egmont (15) (andesitic).

These sources are distinguished using the tephras' mineralogical assemblages and glass and mineral compositions (determined by electron microprobe) chiefly as follows:

Taupo - hypersthene ± augite, sodic plagioclase, glass with rhyolitic composition (part analysis mean weight % ± 1 standard deviation: TiO₂ 0.20 ± 0.04, FeO* 1.66 ± 0.15, MgO 0.17 ± 0.04, CaO 1.26 ± 0.13); **Okataina** - hornblende + hypersthene + augite ± cummingtonite ± biotite, sodic plagioclase, glass with rhyolitic composition (tephras other than Rotorua

Ash: TiO_2 0.11 ± 0.04 , FeO^* 0.90 ± 0.08 , MgO 0.11 ± 0.02 , CaO 0.78 ± 0.07 ;
 Rotorua Ash: TiO_2 0.21 ± 0.04 , FeO^* 1.30 ± 0.14 , MgO 0.21 ± 0.05 , CaO 1.26 ± 0.23); **Maroa** - glass with rhyolitic composition (TiO_2 0.07 ± 0.03 , FeO^* 0.87 ± 0.18 , MgO 0.07 ± 0.02 , CaO 0.68 ± 0.09); **Mayor Island** - aegirine \pm aenigmatite \pm riebeckite \pm olivine, alkali feldspar, glass with peralkaline composition (peralkaline index 1.33 ± 0.1); **Tongariro** - clinopyroxene($\text{Wo}_{42\pm 2}$) + orthopyroxene \pm olivine, calcic plagioclase, Fe-Ti oxides with high Cr_2O_3 (c.0.2-0.3%) and low MnO (c.0.3-0.5%), glass with andesitic composition (SiO_2 $61.38 \pm 2.41\%$); **Egmont** - clinopyroxene($\text{Wo}_{45\pm 2}$) + hornblende \pm orthopyroxene, calcic plagioclase, Fe-Ti oxides with low Cr_2O_3 (<c.0.05%) and high MnO (c.0.5-1.0%), glass with rhyolitic-dacitic composition low in SiO_2 ($70.46 \pm 2.19\%$) and high in K_2O ($4.32 \pm 0.76\%$).

The tephras are correlated with named proximal eruptives using their stratigraphic relationships and radiometric ages (based on multiple ^{14}C dates on enclosing lake sediment) in combination with the mineralogical and chemical criteria. The correlated tephras associated with each source, and the ages adopted (years B.P., old $T\frac{1}{2}$ basis), are: **Taupo** - Taupo (c.1800), Mapara (c.2200), Whakaipo (c.2800), Hinemaiaia (c.4500), Opepe (c.8900); **Okataina** - Whakatane (c.4800), Mamaku (c.7000), Rotoma (c.8500), Waiohau (c.12 200), Rotorua (c.13 300), Rerewhakaaitu (c.14 700), Okareka (c.17 000); **Maroa** - Puketarata (c.14 000); **Mayor Island** - Tuhua (c.6200), uncorrelated (c.14 500); **Tongariro** - Mangamate (?Te Rato Lapilli) (c.9950), Okupata (8 informal units Oa-1 to Oa-8: c.10 100, c.10 500, c.10 800, c.11 050, c.11 200, c.11 700, c.12 100, c.12 700), uncorrelated (c.13 100), Rotoaira (c.13 700); **Egmont** - 15 informal units Eg-1 to Eg-15 (c.2500, c. 3700, c.3750, c.4100, c.4400, c.5250, c. 5850, c.5900, c. 9300, c.9600, c.10 100, c.11 050, c.14 500, c.15 000, c.15 500).

In total, the post c.15 000 year-lacustrine tephras range in thickness from c.20 cm (possibly equivalent to c.37 cm on dry land because of compaction or dissemination in the lakes) in the north of the study area,

to c.25 cm (c.47 cm on dry land) in the south, to c.42 cm (c.78 cm on dry land) in the east. Of these total thicknesses, rhyolitic tephra predominate (c.65-95%); andesitic tephra are more common in the south (c.30-35%), decreasing markedly to the north (c.10-15%) and east (c.5%). These different proportions of andesitic to rhyolitic material may have influenced weathering and argillisation in the tephra-derived soils in the Waikato area.

New, provisional isopach maps for eleven tephra (Whakaipo, Eg-2, Tuhua, Mamaku, Rotoma, Opepe, Mangamate, Waiohau, Oa-8, Rotorua, Rerewhakaaitu) are presented. The thickness resolution of these is generally one to two orders of magnitude greater than in most previous isopach maps in New Zealand, and attests to the value of utilising lake sediments for tephra mapping. Most of the tephra found in the Waikato lakes should persist well beyond the Waikato area. Extrapolated plots of isopach thickness against distance from isopach centre suggest that c.1 mm-isopachs should occur c.200-300 km from source. Many of the tephra were probably emplaced by powerful eruptions (possibly including directed blasts), or were dispersed by strong winds, or both. In some instances, co-ignimbrite ash may have contributed to the resultant lacustrine tephra deposits.

The 41 tephra identified in the Waikato lake cores record, on average, an eruptive event every c.400 years (rhyolitic, 1 per c.1100 years; andesitic, 1 per c.650 years). A number of the tephra, particularly Taupo, Tuhua, Mamaku, Opepe, Mangamate, Waiohau, Rotorua, Rerewhakaaitu, and Okareka, are useful as time-stratigraphic markers in multidisciplinary palaeoenvironmental studies on the lakes and catchments.

Keywords stratigraphy, late Quaternary, tephrostratigraphy, tephrochronology, distal tephra, tephra composition, radiocarbon dates, ferromagnesian mineralogy, glass chemistry, isopach maps, North Island volcanoes, Waikato lakes, palaeolimnology, "Tirau Ash", "Mairoa Ash".

INTRODUCTION

The central Waikato region is upwind and well to the north and northwest of the main tephra-producing volcanoes of central North Island (Fig.1; McCraw 1975). Consequently, most of the late Quaternary airfall tephra deposits found there are relatively thin and have been hard to differentiate. Early reconnaissance mapping of the tephras, chiefly for soil survey purposes, separated two main soil-forming materials which were named Mairoa Ash and Tirau Ash (Grange 1931; Grange & Taylor 1932; Taylor 1933; Grange et al. 1939; N.Z. Soil Bureau 1954). Although each of these deposits was believed to be composed of materials derived from several eruptions, they were arbitrarily named "Ash", rather than "Ashes" or "Ash Beds", for purposes of soil description and classification (Taylor 1953; Gibbs 1968; Gibbs et al. 1982). Tirau Ash, considered to be primarily but not wholly rhyolitic, formed the parent material of soils in eastern parts of the Waikato; Mairoa Ash, thought to contain a greater component of andesitic ash beds of an intermittent origin, extended westward from the Tirau Ash boundary to the west coast (Fig.1). Taupo Pumice was recognised in soil profiles as far north as Putaruru (Grange & Taylor 1932), and as a discrete lapilli layer near the surface of the Rukuhia and Moanatuatua peat bogs by Grange et al. (1939) (see also Tonkin 1967).

More recent studies on stratigraphic sections and soil profiles in the Waikato and adjoining districts (e.g., Pullar 1967, 1978; N.Z. Soil Bureau 1968; Vucetich 1968; Vucetich & Pullar 1969; Pullar & Birrell 1973a,b; Pullar et al. 1973; Hodder & Wilson 1976; Hodder 1978; Lowe 1979, 1981a; Orbell 1982; Parfitt et al. 1982a) confirmed the composite nature of the Mairoa Ash and Tirau Ash, and identified some of the tephras making up the deposits at a number of sites. These identifications were achieved either by careful hand-over-hand field methods (e.g., Vucetich & Pullar 1969; Pullar & Birrell 1973b), or by mineralogical and geochemical methods

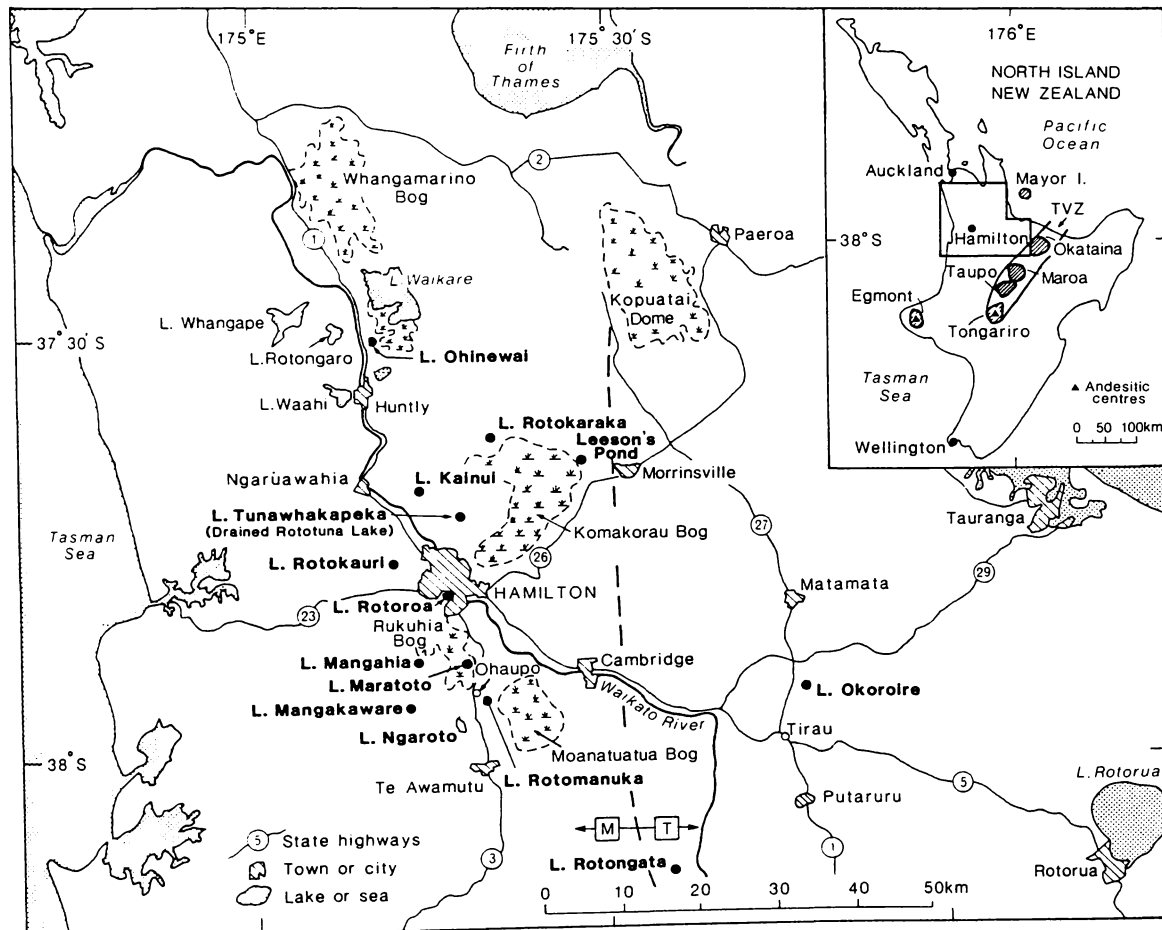


Fig.1. The central Waikato area showing the locations of the lakes cored in this study (bold). Some other lakes and peat bogs are also shown. The dashed line marks the approximate boundary of the two main soil-forming materials described in early soil surveys as "Mairoa Ash" (M) and "Tirau Ash" (T) (after N.Z. Soil Bureau 1954). The inset shows the locations of tephra-producing rhyolitic and andesitic volcanic centres active in the late Quaternary period (after Cole & Nairn 1975 and Hogg & McCraw 1983). TVZ = Taupo Volcanic Zone. Note: Mt. Egmont is also known as Mt. Taranaki.

based on laboratory analyses (e.g., Hodder & Wilson 1976; Lowe 1981a; see also Hogg & McCraw 1983).

Both these approaches have limitations, however. The chief difficulties in the field arise from the loss of identifying characteristics as individual tephras thin away from source towards the Waikato area, collapsing into composite beds (Pullar 1967), and from the masking effects of post-depositional erosion, mixing, and weathering in the soil-forming environment. In the laboratory, detailed grain-by-grain "fingerprinting" methods circumvented these problems to some extent, but relatively few tephras were identified with certainty.

An additional complication has been the necessity to consider the proposal that loess contributed significantly to the surficial deposits in some parts of the region (McCraw 1967; Vucetich 1968; Cowie & Milne 1973). However, this proposal was largely discounted by Lowe (1981a, p.311-313)*.

The obtaining of a 3.2 m-long sediment core from Lake Maratoto, a small peaty lake near Ohaupo (Fig.1), heralded a new approach to elucidating the late Quaternary tepthrostratigraphy of the Waikato area. The core contained a succession of multiple, essentially unweathered, discrete tephra layers separated from one another by fine-grained organic lake sediment (Green 1979; Lowe et al. 1980). Most of the tephras, aged \leq c. 15 000 years,¹ were identified (some tentatively) by their dominant ferromagnesian mineralogy, their stratigraphic position, and by five radiocarbon dates (the first to be obtained on airfall tephras in the Hamilton Basin). Lowe et al. (1980) showed that some of the tephras were derived from Mayor Island, Tongariro, and possibly Mt. Egmont sources in addition to Okataina and Taupo volcanic centres (Fig.1, inset). The core thus revealed that "Mairoa Ash" in the Ohaupo area was likely to contain many more tephras than had previously been considered present, and that these were derived from a variety of North Island volcanic centres (Lowe 1981b).

* See also Lowe, D.J. (1980): Tephric loess. *N.Z. soil news* 28: 217-220.

1. All ages discussed in the text are conventional ages based on the Libby (old) half-life of 5568 years (Hogg et al. 1987).

Since this first core was taken from Lake Maratoto, a further 13 lakes², and several peat bogs, in the Waikato region have been cored (Fig.1) to give a wider picture of tephra occurrence and distribution. The initial findings of Lowe et al. (1980) for Lake Maratoto were partly modified (some tephras were re-identified) and further cores examined in more detail by Green & Lowe (1985). Three diffuse ash layers within gritty muds (colluvium) underlying the lake sediments in some of these cores were analysed by Green & Lowe (1985): the upper two beds (c.10-20 cm thick) were tentatively identified as Hauparu and Tahuna tephras, the lower as Rotoehu Ash (c.30 cm thick). Further data on these three late Pleistocene tephras are to be reported elsewhere. Some analyses of cores from the other Waikato lakes have been reported by Lowe et al. (1981), Lowe (1986a,b,c), and Hogg et al. (1987).

The aim of this paper is to summarise the field properties, stratigraphy, chronology, and composition of the late Quaternary tephras contained in sediments in cores from the lakes in the central Waikato region. The lacustrine tephras described range in age from c.1800-17 000 years B.P., and were erupted from a total of six volcanic centres of both rhyolitic and andesitic composition (Fig.1). Using multiple criteria, the tephras are identified and correlated with named eruptive units elsewhere. The pattern of distribution of the tephras and their emplacement mechanisms are also considered. New isopach maps are presented.

The use of such lake sediments or peats to erect a comprehensive tephrostratigraphy is unusual, and the Waikato lakes have provided the longest and most complete sequence of tephras yet investigated in New Zealand lakes or bogs (cf. Druce 1966; Pullar 1970; Topping 1973; Topping & Kohn 1973; McGlone & Topping 1977; Stewart et al. 1977; Kennedy et al.

2. Several other Waikato lakes, including Hakanoa and Waahi, have also been cored but are not considered here as they are much younger, being formed c.1800 years ago as a result of the deposition of Taupo Pumice Alluvium (Lowe & Green 1987).

1978; Howorth et al. 1980; Kohn et al. 1981; Franks 1984; Lowe & Hogg 1986; Neall & Alloway 1986). Apart from Iceland (e.g., Thorarinsson 1981a), studies specifically on tephras in bogs and lakes overseas have also been relatively sparse, particularly from sites containing more than just a few tephras, but are becoming increasingly important (e.g., see Borchardt et al. 1973; Westgate 1977; Mathewes & Westgate 1980; Fisher & Schmincke 1984; Mangerud et al. 1984; Mehringer et al. 1984; Davis 1985; Riehle 1985).

WAIKATO LAKES AND BOGS

Most of the small, typically peaty lakes in the central Waikato region originated c.15 000-17 000 years ago, during the final stages of alluvial aggradation of the Hinuera Formation by the ancestral Waikato River (McCraw 1967; Green & Lowe 1985; Lowe & Green 1987). The lakes were formed when antecedent valleys draining low Pleistocene hills were blocked off by the volcanoclastic Hinuera deposits, which dammed the valley mouths. The lakes are shallow (<c.8 m) and usually contain around 3-4 m (occasionally 5-6 m) of soft, brownish-black (peaty) to olive-grey lacustrine muds or clays (known as dy or gyttja) containing the remains of small lake-dwelling plants and animals. They have low sedimentation rates (c.0.1-0.2 mm.yr⁻¹) (Green 1979; Boubée 1983; Green & Lowe 1985). Occasionally vivianite is found in the sediments.

The subsequent development of many of these lakes has been affected by the massive growth of large, c.10-12 m-deep ombrogenous peat bogs on the surface of the Hinuera sediments (e.g., see Fig.1 and Davoren 1978). These bogs probably formed first in patches in swampy hollows and around the margins of shallow lakes (such as Lake Maratoto) on the Hinuera surface (McCraw 1967). They rapidly expanded and deepened after c.10 000-12 000 years ago, probably in response to a net increase in rainfall and hence rise in regional water tables (Green et al. 1984; Green & Lowe 1985).

Lakes vs. bogs as tephra recorders

The record of tephra fallout provided by the Waikato lakes is more comprehensive than that of the adjacent peat bogs. Usually only about six or so disseminated tephras, chiefly from substantial rhyolitic eruptions, are detectable in the peat cores.* For tephrostratigraphic purposes, the lakes are advantageous in that:

- (1) they are older hence contain a longer record;
 - (2) they have soft, fine sediment and (in the deeper basins) a relatively undisturbed environment that has allowed the preservation, as separate units, of deposits only a few millimetres in thickness;
 - (3) the continuous lake cores provide unequivocal stratigraphic control.
- Nevertheless, the tephrostratigraphy of the peat bogs is useful where lakes are lacking, especially in mapping and dating tephras not otherwise identifiable in subaerial environments (e.g., Hogg & McCraw 1983). Most results of the peat coring are excluded from this paper, but some preliminary findings are given in Green & Lowe (1985) and Hogg et al. (1987) (see also Tables 4 and 10).

CORING SITES AND METHOD

Locations of the lakes cored in this study are shown in Fig.1. (Grid reference locations are given in Fig.2.) Around 80 cores, usually c.2-4 m in length, were obtained from the lakes with a hand-operated, modified Livingstone piston sampler (after Rowley & Dahl 1956; see also D.J.Lowe & J.D.Green in prep. "Origins and ages of Waikato lakes based on radiocarbon-dated sediment cores and tephrochronology"). The coring tubes comprise lengths of PVC pipe of 50 mm internal diameter that were previously sawn in half longitudinally and held together with waterproof plastic tape. After the coring operation, the cores were split longitudinally using fine wire.

* These include Taupo, Mamaku, Rotoma, Waiohau, and Rotorua tephras in the Hamilton Basin and, in addition, Kaharoa and Whakatane tephras in the Matamata Basin.

Normally, several cores were taken from each lake, usually from the deepest areas, but occasionally from sites in shallower water or at the shoreline.

STRATIGRAPHY AND FIELD PROPERTIES OF THE TEPHRAS

The stratigraphy and main field properties of the tephras in the lake cores are summarised in Table 1 and Fig.2. The stratigraphic sequence, thickness, lithology, and bedding characteristics of the tephra layers are practically identical in all of the lakes examined, hence they are regarded as representing primary airfall tephras. Further support for an airfall origin is given by Lowe (1985) in that the tephras in Lake Maratoto, although uneven in thickness, are laterally continuous and generally follow the lake basin topography. It is possible that some of the tephric material derives from co-ignimbrite ash fall (see Walker 1981a and the section on tephra distribution and implications below).

Most of the tephra layers can be readily correlated from core to core and from lake to lake using their field properties and stratigraphy (e.g., Plate 1). The sources and identifications of the tephras given in Fig.2 and Table 1 are based on their mineralogical and chemical composition and their age, as described in later sections, together with their stratigraphic relationships.

Tephra properties

Generally, most of the tephras occurring within the lake sediment are compact, macroscopic layers ranging in thickness from c.2 mm to c.110 mm. The layers are usually continuous (i.e., go right across the core), but occasionally they are partly dislocated or appear as ashy "pods" within the sediment. Upper contacts are commonly smooth in appearance but the adjacent overlying sediments usually contain indistinct ash grains disseminated over

some millimetres; the lower contacts are often irregular and wavy (Plate 1; see discussions below on tephra thickness and bioturbation).

The thicker tephras, i.e., more than c.5-10 mm, are typically pale coloured (white or grey, sometimes stained yellowish-orange) and stand out against the darker lake sediment (Plate 1; see also fig.3 in Lowe 1985). They are usually glassy, pumiceous, and of rhyolitic origin. (An exception is the Mangamate Tephra which is greyish-black and andesitic.) Texturally, they range from fine ash (<c. 1/16 mm) to fine lapilli (c.2-4 mm), but commonly comprise medium (c. 1/16 - $\frac{1}{2}$ mm) or coarse (c. $\frac{1}{2}$ - 2 mm) ash. Normal or multiple graded bedding occurs frequently (e.g., Plates 2A,B), especially in beds \geq c.15 mm thick. Reverse grading is rare, however. Generally, these thicker tephras are the most distinctive and thus the most useful sediment markers in the cores. They include Taupo, Tuhua, Mamaku, Opepe, Mangamate, Waiohau, Rotorua, Rerewhakaaitu, and Okareka tephras (Fig.2; Green & Lowe 1985).

The thinner tephra beds, i.e., less than c.5 mm, are commonly darker coloured (dark grey, brown), often speckled and more crystal rich, rather indistinct, and of andesitic origin. The dark colour in some cases is due to staining by lake sediment. Some beds are greyish-white and yellowish-brown and can be either andesitic or rhyolitic in composition. Generally, these thinner beds consist of fine or medium to coarse ash and usually show little or no graded bedding, being well sorted.

Other tephras occur as diffuse, gritty zones in the lake sediments that may span up to c.100 mm, or as very thin (<c. 1-2 mm), virtually microscopic layers best seen by x-radiography (Plate 3; Lowe et al. 1981, fig.1).

Table 1. Composite stratigraphic column of late Quaternary tephras identified in cores from Waikato lakes. Some identifications are provisional.

Tephra and Symbol (see Fig. 2)†	Source (see Fig. 1)	Group- Subgroup #	Age (years B.P., old T $\frac{1}{2}$)*	General description and approximate thickness range; comments
Taupo Pumice, Tp	Taupo	1	1800	Yellowish fine lapilli & coarse ash, 5-50 mm thick
Mapara Tephra, Mp	Taupo	1	2200	White fine ash, 2-3 mm
Egmont-1, Eg-1 ^a	Egmont	-	2500	Grey fine-medium ash, 3-5 mm
Whakaipo Tephra, Wo	Taupo	1	2800	Greyish-white fine ash, 2-10 mm
Egmont-2, Eg-2	Egmont	-	3700	Brownish-grey, slightly speckled medium-coarse ash, 3-5 mm
Egmont-3, Eg-3	Egmont	-	3750	Indistinct fine ash, 1-2 mm (found only in L. Okoroire)
Egmont-4, Eg-4	Egmont	-	4100	Dark, medium-coarse ash, 1-3 mm; blotchy
Egmont-5, Eg-5	Egmont	-	4400	Pale yellowish-white, brownish-speckled, fine-medium ash, 3-6 mm
Hinemaiaia Tephra ^b , Hm	Taupo	1	4500	White fine ash, 1-8 mm
Whakatane Ash, Wk	Okataina	2	4800	White fine-medium ash, 10-12 mm in L. Okoroire; possibly microscopic in other lakes
Egmont-6, Eg-6	Egmont	-	5250	Yellow fine ash, 2-3 mm
Egmont-7, Eg-7	Egmont	-	5850	Greyish-brown fine-medium ash, 1-2 mm
Egmont-8, Eg-8	Egmont	-	5900	Indistinct pale yellow fine ash, 1-2 mm
Tuhua Tephra, Tu	Mayor Is.	3	6200	Olive, greenish-grey fine-coarse ash, 5-45 mm
Mamaku Ash, Ma	Okataina	2	7000	Pale yellowish-brown to orange, fine-coarse ash, 20-80 mm; usually bedded
Rotoma Ash, Rm	Okataina	2	8500	Pale yellowish-white fine ash, 3-30 mm
Opepe Tephra, Op	Taupo	1	8900	Greyish fine ash, 10-20 mm (medium-coarse ash in L. Okoroire)
Egmont-9, Eg-9	Egmont	-	9300	Yellowish-white, speckled medium ash, 1-3 mm; may be disseminated (c.10 mm); age approx.
Egmont-10, Eg-10	Egmont	-	9600	Yellowish medium ash, 1-2 mm; age approx.
Mangamate Tephra, Mm ^c	Tongariro	4	9950	Mainly greyish-black, white speckled base, coarse ash, 5-20 mm; scoriaceous
Okupata Tephra, Oa-1 ^d	Tongariro	4	10 100	} Pale grey fine ash, 2-3 mm
Egmont-11, Eg-11	Egmont	-	10 100	
Okupata Tephra, Oa-2	Tongariro	4	10 500	Indistinct brownish fine-medium ash, 1-2 mm; age approx.
Okupata Tephra, Oa-3	Tongariro	4	10 800	Indistinct brownish fine-medium ash, 1-2 mm; age approx.
Okupata Tephra, Oa-4	Tongariro	4	11 050	} Greyish-white, speckled, mainly medium-coarse ash but some fine ash, 4-5 mm
Egmont-12, Eg-12	Egmont	-	11 050	

Okupata Tephra, Oa-5	Tongariro	4	11 200	Pale greyish-white fine ash, 2-3 mm; age approx.; contains traces of Eg-tephra(?)
Okupata Tephra, Oa-6	Tongariro	4	11 700	Yellowish fine ash, 2-3 mm; may be blotchy or disseminated (c.5-10 mm)
Okupata Tephra, Oa-7	Tongariro	-	12 100	Indistinct brownish fine ash, 1 mm; age approx.
Waiohau Ash, Wh	Okataina	2	12 200	White with cream top, fine-medium ash, 10-45 mm; commonly bedded
Okupata Tephra, Oa-8 ^d	Tongariro	4	12 700	Greyish-brown to brown fine ash, 5-20 mm; occasionally disseminated (c.50 mm)
uncorrelated, un	Tongariro	4	13 100	Brownish-grey fine-coarse ash, 3-5 mm; occ. bedded; age approx.
Rotorua Ash, Rr	Okataina	2	13 300	White mainly coarse ash, 15-110 mm; distinctly bedded (see Plate 2)
Rotoaira Lapilli, Rt	Tongariro	4	13 700	Greyish fine-medium ash, 2 mm; usually disseminated (c.30 mm); age approx.
Puketarata Ash, Pk	Maroa	-	14 000	Indistinct disseminated fine ash; contains traces of Eg-tephra(?); age approx.
Egmont-13, Eg-13	Egmont	-	14 500	Indistinct pale yellowish-brown fine to v. fine ash; Mayor Is. tephra occurs as glass only (microscopic); ages approx.
uncorrelated, un	Mayor Is.	3	14 500	
Rerewhakaaitu Ash, Rk	Okataina	2	14 700	White fine-coarse ash, wavy boundaries, 5-30 mm; some biotite flakes visible
Egmont-14; Eg-14	Egmont	-	15 000	Brownish, white-speckled coarse-medium ash, 1-2 mm
Egmont-15, Eg-15	Egmont	-	15 500	Brown fine ash, 1 mm; age approx. (see text & Fig. 3)
Okareka Ash, Ok	Okataina	2	17 000	Yellowish-white fine ash over coarse ash, 50 mm; biotite flakes common; age approx.

* Some ages interpolated from sedimentation rates (see text and Fig. 3).

^a Informally-named Egmont-derived tephras (see text); suggested *provisional* correlations: Eg-1 = Maketawa; Eg-2, Eg-3 = Inglewood; Eg-4 = Korito; Eg-5 = Tariki; Eg-6 = Waipuku; Eg-7, Eg-8 = S1, S2 (?Ahuahu) (based on communications with V.E. Neall & B.V. Alloway 1984-85; see also Neall 1972, 1979; Neall & Geddes 1981; Neall & Alloway 1986).

^b Definition of Froggatt (1981c) and Lowe (1986a).

^c Possibly Te Rato Lapilli member (symbol Tt) (Lowe et al. 1980).

^d Members of Okupata Tephra Formation informally designated Oa-1 to Oa-8; last is tentatively correlated with the "basal lapilli" unit of Topping (1973) (see text).

Group-Subgroup designations: 1 = Lake Taupo Group, Taupo Subgroup; 2 = Okataina Group, Rotorua Subgroup (Howorth et al. 1981); 3 = no formal group status. Tuhua Tephra Formation was defined by Hogg & McCraw (1983); it is probably equivalent to the Oira Pyroclastite Formation (Mayor Island Group) of Buck et al. (1981), which applies to deposits on Mayor Island only; 4 = Tongariro Subgroup (Topping 1973).

† References for definitions of Taupo, Okataina, and Maroa-derived correlative tephras are: Baumgart (1954); Healy (1964); Vucetich & Pullar (1964, 1969, 1973); Lloyd (1972); Froggatt (1981 c, d).

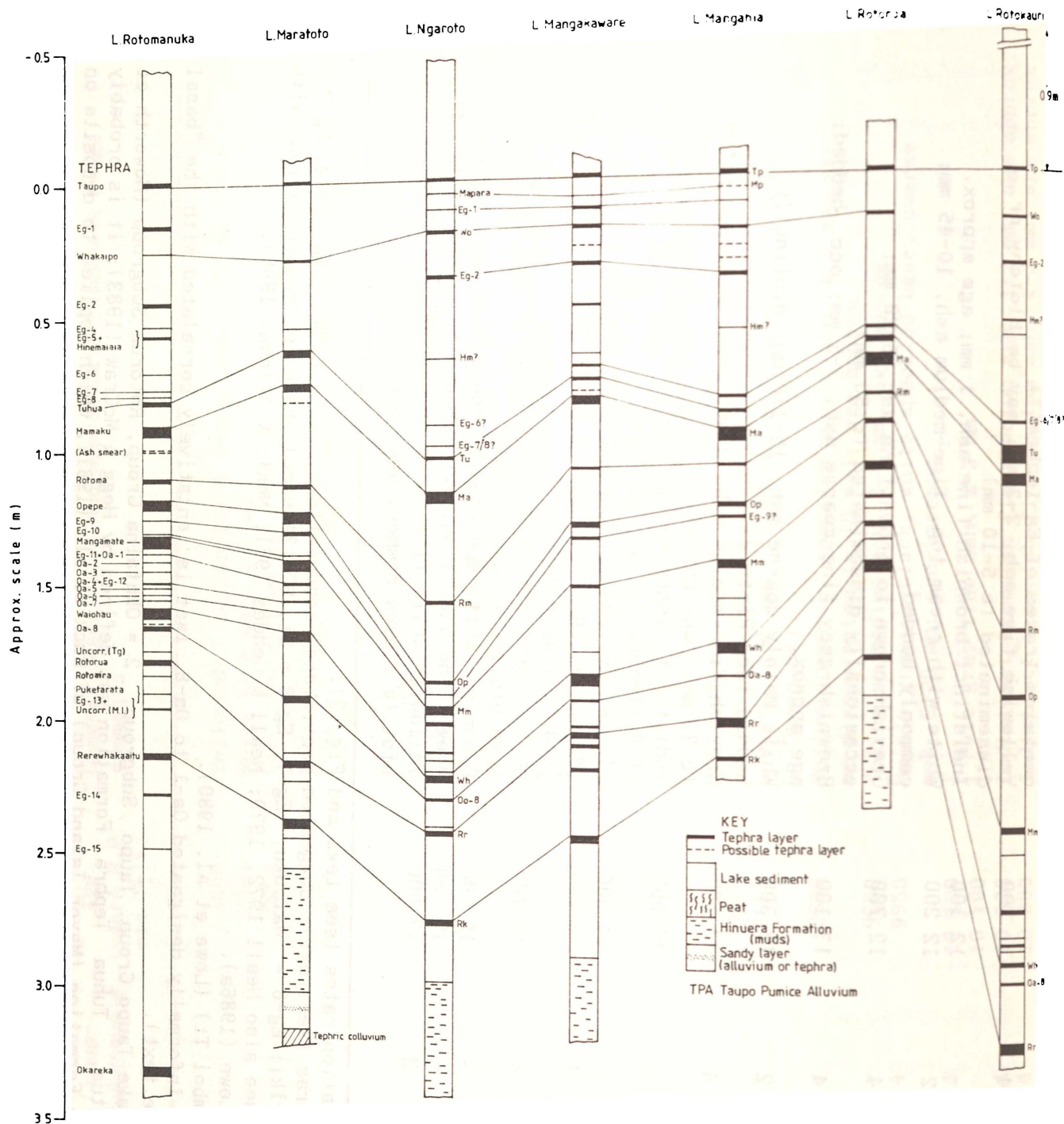


Fig.2. Stratigraphy and correlation of late Quaternary tephras in cores from 14 Waikato lakes (locations are given in Fig.1). Tephras names are explained in full in Table 1; Eg-1 to Eg-15 = Egmont-derived tephras, informally numbered 1-15 with increasing age; Oa-1 to Oa-8 = informal units, numbered 1-8, of Okupata Tephra Formation; uncorr. = uncorrelated tephra (Tg = Tongariro source; M.I. = Mayor Island source). The chronology of the tephras is given in Fig.3; additional ^{14}C dates given here (Wk- numbers) are in years B.P. (old $T\frac{1}{2}$ basis). The columns depicted are composites of two or more cores from each lake (hence scale is approximate because of differences in sediment thicknesses from core to core), as follows: L. Rotomanuka, 14 cores (approximate coring site location S15/136615**); L. Maratoto, 33 (S15/129663; see also Green & Lowe 1985); L. Ngaroto, 2 (S15/583115);

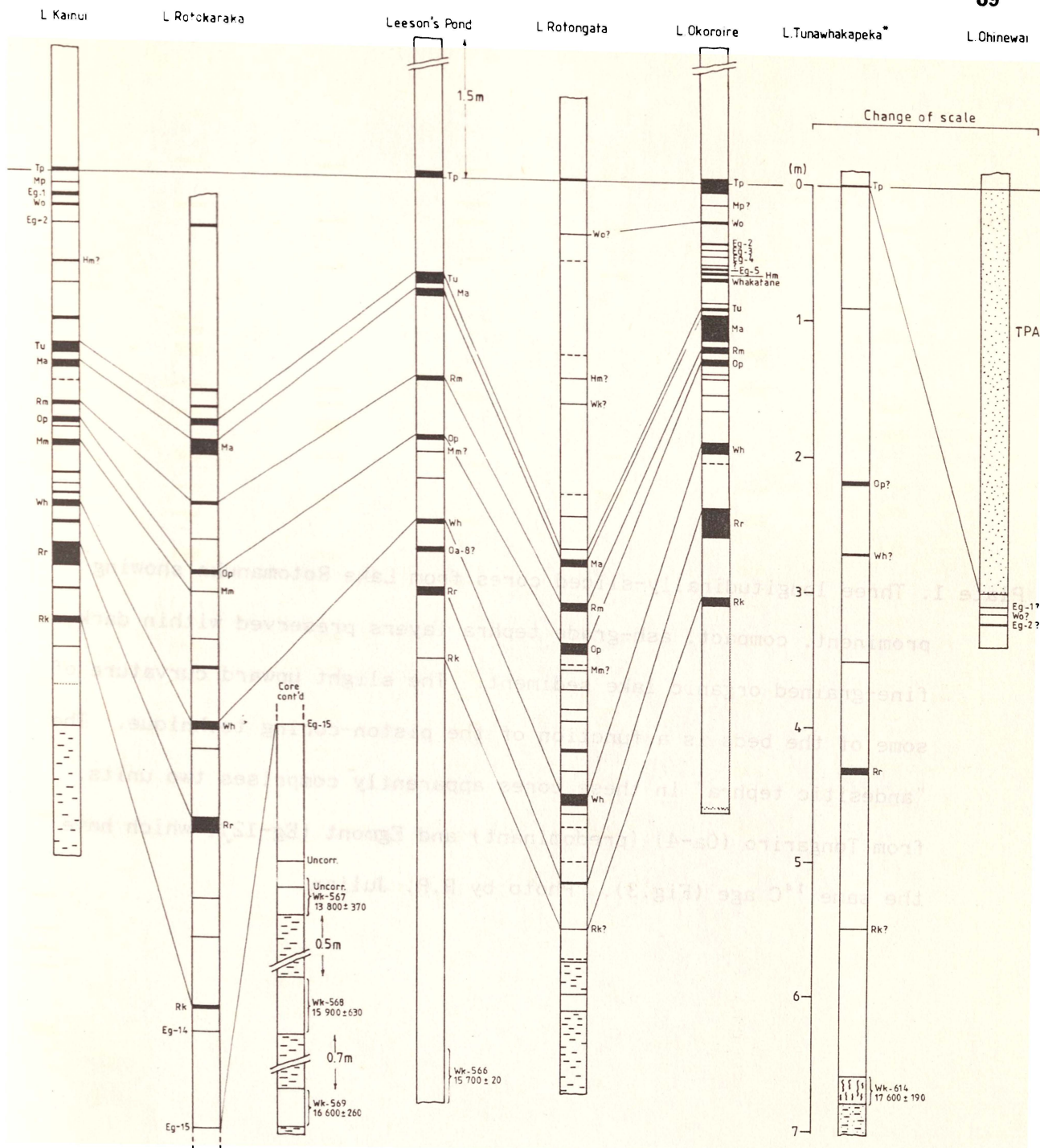


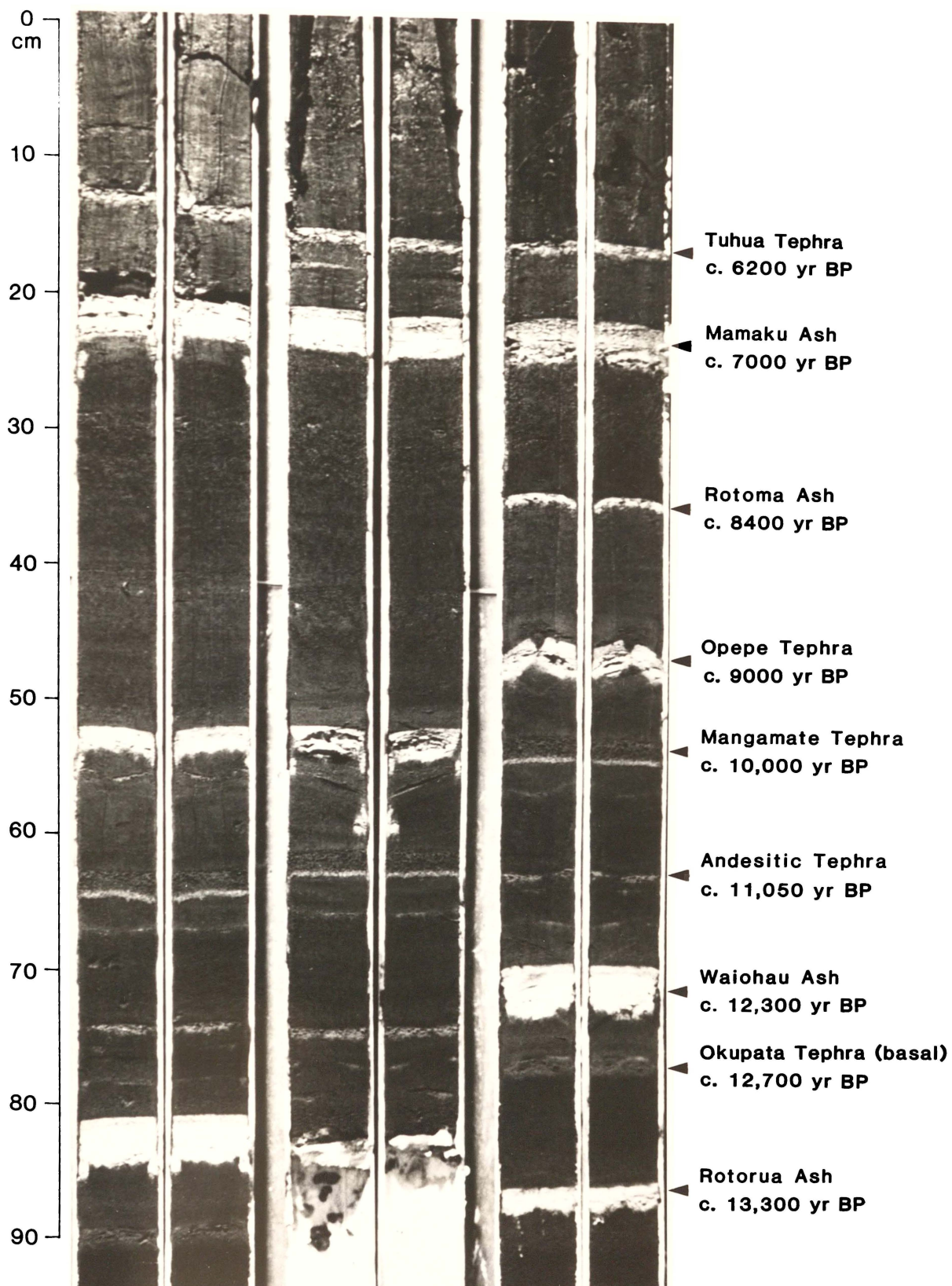
Fig. 2 contd.

L. Mangakaware, 3 (S15/610053); L. Mangahia, 3 (S15/668062); L. Rotoroa (also known as Hamilton Lake), 2 (S14/106755); L. Rotokauri, 2 (S14/037809); L. Kainui (also known as Lake D), 2 (S14/072892); L. Rotokaraka, 4 (S14/166965); Leeson's Pond, 3 (S14/287929); L. Rotongata, 4 (T16/380376); L. Okoroire, 3 (T15/555611; see also Lowe 1986a); L. Tunawhakaepka (drained "Rototuna Lake"), 1* (S14/116853); L. Ohinewai, 2 (S13/024097).

* This lake was cored using a motorised Gidding's auger.

** Grid references based on the national 1000 m grid of the 1:50 000 topographical map series (NZMS 260).

Plate 1. Three longitudinally-sliced cores from Lake Rotomanuka showing prominent, compact, ash-grade tephra layers preserved within dark, fine-grained organic lake sediment. The slight upward curvature of some of the beds is a function of the piston-coring technique. The "andesitic tephra" in these cores apparently comprises two units, from Tongariro (Oa-4) (predominant) and Egmont (Eg-12), which have the same ^{14}C age (Fig.3). Photo by R.R. Julian.



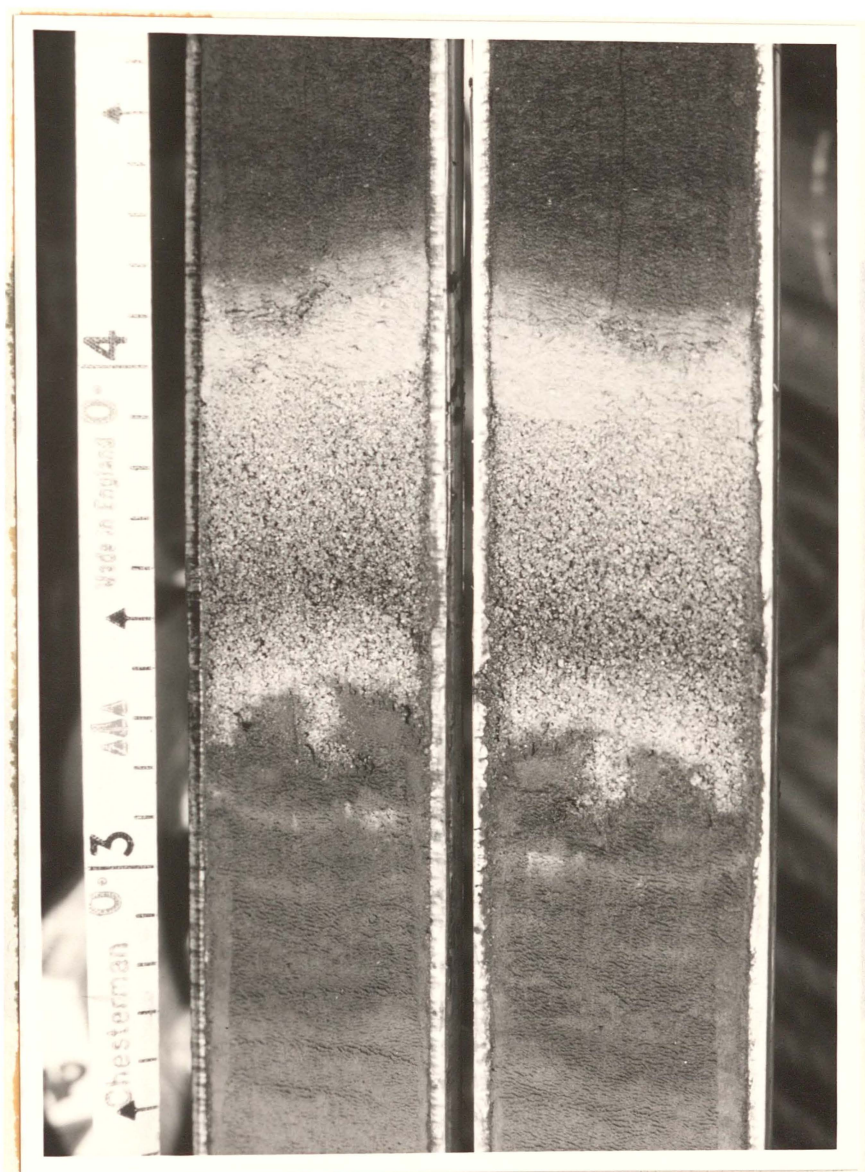
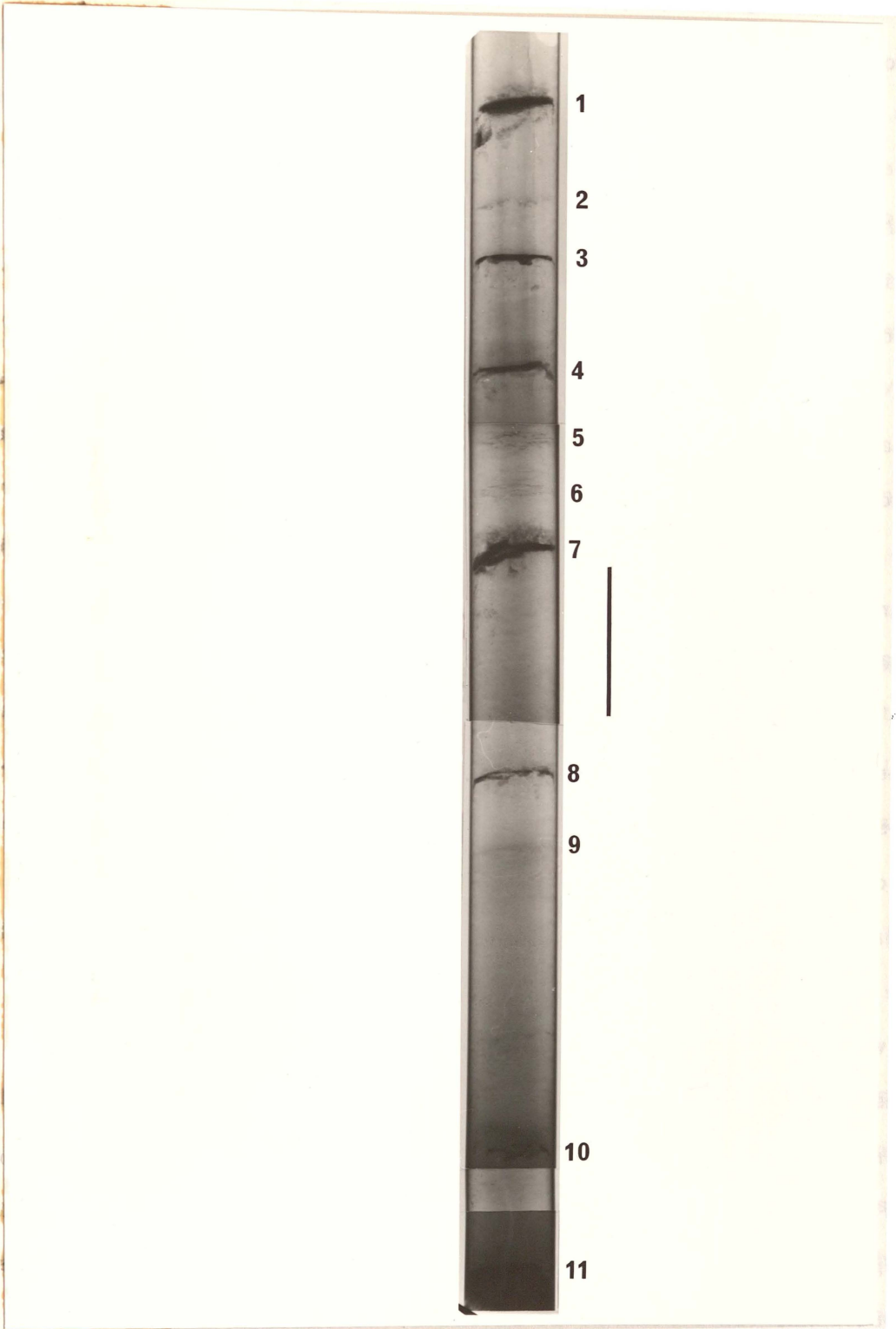


Plate 2.A. Normally-graded Rotorua Ash Formation, Lake Okoroire, comprising mainly pumiceous coarse ash overlain by fine ash (latter contains very sparse fine lapilli). Scale marks are 1 cm apart. Photo by D.J. Lowe.



Plate 2B. Rotorua Ash Formation in two cores from Lake Kainui, showing multiple bedding (from base up have medium ash, fine ash, pumiceous coarse ash, medium ash, fine ash), gas-pocket holes (cores on left), and coarse ash-filled burrow(?) channels underneath the tephra. Scale marks are 1 cm apart. Photo by D.J. Lowe.

Plate 3. Composite x-radiograph of a core from Lake Mangahia. **The numbered** tephtras are provisionally identified from their field character, stratigraphic position, and age (based on estimated sedimentation rates) as follows: 1, Taupo Pumice; 2, Mapara Tephra; 3, **Eg-1**; 4, Whakaipo Tephra; 5,6, uncorrelated; 7, Eg-2; 8, Eg-5 or **Hinemaiaia** Tephra; 9, Eg-6(?); 10, Tuhua Tephra; 11, Mamaku Ash. **Photo by A.O. Vallinga**, Waikato X-ray Clinic, Hamilton. X-ray unit operated at **35 kV**, 300 mA; exposure time 0.6 s; focus-film distance 90 cm. **Scale bar = 10 cm.**



Number of eruptives and total thickness of deposits

A total of 41 tephras, aged \leq c. 17 000 years B.P., have so far been identified in the lakes, and each is likely to represent a **separate eruptive** event (see discussion on stratigraphic reliability below). **A small number** of the tephras are found only as microscopic units, being detected by electron microprobe analysis of sparse glass shards or titanomagnetite grains. Not all of the tephras occur in any one core, nor in one single lake. But the longest and most detailed record of all the lakes cored is found in Lake Rotomanuka (Fig.2), which, together with the centrally-located Lake Maratoto, has been the focus of most laboratory analysis (see below).

The total thickness of the visible lacustrine tephras in the Ohaupo-Hamilton area is, on average, c.25 cm (Table 2). In the northern Waikato (e.g., Lakes Rotokaraka, Leeson's Pond) the average thickness is estimated at c.15-20 cm, and in the east (e.g., Lake Okoroire), c.40-45 cm. These thicknesses are approximate because the irregular boundaries and diffuse nature of some of the tephras can make measurements imprecise. Also, the thickness of individual tephras may differ in cores from the same lake.

Relationship to thickness of subaerial deposits

The very firm, compact nature of most of the lacustrine tephras contrasts with the friability and low bulk densities (c.0.7-0.9 g.cm^{-3}) commonly associated with their subaerial equivalents (e.g., Gradwell 1976). The lacustrine tephras are quite coherent and probably have bulk densities around c.1.5-1.6 g.cm^{-3} , based on their field properties and measurements made on tephras in similar settings by Borchardt et al. (1973) and Anderson et al. (1984). Rai (in Borchardt et al. 1973) estimated from bulk density comparisons that on-land tephras are about 1.75 times as thick as equivalent bog or lacustrine tephras. Similarly, Watkins et al. (1978) converted submarine tephra thicknesses to equivalent dry land thicknesses by multiplying by a factor of 2, and then added a further correction for bioturbation (see also Sparks et al. 1983 and Fisher & Schmincke 1984).

Thus the expected equivalent dry-land tephra thicknesses in the Waikato area may be roughly estimated, in part, by using a compaction correction factor of 1.75 (Table 2). An additional correction for dissemination can be made using the results of x-radiography. In a short core from Lake Mangakaware, the total thickness of visible tephra is 43 mm; the x-radiograph or "true" thickness is 53 mm (see Lowe et al. 1981). Thus, visual measurements of tephra thickness may underestimate the true thickness by c. 20%. Because only a few cores were x-rayed, it is not known if this value applies generally, but it seems reasonable to conservatively adopt 10% as a correction for dissemination. Therefore 10% of the original visible thickness measurements may be added to the compaction-corrected thickness to obtain a total equivalent dry-land thickness (Table 2).

Taking into account the age range of the deposits (mainly \leq c. 15 000 years), these recalculated figures are generally consistent with actual thickness measurements of subaerial tephra profiles at various sites in the Waikato (e.g., Pullar 1967; N.Z. Soil Bureau 1968; Pullar & Birrell 1973b; Bruce 1979; Wilson 1980; Lowe 1986b; see also Figs.6 to 8 below).

Bioturbation and stratigraphic reliability

Many of the tephra have irregular or diffuse contacts, or are manifest as relatively thin, indistinct zones within the sediments. In some cases, ash-filled burrow (?) channels may extend well below the base of a tephra; gas-pocket holes may also occur (Plate 2B). Most of this dissemination and disruption is short-range and is probably attributable to bioturbation. (Other processes such as wave action, particularly near the lake margins, may also be important, e.g., Green & Lowe 1985.) The chief biological mixing agents are probably chironomids (tube formers) and other insect larvae, oligochaete worms, and crustacea (e.g., cladocerans such as chydorids), which tend to predominate in the sediments in shallower water

Table 2. Total thickness of tephras* younger than and including Rerewhakaaitu Ash in the Waikato area based on lake core measurements, and estimated equivalent dry-land thicknesses. Values in millimetres.

Area	Total visible thickness in cores (average)	Compaction - corrected thickness (visible x1.75)	Estimated dissemination thickness (visible x0.1)	Total equivalent dry-land thickness (approximate)
Hamilton-Ohaupo	25	44	2.5	47
Whitikahu-Morrinsville	20	35	2.0	37
Okoroire-Tirau	42	74	4.2	78

* Assumed to represent airfall material only, with no modification to thickness by postdepositional reworking.

near lake shores (Boubée 1983; J.D.Green pers. comm. 1987). In one lake (Rotokaraka), freshwater snail (*Potamopyrgus antipodarum*; C.A.Wallace pers. comm. 1983) and caddis-fly cases were found intermixed with ash from the Rerewhakaaitu eruption.

The effect of this bioturbation on the stratigraphic relationships of the tephras has, in general, been minor, and in most cases is clearly visible and hence avoidable in sampling. The rates of sediment deposition, although slow, have generally been sufficient to separate each successive tephra deposit with an intervening layer of sediment. Where tephras occur very closely together in the cores, i.e., within a few millimetres of one another, they may show some intermixing (detected mainly by electron microprobe analysis). Thin tephras deposited just before or just after the thicker rhyolitic deposits may contain a small "background" scatter of identifiable glass shards derived from the rhyolitic tephras. In some samples, the distinctive peralkaline mineral assemblage associated with Tuhua Tephra (Hogg & McCraw 1983) contains a proportion of calcalkaline minerals (see Table 4), suggesting contamination after deposition (e.g., by the succeeding Egmont-derived deposits).

However, because most tephras in the cores occur as essentially unmixed and discrete units, and because they systematically increase in age with increasing depth (see chronology section below), they clearly represent, to a large degree, a faithful stratigraphic record of tephra deposition (cf. Sarna-Wojcicki & Shipley et al. 1981; Anderson et al. 1984). Even though it is possible that some of the tephric material in the lakes was washed or blown in from the catchment, or reworked by wave action soon after the main fall event, any material so reworked can be considered for stratigraphic purposes to have the same age as the original fallout tephra (Fisher & Schmincke 1984).

Tephra duplication in the cores (e.g., see Anderson et al. 1984) does not seem to have occurred - all but one of the tephra layers identified

could be matched with known eruptions (or with known periods of activity) from the North Island volcanoes. It was eventually concluded that the one "unknown" layer, which intermittently occurred between Mamaku Ash and Rotoma Ash (Fig.2), was probably the result of reworking of one or both of these tephras, either naturally or by a smearing action brought about by the coring method in its initial period of use.*

CHRONOLOGY OF THE TEPHRAS

Sampling

Lake sediment enclosing the tephras was sampled to determine, using the radiocarbon dating method, their age of deposition and thus time of eruption. Stratigraphic columns showing the sampling positions with respect to the tephras identified are given in Fig.3.

The slices of sediment, generally 1-2 cm thick, were carefully extracted from above and below the tephra layers using stainless steel cutters. Although the slices were deliberately kept as thin as possible, they nevertheless represent an accumulation time of perhaps c.100- 200 years because of the slow rates of sedimentation in the Waikato lakes. Consequently, the dates obtained may be limited in their accuracy, with respect to the age of deposition of the tephras, by up to several hundred years. However, this potential reduction in accuracy is partly offset by the obtaining of a stratigraphic succession of dates in the cores from several sites, and by the availability of dates on many of the tephras in other environments (e.g., Pullar et al. 1973; McCraw 1975), which thus act as independent monitors of error (cf. Mathewes & Westgate 1980; Green & Lowe 1985).

To provide sufficient material for dating, slices of sediment from two or more suitable cores (taken in the same lake) were commonly combined

* The possible occurrence of an uncorrelated tephra, c.8000 years B.P., cannot be ruled out, however.

into composite samples (organic contents generally decrease with increasing depth in the cores, with usually only c.10% or less organic matter in the basal lake sediments; Green & Lowe 1985). The distinctive nature of most of the tephras ensured that this procedure could be carried out confidently because the same stratigraphical event in each core could be positively identified. Conversely, some indistinct tephras were accordingly not sampled for dating.

In some samples with very low carbon contents, the slices from above and below the tephra were combined into a "straddle" sample, providing an average age for the tephra. Where tephras were closely spaced in the cores, the entire layer of sediment between two adjacent tephras (i.e., "bridging" them) was occasionally sampled. The date thus obtained applies equally to both tephras, giving a maximum age for one and a minimum age for the other (Hogg et al. 1987).

Once obtained, the samples were oven dried, lightly crushed, and submitted to the University of Waikato Radiocarbon Dating Laboratory (symbol Wk-) for ^{14}C assay. About 70 samples applying to tephras were dated.

Results and interpretation

The dates and associated error terms (one standard deviation) obtained from cores from five lakes are given in Fig.3. Ages adopted in this study for the tephras are summarised in Table 1. In the few cases where specific tephra layers were not dated, their ages of deposition were interpolated using sedimentation rates. Ages so obtained are probably reasonably reliable because they are well constrained by the dates on material in adjacent parts of the core.

The ages generally accord with the stratigraphy (increase down the cores) with few age inversions from tephra to tephra. Commonly, the dates above and below a tephra are statistically indistinguishable (using the

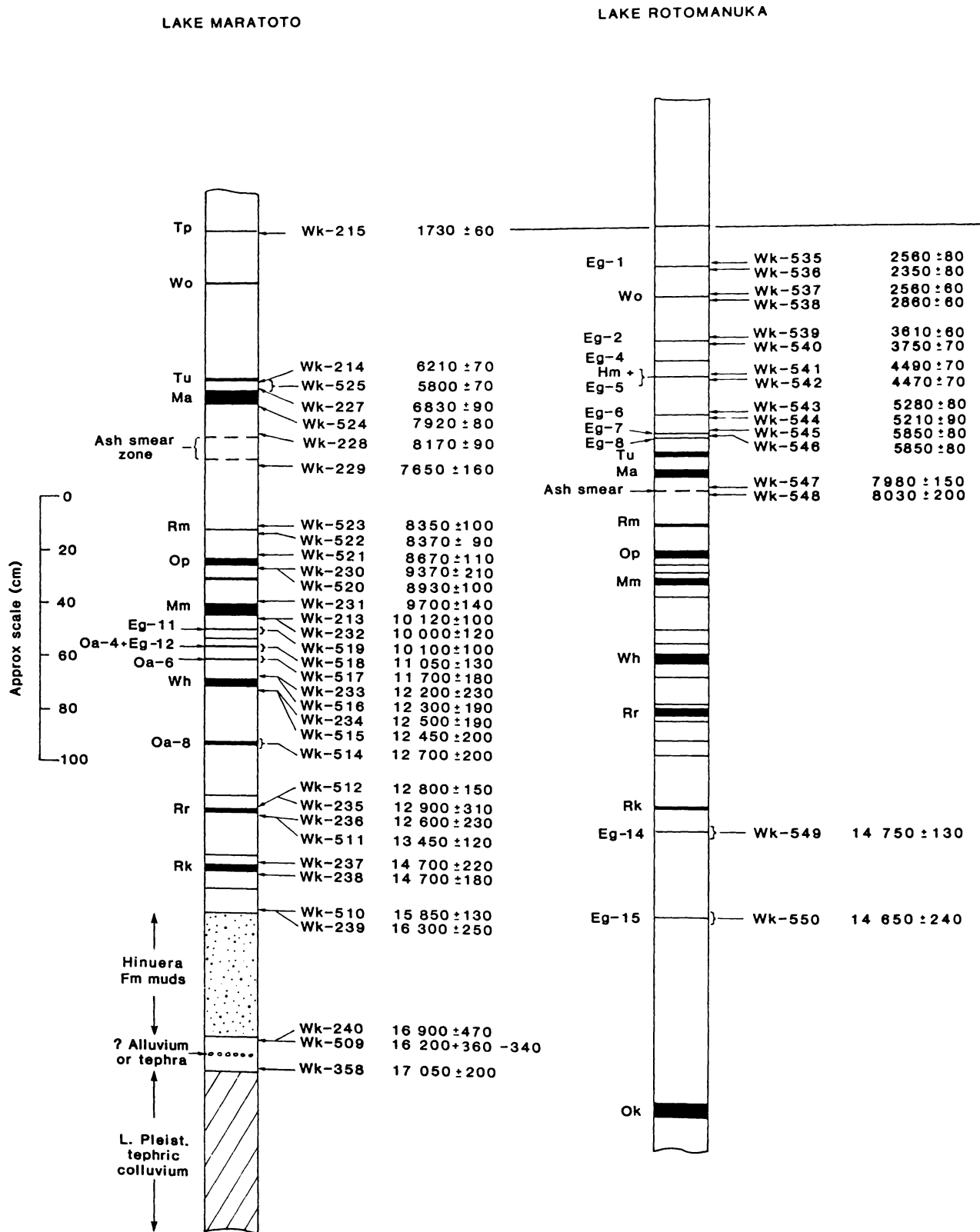


Fig.3 (caption opposite)

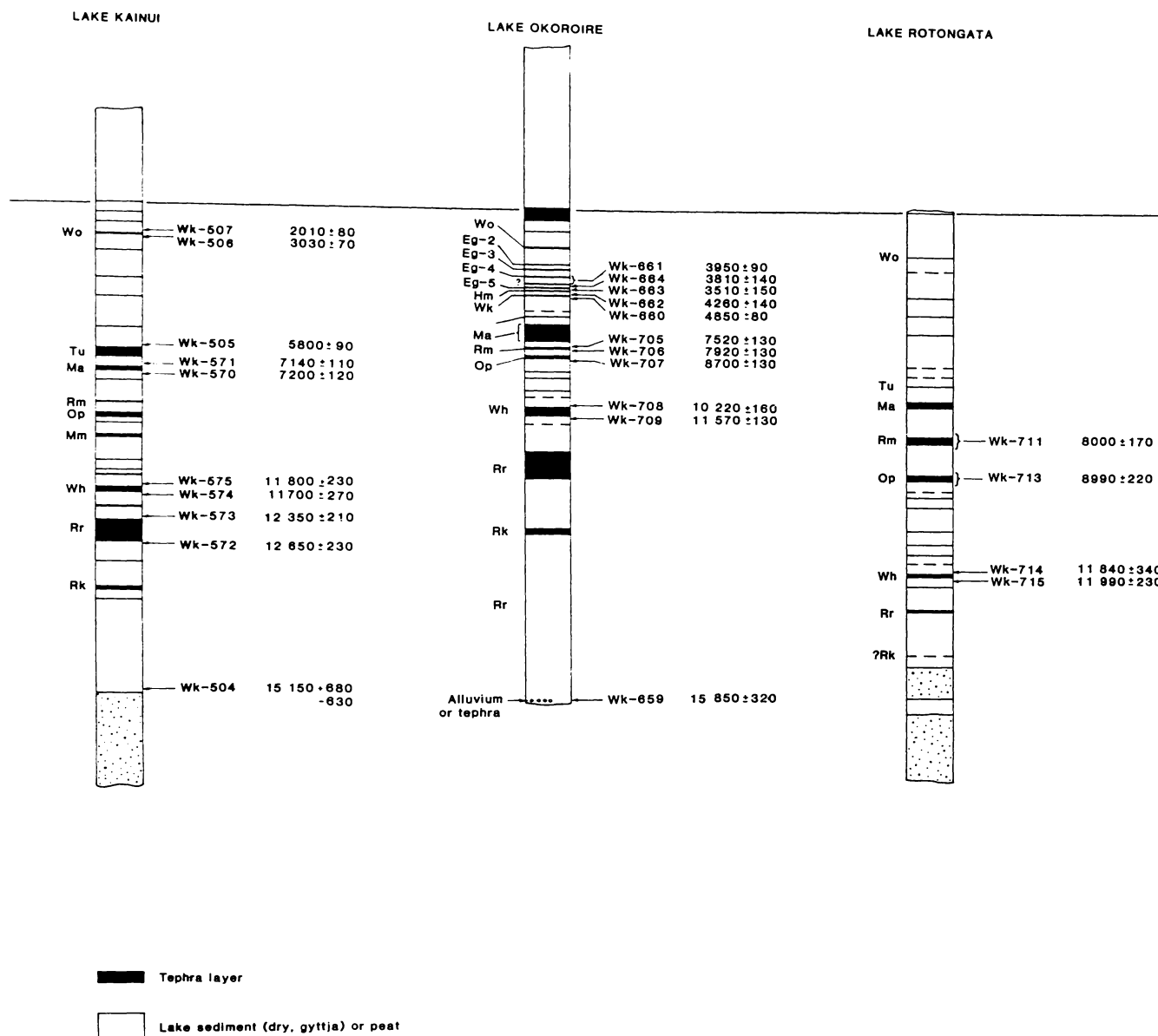


Fig.3. Stratigraphic columns showing sampling positions and dates obtained on tephtras in cores from five Waikato lakes (locations given in Fig.1). The dates presented are conventional radiocarbon ages expressed in years B.P. \pm 1 standard deviation, and are based on the old (Libby) half-life of 5568 years. (True ages based on the new half-life of 5730 years may be estimated by multiplying the old $T_{\frac{1}{2}}$ ages by 1.03.) For detailed discussion on the dates and their significance see Hogg et al. (1987). Symbols for named tephtras are explained in Table 1 and Fig.2.

methods of Polach & Golson 1966 and Currie 1981). Some of the dates on the mainly inorganic basal lake sediments (e.g., Wk-240, -504) have large errors that reflect heavy dilution in the dating procedure because of a low carbon content and a small sample size (see Hogg et al. 1987).

To a large extent the dates agree closely with those obtained for the same tephras elsewhere (e.g., Pullar & Heine 1971; Vucetich & Pullar 1973; Cole & Nairn 1975; Froggatt 1981a; Hogg & McCraw 1983), although relatively few dates are available for andesitic eruptives from Tongariro and Egmont volcanic centres (e.g., Topping 1973; Neall 1979; Neall & Geddes 1981; Neall & Alloway 1986).

Discrepancies in ages are associated with the eruptions of the Okataina-derived Rotoma Ash (c. 8500 years B.P.?) and Waiohau Ash (c.12 200 years B.P.?). The dates obtained on the lake cores for Rotoma Ash are younger, and for Waiohau Ash, older, than those obtained at other sites (e.g., see Pullar & Heine 1971; Nairn 1981); the differences in age amount to c.500-1000 years or so. This problem is discussed more fully in Green & Lowe (1985) and Hogg et al.(1987) (see also Lowe & Hogg 1986). Some of the dates on Rotorua Ash are significantly younger than the normally accepted age of c.13 450 years (Nairn 1980), although errors are quite large.

Okareka Ash, positively identified only in cores from Lake Rotomanuka (Fig.2), was not dated directly in this study because enclosing sediment contained insufficient carbon for normal ^{14}C laboratory requirements. An age of around c.17 000 - 18 000 years is suggested from approximate sedimentation rates. This age range is supported by consideration of the dates obtained for Lake Maratoto sediments, the oldest of which are dated ^{at} _h 17 050 \pm 200 years B.P. (Wk-358; Green & Lowe 1985). Because Okareka Ash is apparently absent from the Lake Maratoto sediments, then it is likely to be older than c.17 000 yeas.

Elsewhere, Okareka Ash has not been dated, but Nairn (1981) estimates its age as c. 17 000 years based on its stratigraphic relationship to dated

overlying (Rerewhakaaitu) and underlying (Te Rere, Kawakawa) tephras (Vucetich & Pullar 1969). An arbitrary age of c.17 000 years is therefore adopted here (Table 1), but an older age may yet eventuate for this tephra (see also Hogg et al. 1987)

TEPHRA COMPOSITION AND IDENTIFICATION

In hand specimen and under the binocular microscope the pale coloured rhyolitic tephras are predominantly vitric with both platy and sparsely porphyritic pumiceous shards. They also contain subordinate feldspar and mafic crystals or crystals fragments, commonly with glass selvages. Lithic fragments are rare. The andesitic tephras, usually darker in colour, are composed mainly of feldspar and mafic crystals, often with narrow glassy selvages, and of greyish, moderately vesicular, "andesitic scoria" comprising microlites or crystallites of feldspar and other constituents in a glassy matrix (see section on light minerals below). Glass shards are relatively uncommon and usually vesicular (e.g., see Kirkman & McHardy 1980), and may have a "dirty" appearance due to slight surficial weathering. Lithics of varying composition may also occur.

Sampling and laboratory analysis

All the tephra layers in cores from Lakes Rotomanuka, Maratoto and Kainui, and some of the tephras in Lakes Okoroire, Rotongata, and Mangahia, were sampled (a total of about 150 samples). The 63-250 μm (2-4 phi) size fractions of the samples of each of the tephras were split into heavy mineral (S.G. > 2.9 g.cm^{-3}) and light mineral (S.G. < 2.9 g.cm^{-3}) components using standard heavy liquid and Frantz electromagnetic methods (e.g., Lowe 1981a; Froggatt & Gosson 1982), and their proportions determined gravimetrically. These components were further separated and prepared as

necessary for analysis by petrographical microscope (point count of detrital mounts), x-ray diffraction (XRD) (powder mounts), scanning electron microscope (SEM)(unpolished and polished mounts), and electron microprobe (EMP) (polished blocks of various constituents) (Lowe 1981a; Hume & Nelson 1982; Froggatt & Gosson 1982; Froggatt 1983).

Correlations with source volcanoes and named eruptives

The analytical results, when considered together and with reference to previous work, permit the correlation of each of the distal tephras to one of six volcanic centres (Fig.1; Lowe 1986c; Lowe submitted). The main diagnostic criteria are summarised at the end of this section (Table 11). By taking into account the tephras' stratigraphic position and age, correlations with named proximal eruptives from each of these source volcanoes have been established (stratigraphic names are summarised in Table 1).

Several modifications to the provisional tephrostratigraphy recorded in Lowe et al. (1980, p.483) are made. "Waimihia Lapilli" is re-identified here as Whakaipo Tephra (see glass chemistry section below). "?Rotoma Ash" and "Unnamed ash" were re-identified as Mamaku Ash and Rotoma Ash, respectively, in Green & Lowe (1985). "?Okato Tephra" is re-identified here as the lowest unit of the Okupata Tephra Formation (Oa-8), taken to be equivalent to the "basal lapilli" bed described by Topping (1973). Dates on Okupata Tephra near source are (NZ1374) 9790 ± 160 years B.P. (minimum) and (NZ1189) $12\,450 \pm 340$ years B.P. (maximum) (Topping 1973, p.410). In addition, the formation is overlain by Karapiti Tephra and underlain by unnamed andesitic tephra and Rotorua Ash (Topping & Kohn 1973; Froggatt & Solloway 1986), and hence its age is further constrained by the ages of these tephras. From these ages and the descriptions in Topping (1973), it appears that Okupata Tephra Formation is time transgressive, with units

erupted at various intervals between about c.10 000 and c.12 500 - 13 000 years B.P.* Consequently, andesitic tephra with Tongariro source characteristics that occur between Mangamate Tephra (?Te Rato Lapilli) and Rotorua Ash in the lake cores might best be considered as representatives of the Okupata Tephra Formation. Oa-8 is assumed to be the correlative of the basal lapilli unit of Topping (1973), and has a date of (Wk-514) 12 700 ± 200 years B.P. (Fig.3). A thin andesitic tephra is found stratigraphically between this tephra (Oa-8) and the underlying Rotorua Ash (Rr) in some of the lake cores (Fig.2) and, based on its proximity to the latter tephra, has an estimated age of c.13 100 years B.P. This tephra is regarded here as an "unnamed tephra" (cf. Topping 1973).

Informal designations are used where correlations are currently uncertain (e.g., for the Egmont eruptives, Eg-1 to Eg-15), and where no formal name has previously been defined (e.g., unnamed members of the Okupata Tephra Formation, Oa-1 to Oa-8). The analytical data providing the basis for these correlations are presented and discussed below.

Heavy minerals

The 2-4 phi heavy mineral fractions consist chiefly of ferromagnesian silicates and ubiquitous Fe-Ti oxides (opaque minerals). Results from the gravimetric and modal analyses are summarised in Tables 3 and 4.

Some samples contained insufficient heavy minerals for analysis.

Proportions of heavy and opaque minerals

Although the figures in Table 3 show considerable variation, some general trends are evident. The tephra from the rhyolitic Taupo and Okataina volcanic centres are relatively low in heavy minerals (<5%) but high in Fe-Ti oxides (c.20-30%), especially Okataina. The opposite applies to the andesitic Tongariro and Egmont-derived tephra, which are high in

* See also Lowe & Hogg (1986) in which a member of Okupata Tephra Formation is dated at c. 10 300 years B.P.

Table 3. Abundances of heavy minerals and opaque minerals in 2-4 phi fractions of tephras in Waikato lake cores. Values are mean \pm 1 standard deviation; n = number of samples of tephras analysed for each volcanic centre.

Volcanic centre	Heavy minerals (wt.%)*	n	Opaque minerals (vol.%)†	n
Taupo	3.6 \pm 4.6	10	18.9 \pm 7.8	24
Okataina	1.7 \pm 1.5	26	26.1 \pm 9.4	38
Maroa	trace	1	0	1
Mayor Island	0.6 \pm 0.5	4	4.3 \pm 4.2	5
Tongariro	15.2 \pm 5.4	15	9.1 \pm 5.5	21
Egmont	22.1 \pm 9.3	11	10.2 \pm 6.1	25

* Proportion of heavy minerals in 2-4 phi fractions. Values for samples containing sparse heavy minerals are liable to have low precision.

† Proportion, by point count, of opaque minerals in the 2-4 phi heavy mineral fraction (see Table 4).

Samples from Lakes Rotomanuka, Maratoto, Kainui, and Okoroire.

Table 4. Dominant ferromagnesian minerals in tephras in cores from Waikato lakes and bogs.

Tephra	Lake & Sample No. ^a	Ferromagnesian silicate minerals (summed to 100%) ^b					Opagues (%) ^c	Total counts
		Hyp	Aug	Hbe	Cgt	Bio		
<i>Taupo-derived tephras</i>								
Taupo	RM-1	81	17	2	-	-	20	306
	MO-1	82	15	3	-	-	30	296
	PO-1	91	2	6	1?	-	35	359
Mapara	KN-1	91	7	2	-	-	14	100
Whakaipo	RM-1	92	6	1	-	1	20	307
	KN-1	86	8	6	-	tr	23	299
	MO-1	70	23	7	-	-	16	258
Hinemaiaia	OK-1	92	3	3	2	-	23	165
Opepe	RM-1	62	33	5	tr	-	30	317
	RM-2	71	27	2	-	-	26	316
	MO-1	68	29	3	-	-	20	400
	OK-1	72	24	4	-	-	11	200
<i>Okataina-derived tephras</i>								
Whakatane	OK-1	9	2	5	84	-	20	369
	PO-1	8	1	12	79	tr	16	319
	KM-1	21	13	10	56	-	18	349
Mamaku	MO-1	56	10	34	-	-	32	308
	MO-2*	75	8	17	tr	-	19	347
	RM-1	64	7	29	-	-	45	347
	RM-2	25	28	47	tr	-	24	310
	PO-1	61	4	35	tr	-	19	359
	KM-1	61	3	36	-	-	28	299
Rotoma	MU-1	73	4	22	1?	-	32	389
	RM-1	44	37	7	13	-	23	314
	RM-2	30	16	14	34	6	14	293
	MO-1	57	29	4	10	tr	25	302
	MO-2	49	27	11	13	-	8	472
	OK-1	8	4	5	81	2	12	155
	RN-1	4	3	5	86	2	24	200

^a RM = L. Rotomanuka; MO = L. Maratoto; KN = L. Kainui; OK = L. Okoroire; MG = L. Mangahia; RN = L. Rotongata; PO = Pohlen bog (G.R. NZMS260 T14/562762); MU = Moanatuatua bog (S15/179582); KM = Kaimai bog (T14/616895). Note: RM-1 = sample from core 1, RM-2 = sample from core 2, and so on. Core numbers and in-house sample numbers are available from the author.

^b Hyp = Hypersthene; Aug = Augite; Hbe = Calcic Hornblende; Cgt = Cummingtonite; Bio = Biotite; tr = trace amount detected (<1%); - = not detected; ? = uncertain identification.

^c Proportion of opaque minerals (Fe-Ti oxides) in 2-4 ϕ heavy mineral fraction (by point count).

Table 4 contd.

Tephra	Lake & Sample No.	Ferromagnesian silicate minerals (summed to 100%) ^d					Opaques (%)		Total counts				
		Hyp	Aug	Hbe	Cgt	Bio							
<i>Okataina-derived tephtras contd.</i>													
Waiohau	RM-1	60	23	17	tr	tr		24	368				
	RM-2	59	36	5	-	-		23	303				
	MO-1	52	18	27	tr	3		27	682				
	MO-2	58	7	31	-	4		42	361				
	MO-3*	73	2	24	-	1		34	163				
	MU-1	34	28	38	-	-		16	326				
Rotorua	RM-1	48	10	30	tr	12		26	300				
	MO-1	59	4	34	tr?	3		29	829				
	MU-1	19	38	34	-	9		6	490				
Rerewhakaaitu	RM-1	2	1	18	-	79		13	450				
	MO-1	13	34	21	-	32		4	387				
Okareka	RM-1	36	22	16	1?	25		22	343				
	RM-2	43	20	17	5	15		22	360				
	RM-3	23	4	32	1	40		31	394				
	Lake & Sample	Opx ^d	Cpx	Hbe	Cgt	Bio	Olv	Aeg	Aen	Rie	Tuh	Opaques (%)	Total counts
<i>Mayor Island-derived tephra</i>													
Tuhua	RM-1	6	29	17	-	-	3	40	1	4	-	2	296
	KN-1	tr	7	2	-	-	2	87	1?	1	-	7	328
	MO-1	2	3	-	-	-	3	86	3	3	tr	1	367
	MG-1 ^e	26	26	16	-	-	1	28	2	1	-	n.k.	n.k.
	OK-1	1	1	-	tr?	-	-	98	-	-	-	1	143

^d Opx = Orthopyroxene; Cpx = Clinopyroxene; Olv = Olivine; Aeg = Aegirine; Aen = Aenigmatite; Rie = Riebeckite; Tuh = Tuhualite.

^e From Hogg (1979, p. 126); n.k. = not known.

* Samples from peat core RJ1 (Rukuhia bog) at L. Maratoto (see Green & Lowe 1985, p.679).

Table 4 contd.

Tephra	Lake and Sample No.	Ferromagnesian silicate minerals (summed to 100%) ^d				Opaques (%)	Total counts	
		Opx	Cpx	Hbe	Olv			
<i>Tongariro-derived tephtras</i>								
Mangamate	RM-1	43	30	1		6	354	
	RM-2	43	27	1		29	290	
	MO-1	44	22	-		34	365	
Okupata-1**	RM-1	49	34	16		1	395	
	RM-2	35	47	16		2	459	
	MO-1	46	39	11		4	308	
Okupata-2	RM-1	30	57	9		4	346	
Okupata-2/3	MO-1	68	29	tr		3	347	
Okupata-3	RM-1	56	34	1		9	309	
Okupata-4**	RM-1	63	34	tr		3	295	
	RM-2	65	32	1		2	397	
	MO-1	64	32	2		2	398	
Okupata-5	RM-1	72	25	3		10	398	
Okupata-6	RM-1	55	34	1		tr	9	1037
	RM-2	82	34	1		10	8	334
Okupata-7	MO-1	50	44	4		-	7	397
	RM-1	61	36	2		2	12	300
	RM-1	56	42	1		1	7	471
Okupata-8	MO-1	67	31	1		1	2	371
	MO-2	61	36	-		1	6	407
	MO-3	65	31	-		3	4	218
uncorrelated	RM-1	70	27	-		4	8	345
	MO-1	69	30	1		2	6	824
Rotoaira	RM-1	49	39	tr		1	3	347
	RM-2 ^f	48	44	8		8	14	294
	MO-1	37	59	3		1?	8	393

^f Sample contains glass of ?Puketarata Ash (Table 10).

** Oa-1, Oa-4 contain glass and Fe-Ti oxide of Eg-11 and Eg-12, respectively.

Table 4 contd.

Tephra	Lake and Sample No.	Ferromagnesian silicate minerals (summed to 100%)					Opagues (%)	Total counts
		Opx	Cpx	Hbe	Olv	Ctg		
<i>Egmont-derived tephras</i>								
Egmont-1	RM-1	2	49	49	tr?	-	1	391
	KN-1	-	57	43	tr?	-	5	350
Egmont-2	RM-1	-	46	52	-	-	11	396
	KN-1	-	42	58	-	-	1	349
	OK-1	tr	55	45	-	-	11	356
Egmont-3	OK-1	6	49	43	-	-	6	67
Egmont-4	RM-1 ^k	2	46	52	-	2?	9	310
	OK-1	-	75	25	-	-	4	359
Egmont-5	RM-1 ^k	16	44	40	-	-	15	455
	KN-1 ^h	6	43	47	-	4	11	162
	OK-1	-	72	28	-	-	2	400
Egmont-6	RM-1	35	47	17	-	1?	4	588
	MO-1	2	64	34	-	-	3	322
Egmont-7	RM-1	tr	89	11	-	-	9	594
	KN-1	4	79	17	-	-	11	349
Egmont-8	RM-1	7	54	39	-	-	18	267
Egmont-9	RM-1	-	57	43	-	-	23	393
	MO-1	8	60	32	-	-	7	630
Egmont-10	MO-1	9	54	37	-	-	12	296
Egmont-13	MO-1	4	75	21	-	-	6	346
	(?)RM-1 ⁱ	48	44	8	-	-	8	393
	RM-2 ^j	13	76	12	-	-	8	396
Egmont-14	RM-1	2	86	12	-	-	22	409
	RM-2	3	84	13	-	-	3	447
	KN-1	23	53	21	3?	-	11	124
Egmont-15	RM-1	7	83	10	-	-	14	375
	RM-2	4	84	12	-	-	12	387
	RM-3	1	93	6	-	-	14	408
	(?)KN-1 ^k	30	47	22	1?	-	29	272

^g Sample contains glass of Hinemaiaia Tephra (Table 10).

^h Cgt suggests Whakatane Ash may be present in trace amounts.

ⁱ Possibly Eg-13; sample also contains glass of ?Puketarata Ash (Table 10).

^j Sample contains glass of unnamed Mayor Island eruptive (Table 10).

^k Possibly Eg-15.

heavies (c.15-25%) and relatively low in oxides (10%). Samples of the pantelleritic Mayor Island-derived tephras are very low in both heavies (1%) and oxides (5%). (The unnamed c.14 500 year-old Mayor Island tephra consists solely of glass, as does, in essence, the Maroa-derived tephra, Puketarata Ash.)

These trends in relative abundances are broadly similar to those of near-source eruptives, taking into consideration differences in methodology, size fractions examined, and type of sample: the andesitic tephras are relatively mafic-rich and Fe-Ti oxide poor, the rhyolitic tephras mafic poor but with variable, sometimes high, Fe-Ti oxide abundances (cf. Clark 1960; Ewart 1963, 1966; Gow 1968; Cole 1970a, 1978; Kohn & Neall 1973; Fry 1977; Buck et al. 1981; Lowe & Hogg 1986; Neall et al. 1986). Some of the variations are likely to be due in part to the effects of aeolian fractionation (e.g., see Fisher & Schmincke 1984), as is evident particularly for the tephras consisting wholly of glass.

Ferromagnesian minerals

The ferromagnesian silicate minerals generally have properties similar to those described in Lowe (1981a, p. 103-4). Most of the minerals are euhedral with glassy rims, and typically contain abundant inclusions such as apatite, glass, and opaque minerals.

The ferromagnesian mineral assemblages (Table 4) can be classed into five main groups, each of which characterises one of the source volcanoes, as follows:

- Group 1: Hypersthene ± augite (Taupo)
- Group 2: Hornblende + hypersthene + augite ± cummingtonite ± biotite (Okataina)
- Group 3: Aegirine ± aenigmatite ± riebeckite ± olivine ± ferrohedenbergite ± tuhualite (Mayor Island)
- Group 4: Orthopyroxene + clinopyroxene ± olivine ± hornblende (Tongariro)
- Group 5: Clinopyroxene + hornblende ± orthopyroxene (Egmont).

(The only recent eruptive from the Maroa volcanic centre, Puketarata Ash, contains mainly biotite and hornblende \pm hypersthene near source; Kohn 1973; Topping & Kohn 1973.) Apatite and zircon may also occur in small amounts (<5%), with zircon being a noticeable constituent in the Okataina-derived tephra in particular. The proportions of minerals within most groups may vary from sample to sample; for example, in group 5, clinopyroxene may normally predominate over hornblende in some Egmont tephra but in others hornblende is dominant. Some of the data from Table 4 are plotted in a ternary diagram (in Lowe (submitted), fig.5) to illustrate the degree of separation and overlap of the groupings.

Some of the ferromagnesian minerals are useful as marker minerals for particular tephra or volcanic centres (Lowe et al. 1980): aegirine is diagnostic of Tuhua Tephra (Mayor Island); cummingtonite occurs as the dominant ferromagnesian mineral in Whakatane Ash and Rotoma Ash (Haroharo Complex, Okataina); biotite is dominant in Rerewhakaaitu and Okareka Ash (Tarawera Complex, Okataina) (it may also amount to c.10% in Rotorua Ash), and characteristically occurs in Puketarata Ash - Kohn 1973); olivine (forsteritic) is found in most of the Tongariro eruptives (e.g., Mangamate Tephra), but usually in only small amounts. (Olivine may also occur in rare quantities in Mayor Island and Egmont eruptives, and is apparently of fayalitic composition: Buck et al. 1981; Weaver in Houghton & Wilson 1986; Wallace et al. 1986.)

The mineralogical results above agree closely with previous findings on pyroclastics and lavas associated with the Taupo, Okataina, and Mayor Island volcanoes (e.g., Ewart 1963, 1966, 1971; Cole 1970a; Ewart et al. 1971; Topping & Kohn 1973; Kohn & Glasby 1978; Howorth et al. 1980; Buck et al. 1981; Froggatt 1981a; Hogg & McCraw 1983; Houghton & Wilson 1986; Lowe & Hogg 1986). The results are also consistent with mineralogical analyses of Tongariro and Egmont eruptives, although most published results relate to work done on near-source rock samples (e.g., Clark 1960; Gow 1968; Kohn &

Neall 1973; Fry 1977; Cole 1978; Neall 1979; Franks 1984; Cole et al. 1986; Neall et al. 1986).

Chemical analyses representative of most of the ferromagnesian mineral phases were obtained by EMP (e.g., Froggatt & Gosson 1982), largely to underpin the optical mineralogy. Also, relatively few such analyses have been published previously for relevant late Quaternary lava or pyroclastic deposits (some EMP analyses are given in Howorth 1976; Howorth & Ross 1981; Houghton & Smith 1981; Lowe 1981a; Froggatt 1982a; Cole et al. 1986; Froggatt & Solloway 1986).

A range of selected analyses is given in Table 5. For various reasons, chemical analyses of ferromagnesian silicates have been used relatively little in attempting to separate the eruptives from different volcanic centres, or successive eruptives from one centre. However, with the increasing availability and sophistication of EMP systems, greater numbers of analyses on such minerals are possible, and their use as an adjunct means of fingerprinting tephras, in appropriate circumstances, should increase (e.g., Smith & Leeman, 1982, used SiO/Al₂O₃ contents in hornblendes and Fe/Mg ratios in hypersthene to aid in distinguishing Pacific Northwest tephras: see also Westgate & Evans 1978; Federman & Scheidegger 1984; Mehringer et al. 1984)*. Consequently, 77 pyroxene grains, commonly zoned, in tephras from the Tongariro and Egmont volcanic centres were examined by EMP to see if these centres could be effectively separated.

The analyses, all done on grain cores, suggest some degree of separation. The Tongariro clinopyroxenes, usually colourless, project mainly as augite (mean Wo_{41.8±1.5}; 14 analyses) in the Wo-En-Fs diagram. The Egmont clinopyroxenes, usually green-lemongreen to bluish green, generally contain more Ca and project as salite or high-Ca augite (Wo_{44.6±2.3}; 38 analyses) (see Lowe submitted, fig.6; cf. Cole et al. 1986; Wallace et al. 1986). The Tongariro orthopyroxenes (21 analyses) usually project as hypersthene (total range En₃₃₋₆₉), but the few available Egmont orthopyroxene

* See also Inoue (1980)

Table 5. Electron microprobe analyses* of ferromagnesian minerals in tephras in cores from Lake Rotomanuka.

Clinopyroxenes

Tephra	Egmont-1*			Egmont-2		Ferrohedenbergite Tuhua	
	Analysis No.						
	1	2	3	4	5	1	2
				(rim)			
SiO ₂	50.38	49.03	49.16	51.02	50.07	48.04	47.91
Al ₂ O ₃	3.26	4.24	4.29	2.65	3.19	0.20	0.21
TiO ₂	0.67	0.76	0.89	0.52	0.56	0.48	0.42
FeO†	7.80	8.94	8.48	8.89	8.50	29.59	29.79
MnO	0.26	0.29	0.49	0.41	0.31	1.13	1.10
MgO	14.60	13.31	13.82	14.07	13.57	0.14	0.11
CaO	22.81	22.23	22.13	22.52	22.73	18.42	18.45
Na ₂ O	0.24	0.57	0.42	0.29	0.31	1.22	1.29
K ₂ O	-	tr	0.01	-	-	-	-
Total	100.02	99.37	99.69	100.37	99.24	99.22	99.28
Cations on the basis of 6 oxygens							
Si	1.880	1.854	1.849	1.904	1.891	2.001	1.998
Al	0.143	0.189	0.190	0.117	0.142	0.010	0.011
Ti	0.019	0.021	0.025	0.015	0.016	0.015	0.013
Fe	0.244	0.283	0.267	0.277	0.268	1.030	1.039
Mn	0.008	0.009	0.016	0.013	0.010	0.040	0.039
Mg	0.812	0.751	0.775	0.783	0.764	0.009	0.007
Ca	0.912	0.901	0.892	0.901	0.920	0.822	0.824
Na	0.017	0.042	0.031	0.021	0.023	0.099	0.105
K	-	-	0.001	-	-	-	-
Total	4.035	4.050	4.046	4.031	4.034	4.026	4.036

* Analyses made with a JEOL JXA-733 Superprobe at Victoria University of Wellington, using a 12 nA beam current at 15 kV. A 3 µm beam was used for all samples except micas for which a 10 µm beam was used. The probe was regularly checked for drift by analysing standards, including PSU 4-190 (Hornblende) and PSU Px-1 (Pyroxene). tr = trace detected; - = not detected or not determined. Analyses done on grain cores unless specified otherwise. Tephra abbreviations given in Table 1.

† Total Fe as FeO

* Samples: Eg-1, L57; Eg-2, L58; Tu, L61 (note: L - samples = EMP block nos.).

Table 5 contd.

Clinopyroxenes

Augite

Tephra	Egmont-6			Egmont-14	
	1	2	3	4	5
SiO ₂	51.85	52.59	52.02	51.52	51.19
Al ₂ O ₃	1.80	1.43	1.87	1.92	2.64
TiO ₂	0.55	0.40	0.44	0.51	0.55
FeO†	7.67	6.70	7.65	7.54	8.61
MnO	0.57	0.63	-	0.50	0.12
MgO	15.83	15.94	15.28	15.75	14.81
CaO	21.14	21.44	22.02	21.13	20.80
Na ₂ O	0.40	0.37	0.29	0.39	0.55
K ₂ O	tr	-	-	-	-
Total	99.81	99.50	99.57	99.26	99.27
Cations on the basis of 6 oxygens					
Si	1.929	1.953	1.938	1.925	1.919
Al	0.079	0.063	0.082	0.084	0.117
Ti	0.015	0.011	0.013	0.014	0.016
Fe	0.238	0.208	0.251	0.236	0.270
Mn	0.018	0.020	-	0.016	0.004
Mg	0.878	0.882	0.848	0.877	0.828
Ca	0.843	0.853	0.879	0.846	0.835
Na	0.029	0.026	0.021	0.029	0.040
K	-	-	-	-	-
Total	4.029	4.016	4.032	4.027	4.029

Samples: Eg-6, L60; Eg-14, L76.

Table 5 contd.

Clinopyroxenes

Augite contd.

Tephra	Mangamate			Oa-4 ^c		Oa-8 ^c	
	6	7	8	9	10	11	12
SiO ₂	51.44	51.55	51.09	51.16	51.26	51.10	50.88
Al ₂ O ₃	2.37	1.86	2.68	1.53	1.99	1.81	2.10
TiO ₂	0.49	0.33	0.36	0.53	0.55	0.55	0.55
FeO†	10.75	9.89	8.87	10.26	11.21	9.38	10.24
MnO	0.35	0.21	0.23	0.33	0.37	0.15	0.35
MgO	15.40	15.03	15.02	14.34	14.17	15.26	14.68
CaO	19.01	20.30	20.67	20.72	20.23	20.91	20.47
Na ₂ O	0.36	0.31	0.39	0.27	0.40	0.27	0.38
K ₂ O	0.01	-	tr	-	0.01	-	-
Total	100.18	99.48	99.31	99.14	100.19	99.43	99.65

Cations on basis of 6 oxygens

Si	1.920	1.936	1.915	1.935	1.922	1.920	1.915
Al	0.104	0.082	0.118	0.069	0.088	0.080	0.093
Ti	0.014	0.009	0.010	0.015	0.015	0.016	0.016
Fe	0.335	0.310	0.278	0.324	0.351	0.295	0.322
Mn	0.011	0.007	0.007	0.011	0.012	0.005	0.011
Mg	0.857	0.841	0.839	0.809	0.792	0.855	0.824
Ca	0.760	0.817	0.830	0.839	0.813	0.842	0.825
Na	0.026	0.022	0.028	0.020	0.029	0.019	0.028
K	0.001	-	-	-	-	-	-
Total	4.028	4.024	4.025	4.022	4.022	4.032	4.034

Samples: Mm, L67; Oa-4, L68; Oa-8, L72

^c Some augites in these samples contain distinctive amounts of Cr₂O₃ (0.2 - 0.5 wt.%); analyses 9 & 10 presumed to represent Oa-4 (see Table 4).

Table 5 contd.

Clinopyroxenes

Aegirine

Tephra	Tuhua			
	1	2	3	4 ^b
SiO ₂	51.90	52.06	51.85	52.60
Al ₂ O ₃	0.31	0.20	0.31	0.20
TiO ₂	0.45	1.00	1.09	0.68
FeO†	31.07	29.80	29.54	31.33
MnO	0.21	0.12	0.18	0.22
MgO	0.03	0.01	0.04	-
CaO	2.11	3.26	2.37	0.53
Na ₂ O	12.82	12.36	12.81	15.41
K ₂ O	-	-	0.03	-
NiO	0.07	0.06	0.04	-
Total	98.97	98.87	98.26	100.97

Cations on the basis of 6 oxygens

Si	2.134	2.132	2.134
Al	0.015	0.010	0.015
Ti	0.014	0.031	0.034
Fe	1.068	1.020	1.017
Mn	0.007	0.004	0.006
Mg	0.002	0.001	0.002
Ca	0.093	0.143	0.104
Na	1.022	0.981	1.022
K	-	-	0.001
Ni	0.002	0.002	0.001
Total	4.357	4.334	4.336

Sample: Tu, L61.

^b Analysed by Dr R.M. Briggs at Auckland University (pers. comm. 1980).

Table 5 contd.

Orthopyroxenes

Bronzite		Hypersthene			Okupata-8		
Tephra	Eg-14	Rr	Mm				
Analysis Number	1	1	2	3	4	5	6
SiO ₂	54.21	50.89	51.29	51.40	52.76	52.09	51.86
Al ₂ O ₃	0.94	1.13	0.81	1.02	0.65	1.18	1.26
TiO ₂	0.23	0.23	0.25	0.30	0.23	0.21	0.34
FeO†	15.00	21.83	24.24	24.22	20.21	21.26	21.15
MnO	0.90	1.26	0.60	0.56	0.49	0.50	0.48
MgO	27.22	20.35	20.11	19.87	23.56	22.59	22.49
CaO	1.34	1.11	1.73	1.81	1.52	1.40	1.60
Na ₂ O	0.01	0.02	0.06	0.05	0.01	tr	0.04
K ₂ O	0.01	-	0.01	0.01	0.02	-	0.01
Total	99.86	99.82	99.10	99.24	99.45	99.23	99.23

Cations on the basis of 6 oxygens

Si	1.961	1.938	1.959	1.959	1.965	1.954	1.947
Al	0.040	0.051	0.036	0.045	0.028	0.052	0.056
Ti	0.006	0.007	0.008	0.009	0.007	0.006	0.010
Fe	0.454	0.791	0.774	0.773	0.629	0.667	0.664
Mn	0.027	0.041	0.020	0.018	0.015	0.016	0.015
Mg	1.468	1.155	1.145	1.130	1.308	1.263	1.258
Ca	0.052	0.045	0.071	0.074	0.061	0.056	0.064
Na	0.001	0.001	0.005	0.003	-	-	0.003
K	0.001	-	-	-	0.001	-	-
Total	4.010	4.029	4.018	4.011	4.014	4.014	4.017

Sample: Eg-14, L76; Rr, L73; Mm, L67; Oa-8, L72.

Table 5 contd.

Orthopyroxenes

Hypersthene contd.

Ferrohypersthene

Tephra	Okupata-4			Rr	
Analysis No.	7	8	9	1	2
SiO ₂	51.70	50.96	51.23	50.75	50.43
Al ₂ O ₃	1.28	1.31	1.93	0.36	0.24
TiO ₂	0.24	0.23	0.26	0.09	0.10
FeO†	21.90	22.91	21.43	28.67	30.89
MnO	0.49	0.53	0.47	1.69	1.76
MgO	21.99	21.41	22.48	16.79	15.26
CaO	1.56	1.70	1.36	1.16	1.06
Na ₂ O	0.02	0.03	-	-	0.02
K ₂ O	-	0.02	tr	-	-
Total	99.18	99.10	99.16	99.51	99.76

Cations on the basis of 6 oxygens

Si	1.947	1.935	1.925	1.978	1.980
Al	0.057	0.059	0.085	0.016	0.011
Ti	0.007	0.007	0.007	0.003	0.003
Fe	0.690	0.727	0.674	0.934	1.015
Mn	0.016	0.017	0.015	0.056	0.059
Mg	1.234	1.212	1.260	0.975	0.893
Ca	0.063	0.069	0.055	0.049	0.045
Na	0.001	0.002	-	-	0.001
K	-	0.001	-	-	-
Total	4.015	4.029	4.021	4.011	4.007

Samples: Oa-4, L68*; Rr, L73.

* Hypersthene presumed to represent Oa-4 tephra (see Table 4).

Table 5 contd.

Olivine

Tephra	Mangamate		
	1	2a (core)	2b (rim)
Analysis Number			
SiO ₂	39.39	39.25	39.31
Al ₂ O ₃	0.02	0.01	0.02
TiO ₂	0.04	0.05	0.04
FeO†	13.14	12.98	13.03
MnO	0.18	0.20	0.22
MgO	47.36	46.88	46.85
CaO	0.15	0.16	0.15
Na ₂ O	-	0.05	0.01
K ₂ O	0.01	0.02	-
Cr ₂ O ₃	0.06	0.04	0.05
NiO	0.18	0.16	0.18
Total	100.53	99.80	99.86
Cations on the basis of 4 oxygens			
Si	0.979	0.982	0.983
Al	0.001	-	0.001
Ti	0.001	0.001	0.001
Fe	0.273	0.272	0.272
Mn	0.004	0.004	0.005
Mg	1.754	1.748	1.746
Ca	0.004	0.004	0.004
Na	-	0.002	-
K	-	0.001	-
Cr	0.001	0.001	0.001
Ni	0.003	0.003	0.004
Total	3.020	3.018	3.016
Atomic%			
Fe	13.5	13.5	13.5
Mg	86.5	86.5	86.5

Sample: Mm, L67 (L. Rotomanuka); an olivine grain in Mangamate Tephra from Lake Maratoto (sample Mo 1.45) has a composition Fo₈₄ based on an analysis at Auckland University by Dr R.M. Briggs (pers. comm. 1980).

Table 5 contd.

Biotite

Tephra	Rerewhakaaitu		
	1	2	3
Analysis Number			
SiO ₂	34.48	35.64	35.35
Al ₂ O ₃	13.64	13.29	13.49
TiO ₂	4.47	4.31	4.44
FeO†	21.82	21.88	21.51
MnO	0.28	0.33	0.42
MgO	10.23	10.46	10.29
CaO	0.01	0.03	0.01
Na ₂ O	0.54	0.54	0.50
K ₂ O	8.70	8.37	8.44
Cl	0.21	0.28	0.20
Total	94.38	95.13	94.65
Ions on the basis of 22 oxygens			
Si	5.509	5.546	5.522
Al	2.496	2.437	2.484
Ti	0.521	0.504	0.522
Fe	2.834	2.848	2.810
Mn	0.037	0.043	0.056
Mg	2.367	2.426	2.396
Ca	0.002	0.005	0.002
Na	0.162	0.163	0.150
K	1.723	1.662	1.681
Cl	0.054	0.073	0.052
Total	15.705	15.707	15.675

Sample: Rk, L75.

Table 5 contd.

Calcic Amphiboles (Hornblende)^d

Tephra	Rotorua			Eg-1		Eg-6	Eg-9		Eg-14	
	1	2	3	4	5	6	7	8	9	10
SiO ₂	46.59	47.16	46.89	40.12	40.54	39.93	40.76	39.47	39.99	39.19
Al ₂ O ₃	7.18	6.59	7.65	13.41	12.89	13.62	12.45	13.06	14.25	14.25
TiO ₂	1.65	1.23	1.47	2.62	3.44	2.62	2.86	2.61	2.48	2.52
FeO†	14.03	13.80	14.93	11.60	11.56	12.05	12.37	13.96	11.17	11.85
MnO	0.50	0.45	0.57	0.18	0.20	0.04	0.21	0.23	0.17	0.14
MgO	14.23	15.02	14.35	13.68	13.86	13.50	13.54	12.37	13.92	13.40
CaO	10.86	11.00	10.95	11.85	11.54	12.09	11.84	12.04	12.03	12.36
Na ₂ O	1.70	1.45	1.76	2.56	2.44	2.41	2.58	2.48	2.46	2.35
K ₂ O	0.26	0.24	0.31	0.92	0.94	0.89	0.88	0.95	1.04	1.01
Total	97.00	96.94	98.88	96.94	97.41	97.15	97.49	97.17	97.51	97.07

Cations on the basis of 23 oxygens

Si	6.903	6.976	6.847	5.994	6.019	5.969	6.072	5.966	5.929	5.868
Al	1.254	1.148	1.316	2.360	2.256	2.398	2.185	2.327	2.491	2.515
Ti	0.184	0.137	0.161	0.294	0.384	0.295	0.321	0.296	0.277	0.284
Fe	1.739	1.706	1.823	1.449	1.435	1.505	1.541	1.764	1.384	1.484
Mn	0.063	0.057	0.071	0.023	0.025	0.005	0.026	0.029	0.022	0.017
Mg	3.143	3.312	3.122	3.047	3.069	3.006	3.007	2.786	3.077	2.991
Ca	1.724	1.744	1.712	1.897	1.836	1.934	1.890	1.949	1.911	1.983
Na	0.488	0.415	0.498	0.740	0.703	0.697	0.745	0.727	0.707	0.681
K	0.048	0.045	0.057	0.174	0.179	0.169	0.168	0.183	0.197	0.193
Total	15.546	15.540	15.607	15.978	15.906	15.974	15.955	16.027	15.995	16.016
Class ^d	← Edenite →			← Ferroan Pargasite →						

Samples: Rr, L73; Eg-1, L57; Eg-6, L60; Eg-9, L66; Eg-14, L76.

^d Green-brown hornblendes; classification based on Leake (1978) and assumes all FeO(total) in Fe²⁺ form.

Note: Analyses of cummingtonite, an Fe-Mg-Mn Amphibole, are given in table 2 of Paper 7.

Table 5 contd.

Calcic Amphiboles (Hornblende) contd.

Tephra	Eg-6		Eg-2	
	11	12	13	14
SiO ₂	42.34	42.42	42.65	42.19
Al ₂ O ₃	11.18	10.51	9.92	10.25
TiO ₂	2.61	3.49	2.94	3.04
FeO†	12.07	11.34	12.64	12.56
MnO	0.30	0.40	0.51	0.32
MgO	14.00	14.60	13.77	13.58
CaO	11.92	11.21	11.41	11.56
Na ₂ O	2.47	21.46	2.36	2.43
K ₂ O	0.81	0.93	0.92	0.91
Total	97.70	97.36	97.12	96.84

Cations on the basis of 23 oxygens

Si	6.268	6.284	6.375	6.321
Al	1.950	1.834	1.747	1.811
Ti	0.291	0.389	0.330	0.343
Fe	1.495	1.405	1.580	1.574
Mn	0.038	0.051	0.064	0.041
Mg	3.091	3.223	3.067	3.033
Ca	1.891	1.780	1.826	1.857
Na	0.710	0.705	0.682	0.705
K	0.154	0.175	0.175	0.174
Total	15.888	15.846	15.846	15.859
Class	← Ferroan Pargasitic Hornblende →			

Samples: Eg-6, L60; Eg-2, L58.

Table 5 contd.

Calcic Amphiboles ("Oxyhornblendes")*

Tephra	Eg-2	Eg-14		Eg-2
	1	2	3	4
SiO ₂	40.77	40.39	39.46	42.63
Al ₂ O ₃	11.43	12.84	13.95	9.71
TiO ₂	2.78	3.10	2.73	2.84
FeO†	14.50	12.88	12.33	12.91
MnO	0.36	0.19	0.10	0.45
MgO	12.44	13.12	13.37	13.77
CaO	11.45	11.58	11.73	11.56
Na ₂ O	2.28	2.51	2.55	2.17
K ₂ O	1.01	1.06	0.98	0.90
Total	97.02	97.67	97.20	96.94

Cations on the basis of 23 oxygens

Si	6.168	6.024	5.906	6.386
Al	2.037	2.256	2.460	1.714
Ti	0.316	0.348	0.307	0.320
Fe	1.834	1.607	1.543	1.617
Mn	0.047	0.023	0.012	0.057
Mg	2.806	2.917	2.983	3.076
Ca	1.857	1.850	1.881	1.856
Na	0.670	0.725	0.739	0.631
K	0.194	0.202	0.188	0.172
Total	15.929	15.952	16.019	15.839
Class*	← Magnésio-Hastingsite		→ Magnésio-Hastingsite	Hornblende

Samples: Eg-2, L58; Eg-14, L76.

* Red-brown hornblendes assumed to be oxyhornblendes; classification based on Leake (1978) and assumes an Fe¹⁺:Fe²⁺ ratio of ~4 : 1 (see text).

analyses (4) show variable composition (En_{46-75}) (Lowe submitted). Thus, taken in conjunction with other criteria, the potential use of ferromagnesian silicate chemical analyses for tephra fingerprinting (and petrological) purposes could be worthy of further investigation.

A number of Egmont hornblendes were additionally examined by EMP (32 analyses), mainly to characterise and classify the types present. (Too few samples from individual eruptives were probed to potentially detect any meaningful compositional or inter-tephra trends -cf. Wallace et al. 1986.) Most are optically green-brown "calcic hornblendes" and, based on Leake's (1978) nomenclature and assuming all FeO (total iron) is in the Fe^{2+} form, include ferroan pargasite, pargasite, and ferroan pargasitic hornblende varieties (Table 5: Lowe submitted). A second, subordinate, group of dark reddish-brown amphiboles are probably "oxyhornblendes" (Deer et al. 1963), and are classed as magnesio-hastingsite or magnesio-hastingsitic hornblende (assuming an $Fe^{3+}: Fe^{2+}$ ratio of about 4:1, hence $Fe^{3+} > Al^{VI}$; Leake 1978).

Fe-Ti oxides

The Fe-Ti oxides comprise mostly titanomagnetite with rare magnetite and ilmenite, based on EMP studies. Very few grains showed exsolution features (Plate 4A), although inclusions are relatively common (Plate 4B). Selected analyses for some Tongariro and Egmont tephtras are listed in Table 6.

Fe-Ti oxide compositions, determined in various ways, have proved useful in tephra correlation studies in New Zealand and overseas (e.g., Kohn 1970, 1973; Topping & Kohn 1973; Westgate & Fulton 1975; Westgate & Gorton 1981; Smith & Leeman 1982; King et al. 1982; Hogg & McCraw 1983; see also Hodder 1981). Kohn & Neall (1973) demonstrated that Tongariro tephtras could be distinguished from those of Egmont by titanomagnetite chemistry as measured by emission spectrographic analysis. The Tongariro titanomagnetites contain more Cr (especially), V, and Ni, but less Mn, than titanomagnetites from Egmont eruptives (see also additional unpublished analyses in Kohn 1973).

Table 6. Electron microprobe analyses* of titanomagnetites in some Egmont and Tongariro tephras. Analyses are recalculated using the method of Carmichael (1967).

	Egmont				Tongariro	
	Eg-4	Eg-7	Eg-9	Eg-14	Mm	Oa-8
SiO ₂	0.05 (0.01)	0.06 (0.02)	0.06 (0.02)	0.09 (0.02)	0.10 (0.07)	0.15 (0.12)
TiO ₂	7.81 (0.22)	9.39 (0.65)	8.64 (1.15)	9.66 (0.89)	8.00 (5.05)	12.75 (3.57)
Al ₂ O ₃	2.85 (0.07)	2.46 (0.38)	2.99 (0.49)	3.97 (0.16)	2.68 (0.56)	2.16 (1.19)
Cr ₂ O ₃	0.04 (0.03)	0.02 (0.02)	0.02 (0.03)	0.02 (0.02)	0.27 (0.11)	0.39 (0.17)
FeO	80.74 (0.40)	79.14 (0.91)	79.68 (0.26)	76.87 (0.76)	80.21 (4.67)	76.34 (4.10)
MnO	0.77 (0.07)	0.82 (0.08)	0.69 (0.04)	0.66 (0.05)	0.33 (0.07)	0.46 (0.16)
MgO	2.65 (0.04)	2.74 (0.19)	2.77 (0.30)	3.67 (0.36)	2.00 (0.72)	2.26 (1.59)
CaO	0.02 (0.01)	0.09 (0.17)	0.02 (0.02)	0.03 (0.05)	0.01 (0.01)	0.01 (0.01)
NiO	0.02 (0.03)	0.01 (0.02)	0.02 (0.03)	0.03 (0.03)	0.06 (0.06)	0.03 (0.03)
Total	94.95	94.73	94.89	95.00	93.66	94.55
n	10	9	7	6	5	6
Recalculated analyses						
<i>Ulvospinel basis</i>						
Fe ₂ O ₃	51.95 (0.38)	49.06 (1.47)	50.04 (1.67)	47.24 (1.29)	49.96 (9.14)	41.40 (6.65)
FeO	34.00 (0.36)	34.99 (0.50)	34.65 (1.44)	34.37 (0.42)	35.25 (3.74)	39.09 (3.90)
Total	100.13 (0.52)	99.66 (0.53)	99.91 (0.36)	99.71 (0.30)	98.78 (0.84)	98.68 (1.07)
Mol%						
Usp	21.8 (5.5)	26.4 (1.9)	24.1 (3.2)	26.7 (2.3)	22.8 (13.8)	36.5 (10.3)

* Analyses obtained using a JEOL-733 Superprobe with a 12 nA beam current at 15 kV and a 3 μm beam. n = number of analyses in mean with 1 standard deviation in parentheses; individual analyses are available from the author. Samples as follows: Eg-4, L84 (L. Rotomanuka); Eg-7, L85 (L. Rotomanuka); Eg-9, L86 (L. Rotomanuka); Eg-14, L88 (L. Rotomanuka); Mm, L91 (L. Rotomanuka); Oa-8, L98 (L. Maratoto). See Table 1 for tephra abbreviations.

These findings are used here to attempt to distinguish Tongariro and Egmont-derived tephras - the respective sources being indicated by the ferromagnesian mineralogy - by EMP analysis of their titanomagnetites. No attempt is made to distinguish between the individual eruptives pertaining to one or to the other of these centres. Note that the EMP has limited capabilities for measuring elements other than major elements and certain transition or heavy metals (e.g., see Westgate & Gorton 1981). Thus vanadium was not analysed, and measurements of nickel, almost always below the probe's accurate detection limits, are accordingly of little value. About 200 analyses were obtained from 18 tephra samples. Usually 10-15 grains in each sample were probed, but in samples containing very sparse Fe-Ti oxides fewer analyses were obtainable.

The results support Kohn & Neall (1973) and generally indicate that Tongariro and Egmont eruptives may be separated using Cr (as Cr_2O_3) and Mn (MnO) abundances in particular. Cr_2O_3 always occurs in measurable quantities (c.0.2 - 0.3%) in the Tongariro-derived samples, but is invariably very low (usually present in trace quantities but below accurate detection limits) in Egmont-derived samples (<c.0.05%). MnO concentrations in the Egmont samples (range c.0.4-1.0%) usually exceed those of the Tongariro samples (c.0.3 - 0.5%) (Fig.4; Table 6). Recent chemical analyses of titanomagnetites in Taranaki tephras by Franks (1984, p.98) show corroborative values: MnO concentrations average 0.8% and Cr_2O_3 concentrations average 0.028% (280 ppm). Note that the results should be treated with caution because the differences in element concentration are small in absolute terms. More work is required to determine if other elements may be used to discriminate between tephra sources or between individual tephras.

Because the EMP is a grain-discrete method, mixed populations in samples may be readily detected (e.g., Kohn 1979; Westgate & Gorton 1981; King et al. 1982; Hogg & McCraw 1983). Assuming that the above differences in Cr_2O_3 and MnO concentrations in the titanomagnetites are reliable indicators of

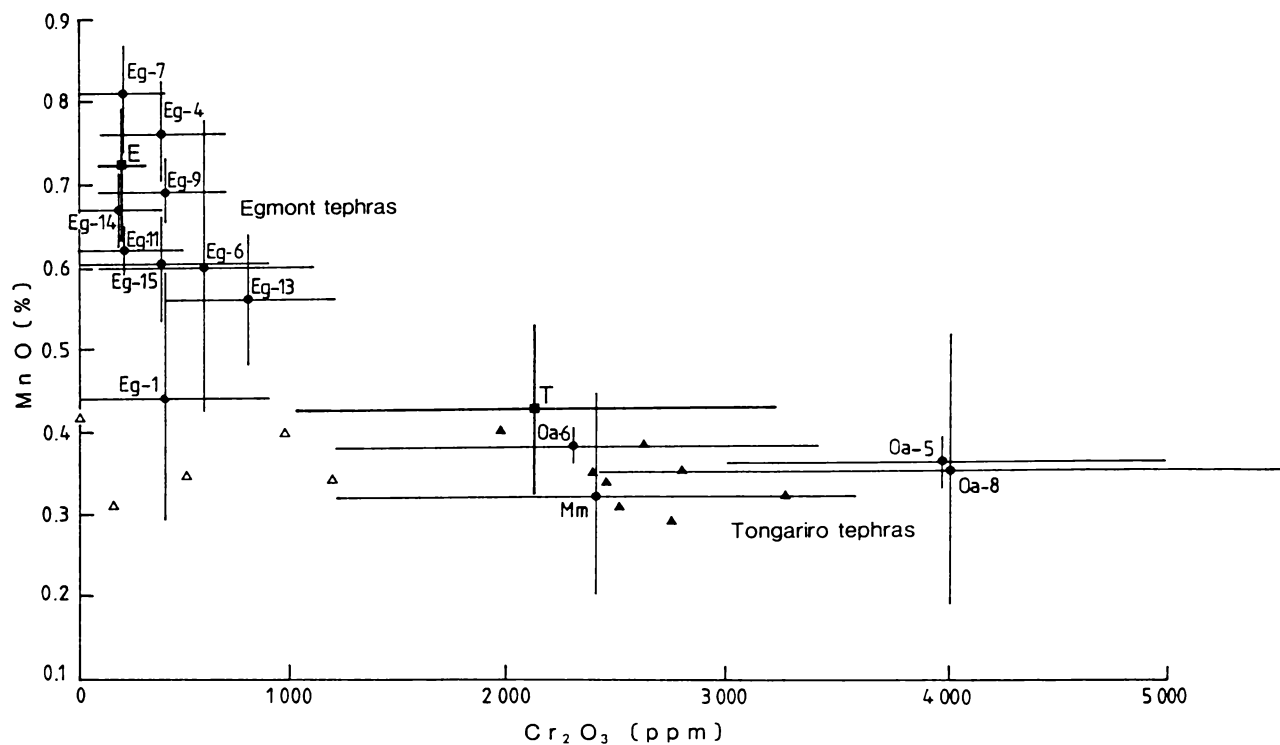


Fig.4. MnO vs Cr₂O₃ plot for Ti-magnetites of some Egmont and Tongariro-derived tephtras in Lake Rotomanuka. Bars represent one standard deviation from the mean. Numbers of grains analysed in Egmont tephtras: Eg-1, 11; Eg-4, 10; Eg-7, 8; Eg-9, 7; Eg-11, 10; Eg-13, 12; Eg-14, 10; Eg-15, 10. Tongariro tephtras: Mm, 8; Oa-5, 4; Oa-6, 3; Oa-8, 12 (abbreviations are explained in Table 1 and Fig.2). Note that the Cr₂O₃ analyses of the Egmont tephtras are approximate (usually below accurate detection limits).

Triangles mark analyses of individual grains from a "single" tephtra layer in a core from Lake Rotomanuka, which apparently contains two admixed tephtras: Oa-4 (closed triangles), Eg-12 (open triangles). Ferromagnesian mineralogical data (Table 4) indicates that Oa-4 is dominant, however.

E = mean \pm 1 std. dev. of Kohn & Neall's (1973) analyses of Egmont-derived tephtras younger than c.16 000 yrs B.P. (n = 23); T = mean \pm 1 std. dev. of Kohn's (1973) analyses of Tongariro-derived tephtras younger than c.15 000 yrs B.P. (n = 20).

a Tongariro or Egmont source, the analyses showed some samples to contain admixed Tongariro and Egmont-derived grains (e.g., Fig.4; see also Table 10). This was evident mainly in samples of tephra deposited in the period c.10 000 - 12 000 years B.P. (cf. tephrostratigraphy of Stewart et al. 1977, p.184). Analyses from several other samples suggest that Egmont eruptives may have "dusted" the Waikato lakes between c.13 500 - c.14 500 years ago, around the same time that various tephras from other sources were being deposited (Table 1). The mixing so indicated probably arises because such concentrations of eruptions over relatively short time intervals mean that the deposits are very closely spaced in the lake sediments - hence they are potentially subject to the bioturbation and other short-range mixing processes noted earlier.

Analyses of suitable Fe-Ti oxide pairs enable pre-eruptive temperature estimates, and oxygen fugacities, to be determined by geothermometry (Buddington & Lindsley 1964; Spencer & Lindsley 1981). Besides their petrological and volcanological value, these parameters may be a useful aid in correlating tephras (e.g., Lerbekmo et al. 1975; Smith & Leeman 1982; Froggatt & Solloway 1986). Results from a limited number of Tongariro and Egmont Fe-Ti oxide pairs are given in Table 7, and are based on calculation procedures of Carmichael (1967) and Anderson & Lindsley (1985) using computer programmes written by J.C. Stormer. The Ti-magnetite/ilmenite sample pairs are assumed to have co-existed in equilibrium in the magma. Support for this equilibrium is shown by the semi-parallelism of tie lines in a triangular plot of the samples' minor elements Mn, Mg, and Al + Cr (cf. Storey 1985, p.241-242).

Estimated oxide equilibrium temperatures for two pairs from the same tephra sample (0a-4) show close agreement. Other Tongariro and Egmont eruptives show a range of temperatures and oxygen fugacities (Table 7; see Lowe submitted).

Plate 4.A. Two sets of exsolution lamellae in polished Ti-magnetite grain.

(Mangamate Tephra, L. Rotomanuka.) Scale 10 mm = 15.5 μm ;

magnification X670.

B. Inclusions in polished Ti-magnetite grain with a narrow glassy rim.

(Mangamate Tephra, L. Rotomanuka.) Scale 10 mm = 24 μm ; magnification

X420.

C. Biogenic (?) borings in labradorite or bytownite grain. The grooves are

about 1.5-2 μm in width. (Eg-2 tephra, L. Rotomanuka.) Scale 10 mm =

15.5 μm ; magnification X670.

D. Enlargement of lower left part of micrograph C. Scale 10 mm = 8 μm ;

magnification X1260.

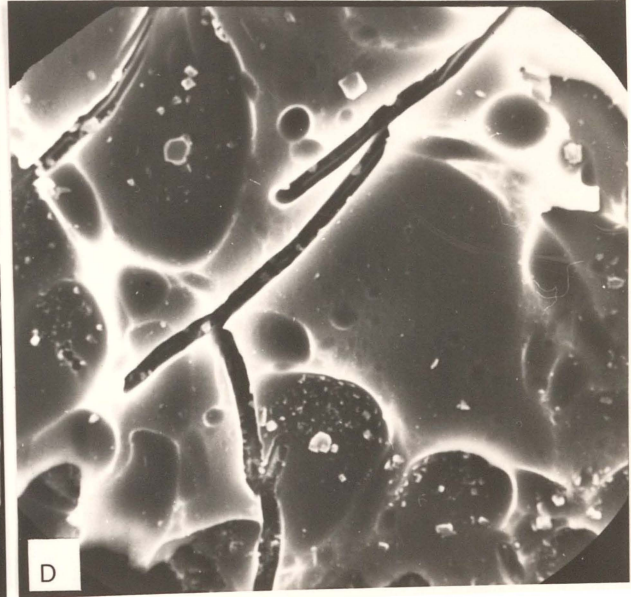
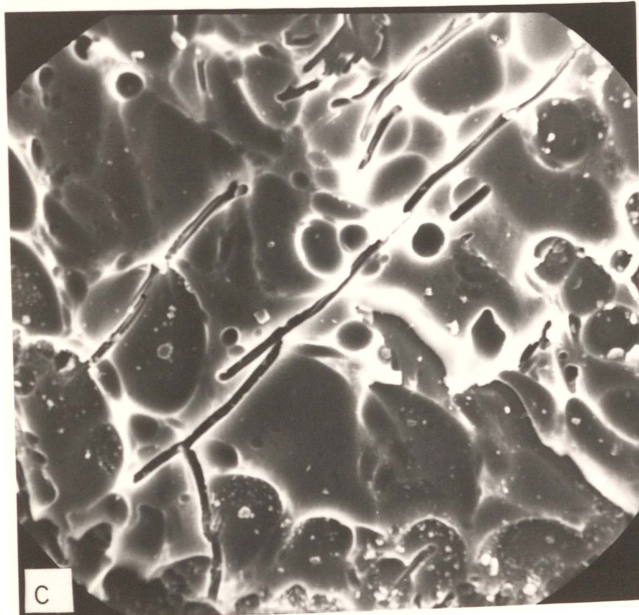
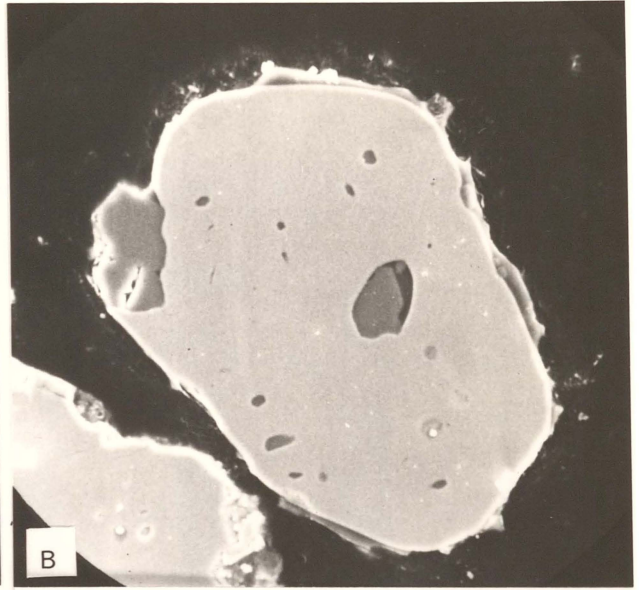
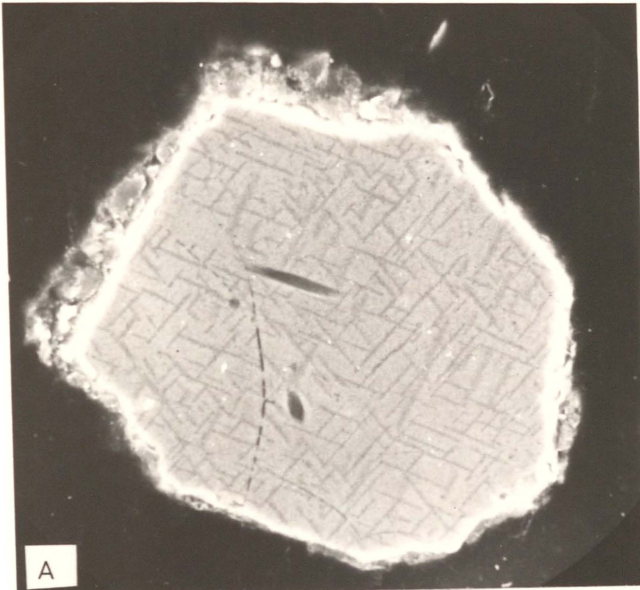


Table 7. Electron microprobe analyses of co-existing titanomagnetite - ilmenite pairs, recalculated after Carmichael (1967). Oxide equilibrium temperatures and oxygen fugacities were deduced from curves of Spencer & Lindsley (1981) as modified by Anderson & Lindsley (1985), using a computer programme written by J.C. Stormer.

Sample*	Egmont tephra			Tongariro tephra			
	Eg-2	Eg-13	Mm	Oa-4	Oa-4	Oa-5	Oa-8
<i>Spinel phase</i>							
SiO ₂	0.04	0.08	0.09	0.08	0.16	0.05	0.09
TiO ₂	7.97	11.09	4.89	13.13	13.23	13.72	18.01
Al ₂ O ₃	2.14	4.00	2.28	2.35	2.35	2.77	1.16
Cr ₂ O ₃	0.04	0.00	0.30	0.24	0.26	0.37	0.28
Fe ₂ O ₃	52.43	44.49	55.39	40.89	40.98	40.31	32.71
FeO	34.68	35.88	33.16	39.90	40.30	39.78	43.66
MnO	1.11	0.63	0.28	0.34	0.38	0.40	0.50
MgO	2.06	3.62	1.25	2.05	2.08	2.66	2.29
CaO	0.02	0.00	0.02	0.03	0.00	0.02	0.01
NiO	0.04	0.00	0.00	0.05	0.00	0.10	0.01
Total	100.53	99.78	97.66	99.06	99.75	100.16	98.71
Mol%							
Usp	22.3	30.6	14.5	37.1	37.4	37.9	51.0
<i>Rhombohedral phase</i>							
SiO ₂	0.02	0.04	0.08	0.01	0.04	0.05	0.02
TiO ₂	30.52	35.74	21.24	44.41	44.62	33.81	37.71
Al ₂ O ₃	0.48	0.46	1.49	0.41	0.36	0.54	0.60
Cr ₂ O ₃	0.08	0.26	0.23	0.08	0.13	0.03	0.14
Fe ₂ O ₃	42.21	32.00	59.77	19.24	17.55	36.90	29.13
FeO	24.07	30.51	14.54	30.31	33.78	25.55	26.59
MnO	0.51	0.18	0.57	0.34	0.28	0.21	0.17
MgO	1.46	0.84	2.29	5.17	3.42	2.60	4.00
CaO	0.13	0.00	0.00	0.04	0.00	0.00	0.01
NiO	0.11	0.00	0.00	0.04	0.01	0.07	0.03
Total	99.58	100.04	100.20	100.03	100.19	99.76	98.40
Mol%							
R ₂ O ₃	41.4	31.6	59.4	18.4	17.0	35.8	28.6
Temp. (°C)	934	948	974	917	908	1020	1095
log fO ₂	-9.27	-9.62	-8.06	-10.80	-11.04	-8.84	-8.68

* Eg-2, L83 (L. Rotomanuka); Eg-13, L101 (L. Rotomanuka); Mm, L91 (L. Rotomanuka); Oa-4, L95 (L. Rotomanuka); Oa-5, L96 (L. Rotomanuka); Oa-8, L98 (L. Maratoto); see Table 1 for tephra abbreviations.

Light Minerals

Based on XRD analysis and examination by petrological microscope, the light minerals of the 2-4 phi fractions of tephrae from the rhyolitic volcanoes comprise mainly glass (usually \geq c.80 wt. %) plus small amounts of plagioclase feldspar, quartz, and rare alkali-feldspar.

Tephrae from the andesitic volcanoes are dominated by plagioclase feldspar (usually c.55 - 85%). Plagioclase is usually the most abundant phenocryst in Tongariro and Egmont lavas (Cole et al. 1986; Neall et al. 1986). Glassy (isotropic) material makes up c.15-45% of the tephrae's light mineral fractions, and is commonly vesicular and softish and fragile-looking; many grains contain semi-oriented lathlike feldspar microlites. The Tongariro tephrae generally contain the least glass. Many plagioclase grains have narrow glassy mantles.

SEM photomicrographs illustrating some of these features are given in Plates 5A-H.

Generally, the tephric material looks fresh and unaltered, but occasionally the SEM showed evidence of incipient weathering in the form of micropits and tiny fragments ("adhering dust") on grain surfaces (e.g., Plate 5H; cf. Heiken & Wohletz 1985). Some calcic-plagioclase grains in an Egmont-derived sample have unusual tubular, "box-canyon" grooves (Plates 4C,D). These are interpreted as biogenic - perhaps marking micro-borings by calcium-seeking filamental algae, e.g., charophyte rhizomes (?*nitella*) (cf. Ross & Fisher 1986). Vesicle fillings (including diatom frustules) may also occur, particularly in the andesitic scoriaceous/pumiceous pyroclasts.

Elongated, parallel vesicles characterise many shards in samples of Tuhua Tephra.

Feldspar composition

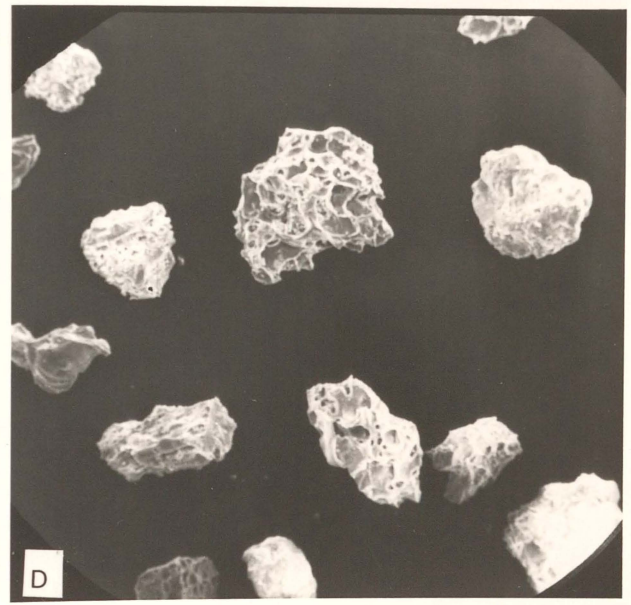
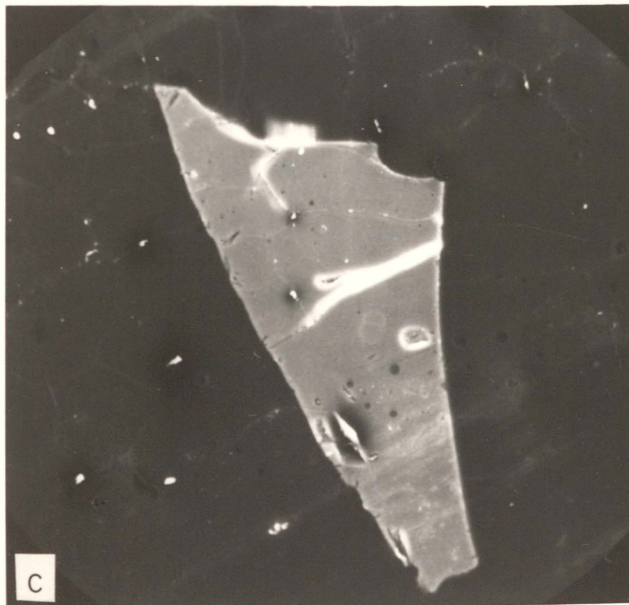
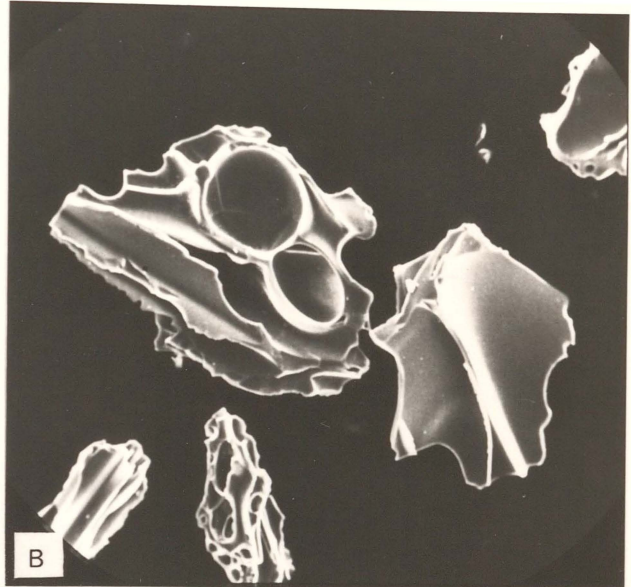
Feldspar composition was investigated by EMP. In total about 130 analyses were obtained, around 90% of these being on samples of the

Plate 5.A Pumiceous, platy, and cusplate rhyolitic glass shards with varying degrees of vesicularity (cf. Nelson et al. 1985); some show elongated, parallel vesicles. (Taupo Pumice, L. Rotomanuka.) Scale 10 mm = 150 μm ; magnification X67.

B. Cusplate and vesicular rhyolitic pumice shards (Taupo Pumice, L. Rotomanuka.) Scale 10 mm = 60 μm ; magnification X170.

C. Platy, rhyolitic shard (polished) of peralkaline composition. (Unnamed Mayor Island-derived tephra, L. Rotomanuka.) Scale 10 mm = 50 μm ; magnification X200.

D. Blocky, andesitic pumiceous/scoriaceous glass shards. (Okupata Tephra, Oa-8, L. Maratoto.) Scale 10 mm = 134 μm ; magnification X75.



plagioclase-rich Tongariro and Egmont-derived tephras. Mainly grain cores were probed. Selected representative analyses are given in Table 8.

The Tongariro and Egmont-derived tephras show a range of plagioclase compositions, with both groups containing andesine, labradorite, and bytownite (Fig.5). The Tongariro samples (68 analyses) range from An_{35-85} with the mean of all analyses being $An_{61\pm 8}$; Egmont samples (49 analyses) are similar, having a range of An_{33-81} and a mean of $An_{57\pm 9}$ (Lowe submitted). These results are in close agreement with the findings of Cole et al. (1986) and Neall et al. (1986) for Tongariro and Egmont lavas, respectively.

The few analyses obtained on the tephras derived from rhyolitic sources indicate that the feldspars are generally much less calcic. The Taupo and Okataina-derived tephras usually contain oligoclase and andesine (An_{23-38} ; Lowe 1986b, p.297) (cf. Ewart 1969; Cole & Nairn 1975). The peralkaline Mayor Island-derived Tuhua Tephra contains alkali feldspar, both sanidine (Or_{53-73}) and anorthoclase (Or_{35}) (Fig.5) (cf. Ewart et al. 1968b; Buck et al. 1981; Hogg & McCraw 1983; Houghton & Wilson 1986).

Glass chemistry

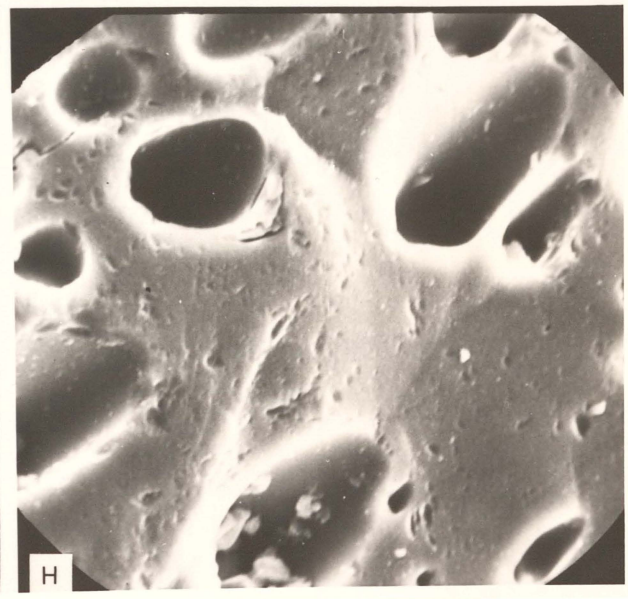
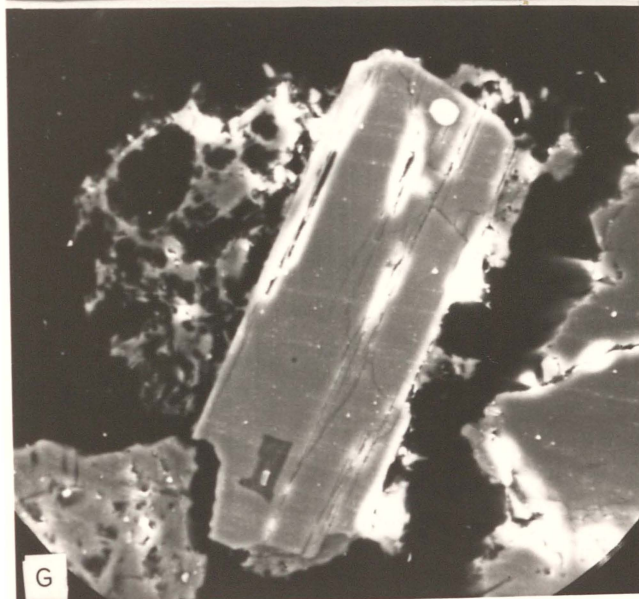
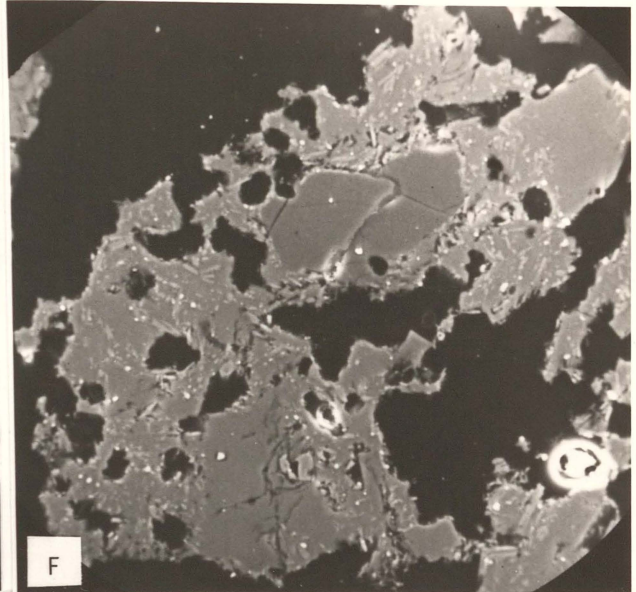
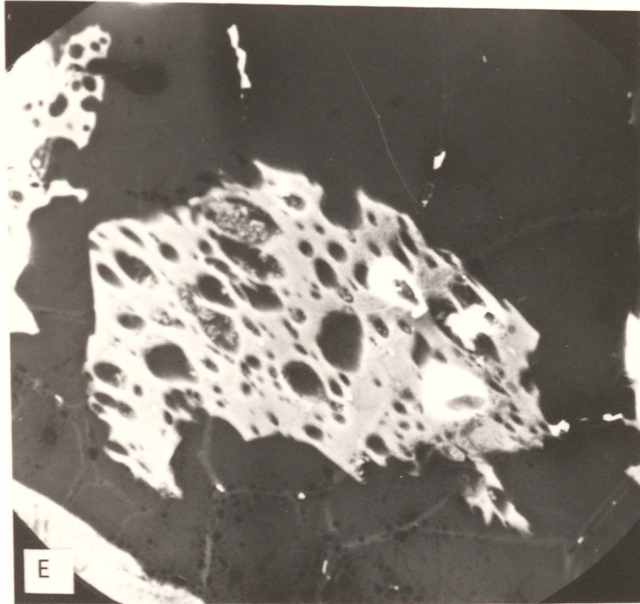
The suitability of the EMP for analysing glass for the characterisation and correlation of tephras has been well documented since the early work by Smith & Westgate (1969) and others (e.g., see recent studies by Federman & Carey 1980; Self & Sparks 1981; Froggatt 1983; Kyle & Seward 1984; Mangerud et al. 1984; Sarna-Wojcicki et al. 1984; Davis 1985; Ledbetter 1985; Nelson et al. 1985; Riehle 1985; Vinci 1985; Froggatt et al. 1986). For several reasons, the method was seen to be potentially very useful for studying the tephras in this project. Firstly, the tephras in the Waikato region derive from multiple sources, and were thus ~~were~~ likely to show a range of chemically distinct units. Where glass major element compositions proved too similar to distinguish one tephra from another, the continuous cores would enable them to be distinguished stratigraphically. Secondly, glass is the main constituent in the rhyolitic tephras and is easily separated. Thirdly, the EMP provides

Plate 5. E. Highly vesicular andesitic pumiceous glass shard (polished) illustrating limited potential for probing with 10-20 μm beam. (Rotoaira Lapilli, L. Rotomanuka.) Scale 10 mm = 33 μm ; magnification X300.

F. Vesicular, andesitic glassy material containing abundant plagioclase microlites (polished). (Okupata Tephra, Oa-1, L. Maratoto.) Scale 10 mm = 41 μm ; magnification X250.

G. Calcium-rich, inclusion-bearing, plagioclase grain with fragmentary, vesicular andesitic glassy rim (polished). (Eg-2 tephra, L. Kainui.) Scale 10 mm = 24 μm ; magnification X420.

H. Surface of part of moderately vesicular rhyolitic pumice shard (peralkaline) showing surface micropitting. (Tuhua Tephra, L. Rotomanuka.) Scale 10 mm = 8 μm ; magnification X1340.



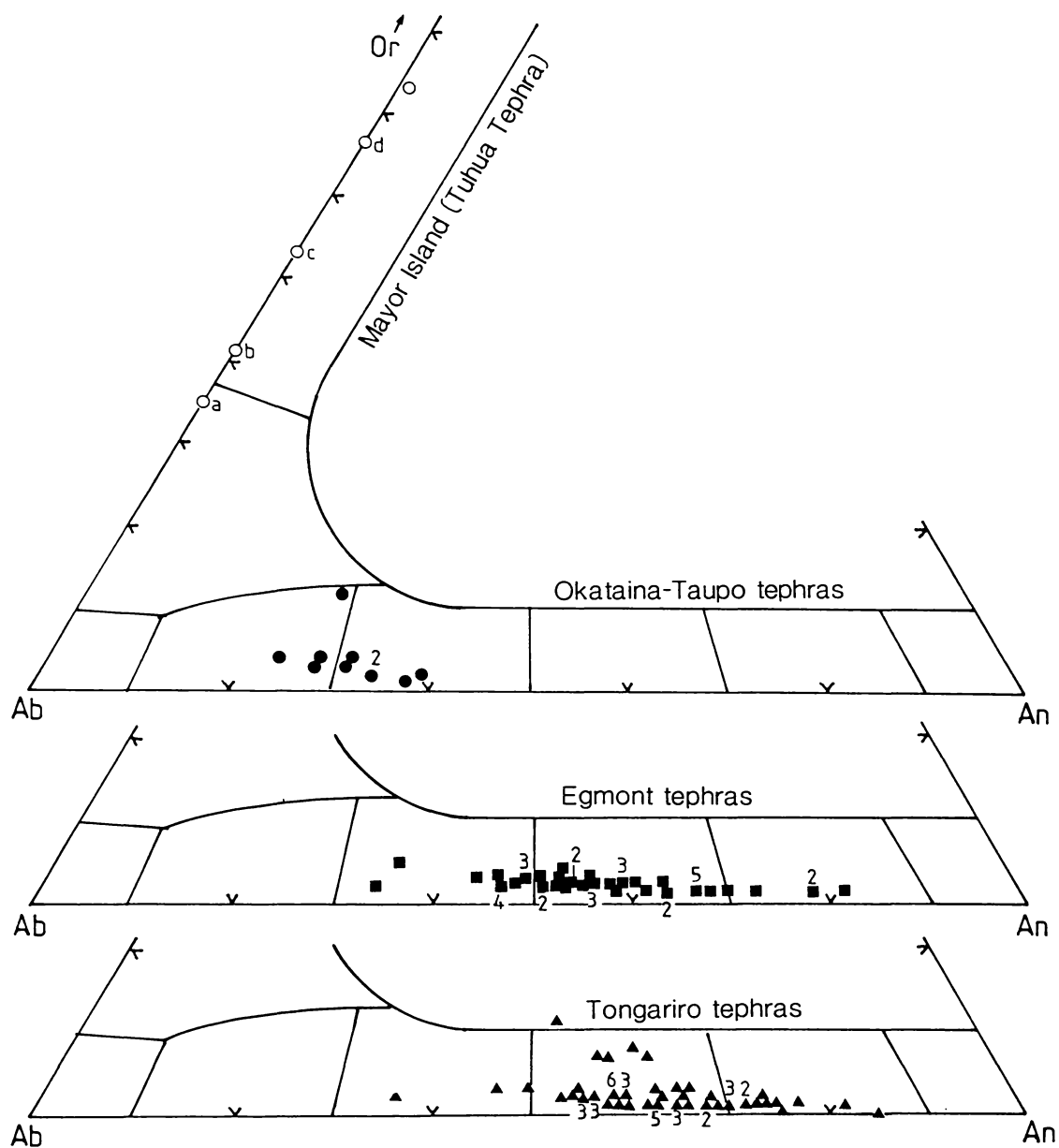


Fig.5. Electron microprobe analyses of feldspars (molecular %). Only analyses from grain cores are plotted. Numbers indicate that two or more grains have essentially identical Ab-An-Or compositions. Analyses a-d (Tuhua Tephra) were determined by Dr R.M. Briggs at Auckland University (University of Waikato, pers. comm. 1980); anal. a & b are from a subaerial deposit of Tuhua Tephra on Coromandel Peninsula (sample K2, site 37: Hogg 1979).

Table 8. Some representative electron microprobe analyses* of feldspars in tephras in Waikato lakes (see also Fig. 5).

Sample Number ^b	Alkali feldspar		Plagioclase feldspar									
	Sanidine ^a		Andesine									
	L11	H2	L4	L5					L38	L9	L18	L40
Analysis Number	1	2	1	2	3a	3b	4	5	6	7	8	9
SiO ₂	71.23	72.32	60.18	57.15	56.10	57.12	55.93	56.27	58.18	54.86	55.73	55.16
Al ₂ O ₃	19.14	19.60	24.90	27.07	26.85	26.52	26.81	27.08	25.58	26.91	27.22	27.69
TiO ₂	-	-	0.02	0.04	0.04	0.03	-	0.06	0.02	0.04	0.02	0.04
FeO [†]	0.72	0.71	0.24	0.41	0.40	0.43	0.50	0.45	0.28	0.62	0.51	0.35
MgO	-	-	0.01	0.02	0.03	0.03	0.04	0.05	0.01	0.17	0.03	0.06
CaO	-	-	6.69	9.45	9.47	9.08	9.70	9.45	7.87	9.91	9.45	9.99
Na ₂ O	3.19	1.90	7.31	5.98	6.02	6.42	5.87	6.02	7.02	5.64	5.90	5.57
K ₂ O	5.44	5.52	0.35	0.36	0.35	0.45	0.42	0.42	0.37	0.51	0.43	0.51
Total	99.72	100.05	99.70	100.48	99.26 (core)	100.08 (rim)	99.27	99.80	99.33	99.66	99.29	99.37
Or	53	66	2	2	2	2	2	2	2	3	2	3
Ab	47	34	65	52	52	55	51	52	60	49	52	49
An	0	0	33	46	46	43	47	46	38	48	46	48
Cations on the basis of 8 oxygens												
Si			2.688	2.558	2.546	2.570	2.541	2.541	2.625	2.514	2.530	2.506
Al			1.310	1.428	1.436	1.406	1.436	1.441	1.360	1.454	1.456	1.482
Ti			0.001	0.002	0.001	0.001	-	0.002	0.001	0.002	0.001	0.002
Fe			0.009	0.015	0.015	0.016	0.018	0.017	0.010	0.024	0.019	0.013
Mg			0.001	0.001	0.002	0.002	0.002	0.003	0.001	0.011	0.002	0.004
Ca			0.320	0.454	0.461	0.438	0.472	0.457	0.381	0.486	0.460	0.486
Na			0.633	0.519	0.530	0.560	0.518	0.527	0.614	0.501	0.520	0.490
K			0.020	0.021	0.020	0.026	0.024	0.024	0.021	0.030	0.025	0.030
Total			4.982	4.998	5.010	5.019	5.011	5.012	5.013	5.022	5.013	5.013

* Analyses by JEOL JXA-733 Superprobe at Victoria University of Wellington with a 12 nA beam at 15 kV defocused to 10 μ m. Or-1A (orthoclase) standard was used to regularly check probe calibration. Analyses done on grain cores unless specified otherwise; analyses 3a, 3b done on same grain. - = not detected. A complete set of analyses is available from the author on request.

[†] Total Fe as FeO

^a These analyses made by Dr R.M. Briggs (University of Waikato) at Auckland University.

^b Tephra from which sample obtained (all from Lake Rotomanuka unless noted otherwise; see Table 1 for tephra abbreviations): L11, Tu; H2, Tu (Hauraki Bog, Hogg 1979); L4, Wo; L5, Eg-2; L38, Rk; L9, Eg-7; L18, Eg-10 (L. Maratoto); L40, Eg-14.

Table 8 contd.

Plagioclase contd.

Labradorite

Sample Number ^c	L6	L8			L108	L10	L109		L106	L105	L25
Analysis Number	1	2	3	4	5	6	7	8	9	10	
SiO ₂	54.96	53.83	55.29	50.93	50.86	52.93	52.07	54.05	51.93	53.07	
Al ₂ O ₃	27.63	28.04	28.19	30.09	30.73	28.63	29.17	28.08	28.87	28.86	
TiO ₂	-	0.07	-	0.05	0.04	0.02	0.04	0.08	0.11	0.02	
FeO†	0.50	0.52	0.43	0.60	0.52	0.39	0.59	0.56	1.07	0.58	
MgO	0.03	0.06	0.05	0.04	0.04	0.06	0.08	0.08	0.15	0.06	
CaO	10.46	11.37	10.28	13.43	13.71	12.16	12.82	11.26	13.05	12.72	
Na ₂ O	5.47	4.97	5.48	3.79	3.86	4.70	4.16	4.89	3.82	4.32	
K ₂ O	0.42	0.37	0.33	0.12	0.20	0.15	0.21	0.45	0.26	0.22	
Total	99.47	99.23	100.35	99.05	99.96	99.04	99.14	99.45	99.26	99.85	
Or	2	2	2	1	1	1	1	3	2	1	
Ab	48	43	48	33	33	41	37	43	34	38	
An	50	55	50	66	66	58	62	54	64	61	

Cations on the basis of 8 oxygens

Si	2.498	2.460	2.499	2.344	2.323	2.425	2.390	2.463	2.387	2.416
Al	1.480	1.510	1.493	1.632	1.654	1.546	1.578	1.508	1.564	1.549
Ti	-	0.002	-	0.002	0.001	0.001	0.001	0.003	0.004	0.001
Fe	0.019	0.020	0.016	0.023	0.020	0.015	0.022	0.021	0.041	0.022
Mg	0.002	0.004	0.003	0.003	0.003	0.004	0.005	0.006	0.010	0.004
Ca	0.509	0.557	0.495	0.662	0.671	0.597	0.630	0.550	0.642	0.620
Na	0.482	0.440	0.478	0.338	0.342	0.418	0.370	0.432	0.341	0.381
K	0.024	0.021	0.019	0.007	0.012	0.009	0.012	0.026	0.015	0.013
Total	5.015	5.014	5.002	5.010	5.026	5.014	5.011	5.009	5.004	5.006

^c L6, Eg-4; L8, Eg-6; L108, Eg-7 (L. Kainui); L10, Eg-9; L109, Mm (L. Maratoto); L106, Eg-11 or Oa-1 (L. Maratoto); L25, Eg-12 or Oa-4; L105, Oa-2 (L. Maratoto).

Table 8 contd.

Plagioclase contd.

Labradorite contd.

Sample Number ^d	L29	L27			L110		L40			L42
Analysis Number	11	12	13	14	15	16	17	18	19	20
SiO ₂	50.90	53.19	51.91	52.84	50.50	51.09	53.70	53.07	54.04	50.72
Al ₂ O ₃	29.81	28.45	29.72	29.00	30.22	30.19	28.55	28.94	28.03	30.49
TiO ₂	-	0.11	0.07	0.05	0.07	0.07	0.03	-	-	0.03
FeO†	0.72	0.73	0.60	0.62	0.61	0.48	0.47	0.56	0.65	0.63
MgO	0.09	0.10	0.07	0.10	0.08	0.07	0.07	0.08	0.09	0.11
CaO	13.94	11.86	12.46	11.93	14.07	13.52	11.23	11.82	10.94	13.54
Na ₂ O	3.44	4.61	4.13	4.74	3.45	3.53	4.94	4.76	5.09	3.73
K ₂ O	0.21	0.31	0.18	0.33	0.13	0.17	0.34	0.37	0.40	0.23
Total	99.11	99.36	99.14	99.61	99.13	99.12	99.33	99.60	99.24	99.48
Or	1	2	1	2	1	1	2	2	2	1
Ab	31	40	37	41	30	32	43	41	45	33
An	68	58	62	57	69	67	55	57	53	66

Cations on the basis of 8 oxygens

Si	2.345	2.432	2.379	2.411	2.326	2.347	2.449	2.421	2.467	2.327
Al	1.619	1.533	1.605	1.560	1.641	1.634	1.534	1.556	1.508	1.649
Ti	-	0.004	0.002	0.002	0.002	0.002	0.001	-	-	0.001
Fe	0.028	0.028	0.023	0.023	0.024	0.018	0.018	0.021	0.025	0.024
Mg	0.006	0.006	0.005	0.007	0.005	0.005	0.005	0.006	0.006	0.007
Ca	0.688	0.581	0.612	0.583	0.695	0.665	0.549	0.578	0.535	0.666
Na	0.307	0.409	0.367	0.419	0.308	0.315	0.436	0.421	0.450	0.332
K	0.012	0.018	0.010	0.019	0.007	0.010	0.020	0.022	0.023	0.013
Total	5.005	5.011	5.004	5.024	5.009	4.996	5.011	5.025	5.014	5.020

^d L29 & L27, Oa-5; L110, Oa-8 (L. Maratoto); L40, Eg-14; L42, Eg-15.

Table 8 contd.

Plagioclase contd.

Bytownite

Sample Number ^e	L104	L27		L40		L42
Analysis Number	1	2	3	4	5	6
SiO ₂	49.01	49.08	49.18	46.94	47.48	47.69
Al ₂ O ₃	31.17	31.84	31.25	33.13	32.73	32.45
TiO ₂	0.06	0.05	0.03	-	0.03	0.04
FeO†	0.60	0.69	0.71	0.53	0.48	0.65
MgO	0.05	0.07	0.04	0.03	0.03	0.04
CaO	15.57	15.13	14.72	16.54	16.00	15.78
Na ₂ O	2.86	2.82	2.97	2.10	2.42	2.38
K ₂ O	0.14	0.13	0.24	0.12	0.08	0.14
Total	99.46	99.81	99.14	99.39	99.25	99.17
Or	1	1	2	1	1	1
Ab	25	25	26	18	21	21
An	74	74	72	81	78	78

Cations on the basis of 8 oxygens

Si	2.262	2.254	2.273	2.174	2.197	2.210
Al	1.696	1.723	1.702	1.808	1.786	1.771
Ti	0.002	0.002	0.001	-	0.001	0.002
Fe	0.023	0.026	0.027	0.020	0.018	0.025
Mg	0.003	0.005	0.002	0.002	0.002	0.002
Ca	0.770	0.744	0.729	0.821	0.793	0.783
Na	0.256	0.251	0.266	0.188	0.217	0.214
K	0.008	0.007	0.014	0.007	0.005	0.008
Total	5.021	5.012	5.014	5.020	5.020	5.015

^e L104, Eg-12 or Oa-4 (L. Maratoto); L27, Oa-5; L40, Eg-14; L42, Eg-15.

the only means of detecting and potentially correlating any distal deposits present as sparse glass shards only.

Accordingly, glass was analysed by EMP for nine elements using methods and conditions described in Froggatt & Gosson (1982) and Froggatt (1983). These included using an 8 nA beam at 15 kV, usually defocussed to 10 μm but occasionally to 20 μm , to minimise loss of Na and K. These last two elements were always analysed first and second, respectively. Peak searches were carried out regularly, and glass and elemental standards frequently analysed to check and correct for machine drift. (Glass standards used were: KN-18, comenditic glass; VG-99, basaltic glass; VG-568, Yellowstone rhyolitic glass.) Froggatt (1982a, 1983) has demonstrated that the EMP technique has good reproducibility. Duplicate analyses on three glass shards from Mapara Tephra in Lake Kainui are given in Table 9.

Around 350 individual analyses were made, some 300 of these being on glass from the rhyolitic tephtras. Only c.50 reliable analyses were obtained on glass in tephtras from the andesitic sources - the sparseness of suitable glass in these samples, its high vesicularity and sometimes quasi-fragmented nature (e.g., see Plates 5E,F), plus the presence of microlites, combine to make it difficult to probe. Occasionally, glass rims on plagioclase grains were probed.

Usually a minimum of 10-12 analyses (each on an individual shard) were obtained for each of the rhyolitic tephtras present. However, for the reasons noted above, the andesitic eruptives are less well represented, and, in some cases, only 1 or 2 analyses per sample were obtainable.

Some of the analyses obtained are listed (in anhydrous form) in Table 10 (see also Green & Lowe 1985; Lowe 1986a; Lowe & Hogg 1986). The results are generally consistent with previous work on eruptives from the source volcanoes, although relatively few analyses on glass (as distinct from whole rock) have been published (cf. Ewart 1963; Ewart et al. 1968a,b; McCraw & Whitton 1971; Topping 1974; Cole & Nairn 1975; Neall 1977; Cole 1979; Kohn

Table 9. Duplicate electron microprobe analyses of three glass shards in Mapara Tephra in a core from Lake Kainui (normalised to 100%-loss free).

Shard No. Analysis	1		2		3		Mean \pm 1 S.D. (n = 6)
	a	b	a	b	a	b	
SiO ₂	77.03	77.18	76.68	76.47	76.63	76.23	76.70 \pm 0.35
Al ₂ O ₃	13.04	12.90	13.35	13.27	13.27	13.09	13.15 \pm 0.17
TiO ₂	0.17	0.19	0.19	0.19	0.19	0.18	0.19 \pm 0.01
FeO*	1.73	1.50	1.74	1.78	1.69	1.85	1.72 \pm 0.12
MgO	0.15	0.16	0.20	0.14	0.16	0.19	0.17 \pm 0.02
CaO	1.24	1.20	1.30	1.29	1.25	1.47	1.29 \pm 0.09
Na ₂ O	3.56	3.79	3.44	3.75	3.84	3.98	3.73 \pm 0.20
K ₂ O	2.94	2.96	2.95	2.99	2.86	2.89	2.93 \pm 0.05
Cl	0.14	0.12	0.13	0.12	0.11	0.13	0.13 \pm 0.01
Water†	--	--	0.54	1.22	1.55	0.20	0.59 \pm 0.66
Total	100.17	101.26	99.46	98.78	98.45	99.80	

* Total Fe as FeO

† Difference between analytical total as measured (given) and 100.

Each shard was analysed in two different spots (a, b) using an 8 nA beam at 15 kV defocussed to 10 μ m (see text). Sample L2.

Table 10. Electron microprobe analyses* of glass in tephras sampled from Lakes Rotomanuka, Kainui, or Maratoto. The analyses are normalised to 100% volatile free.

Taupo-derived tephras					
	Tp	Mp	Wo	Hm**	Op
SiO ₂	76.43 (0.64)	76.54 (0.36)	77.91 (0.26)	77.01 (0.67)	76.51 (0.40)
Al ₂ O ₃	13.05 (0.23)	13.15 (0.17)	12.48 (0.07)	12.88 (0.33)	13.01 (0.32)
TiO ₂	0.23 (0.05)	0.21 (0.04)	0.16 (0.05)	0.17 (0.03)	0.18 (0.03)
FeO†	1.81 (0.19)	1.76 (0.12)	1.52 (0.08)	1.68 (0.14)	1.73 (0.06)
MgO	0.22 (0.05)	0.19 (0.04)	0.13 (0.01)	0.16 (0.05)	0.20 (0.02)
CaO	1.31 (0.16)	1.32 (0.10)	0.98 (0.03)	1.30 (0.16)	1.41 (0.12)
Na ₂ O	3.97 (0.31)	3.76 (0.25)	3.62 (0.11)	3.71 (0.17)	3.86 (0.28)
K ₂ O	2.84 (0.17)	2.94 (0.10)	3.09 (0.10)	3.00 (0.25)	2.94 (0.13)
Cl	0.14 (0.03)	0.13 (0.02)	0.12 (0.02)	0.11 (0.03)	0.16 (0.03)
Water‡	3.21 (1.83)	1.65 (2.20)	1.55 (0.79)	1.70 (1.97)	6.33 (3.90)
n	10	9	11	20	7

* Analyses made with a JEOL JXA-733 Superprobe using an 8 nA beam current at 15 kV and defocussed to 10 µm (several shards were analysed at 20 µm) (see Froggatt & Gosson 1982; Froggatt 1983; and text). n = number of analyses in mean; numbers in parentheses = 1 standard deviation.

† All Fe calculated as FeO.

‡ Difference between original analytical total and 100. Tephra abbreviations are given in Table 1. Samples: Tp, L1 (L. Rotomanuka); Mp, L2 (L. Kainui); Wo, L4 (L. Rotomanuka); Hm, L6-7 (L. Rotomanuka); Op, L16 (L. Rotomanuka).

** See also Lowe (1986a, p.67) and Lowe & Hogg (1986, p.32).

Table 10 contd.

Okataina-derived tephras						
	Ma	Rm	Wh ^c	Rr	Rk	Ok
SiO ₂	78.87 (0.50)	78.63 (0.16)	78.61 (0.30)	77.57 (0.58)	78.34 (0.41)	78.53 (0.47)
Al ₂ O ₃	12.05 (0.17)	12.33 (0.10)	12.35 (0.13)	12.68 (0.32)	12.41 (0.18)	12.34 (0.08)
TiO ₂	0.12 (0.02)	0.10 (0.05)	0.13 (0.03)	0.21 (0.05)	0.14 (0.04)	0.11 (0.04)
FeO†	0.87 (0.07)	0.87 (0.07)	0.92 (0.08)	1.26 (0.09)	1.00 (0.13)	0.87 (0.06)
MgO	0.10 (0.02)	0.12 (0.02)	0.14 (0.01)	0.20 (0.08)	0.13 (0.03)	0.11 (0.03)
CaO	0.69 (0.10)	0.71 (0.07)	0.89 (0.04)	1.20 (0.33)	0.88 (0.07)	0.82 (0.06)
Na ₂ O	3.80 (0.20)	3.76 (0.06)	3.60 (0.28)	3.55 (0.29)	3.42 (0.34)	3.37 (0.26)
K ₂ O	3.38 (0.43)	3.37 (0.09)	3.26 (0.10)	3.19 (0.44)	3.56 (0.34)	3.71 (0.32)
Cl	0.12 (0.02)	0.11 (0.05)	0.10 (0.03)	0.14 (0.03)	0.12 (0.03)	0.14 (0.02)
Water‡	1.13 (1.40)	0.70 (0.43)	4.99 (3.00)	7.07 (1.71)	3.38 (2.12)	5.79 (1.66)
n	14	10	10	10	12	9

Samples: Ma, L12 (L. Rotomanuka); Rm, L15 (L. Rotomanuka); Wh, L31 (L. Rotomanuka); Rr, L34 (L. Rotomanuka); Rk, L38 (L. Rotomanuka); Ok, L43 (L. Rotomanuka).

c See also Appendix to Table 10.

Table 10 contd.

	Mayor Island-derived tephras			
	Maroa-tephra	Tu	Tu ^a	Un
	Pk			
SiO ₂	78.49 (0.45)	75.40 (0.38)	74.74 (0.21)	75.99 (0.37)
Al ₂ O ₃	12.28 (0.10)	9.43 (0.26)	9.26 (0.09)	9.68 (0.15)
TiO ₂	0.08 (0.02)	0.29 (0.05)	0.22 (0.05)	0.19 (0.01)
FeO [†]	0.90 (0.10)	5.65 (0.33)	5.64 (0.08)	4.71 (0.36)
MgO	0.07 (0.03)	0.02 (0.01)	0.01 (0.01)	0.01 (0.01)
CaO	0.64 (0.04)	0.24 (0.04)	0.20 (0.09)	0.19 (0.02)
Na ₂ O	3.23 (0.38)	4.86 (0.31)	5.51 (0.10)	4.75 (0.30)
K ₂ O	4.17 (0.48)	3.94 (0.42)	4.24 (0.11)	4.28 (0.13)
Cl	0.15 (0.03)	0.17 (0.06)	0.17 (0.10)	0.20 (0.01)
Water [‡]	5.07 (1.09)	0.73 (1.16)	1.97 (0.92)	1.87 (1.08)
n	12	16	7	5
	<i>Peralk. Index^b</i>	1.30 (0.06)	1.47 (0.02)	1.28 (0.08)

Samples: Pk, L33, L36 (L. Rotomanuka); Tu, L11 (L. Rotomanuka); Tu^a, L111 (L. Kainui; analyst P.C. Froggatt); Un, L37 (L. Rotomanuka).

^b Peralkaline Index = $(Na_2O + K_2O)/Al_2O_3$

Table 10 contd.

	Tongariro-derived tephras		
	Oa-1 ^b	Oa-4 ^b	Oa-8
SiO ₂	56.18 (2.50)	62.61 (2.96)	61.78 (1.17)
Al ₂ O ₃	20.92 (1.63)	21.19 (2.11)	16.18 (1.36)
TiO ₂	0.69 (0.32)	0.40 (0.01)	0.98 (0.10)
FeO [†]	5.28 (0.74)	1.82 (0.38)	6.41 (0.51)
MgO	2.39 (0.84)	0.39 (0.13)	2.71 (0.50)
CaO	10.19 (1.41)	7.89 (2.25)	6.44 (0.94)
Na ₂ O	3.42 (0.10)	3.33 (0.76)	3.52 (0.21)
K ₂ O	0.88 (0.37)	2.28 (0.10)	1.89 (0.23)
Cl	0.07 (0.06)	0.11 (0.01)	0.09 (0.05)
Water [‡]	2.19 (0.33)	0.63 (0.53)	1.97 (0.82)
n	2	2	10

^b Analyses may be influenced by presence of plagioclase microlites.

Samples: Oa-1, L106 (L. Maratoto); Oa-4, L25 (L. Rotomanuka); Oa-8, L110 (L. Maratoto).

Table 10 contd.

	Egmont-derived tephras				
	Eg-2	Eg-6	Eg-7	Eg-11	Eg-12
SiO ₂	70.74 (0.99)	67.71 (1.65)	70.25 (2.48)	70.32 (3.83)	71.85 (0.89)
Al ₂ O ₃	15.60 (0.52)	16.54 (1.31)	15.44 (0.85)	15.03 (1.04)	14.08 (0.38)
TiO ₂	0.39 (0.07)	0.56 (0.10)	0.52 (0.07)	0.61 (0.10)	0.60 (0.10)
FeO†	1.66 (0.13)	2.52 (0.40)	1.92 (0.41)	2.52 (0.80)	2.84 (0.38)
MgO	0.38 (0.14)	0.91 (0.41)	0.64 (0.53)	0.75 (0.76)	0.64 (0.13)
CaO	1.70 (0.24)	3.08 (0.97)	1.88 (1.32)	2.28 (0.62)	2.44 (0.34)
Na ₂ O	4.47 (0.37)	4.39 (0.37)	4.32 (0.29)	3.89 (0.99)	3.58 (0.13)
K ₂ O	4.88 (0.81)	4.17 (0.67)	4.85 (0.79)	4.79 (0.91)	3.84 (0.25)
Cl	0.18 (0.04)	0.12 (0.05)	0.18 (0.08)	0.14 (0.20)	0.13 (0.05)
Water‡	1.69 (1.09)	3.02 (1.66)	2.83 (2.47)	3.60 (1.33)	3.24 (2.61)
n	7	6	6	4	9

Samples: Eg-2, L103 (L. Kainui); Eg-6, L8 (L. Rotomanuka); Eg-7, L108 (L. Kainui); Eg-11, L106 (L. Maratoto); Eg-12, L25 (L. Rotomanuka).

Appendix to Table 10. Glass chemistry of Waiohau Ash sampled from Waikato peat cores.

	Wh ^d	Wh ^e
SiO ₂	78.32 (0.33)	78.33 (0.17)
Al ₂ O ₃	12.38 (0.13)	12.38 (0.05)
TiO ₂	0.11 (0.05)	0.11 (0.06)
FeO†	0.87 (0.07)	0.86 (0.10)
MgO	0.10 (0.03)	0.11 (0.03)
CaO	0.82 (0.05)	0.84 (0.10)
Na ₂ O	3.55 (0.16)	3.45 (0.12)
K ₂ O	3.73 (0.41)	3.81 (0.43)
Cl	0.12 (0.01)	0.11 (0.01)
Water‡	3.05 (1.58)	2.68 (1.43)
n	11	6

^d Sample L48 (RJ1-3) from Rukuhia peat core, L. Maratoto (see Green & Lowe 1985, p.680).

^e Sample L49 (Muir-169) from Moanatuatua peat core, Muir Road.

1979; Froggatt 1983; Froggatt & Solloway 1986; Houghton & Wilson 1986)³. Taking into account the inherent variability normally associated with the EMP analysis of Na₂O, K₂O, and SiO₂ in particular (Smith & Westgate 1969), the glass populations of most of the rhyolitic tephtras are relatively homogenous, as indicated by the generally low standard deviations (Table 10), hence unmixed.

The Tongariro glasses (mean of all analyses SiO₂ = 61 ± 2%) can be classed as andesitic (Table 10 and table 1 in Lowe submitted). The Egmont glasses are noticeably more silicic (mean of all analyses SiO₂ = 70 ± 2%), hence are rhyolitic-dacitic, but otherwise chemically resemble andesitic glass; they have generally high K₂O contents (mean of all analyses 4.32 ± 0.76%).

The analyses show that the eruptives associated with each volcanic centre can be distinguished by their major element chemistry, particularly using TiO₂, FeO*(total iron), MgO, and CaO, which typically have small standard deviations (see Lowe submitted). In considering individual eruptives from the Okataina and Taupo volcanic centres, the glass major element chemistry is usually insufficient on its own to identify a particular named unit. Rotorua Ash (Okataina) and Whakaipo Tephra (Taupo) appear to differ to some extent in this regard, however (see also Green & Lowe 1985; Lowe 1986a). Whakaipo Tephra, rather than Waimihia Lapilli as identified originally by Lowe et al. (1980) from its hypersthene-rich mineralogy, is re-identified here from the slightly lower concentrations of CaO and FeO* in its glass (Table 10), and from the new radiocarbon dates obtained for it (c.2800 years B.P.; Fig.3). The individual Egmont tephtras show some variations in glass chemistry (e.g., cf. Eg-2 and Eg-12, Table 10), but such differences are statistically uncertain because of the generally high standard deviations and the low numbers of shards analysed.

-
3. Unpublished analyses of glass from near-source Okataina and Taupo tephtras (P.C. Froggatt 1982a and pers. comm. 1984) closely match those obtained on their distal counterparts in this study. This compositional homogeneity is analogous to that obtained by Sarna-Wojcicki & Meyer et al. (1981) and Sarna-Wojcicki et al. (1983) on widespread samples of the May 18 1980 Mt. St. Helens' glasses.

Correlation with named units can generally only be made using stratigraphic position, ^{14}C age, and other data (e.g., ferromagnesian mineralogy, abundance of feldspar) taken together (e.g., see Lowe 1986a, submitted).

The only eruptive from Mayor Island previously known to have reached the North Island mainland is the c.6200 year-old Tuhua Tephra (Lowe et al. 1980; Hogg & McCraw 1983). However, the occurrence of a tiny number of glass shards of peralkaline composition (Table 10; Plate 5C) in a tephra c.14 500 years old in Lake Rotomanuka suggests the presence of a second Mayor Island eruptive on the mainland (albeit as a very light dusting in the Waikato).

Puketarata Ash, derived from the Puketarata dome in the Maroa volcanic centre (Lloyd 1972; Wilson et al. 1986), is provisionally identified in the cores mainly on the basis of its slightly unusual glass chemistry in a sample from Lake Rotomanuka. (A trace amount of biotite was also present.) The very low TiO_2 and MgO concentrations (Table 10) correspond to similarly low levels in residual glass of lava from Puketarata dome analysed by Ewart (1969) and Ewart et al. (1968a), and in glass from near-source Puketarata Ash (P.C.Froggatt pers.comm. 1984). Thus the deposits may be correlatives. The shards tentatively identified as representing Puketarata Ash in Lake Rotomanuka occur in a zone stratigraphically between the Rotoaira and Rerewhakaaitu tephras. An age of around c.14 000 years is suggested. This stratigraphic position and age is consistent with findings from recent mapping near the Puketarata dome (C.G. Vucetich pers. comm. 1983), although previously the stratigraphic relationship of Puketarata Ash to certain other tephras was ambiguous (e.g., see Vucetich & Pullar 1969, 1973; Topping & Kohn 1973; Nathan 1976). The postulated occurrence of Puketarata Ash in the Hamilton Basin seems remarkable, given the very small volume (0.22 km^3) and sub-plinian nature of the deposit (Wilson et al. 1986).

Parker's Index (P.I.) values (Parker 1970) for mean glass analyses from the tephras derived from each volcanic centre are as follows: Taupo, 64.0; Okataina, 64.4; Maroa, 67.2; Mayor Island, 81.4; Tongariro, 71.8; Egmont,

81.7 (higher values generally indicate greater susceptibility to weathering). The Mayor Island glasses have a mean peralkaline index (e.g., see Smith 1976) of 1.33 ± 0.1 (Table 10).

Summary of compositional criteria characterising tephra sources

Taken together, the compositional features of the lacustrine tephras enable them to be matched to a source volcano. The main diagnostic criteria are summarised in Table 11. As emphasised earlier, the individual tephras derived from each centre may be identified by additionally considering their stratigraphic position and radiometric age.

TEPHRA DISTRIBUTION AND IMPLICATIONS

Distribution of rhyolitic and andesitic tephras

Bar graphs showing the relative thicknesses of rhyolitic (plain bars) to andesitic (stippled bars) tephras at each lake coring site are plotted in Fig.6. Note that the dashed bar lines represent thicknesses adjusted for compaction or dissemination (see text and Table 2 above) to give the approximate equivalent thickness of dry tephra on land.

Generally, andesitic tephras are thickest in the southern part of the study region, decreasing in proportion to the thickening rhyolitic tephras to the east and southeast. For example, at Lake Rotomanuka the andesitic material comprises c.35% of the total thickness of the deposits and, at Lake Ngaroto, c.36%. In Lake Okoroire, however, the andesitic component is only c.6%, although a similar number of andesitic tephras are present. The proportion of andesitic tephras also diminishes northwards (e.g., the andesitic tephras in Lake Kainui and Leeson's Pond account for c.15% and c.11%, respectively, of the total thickness of tephras in these lakes; see

Table 11. Mineralogical and compositional criteria characterising tephra sources: a summary.

Source Volcano	Heavy Minerals				Light Minerals			P.I. (mean)*	
	H.M. ^a in 2-4φ (%) ^a	Opagues ^a in H.M. (%) ^a	Dominant ferromagnesian minerals ^b	Clino- pyroxene composition	Fe-Ti oxide composition	Glass: Feldspar ratio ^c	Glass composition (mean%) ^d		Feldspar composition
Taupo	4 ± 5	19 ± 8	Hyp ± Aug	-	-	H	Rhyolitic: SiO ₂ 76.90 ± 0.52 TiO ₂ 0.20 ± 0.04 FeO 1.66 ± 0.15 MgO 0.17 ± 0.04 CaO 1.26 ± 0.13	Sodic plagioclase (olig. - and.)	64.0
Okataina	2 ± 2	26 ± 9	Hbe + Hyp + Aug ± Cgt ± Bio	-	-	H	Rhyolitic: SiO ₂ 78.52 ± 0.32 A. TiO ₂ 0.11 ± 0.04 FeO 0.90 ± 0.08 MgO 0.11 ± 0.02 CaO 0.78 ± 0.07 B. TiO ₂ 0.21 ± 0.04 FeO 1.30 ± 0.14 MgO 0.21 ± 0.05 CaO 1.26 ± 0.23	Sodic plagioclase (olig. - and.)	64.4
Maroa	-	-	(Bio + Hbe ± Hyp) ^f	-	-	(H)	Rhyolitic: SiO ₂ 78.46 ± 0.49 TiO ₂ 0.07 ± 0.03 FeO 0.87 ± 0.18 MgO 0.07 ± 0.02 CaO 0.68 ± 0.09	-	67.2
Mayor Is.	0.6 ± 0.5	4 ± 4	Aeg ± Aen ± Rie ± Oliv	-	-	H	Rhyolitic: SiO ₂ 75.35 ± 0.53 Peralkaline [Na ₂ O + K ₂ O]/Al ₂ O ₃ >1 (mean 1.33 ± 0.1)	Alkali (sanidine- anorth.)	81.4
Tongariro	15 ± 5	9 ± 6	Opx + Cpx ± Oliv(Fo) ± Hbe	Wo _{42±2}	Cr ₂ O ₃ 0.2-0.3% MnO 0.3-0.5%	L	Andesitic: SiO ₂ 61.38 ± 2.41 K ₂ O 1.82 ± 0.43	Calcic plag. (labrad.-bytown.) mean An _{61±8}	71.8
Egmont	22 ± 9	10 ± 6	Cpx + Hbe ± Opx	Wo _{45±2}	Cr ₂ O ₃ <0.05% MnO 0.5-1.0%	L	Rhyo.-dacitic: SiO ₂ 70.46 ± 2.19 K ₂ O 4.32 ± 0.76	Calcic. plag. (labrad.-bytown.) mean An _{57±9}	81.7

a H.M. = Heavy minerals (see Table 3).

b Hyp = Hypersthene; Aug = Augite; Hbe = Hornblende; Cgt = Cummingtonite (dominant in Whakatane and Rotoma tephras: Table 4); Bio = Biotite (dominant in Rerewhakaaitu and Okareka tephras; also important in Rotorua Ash; Table 4); Aeg = Aegirine; Aen = Aenigmatite; Rie = Reibeckite; Oliv = Olivine; Cpx = Clinopyroxene; Opx = Orthopyroxene.

c H = High (glass >c.80% of 2-4φ fraction); L = Low (glass c.15-45% of 2-4φ fraction).

d Anhydrous basis: A = tephras other than Rotorua Ash; B = Rotorua Ash (Okataina source); total Fe as FeO.

e Parker Index: $\left[\frac{(Na)_x}{(Na-O)_b} + \frac{(Mg)_x}{(Mg-O)_b} + \frac{(K)_x}{(K-O)_b} + \frac{(Ca)_x}{(Ca-O)_b} \right] \times 100$

where (X)_x = atomic proportion of element X, and (X-O)_b = bond strength of element X with oxygen (Na-O = 0.35; Mg-O = 0.9; K-O = 0.25; Ca-O = 0.7) (Parker 1970).

f Based on Kohn (1973) and Topping & Kohn (1973).

- indicates not measured or insufficient data.

* These properties are quite variable, probably because of the effects of aeolian fractionation etc., i.e., the proportions are not likely to be entirely persistent.

also Lowe 1986b, fig.6b). These differences probably reflect changes in distance from the source volcanoes, and the distributional pattern of fallout (e.g., see Fig.7).

Implications for weathering

The broad changes in the ratio of andesitic to rhyolitic material across the central Waikato region, based on the lacustrine tephra compositions, support the findings of most studies on the subaerial tephra-derived soils - those formed from the so-called "Mairoa Ash" and "Tirau Ash" beds as described earlier (e.g., Grange 1931; Taylor 1933; Hodder & Wilson 1976; Lowe 1981a). The possible influence of this "compositional gradient" on weathering and argillisation processes in the tephra-derived soils in the central-eastern Waikato is discussed in detail in Lowe & Nelson (1983) and Lowe (1986b) (see also Birrell & Pullar 1973; Parfitt et al. 1982b, 1983).

The P.I. values of glass in the lacustrine tephtras indicate that the Egmont, Tongariro, and Mayor Island glasses (P.I.s = 71.8-81.7) are more susceptible to weathering than are the Maroa (P.I.= 67.2) or Taupo and Okataina-derived glasses (P.I.s = 64.0-65.4). This implies that in tephra studies involving detailed analysis of glass from weathering environments (e.g., Hodder & Wilson 1976), glasses from these first three centres in particular are liable to be under-represented. Similarly, olivine, which is found in small amounts in some of the Tongariro-derived tephtras in the lake cores, has not been recorded in any subaerial tephra deposits in the Waikato area (e.g., Lowe 1981a), presumably having been rapidly weathered in the soil-forming environment (cf. Wilson 1975).

Isopach maps and tephra dispersal mechanisms

Provisional isopach maps of eleven tephtras, including the main marker tephtras, are given in Fig.7. Thicknesses adjusted for compaction and dissemination are given in parentheses. The isopach contours are tentative

Fig.6. Bar graphs illustrating tephra thickness-compositional relationships in the Waikato area based on approximate measurements of lacustrine tephtras aged \leq c.15 000 years (i.e., younger than and including Rerewhakaaitu Ash). Bars with hatching = total thickness of tephtras from all sources; blank bars = total thickness of rhyolitic tephtras; stippled bars = total thickness of andesitic tephtras. Solid bar lines represent actual thickness measurements; dashed bar lines represent thicknesses adjusted for compaction and dissemination to obtain an equivalent dry-land tephtra thickness (approximately 2X actual measurements - see text). Dashed lines are isopach contours (in millimetres) of the sum of tephtras erupted during the last c.15 000 years, as measured at subaerial sites by Pullar (1967, p.28). Lake sites are: 1, L. Maratoto; 2, L. Rotomanuka; 3, L. Ngaroto; 4, L. Mangakaware; 5, L. Mangahia; 6, L. Rotoroa; 7, L. Rotokauri (note: thickness measurements do not include Rerewhakaaitu Ash); 8, L. Kainui; 9, L. Rotokaraka; 10, Leeson's Pond; 11, L. Okoroire; 12, L. Rotongata.

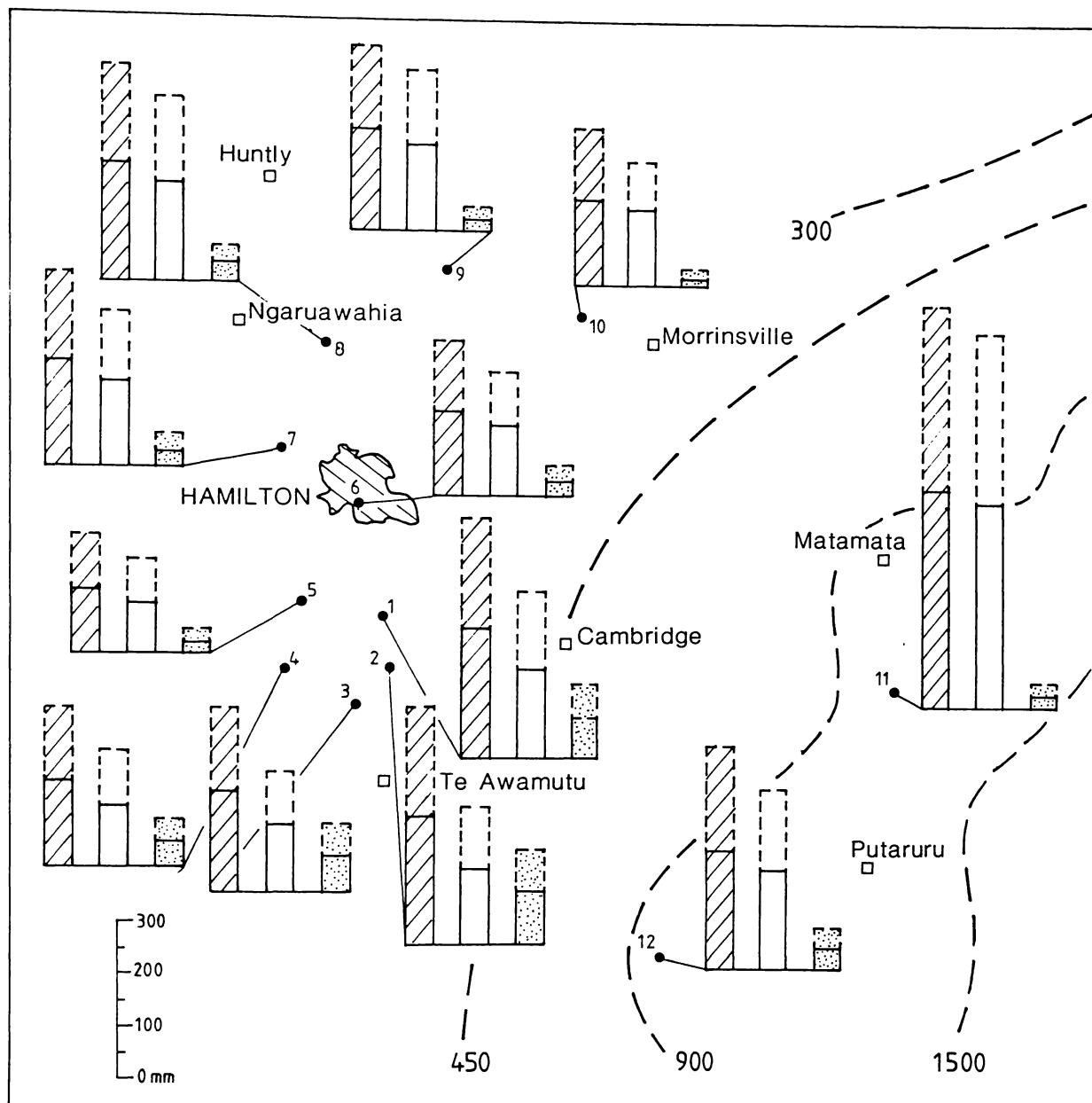
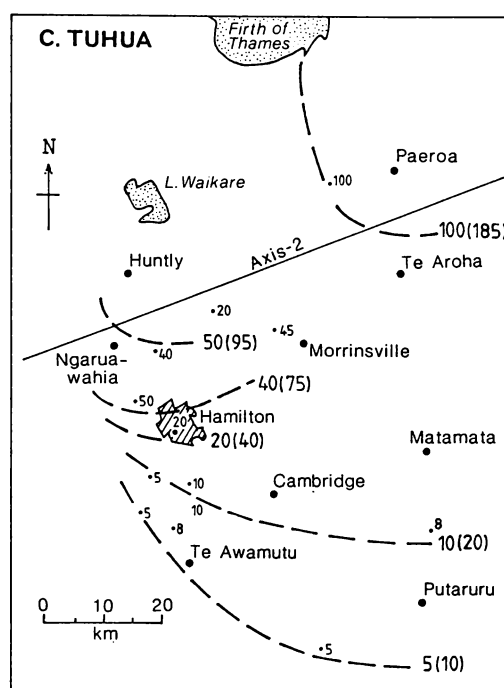
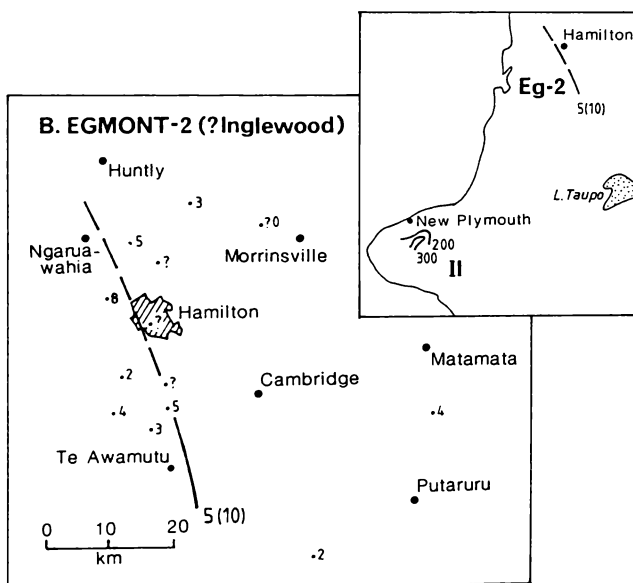
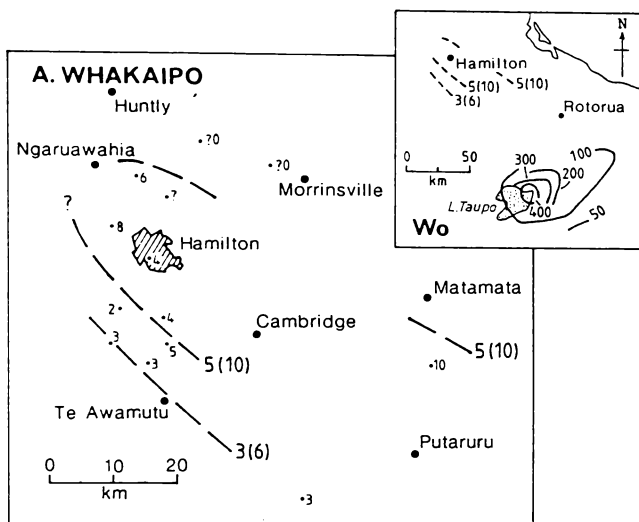


Fig. 6

Fig.7. Provisional isopach maps for eleven tephras in the Waikato area, based on measurements from lake sediment cores (see Fig.6 for lake names and locations). Insets, all drawn to the same scale, allow comparison with isopachs of the same tephras in the Taupo-Rotorua-Gisborne-Taranaki districts (B after Neall 1972; A,F after Vucetich & Pullar 1973; D,E,H,J,K after Pullar & Birrell 1973a; G,I after Topping 1973). All measurements are in millimetres; numbers in parentheses are thicknesses adjusted for compaction and dissemination to give an estimate of dry-land tephra thicknesses (see text).

Axis-2 line and 100 mm isopach contour in Map C (Tuhua Tephra) are based on Hogg & McCraw (1983). Map J (Rotorua Ash) isopach contours appear to straddle a NW-SE axis (indicated in inset), perhaps reflecting the effect of strong directional winds, a directed blast, or possibly co-ignimbrite ash fall generated by near-source pyroclastic flows resulting from column collapse. Pullar & Birrell (1973a) appear to have possibly overestimated the thickness of Rotorua Ash in the eastern Waikato (dotted isopach; see also Fig.8D).

Isopach maps of Taupo Lapilli are given by Pullar & Birrell (1973a) and Pullar et al. (1977).



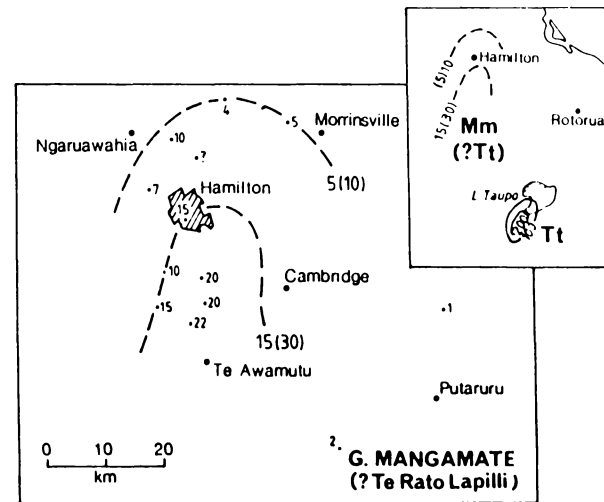
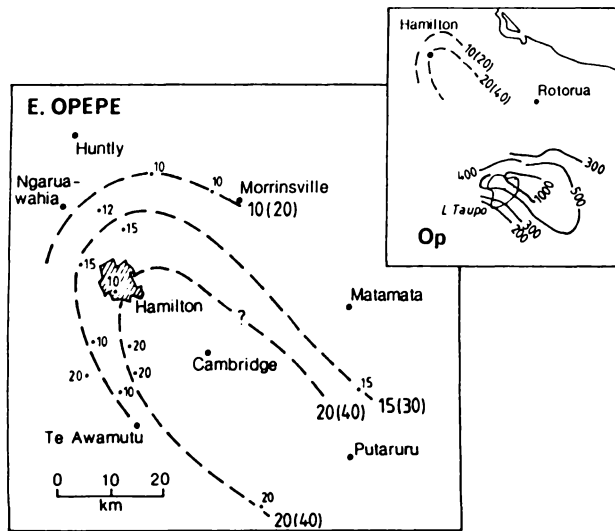
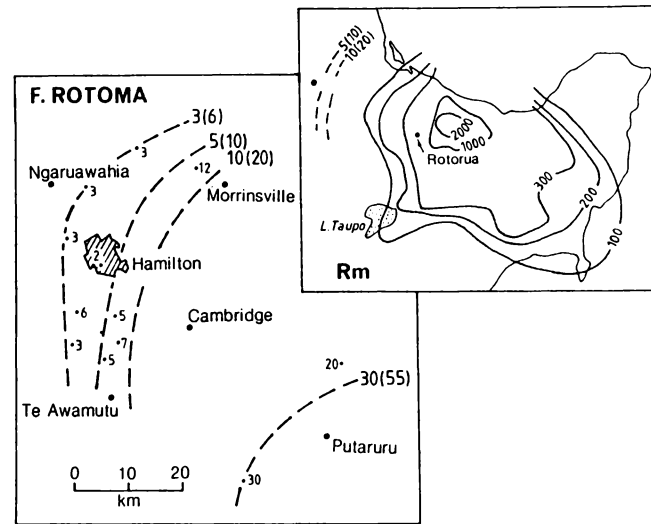
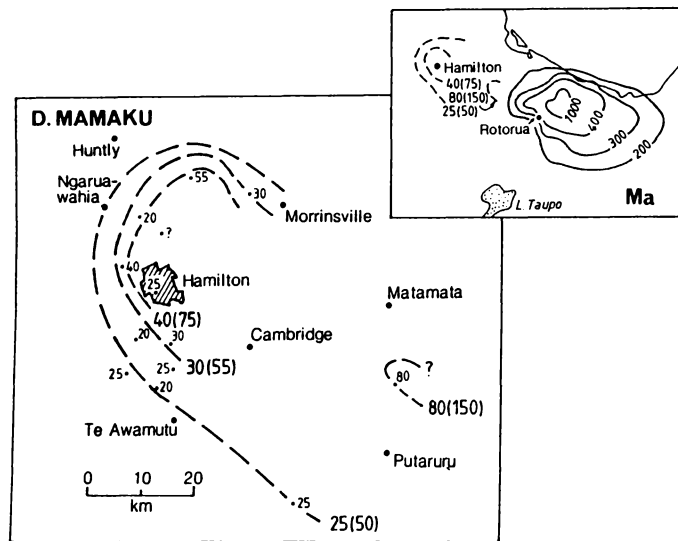


Fig. 7 contd.

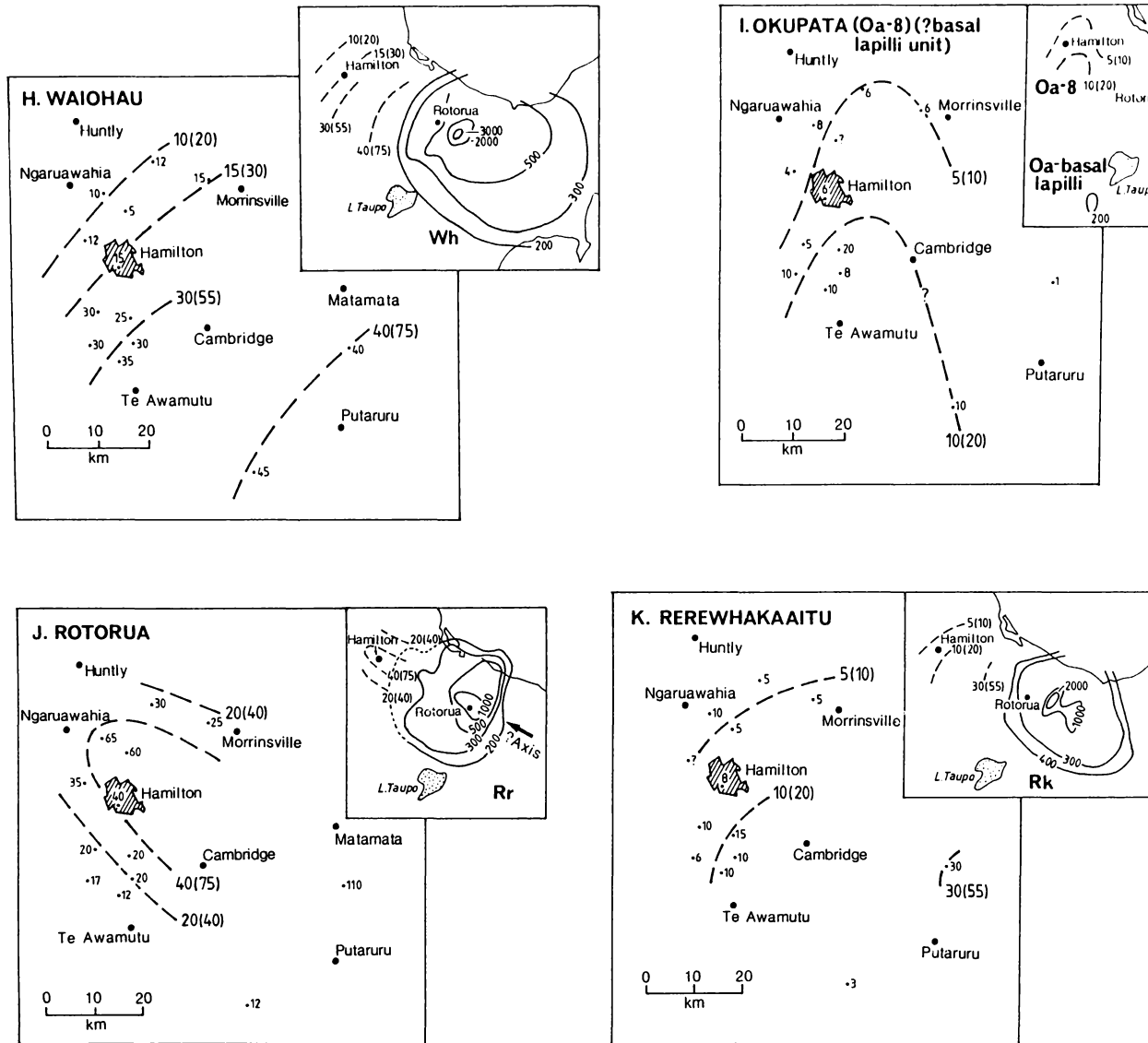


Fig. 7 contd.

because the number and geographic spread of the sites is relatively limited, and because the tephra thickness measurements may differ by small amounts in cores from the same lake (an average thickness was used in such cases). It is assumed that all of the tephric material is essentially airfall in origin, i.e., it has not been overthickened (or thinned) by post-depositional wave action or by inwashing from the catchment.

The outer limits of previous isopach maps (e.g., insets in Fig.7) are generally restricted to c.100-200 mm thickness contours. The new isopach maps presented here have improved on this degree of resolution by around 10 to 100 times, and include isopachs as thin as 3-5 mm (e.g., Figs. 7B,E). The maps generally "conform" with the previous ones in that the more distal deposits in the Waikato are usually thinner than the outermost contours of the earlier maps. In the case of Rotorua Ash, the outermost isopach (c.200 mm) of Pullar & Birrell (1973a) appears to conflict with the lake measurements (Fig.7J, inset). The 300 mm isopach distribution pattern in Fig.7J, with a possible NW-SE trending fallout axis (arrowed), is more consistent with the lake data, however. In Fig.7E (Rotoma Ash), the outermost isopach of Pullar & Birrell (1973a) of 100 mm may similarly have been overestimated (cf. approximately 55 cm dry-land equivalent thickness from lake core data). (See also Figs. 8C,D.)

Graphs showing isopach thicknesses plotted against distance from isopach centre for twelve tephrae are given in Fig.8. These combine the approximate thickness data from the Waikato lake cores with measurements from the previously-published isopach maps as referenced in the caption to Fig.7. The isopach thicknesses are plotted along a transect from the isopach centres towards Hamilton. These transects do not, therefore, necessarily coincide with a major or minor fallout axis (cf. Froggatt 1982b). The dashed curves link adjusted thickness measurements (open symbols) for the lacustrine tephrae.

Near-linear semi-log plots indicate an exponential decrease in tephra thickness (T) with increasing distance (x) from source i.e., $T = ae^{-kx}$ (Fisher

& Schmincke 1984). Various workers have suggested that a change in slope reflects a change in dispersal mechanism of the tephra, perhaps from turbulent transport near source to normal wind dispersal of finer material further from source. More recently, however, this flatter-lying "fine tail" has been interpreted as representing co-ignimbrite ash fall rather than Plinian-type fallout material (Sparks & Walker 1977; Froggatt 1982a; Fisher & Schmincke 1984).

In Fig.8 some of the plots are approximately linear (with essentially little effective difference in shape between the actual and adjusted thickness plots), and hence generally fit an exponential decay model (e.g., Fig.8A). However, the distal fallout deposits of other tephras are thicker than the exponential would predict, indicating either a change in dispersal mechanism or a contribution from co-ignimbrite ash associated with the eruptions. Mamaku Ash (Fig.8B). Rotorua Ash, Rerewhakaaitu Ash, Okareka Ash (Fig.8 D), and possibly Waiohau Ash (Fig.8C) show this latter pattern to a greater or lesser extent. The Mamaku and Waiohau eruptions included ignimbritic events (Nairn 1981), and Rotorua Ash local near-vent pyroclastic flow and surge events (Nairn 1980), so it is possible that the "fine tail" for these tephras in the Waikato area partly represents co-ignimbrite ash. However, a change in dispersal mechanism (see further discussion below) cannot be excluded. The plots of the Tongariro-derived tephras in Fig. 8E also appear to show slope breaks, but more measurements at intermediate sites are needed to corroborate this.

Tuhua Tephra (not plotted in Fig.8) is thickest to the north-northeast of Hamilton City, but drops off markedly to the south (Fig.7C). The Waikato lakes' measurements generally support the onland distribution pattern in Hogg & McCraw (1983, p. 182), which shows a postulated depositional axis (Axis-2 in Fig.7C) extending southwestwards from Mayor Island and passing to the north of Hamilton. Tuhua Tephra has recently been identified in Rotorua City, c. 5-10 mm thick (Kennedy & Froggatt 1984).

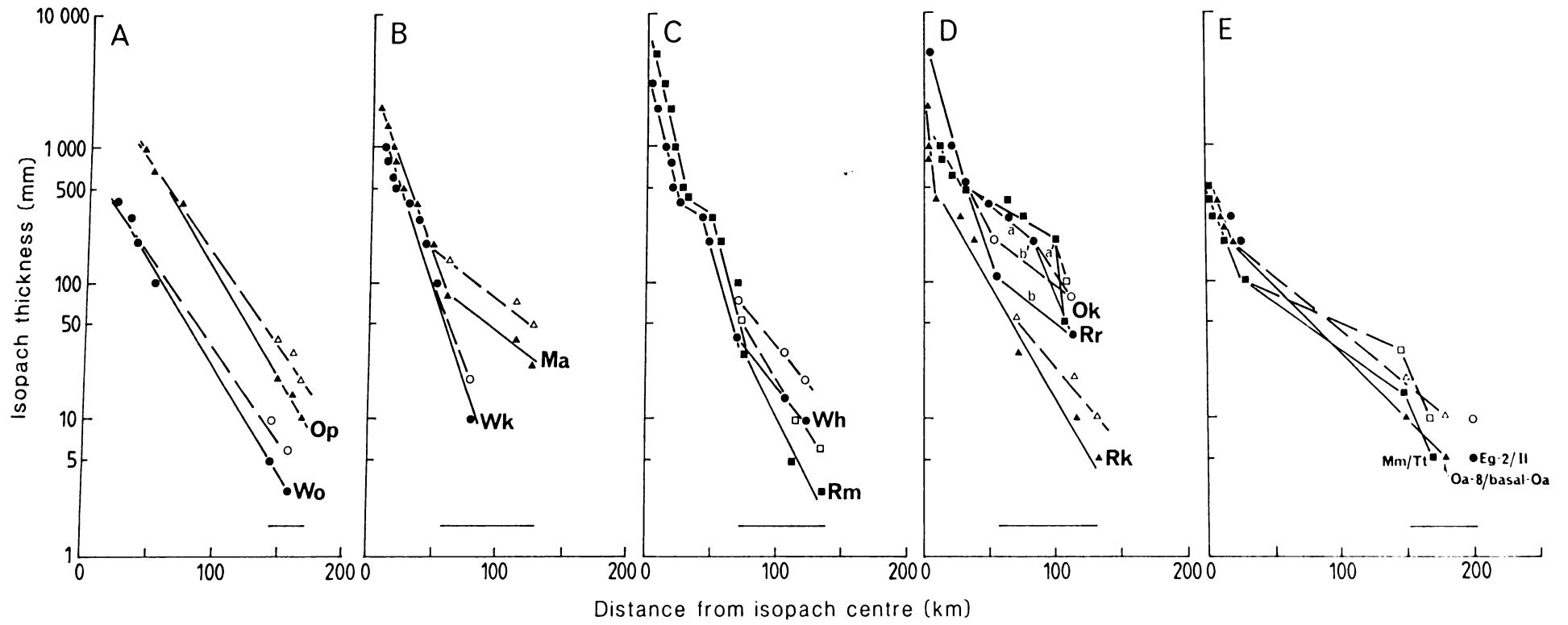


Fig.8. Plots of isopach thickness against distance from isopach centre for 12 tephras (see also plots for Whakaipo and Taupo tephras in Froggatt 1982b, p.305). Dashed curves join adjusted thicknesses (open symbols) for tephras in Waikato lakes. Horizontal bars indicate region of Waikato lake core measurements. Symbols for tephras are: Wo, Whakaipo; Op, Opepe; Wk, Whakatane; Ma, Mamaku; Rm, Rotoma; Wh, Waiohau; Rr, Rotorua*; Rk, Rerewhakaaitu; Ok, Okareka; Mm/Tt, Mangamate (Waikato lakes) and possible near-source correlative, Te Rato Lapilli; Oa-8/basal-Oa, Okupata (informal unit 8, Waikato lakes) and possible near-source correlative, the basal lapilli unit of Okupata Tephra; Eg-2/I1, Egmont-2 (Waikato lakes) and possible near-source correlative, Inglewood Tephra (references given in Fig.7).

* ✓ Curves a,a' are drawn through Pullar & Birrell's (1973a) 200-400 mm isopachs (Lake Okoroire measurement ignored); curves b,b' are drawn through the isopach based on the Lake Okoroire measurement (Pullar & Birrell's 1973a 200-400 mm isopachs ignored).

The curves in Fig.8 suggest that many of the tephras found in the Waikato lakes are likely to persist well beyond the Waikato area. Extrapolation of the graphs indicate that for the Taupo and Okataina-derived tephras the c.1 mm isopach is likely to occur c.200-250 km from source (probably c.300 km or so for Mamaku Ash): for the andesitic tephras, the c.1 mm isopach could occur c.250 - 300 km from source. The new isopach maps may allow estimates of tephra volumes to be improved (e.g., Froggatt 1982b), but such calculations are not considered here.

Possible dispersal mechanisms

The identification of the distal tephras in the Waikato lakes has enabled most tephra distributions to be extended well beyond previously mapped limits, as is shown in Figs. 7 & 8. This is especially so for the Tongariro and Egmont-derived tephras (cf. Neall 1972; Topping 1973; Neall & Geddes 1981; Geddes & Neall 1982; Neall & Alloway 1986). Indeed, the presence of so many tephras from the various sources, apart perhaps from the relatively close Okataina centre, is initially surprising. However, upon consideration of the highly active nature of the Tongariro and Egmont volcanic centres in particular (e.g., Cole & Nairn 1975), and with the benefit of hindsight, it seems that such a record might have been expected, provided favourable sites for preservation (e.g., lake sediments) could be found. Even so, the Waikato area is essentially upwind of the source volcanoes, and a good proportion of the distal lacustrine tephras present relate to relatively minor deposits (in terms of thickness) near source. Consequently, their deposition in the Waikato must depend on certain eruption conditions or wind regimes applying.

Although the prevailing winds in the North Island are presently southwesterly-westerly (and are likely to have been so for at least the past c.20 000 years, e.g., see Salinger 1984 and Stewart & Neall 1984), the predominant wind direction at altitudes greater than c.20 km is usually easterly (Nelson et al. 1985; Buck 1985). Thus, one explanation for the deposition of many of the late Quaternary tephras in the Waikato is that they

derive largely from eruptions that were powerful enough to produce eruption columns exceeding c.20 km in height (the dispersion of tephras being mainly a function of column height and the atmospheric wind regime, e.g., Walker 1973, 1981a; Wilson et al. 1978; Sarna-Wojcicki & Shipley et al. 1981; Fisher & Schmincke 1984; Carey & Sparks 1986). This was evidently the case for the "ultraplinian" Taupo eruption (Walker 1980; Wilson & Walker 1985) and the Tuhua eruption (Buck 1985; Houghton & Wilson 1986), and possibly for the Rotorua and Hinemaiaia eruptions (Nairn 1980; Lowe 1986a), at least (see also Wilson et al. 1986). The possible role of water-magma interactions in producing very powerful (phreatomagmatic) eruptions may also be relevant in some cases here (cf. Walker 1981c; Self 1983).

Alternatively, or in addition, some of the tephras may have originated from less powerful eruptions but were ejected obliquely (directed blasts) or were emplaced by strong northeasterly, southeasterly, or southwesterly lower atmosphere winds. Strong southerly winds blowing during the modest February 1975 eruption of Mt. Ngauruhoe resulted in fine ash being deposited as far north as Hamilton and Tauranga cities (Nairn & Self 1978). (Note: this ash has not been detected in the Waikato lakes.) The curves in Fig.8E suggest that such winds may have been responsible for depositing Mangamate and Okupata (Oa-8) eruptives in the central Waikato lake sites (see also Topping 1973). As noted above, co-ignimbrite ash fall may also have had an effect on tephra dispersal patterns and thickness variations (e.g., for Mamaku Ash, Fig.8B?).

A number of known rhyolitic eruptives from the Taupo and Okataina volcanoes do not appear to be present as macroscopic tephras in the Waikato lakes studied, i.e., the Kaharoa⁴ (Okataina) and the Waimihia, Motutere, Poronui, and Karapiti (Taupo) tephras. Two of these eruptions, Kaharoa and Waimihia, were evidently quite powerful but probably strongly controlled by

4. Kaharoa Ash does probably occur in the northeastern Waikato, being tentatively identified in surficial peat deposits at three localities: the Hauraki bog (Lowe et al. 1981; Hogg & McCraw 1983); the Pohlen bog (near Matamata); and an unnamed bog in the Kaimai Range (D.J.Lowe, unpublished data). Its apparent absence in the Lake Okoroire cores (Fig.2) may be attributable to the difficulty of coring the very sloppy surficial lake sediments. Close inspection of all the cores taken from the other lakes has, so far, revealed no trace of Kaharoa Ash.

contemporary winds (see Cole 1970b; Pullar et al. 1977; Walker 1981b). The other eruptions were moderate to weak in nature, producing plinian or subplinian deposits (e.g., Vucetich & Pullar 1973; Froggatt 1981b,c; Froggatt & Solloway 1986; Wilson et al. 1986).

Clearly, an important lesson reinforced here is that eruptions represented by substantial deposits near source will not necessarily persist far (nor in all directions), whereas apparently minor deposits near source may represent powerful sheet-forming eruptions and be quite widely dispersed (see Walker 1973, 1980; Fisher & Schmincke 1984).

TEPHRA ACCUMULATION RATE

The average rate of accumulation of tephras in the Waikato area over the last c.17 000 years has been approximately one event per c. 400 years. Rhyolitic tephras are deposited, on average, once every c.1100 years. Andesitic tephras are deposited more frequently, every c.650 years on average, but in relatively concentrated bursts of activity, especially from Tongariro (see discussion in Lowe submitted). Based on the average depositional rate of one event per c.400 years, the Waikato area can possibly expect to receive a "significant" ash fallout event (i.e., substantial enough to be recorded in the lake sediments) at any time because the last such event recorded was deposited c.1800 years ago (Taupo Pumice). It is hard to say which volcanic centre is likely to produce this next event because all can be considered active and capable of producing a widespread deposit under certain conditions (see also Froggatt 1982b and Latter 1986)*. The Maroa centre, with only one relatively small eruption in the past c.17 000 years, might be considered least likely, but such a low frequency does not preclude the possibility of a large, widespread eruption in the near future. For the reasons outlined previously, any tephra erupted from one of the six volcanic centres in question may not be carried to the Waikato in significant quantities.

* See also review by Dibble & Neall (1984)

However, because the lake record represents approximately 60% of the known *major* tephra-producing eruptions (e.g., McCraw 1975; Cole & Nairn 1975), there is perhaps a better-than-even chance that another significant eruption from any of these volcanic centres will result in tephra fallout in the Waikato area.

TEPHROCHRONOLOGICAL APPLICATIONS TO PALAEOENVIRONMENTAL STUDIES

The value of tephra layers as isochronous marker horizons for palaeoecological studies was recognised earlier this century by the founder of tephrochronology, S. Thorarinsson, who worked initially with L. von Post on the correlation of pollen records using Icelandic tephra layers (Buckland et al. 1981; Thorarinsson 1981b; see also, e.g., Oldfield et al. 1980; Watts & Bradbury 1982; Horie 1984; Leonard 1986). In New Zealand, a number of palaeoecological studies utilising tephrochronology have been done largely on peat bogs (e.g., McGlone & Topping 1977, 1983; McGlone 1981, 1983; Pocknall & Millener 1984). Palaeolimnological studies in New Zealand have begun only comparatively recently, however (e.g., see Lowe & Green 1987, p.54). The Waikato lakes have been the focus of many of these studies, chiefly because the dated tephtras contained in the lake sediments provide an exceptionally detailed and, within the constraints of ^{14}C dating, accurate time-stratigraphic framework. In addition, because most of the lakes are c.16 000-17 000 years old, they provide a record of both late-glacial and postglacial changes in the lakes and their catchments.

Palaeoenvironmental studies on the lake sediments that have utilised the dated tephtras as time-parallel marker beds include Green (1979), Boubée (1983), Green et al. (1984), Green & Lowe (1985), Kellett (1985), McCabe (1985), Lowe & Green (1987), and Newnham (1987). These and further studies in progress involve a "team approach" (Frey 1974) in which various specialists study different aspects of the same cores. Ultimately, it is hoped to reach an integrated interpretation.

CONCLUSIONS

Cores from 14 Waikato lakes have provided a new record of tephra deposition in the Waikato area over the past c.17 000 years. A total of 41 distal tephras of rhyolitic or andesitic composition have been identified (Table 1). They originated from six North Island volcanic centres as follows: Taupo, 5 tephras (Taupo, Mapara, Whakaipo, Hinemaiaia, and Opepe); Okataina, 7 tephras (Whakatane, Mamaku, Rotoma, Waiohau, Rotorua, Rerewhakaaitu, and Okareka); Maroa, 1 tephra (Puketarata); Mayor Island, 2 tephras (Tuhua and uncorrelated); Tongariro, 11 tephras (Mangamate, Okupata (8 informal units, Oa-1 to Oa-8), uncorrelated, Rotoaira); Egmont, 15 tephras (15 informal units, Eg-1 to Eg-15⁵). These sources and correlations were distinguished using the tephras' mineralogy and composition (Table 11) together with stratigraphic position and ¹⁴C chronology (Figs.2 & 3).

In terms of thickness, the rhyolitic tephras predominate at all sites, but the proportion of andesitic to rhyolitic eruptives differs across the region: c.30-35% in the south, c.10-15% in the north, and c.5% in the east (Fig.6). The compositional variations associated with these differences may have influenced weathering and argillisation in the late Quaternary tephra-derived soils in the region (Lowe 1986b).

In the Ohaupo-Hamilton area, the total thickness of the lacustrine tephras younger than c.15 000 years is c.25 cm (approximately equivalent to c.47 cm on dry land); in the Whitikahu-Morrinsville area, the thickness is c.20 cm (c.37 cm); and near Tirau the thickness is c.42 cm (c.78 cm). Detailed thickness distribution patterns for eleven of the tephras are given in provisional isopach maps for the central Waikato area (Fig.7). These improve on the resolution of most existing maps for other parts of the North Island by one to two orders of magnitude. Isopach thickness-distance plots show some tephras to have an exponential rate of thickness decrease away from source;

5. Possible tentative correlatives are: Eg-1 = Maketawa; Eg-2, Eg-3 = Inglewood; Eg-4 = Korito; Eg-5 = Tariki; Eg-6 = Waipuku; Eg-7, Eg-8 = S1 & S2 (?Ahuahu) (V.E.Neall & B.V.Alloway pers. comm. 1984-5; Neall & Alloway 1986).

others have an "overthickened" fine tail possibly reflecting either a change in dispersal mechanism (e.g., strong directional surficial or high altitude winds) or the addition of co-ignimbrite ash.

The tephras preserved by the lake sediments are useful as time-stratigraphic markers in multidisciplinary palaeoenvironmental studies in the Waikato area.

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- Green, J.D.; Lowe, D.J. 1985 = Paper 9
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- Lowe, D.J. 1986b = Paper 11
- Lowe, D.J. submitted = Paper 12
- Lowe, D.J.; Green, J.D. 1987 = Appendix B
- Lowe, D.J.; Hogg, A.G. 1986 = Paper 5
- Lowe, D.J.; Nelson, C.S. 1983 = Appendix A
- Lowe, D.J. *et al.* 1980 = Paper 1
- Lowe, D.J.; Hogg, A.G.; Hendy, C.H. 1981 = Paper 3

PAPER 5

Tephrostratigraphy and chronology of the Kaipo Lagoon, an 11,500 year-old montane peat bog in Urewera National Park, New Zealand.

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Tephrostratigraphy and chronology of the Kaipo Lagoon, an 11,500 year-old montane peat bog in Urewera National Park, New Zealand

David J. Lowe* and Alan G. Hogg**

Eleven well-preserved Holocene tephtras occur interbedded with peat in the Kaipo Lagoon bog in Urewera National Park, North Island. They are identified chiefly by their field appearance, stratigraphy, and ferromagnesian mineralogy. Glass shards from one tephtra (Hinemaiaia) were analysed by electron microprobe.

The tephtras originate from the Taupo, Okataina, and Tongariro Volcanic Centres and, from youngest to oldest, are: Kaharoa Ash, Taupo Pumice, Mapara Tephtra, Waimihia Lapilli, Hinemaiaia Tephtra, Whakatane Ash, Rotoma Ash, Opepe Tephtra, Poronui Tephtra, Karapiti Tephtra, and Okupata Tephtra. Thirteen new radiocarbon ages were obtained on six of the tephtras (old $T\frac{1}{2}$, years B.P.): Waimihia, $3,250 \pm 70$ (Wk498), $2,910 \pm 60$ (Wk499), $3,040 \pm 50$ (Wk500); Hinemaiaia and Whakatane, $4,490 \pm 60$ (Wk496), $4,530 \pm 60$ (Wk497); Whakatane, $4,860 \pm 70$ (Wk501); Rotoma, $5,440 \pm 170$ (Wk493), $7,380 \pm 80$ (Wk494), $7,560 \pm 100$ (Wk495) (Wk493-495 are all considered anomalously young); Opepe, $8,710 \pm 80$ (Wk492); Poronui, $10,160 \pm 130$ (Wk351), $9,960 \pm 90$ (Wk352), $9,560 \pm 80$ (Wk491). Estimated ages, assuming constant sedimentation rates, for Karapiti Tephtra and Okupata Tephtra are 10,100 and 10,300 years, respectively. Two peat horizons below the Okupata Tephtra were dated at (old $T\frac{1}{2}$) $10,600 \pm 90$ years B.P. (Wk263) and $11,500 \pm 80$ years B.P. (Wk264) and date the initial growth of the Kaipo Lagoon bog. Peat accumulation rates have been slow (average 0.19 mm/year) but variable.

The identification and dating of the tephtras at Kaipo extends their known distribution in eastern North Island, and improves their potential usefulness as isochronous stratigraphic marker units.

Keywords: pyroclastics, tephtra, volcanic ash, stratigraphy, radiocarbon dates, Holocene, Taupo Volcanic Zone, ferromagnesian mineralogy, glass chemistry, sedimentation rates.

INTRODUCTION

Late Quaternary tephtras (volcanic ashes) erupted from the Taupo Volcanic Zone (Fig.1A) have been intensively studied over the past 20 years, and are becoming increasingly useful as datable stratigraphic marker beds for a wide variety of purposes (*e.g.*, see Howorth *et al.*, 1981). Many studies have concentrated on the stratigraphy, age, and distribution of the tephtras near their volcanic source areas (*e.g.*, Healy, 1964; Vucetich and Pullar, 1964, 1973; Topping, 1973; Howorth, 1975; Froggatt, 1981a, b) whereas comparatively few have examined them in detail as distal deposits far (~ 100 km or more) from their source areas

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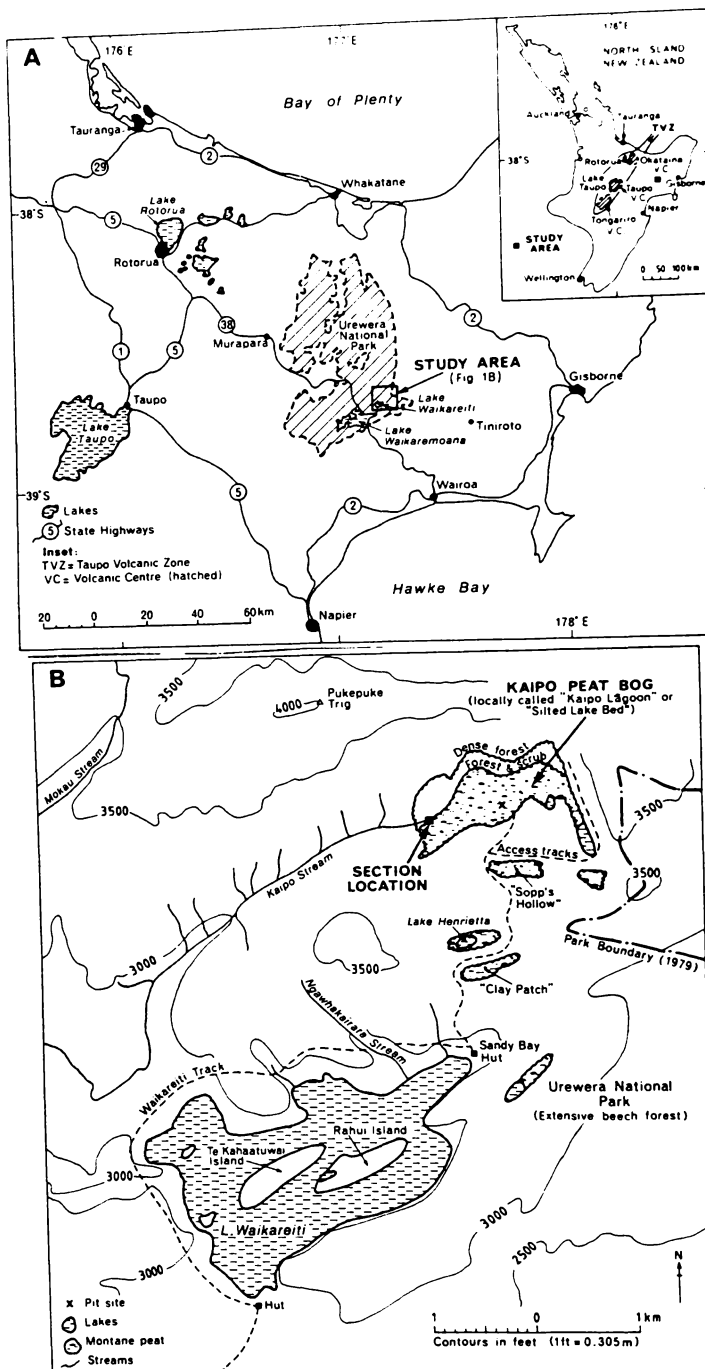


Fig. 1 - Location of the Kaipo Lagoon in the Urewera National Park, North Island. A. Location map of eastern North Island. The inset (based on Cole and Nairn, 1975) shows the relationship of the study area to the Taupo Volcanic Zone (TVZ) and the volcanic centres (V.C.) that were sources of the tephras deposited at Kaipo. B. Map of the south-eastern part of the Urewera National Park showing access to the Kaipo Lagoon and the location of the reference section investigated. Other wetland clearings in the area are shown also. (Based on sheet N96 of the topographical map series NZMS 1).

(e.g., Pullar *et al.*, 1977; Howorth *et al.*, 1980; Lowe *et al.*, 1980; Hogg and McCraw, 1983). Some of these latter studies have utilised cores or sections of peat and organic lake sediments to provide a detailed stratigraphy and an improved chronology for many of the tephras. A similar approach is evident in several overseas studies (e.g., Borchardt *et al.*, 1973; Mathewes and Westgate, 1980; Mehringer *et al.*, 1984). In addition to extending the known distribution of Late Quaternary tephras in New Zealand, peat and lake sediment cores can also provide an accurate record of the stratigraphic relationships of interbedded tephras derived from different volcanic centres (e.g., Lowe, 1986).

In this paper we examine the stratigraphy and chronology of 11 distal, rhyolitic and andesitic tephras interbedded with peat in a section through an 11,500 year old* peat bog, the Kaipō Lagoon, in the Urewera National Park (Fig. 1A,B).

The main purposes of the study are to establish a more certain Holocene tepthrostratigraphy for the Urewera-Waikaremoana area, and to obtain new dates on several tephras that have few or no previous dates, thus improving their potential usefulness as time stratigraphic marker beds. In addition, we provide a detailed chronology for further studies on the paleoecological history of the Kaipō Lagoon area. Such a chronology is important because many previous palynological studies in New Zealand have been hampered by limited time control (McGlone and Topping, 1977).

KAIPŌ LAGOON STUDY AREA

The Kaipō Lagoon is a 73 ha montane peat bog lying at an altitude of 1,100 m in the south-eastern part of Urewera National Park (Fig. 1). It is the largest of a group of natural enclosed clearings in the vicinity of Lake Waikareiti that form

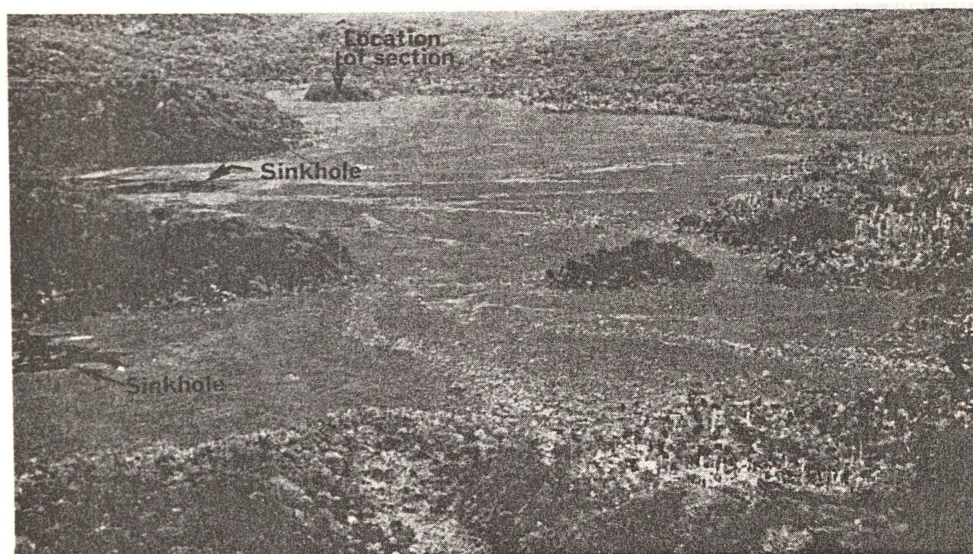


Fig. 2 – Westward view of the Kaipō Lagoon and surrounding beech forest. The bog's hummocky surface has a shrub bog vegetation with numerous small pools; surface channels drain towards sinkholes on the southern margins (on the left). White Kaharoa Ash occurs in patches on the bog's surface and is especially evident around the upper sinkhole. (Photo courtesy of N. B. Rogers).

* All ^{14}C ages discussed in the text are conventional ages based on the (old) Libby half-life of 5,568 years (Hogg, 1982).

distinctive, small peaty wetlands and lakelets surrounded largely by mature silver beech (*Nothofagus menziessi*) and red beech (*N. fusca*) forest (N.Z. Forest Service, 1969; Rogers, 1984). The block-faulted valley in which the bog has formed (Fig. 2) mainly comprises sandy to muddy soft blue-grey siltstones of Miocene age (Grindley, 1960). It is thought that erosion of these sediments, perhaps accelerated by a post-glacial increase in rainfall, empounded the valley sometime before or about 11,500 years ago impeding drainage and creating boggy conditions (Rogers, 1984). Alternatively, an earthquake many have triggered a landslide to form the initial bog basin (*cf.* Adams, 1981).

Although the Kaipō Lagoon is neither a lagoon nor a silted lake bed as noted on topographic maps, the name is retained here because of its common colloquial usage. It is essentially an ombrogenous shrub bog dominated by *Empodisma minus* (a rush) and *Gleichenia dicarpa* (a fern), with occasional *Sphagnum spp.*, which form unusual hummocks amidst numerous small, permanent pools (Rogers, 1984). Marginal sinkholes allow subterranean drainage of water from channels draining the surface of the bog (Fig. 2). A more detailed description of the vegetation and ecology of Kaipō Lagoon is reported by Rogers (1984).

Tephra exposure in the Waikaremoana-Kaipō Lagoon area

The landscape in the Waikaremoana area is mantled with Late Quaternary tephras, which are exposed in limited road cuttings and above slip scarps in generally steep terrain. These tephras, up to about 3 m total thickness, have been described and mapped by Gibbs (1959), Vucetich and Pullar (1964, 1969), and Pullar and Birrell (1973) as part of wider surveys in the Bay of Plenty-Gisborne region. Rijkse (1979) has described the soils in part of the Urewera area and mapped them at a scale of 1:100,000. At Tiniroto, 35 km east of Urewera National Park (Fig. 1A), a sequence of Holocene tephras preserved within muddy organic lake sediments has been examined by various workers (Vucetich and Pullar, 1964, 1973; Howorth and Ross, 1981; Kohn *et al.*, 1981) but positive tephra identifications have proved problematical (*see* Lowe, 1986).

Kaharoa Ash, the most recent tephra deposited in the region* occurs on the bottom of Lake Waikareiti and in patches on the surface of Kaipō Lagoon (Fig. 2). At the western end of Kaipō Lagoon (Fig. 1B), a small stream (Kaipō Stream) draining from it has exposed a 2.8 m-high section that exhibits interbedded tephras and peats overlying muddy peats and muds (Fig. 3). The description, correlation, and dating of the well-preserved tephras in this reference section, and in a pit dug near the centre of the bog (Fig. 1B), forms the basis of this report.

STRATIGRAPHY AND CORRELATION OF THE TEPHRAS

Eleven tephra formations are recognised in the Kaipō Lagoon. From youngest to oldest these are: Kaharoa Ash, Taupo Pumice, Mapara Tephra, Waimihia Lapilli, Hinemaiaia Tephra, Whakatane Ash, Rotoma Ash, Opepe Tephra, Poronui Tephra, Karapiti Tephra, and Okupata Tephra (defined in Healy, 1964; Vucetich and Pullar, 1964, 1973; Topping 1973; Froggatt, 1981a, b, d).

The tephras, illustrated and described in Figs. 3 and 4, are compact, predominantly medium to coarse ash with a pumiceous or vitric character, and often with normal but occasionally reverse bedding. They range in thickness from 1-20 cm and have a total thickness of about 1.2 m. Some of the tephra layers, particularly the very thin ones, are hard to distinguish visually from the enclosing peat because of brownish staining (Fig. 3).

The top three tephras are only poorly represented in the reference section

*Apart from a dusting of ash fallout (<c.5 cm) from the Tarawera eruption of A.D. 1886 (*see* Pullar & Birrell, 1973).

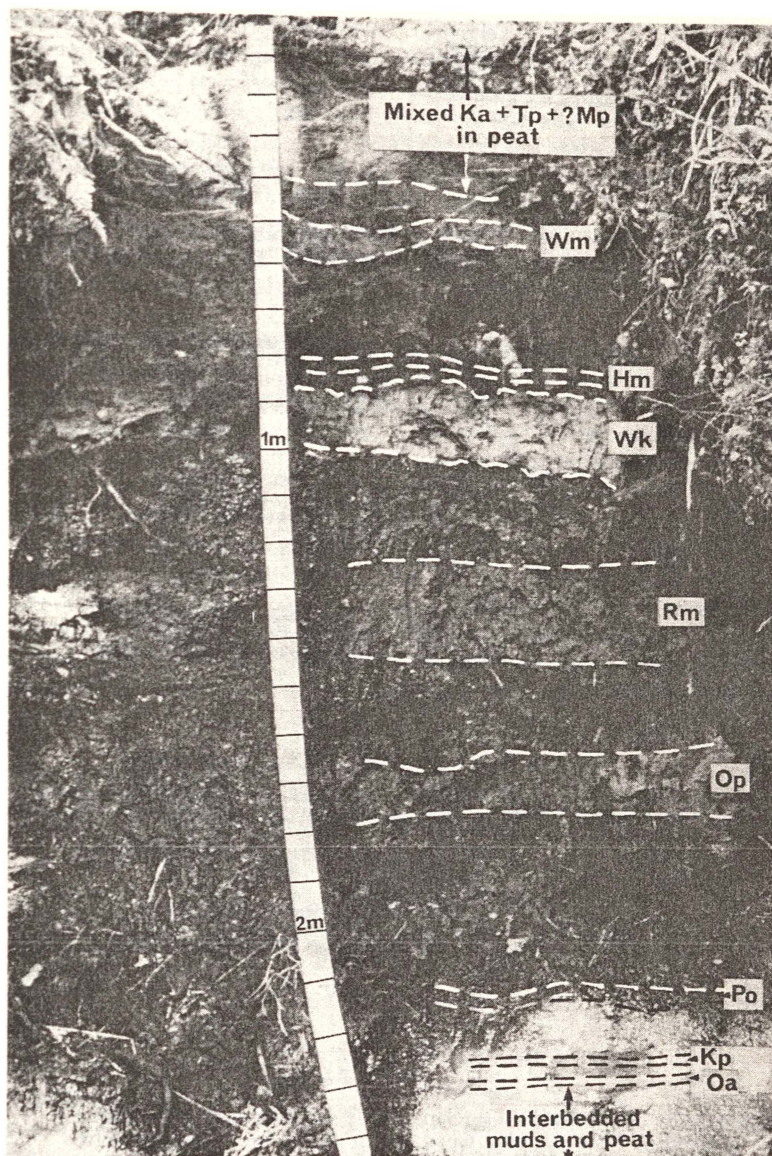


Fig. 3 – Photograph of the Kaipō Lagoon section showing the interbedded tephra and peat overlying muddy peats and muds. The scale is in 10 cm units. The lowest peat layer in the section (at 2.7 m depth) has been dated (Wk264) at $11,500 \pm 80$ years B.P. (see Figs. 4 and 5). Note the coarse roots and sticks protruding from parts of the section face. Tephra symbols are: Ka, Kaharoa Ash; Tp, Taupo Pumice; ?Mp, possibly Mapara Tephra; Wm, Waimihia Lapilli; Hm, Hinemaiaia Tephra; Wk, Whakatane Ash; Rm, Rotoma Ash; Op, Opepe Tephra; Po, Poronui Tephra; Kp, Karapiti Tephra; Oa, Okupata Tephra.

(Fig. 3), which has probably been truncated by erosion; however, they can be found as discrete units elsewhere in the bog (*e.g.*, in the central pit, and also in an 85 cm-long core taken by N.B. Rogers) (Fig. 4).

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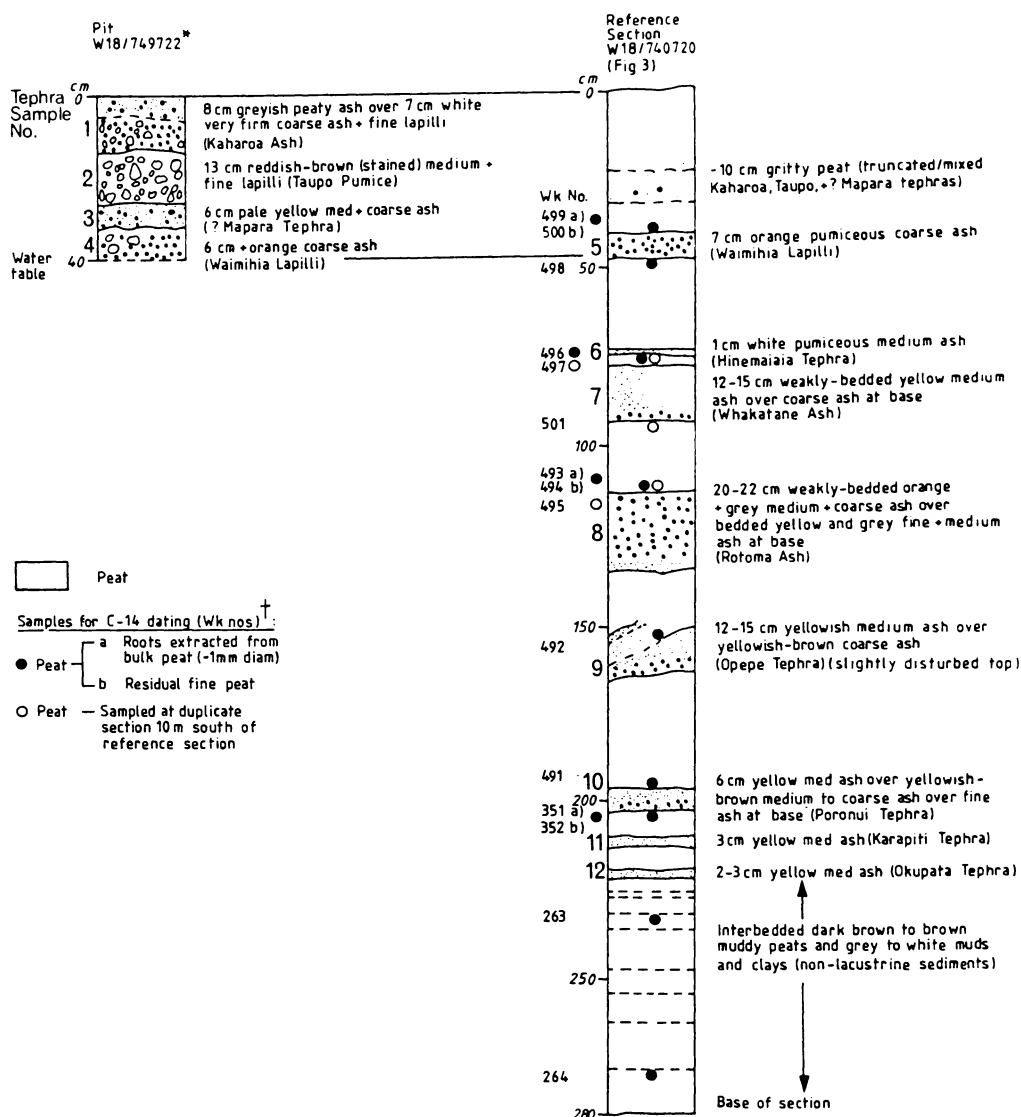


Fig. 4 – Peat and tephra stratigraphy of the Kaipo Lagoon. The positions at which tephra and peat were sampled are indicated. Peat samples were about 2 cm in thickness. The basal muds and clays, which lack diatom remains (Rogers, 1984), appear to grade into massive blue-grey silt below 2.8 m depth. The grain size descriptions are approximate and based on: fine and medium lapilli 2-16 mm; coarse ash $\frac{1}{2}$ –2 mm; medium ash $\frac{1}{16}$ – $\frac{1}{2}$ mm; fine ash $<\frac{1}{16}$ mm. Note: med = medium.

* Grid reference based on the 1,000 m grid of the 1:50,000 topographical map series (NZMS 260).

† Numbers prefixed Wk refer to the University of Waikato Dating Laboratory number. In the text, numbers prefixed NZ are New Zealand Radiocarbon Dating Laboratory numbers.

Recognition of the tephras was based on field appearance and stratigraphic position (Fig. 4) together with ferromagnesian silicate mineralogy. The identifications were supported by radiocarbon dates. In addition, glass shards from one of the tephras (Hinemaiaia) were analysed by electron microprobe to help confirm its identification.

Tephra sources and identifications

The lowermost tephra, Okupata Tephra, is andesitic and derives from the Tongariro Volcanic Centre; it is included in the Tongariro Subgroup (Topping, 1973). The others are all rhyolitic, derived from either the Taupo Volcanic Centre (Taupo Subgroup: Howorth *et al.*, 1981) or the Okataina Volcanic Centre (Rotorua Subgroup: Howorth *et al.*, 1981). The three volcanic centres are located between 100-150 km distance from Kaipo Lagoon (Fig. 1A).

The topmost tephra in the stratigraphic column, Kaharoa Ash, is distinguished by its hard, white pumice grains and the dominance of biotite in its ferromagnesian mineralogical assemblage (Table 1). It has an Okataina Volcanic Centre source (Cole, 1970).

Underlying Kaharoa Ash are Taupo Lapilli, Mapara Tephra, Waimihia Lapilli, and Hinemaiaia Tephra, each with an hypersthene-dominant mineralogy (Table 1) characteristic of a Taupo source (Ewart, 1963; Froggatt, 1981c). The identification of Mapara Tephra is tentative, as its close stratigraphic proximity to the overlying Taupo Lapilli (tephra 2 in Fig. 4) suggests that it may represent Hatepe Tephra, the lowest member of the Taupo Pumice Formation (Froggatt, 1981d; Walker, 1981). We prefer Mapara Tephra, however, because this tephra has been identified in another montane peat deposit in the Urewera National Park (at Te Rangaakapua)*clearly separated from Taupo Lapilli by a layer of peat 3-6 cm thick (W. B. Shaw and D. J. Lowe, unpublished data). Also, Mapara Tephra is known to occur well beyond the Kaipo Lagoon area, in organic-rich sediments at Lake Poukawa (Howorth *et al.*, 1980) and at Tiniroto (Howorth and Ross, 1981; Kohn *et al.*, 1981), whereas Hatepe Tephra is not recorded at either of these

Table 1 – Dominant ferromagnesian mineral abundances of the tephtras at Kaipo Lagoon.*

Tephra	Sample No. (See Fig.4)	Ferromagnesian silicate minerals (summed to 100%)					Opakes (vol%)†	H.M.§
		Hyp	Aug	Hbe	Cgt	Bio		
Kaharoa Ash	1	37	5	12	—	46	15	Low
Taupo Lapilli	2	100	—	—	—	—	9	Low
Mapara Tephra	3	97	2	1	—	—	13	Low
Waimihia	4	94	6	—	—	—	14	Low
Lapilli	5	100	—	—	—	—	12	Low
Hinemaiaia Tephra	6	95	5	—	—	—	17	Low
Whakatane Ash	7	30	1	4	65	—	19	Low
Rotoma Ash	8	5	—	8	87	—	21	Low
Opepe Tephra	9	84	16	—	—	—	14	Low
Poronui Tephra	10	83	17	—	—	—	7	Low
Karapiti Tephra	11	84	13	2	1	—	10	Low
Okupata Tephra	12	72	28	—	—	—	2	High

* Determined by point-count of the 2-4 ϕ size fraction of the heavy mineral assemblage (≥ 2.95 g.cm⁻³). Between 200 and 500 grains were counted.

† Proportion of opaque minerals (mainly titanomagnetite) in 2-4 ϕ heavy mineral fraction.

§ Approximate abundance of heavy minerals in the whole 2-4 ϕ fraction. Low = 1-5%; High = 20-30% (by weight).

Hyp = Hypersthene; Aug = Augite; Hbe = Calcic Hornblende; Cgt = Cumingtonite; Bio = Biotite; — = not observed.

* See Appendix to Kaipo Lagoon study after References.

Table 2 – Chemical analyses of glasses from Hinemaiaia Tephra at Kaipō Lagoon as determined by electron microprobe.* The analyses are presented on a normalised 100%-loss-free basis.

	1	2	3	4	5	6	7	8	9	10	11	12	13	Mean(Isd)
SiO ₂	76.88	76.93	77.03	77.12	77.22	76.30	77.08	76.70	76.83	76.99	76.93	77.00	76.84	76.90(0.23)
Al ₂ O ₃	12.98	13.01	13.07	12.80	12.97	13.20	12.86	13.03	12.95	12.99	13.01	12.97	13.00	12.99(0.10)
TiO ₂	0.15	0.18	0.17	0.20	0.14	0.20	0.18	0.25	0.23	0.18	0.22	0.15	0.22	0.19(0.03)
FeO†	1.58	1.52	1.52	1.50	1.56	1.72	1.54	1.69	1.65	1.54	1.68	1.56	1.67	1.60(0.08)
MgO	0.21	0.14	0.15	0.19	0.12	0.18	0.19	0.18	0.18	0.18	0.17	0.17	0.16	0.17(0.02)
CaO	1.32	1.26	1.27	1.31	1.42	1.39	1.21	1.25	1.21	1.26	1.34	1.36	1.25	1.30(0.07)
Na ₂ O	3.81	3.87	3.68	3.71	3.44	3.85	3.82	3.76	3.84	3.79	3.59	3.74	3.81	3.75(0.12)
K ₂ O	2.97	2.98	3.01	3.07	3.02	3.00	3.00	3.06	2.97	2.98	2.94	2.94	2.96	2.99(0.04)
Cl	0.10	0.11	0.10	0.10	0.11	0.16	0.12	0.08	0.14	0.09	0.12	0.10	0.09	0.11(0.02)
Water§	1.40	1.77	2.93	3.81	2.16	1.62	2.48	2.18	4.84	1.61	2.24	2.36	3.01	2.50(0.96)

* Glass shards in the 2-4φ size fraction of sample 6 (Fig.4) were mounted in epoxy resin, polished, carbon-coated, and analysed using a JEOL JXA-733 SUPERPROBE at Victoria University of Wellington (Froggatt and Gosson, 1982). A 10 μm beam diameter and 8.0 nA beam current, and other analytical conditions as described in Froggatt (1983), were used. Concentrations are given in oxide weight percent except for Cl which is in atomic weight percent. Isd = 1 standard deviation of the mean of analyses 1-13.

† All Fe calculated as FeO

§ Difference between original analytical total and 100. The glasses also contain detectable Mn and P (not analysed).

localities. (Isopach maps show thin deposits of Hatepe Lapilli extended to Gisborne: Vucetich and Pullar, 1964; Walker, 1981).

Hinemaiaia Tephra (as defined by Froggatt, 1981a) occurs stratigraphically just above Whakatane Ash at Kaipo Lagoon (Fig. 4). Until recently, Hinemaiaia Tephra (definition of Froggatt, 1981a) had been tacitly regarded as underlying Whakatane Ash, following the stratigraphic and chronologic relationships described by Vucetich and Pullar (1973) for Hinemaiaia Ash. However, Lowe (1986) has demonstrated that it stratigraphically overlies Whakatane Ash and is probably widespread over much of the North Island. Lowe (1986) based his correlation in part on the electron microprobe analyses of glass shards from the Hinemaiaia Tephra at Kaipo Lagoon (Table 2). The 13 chemical analyses reported in Table 2 show it to be of rhyolitic composition and support an origin in the Taupo Volcanic Centre (*cf.* glass chemistry analyses of Taupo-derived tephtras in, for example, Ewart, 1963, Froggatt, 1983, and Lowe, 1986). The close similarity of each of the analyses, and the consequent low standard deviations (Table 2; *cf.* Froggatt and Gosson, 1982), indicate that the sample is relatively pure, despite the inherent problems that may be associated with probing glass (Froggatt, 1983). These analyses, together with those on the same tephra elsewhere, confirm its identification as Hinemaiaia Tephra (Lowe, 1986).

Underlying Hinemaiaia Tephra are the Whakatane and Rotoma tephtras, which are positively identified by their high cummingtonite content (Table 1). This amphibole, diagnostic of tephtras derived from the Haroharo complex in the Okataina Volcanic Centre (Ewart, 1971), occurs in only these 2 tephtras in the Rotorua Subgroup (Kohn and Glasby, 1978; Howorth *et al.*, 1980).

The next 3 tephtras below Rotoma Ash are Opepe Tephra, Poronui Tephra, and Karapiti Tephra. Each of these has an hypersthene-rich ferromagnesian mineralogy (Table 1) characteristic of a Taupo source (Froggatt, 1981c).

The oldest tephra observed in the Kaipo section differs from the others in having a high proportion of heavy minerals (20-30%) in the whole 2-4 ϕ (63-250 μ m) size fraction, a very low abundance (2%) of opaque minerals in the heavy mineral suite, and at least twice as much augite (28%) in the ferromagnesian mineral assemblage (Table 1). These properties indicate an andesitic rather than rhyolitic origin, and Tongariro Volcanic Centre is the likeliest source — its eruptives typically contain abundant phenocrysts of hypersthene and augite but low concentrations of opaque minerals (Clark, 1960; Lowe *et al.*, 1980). We consider that the tephra is a member of Topping's (1973) Okupata Tephra Formation, which immediately underlies Karapiti Tephra in the Tongariro area (Topping and Kohn, 1973). The "unnamed andesitic ashes" that underlie Karapiti Lapilli to the east of Lake Taupo, and described by Vucetich and Pullar (1973), are hence probably correlatives of the Okupata Tephra.

CHRONOLOGY

Radiocarbon dating and sample reliability

To support the identification of the tephtras, and to determine rates of peat accumulation, 15 new radiocarbon dates have been determined (Fig. 5). Whilst nine samples comprised bulk peat, the other three samples, taken from the top, middle, and bottom of the section exposure, were each split into a coarse and fine fraction. The coarse fraction consisted of handpicked roots generally larger than about \sim 1 mm in diameter, and the fine fraction residual peat after the root extraction (Fig. 5). This splitting procedure was done to determine whether the abundant coarse root-like material and occasional sticks present in the reference

Tephra (source)	Waikato Radiocarbon Lab. No	Age (years B.P.)		Sample*	Comments
		Old T $\frac{1}{2}$	New T $\frac{1}{2}$		
Kaharoa (Okataina)					Age is c 700 years old (Mc Glone, 1983)
Taupo (Taupo)					Age is c 1800 years old (Healy, 1964)
Mapara (Taupo)					Age is c 2100 years old (Vucetich & Pullar, 1973)
Waimihia (Taupo)	Wk 499	2910 \pm 60	2990 \pm 60	{ PR	Sample severely diluted (24% sample)
	Wk 500	3040 \pm 50	3130 \pm 60		
	Wk 498	3250 \pm 70	3340 \pm 70	P	
Hinemaiaia (Taupo)	Wk 496	4490 \pm 60	4620 \pm 60	P	
	Wk 497	4530 \pm 60	4660 \pm 60	P	
Whakatane (Okataina)	Wk 501	4860 \pm 70	5000 \pm 70	P	
	Wk 493	5440 \pm 170	5600 \pm 170	{ PR	
Rotoma (Okataina)	Wk 494	7380 \pm 80	7590 \pm 80	{ PF	
	Wk 495	7560 \pm 100	7780 \pm 100	P	
	Wk 492	8710 \pm 80	8970 \pm 80	P	
Opepe (Taupo)					
Poronui (Taupo)	Wk 491	9560 \pm 80	9840 \pm 80	{ P	
	Wk 351	10160 \pm 130	10500 \pm 130		{ PR
Karapiti (Taupo)	Wk 352	9960 \pm 90	10290 \pm 90	{ PF	
Okupata (Tongariro)	Wk 263	10600 \pm 90	10900 \pm 90	P	
	Wk 264	11500 \pm 80	11900 \pm 90	P	

Fig. 5 – Radiocarbon dates on peaty material associated with the various tephras identified at the Kaipo Lagoon section. Tephra sources are indicated in Fig. 1A (inset). The reliability of the dates is discussed in the text. *P = Peat (bulk sample); PR = Roots (coarser than ~1 mm diameter) extracted from the bulk peat; PF = Fine peat residual from the bulk peat after root extraction.

section (Fig. 3) represented contemporary (*i.e.*, autochthonous) or modern vegetation growth. As a further precaution, we also took three bulk peat samples from a nearby duplicate section that had fewer obvious roots in the Hinemaiaia Tephra-Rotoma Ash zone (Fig. 4).

The results indicate that, apart perhaps from the zone of peat between the Whakatane and Rotoma tephras, very little mixing or contamination has taken place in the section. The dates progressively increase in age down the section with no stratigraphic inversions from tephra to tephra. Comparison of the three coarse and fine pairs of dates, using the statistical method in Currie (1981), shows that both the top pair (Wk 499-500) and the bottom pair (Wk 351-352) are probably not significantly different at a 90% significance level. The middle pair of samples (Wk 493-494) are significantly different from each other, with Wk 493 several thousand years younger than either Wk 494 or Wk 495. Presumably the rootlets making up Wk 493 represent natural contamination of the peat overlying the Rotoma Ash deposit (see further discussion below). The large counting errors

on Wk493 stem from its small sample size and consequent severe dilution in the dating procedure (Fig. 5).

Ages of tephra deposition

The Kaharoa, Taupo, and Mapara tephtras were not dated at Kaipo Lagoon, but have been dated elsewhere at ~ 700 , $\sim 1,800$, and $\sim 2,100$ years B.P., respectively (Fig. 5).

The three dates associated with Waimihia Lapilli (Wk498, 499, 500) all fall within the range of previous dates for this tephra (Froggatt, 1981c), although their average of $\sim 3,070$ years is younger than the commonly accepted age of $\sim 3,400$ years (Pullar and Heine, 1971; Vucetich and Pullar, 1973; Walker, 1981).

The two dates on the thin (3 cm) layer of peat between Hinemaiaia Tephra and Whakatane Ash (Wk496, 497) apply to both tephtras, and average $\sim 4,510$ years. This average is thus a maximum age for Hinemaiaia Tephra and a minimum for Whakatane Ash. Hinemaiaia Tephra has an average age, based on reliable dates from several sites elsewhere, of $\sim 4,500$ years (Lowe, 1986).

A maximum age on the Whakatane Ash at Kaipo is (Wk501) $4,860 \pm 70$ years B.P., which agrees closely with the previously accepted best estimate of $\sim 4,800$ years for this tephra (Cole and Nairn, 1975; Lowe, 1986).

Disregarding Wk493, the other 2 dates on Rotoma Ash (Wk494, 495) average $\sim 7,470$ years. This age concurs with initial age estimates of (NZ1152) $7,050 \pm 77$ years B.P. and (NZ1199) $7,330 \pm 235$ years B.P. for Rotoma Ash (Pullar and Heine, 1971; Vucetich and Pullar, 1973), but is considerably younger than more recently obtained dates of (Wk522) $8,370 \pm 90$ and (Wk523) $8,350 \pm 100$ years B.P. (Green and Lowe, 1985) and (NZ1945) $8,860 \pm 120$ years B.P. (Nairn, 1980) that are probably more accurate because of better stratigraphic control. Consequently, we regard all of the dates on the peaty material above Rotoma Ash, particularly Wk493, as too young — with respect to the deposition of Rotoma Ash — by possibly 1,000 years or more. The explanation for this apparent anomaly is uncertain, although it may be partly the consequence of an excessive sample size given the particularly slow peat accumulation rate (between 0.06 — 0.07 mm/year) evident for this period (see Fig. 6 below).

The minimum date we obtained for Opepe Tephra is (Wk492) $8,710 \pm 80$ years B.P. Taking errors into account, this is not significantly different from the previously published date of (NZ185) $8,850 \pm 1,000$ years B.P. on Opepe Tephra near Taupo (Pullar and Heine, 1971; Vucetich and Pullar, 1973), and is only slightly younger than a maximum age of (Wk230) $9,370 \pm 210$ years B.P. obtained for Opepe Tephra in Lake Maratoto (Green and Lowe, 1985).

The three dates associated with Poronui Tephra (Wk351, 352, 491) are the first to be obtained on it and average $\sim 9,900$ years. Previously, Poronui Tephra had an extrapolated age estimated to be about 9,740 years (Topping and Kohn, 1973).

Neither Karapiti Tephra nor Okupata Tephra were dated directly, but their stratigraphic positions within a few centimetres of Poronui Tephra and the underlying ^{14}C sample Wk263 ($10,600 \pm 90$ years B.P.) (Fig. 4) allow their ages to be estimated reasonably accurately. Assuming uniform accumulation rates, Karapiti Tephra has an estimated age of $\sim 10,100$ years, and Okupata Tephra $\sim 10,300$ years (Fig. 6). Karapiti Tephra has only one previous direct date, being (NZ4847) $9,910 \pm 130$ years B.P. (Froggatt, 1981b). Okupata Tephra, consisting of multiple units near source, has previously been dated between (NZ1374) $9,790 \pm 160$ years B.P. and (NZ1189) $12,450 \pm 340$ years B.P. (Topping, 1973), and the age of $\sim 10,300$ years is consistent with these dates.

Age of bog formation and peat sedimentation rates

The date (Wk264) $11,500 \pm 80$ years B.P. from the base of the section was from the lowest peaty horizon we observed in the area, and is assumed to represent a minimum age for the beginning of bog formation. The sediments overlying this horizon and underlying Okupata Tephra (Fig. 4) are muddy, suggesting that permanent bog-forming conditions were not attained for another thousand years or so, probably at around 10,500 years. This 11,500-10,500 year age for the initiation of bog growth at Kaipo is similar to dates of inception of bogs in other parts of the North Island (McGlone and Topping, 1977; Green and Lowe, 1985), and may indicate a response to post-glacial climatic change such as an increase in

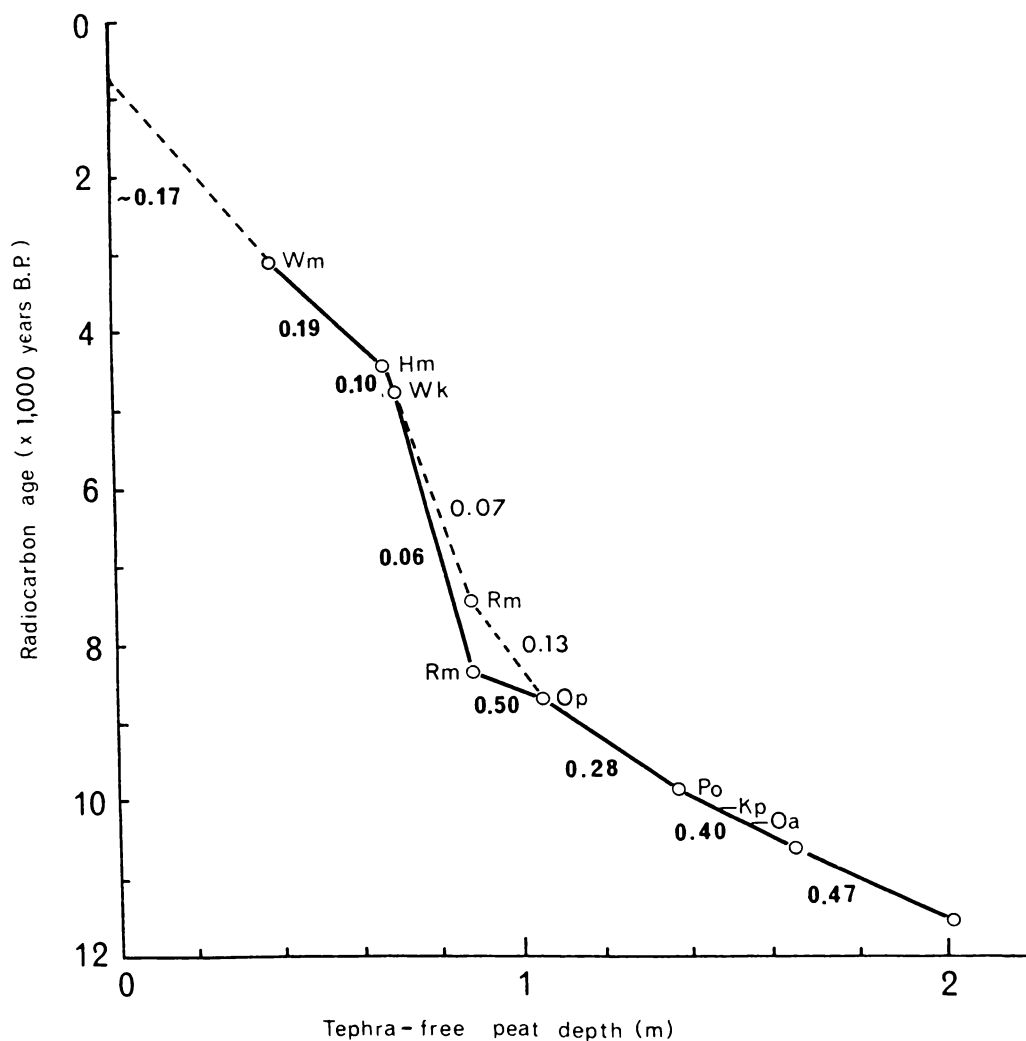


Fig. 6 – Peat accumulation rate curve for the Kaipo Lagoon reference section. Average rates of deposition, in mm/year, are shown between the dated points. The dates are based on average ages from Fig. 5. In the Opepe-Whakatane tephra period, the 2 curves drawn use ages of 7,500 years (dashed) and 8,400 years (solid — and preferred) for Rotoma Ash deposition. The post-Waimihia sedimentation rate is only approximate because of mixing, shrinkage, and possible erosion of the peat in the upper part of the section (the top surface is assumed to be aged ~ 700 years). Tephra symbols are as in Fig. 3.

rainfall, resulting in higher catchment erosion rates or higher water table levels, or both.

The rate of peat accumulation in the bog since 11,500 years ago is plotted in Fig. 6; the average rate for the whole section is 0.19 mm/year. The rates for separate periods are variable, ranging from 0.47 mm/year (for the muddy peats at the base of the section) to only 0.06-0.07 mm/year in the Rotoma-Whakatane period. The average sedimentation rate between 11,500 years and Opepe Tephra (8,700 years) is 0.37 mm/year, but between Opepe Tephra and the bog's surface (marked by Kaharoa Ash) the average rate is much slower, about 0.13 mm/year. Assuming an age of 8,400 years for the deposition of Rotoma Ash, the bog growth rate in the short interval between this tephra and Opepe Tephra was apparently at a maximum 0.50 mm/year.

The fluctuations in accumulation rates may have several causes, such as variations in local drainage conditions, the effects of tephra fall, peat decomposition or erosion, or changes in climate, and we do not know which, if any, is dominant. However, the broad pattern of change, with relatively fast rates peaking between Opepe-Rotoma tephra depositions, then slowing considerably, is similar to the pattern of sediment accumulation in Lake Maratoto (Green *et al.*, 1984; Green and Lowe, 1985), and in peat deposits in the Tongariro region (McGlone and Topping, 1977). In these studies the changes in sedimentation rates were related largely to post-glacial climatic changes; in Lake Maratoto, Green and Lowe (1985) attributed the maximum sedimentation rate at around Opepe Tephra time to a short period of increased rainfall and windiness with enhanced catchment erosion. This climatic change explanation may thus apply also to the Kaipō Lagoon peat sequence.

The average sedimentation rate of 0.19 mm/year for the Kaipō bog is slow compared with rates of about 0.8-0.9 mm/year reported for the 10,000-11,000 years-old Rukuhia and Hauraki bogs in the Waikato region (Harris, 1963; Hogg and McCraw, 1983; Green and Lowe, 1985), about 1 mm/year for peat at Lake Poukawa (Howorth *et al.*, 1980; Froggatt and Howorth, 1980), and 0.36-0.75 mm/year for post-4000 year-old peat at Turakirae Head, Wellington (Mildenhall and Moore, 1983). Elsewhere in New Zealand, however, such relatively slow rates of peat accumulation have been recorded in Holocene-aged deposits at various localities (*e.g.*, 0.19 mm/year, Holden's Bay, Rotorua: McGlone, 1983; 0.03-0.15 mm/year, Longwood Range, Southland: McGlone and Bathgate, 1983).

Implications of the absence of Waiohau Ash at Kaipō

The basal peat date of 11,500 years has implications with regard to the age of the Waiohau Ash Formation. This tephra, which does not occur in the Kaipō section, was identified in a road cutting near Lake Waikaremoana, by Vucetich and Pullar (1964:71) only 10 km from the Kaipō Lagoon, and has been dated near source at $11,250 \pm 200$ years B.P. (NZ568), $11,100 \pm 210$ years B.P. (NZ878), and $11,800 \pm 150$ years B.P. (NZ1135) (Pullar and Heine, 1971). Its generally accepted age is around 11,300 years (Pullar and Birrell, 1973); the last date (11,800 years) has a less certain stratigraphy than the others and is rarely quoted.

Consequently, the apparent absence of Waiohau Ash from the Kaipō Lagoon section implies that either it was misidentified at Lake Waikaremoana by Vucetich and Pullar (1964), and also by Pullar and Birrell (1973), or the previous age determinations (done on charcoal) underestimated its real age by several hundred years at least. Assuming that there is no erosional unconformity above the 11,500

year date at Kaipo, we favour the second option because Green and Lowe (1985) report an age of about 12,400 years for Waiohau Ash in Lake Maratoto (based on four dates).

CONCLUSIONS

Eleven Holocene tephtras occurring at Kaipo Lagoon are derived from the Taupo (7), Okataina (3), and Tongariro (1) Volcanic Centres, and have been identified chiefly from their field appearance, stratigraphy, and dominant ferromagnesian mineralogy. In addition, the glass chemistry of one of the tephtras, Hinemaiaia Tephtra, was analysed by electron microprobe. Six of the tephtras have been radiocarbon dated by 13 new dates on enclosing peat or peaty material; two more tephtras were dated by extrapolation assuming constant sedimentation rates. Three dates obtained on Rotoma Ash deposition are considered to be inexact, however, being at least 1,000 years too young in comparison with reliable dates on this tephtra elsewhere. The other new dates obtained on the tephtras generally accord with previous determinations.

The Kaipo Lagoon bog formed between about 11,500 and 10,500 years ago, perhaps partly in response to the effects of post-glacial climatic change, and peat has accumulated since then at a variable but mainly slow rate (average 0.19 mm/year). The pattern of change of sedimentation rates, relatively fast before and slow after the Opepe-Rotoma maximum, may relate to climatic change, but variation in local conditions could also have been important influences.

The positive identification of the tephtras in the Kaipo Lagoon using diagnostic laboratory methods to supplement the field observations has resulted in a more certain Holocene tephtrstratigraphy for the Urewera-Waikaremoana area. The identification of Opepe, Poronui, Karapiti, and Okupata tephtras in particular has extended their known distribution in eastern North Island. Such improvements to tephtra dispersal maps are potentially helpful in interpretations regarding volcanological processes associated with eruptions of tephtra (*e.g.*, Walker, 1981; Lowe, 1986). The dates on Poronui Tephtra, the first obtained for it, and most of those on the other tephtras, are valuable additions to the few dates presently available, although the specific age of the Rotoma Ash eruption is still uncertain.

Finally, the identification and ^{14}C dating of the tephtras in the Kaipo Lagoon provides an exceptionally detailed chronology for associated studies on the vegetational and climatic history of the Kaipo-Waikareiti area.

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Cross referencing to thesis papers

Green, J.D.; Lowe, D.J. 1985 = Paper 9

Lowe, D.J. 1986 = Paper 6

Lowe, D.J. *et al.* 1980 = Paper 1

Errata

- p.27, line 2 : "MCraw" should read "McCraw"
 p.28, line 8 : "many" should read "may"
 p.31, line 9 : "it" should read "its"
 p.31, line 19 : "another montane" should read "a sub-alpine"

Appendix to Kaipo Lagoon study - Tephrostratigraphy of Te Rangaakapua sub-alpine peat bog, Urewera National Park.

A tephra-bearing sub-alpine bog at Te Rangaakapua was excavated, described, and sampled by Mr. W.T.Shaw (Biological Sciences, University of Waikato) in 1984. I examined samples of the tephtras supplied by Mr. Shaw and identified their source volcanoes and likely correlatives using dominant ferromagnesian mineralogy (Table 1) and field relationships and ages (Fig.1). Two ^{14}C dates were obtained (Fig.1; Hogg et al. 1987).

The tephrostratigraphy is consistent with that described at Kaipo Lagoon by Lowe and Hogg (1986), except that Hinemaiaia Tephra, found at Kaipo, was not identified at Te Rangaakapua (see also Lowe 1986). A pollen analysis of peat samples is being undertaken by Dr M.S.McGlone (Botany Division, DSIR, Christchurch).

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Table 1. Dominant ferromagnesian mineral abundances in tephras at Te Rangaakapua (Profile 1).¹

Tephra Formation	Sample No. (Fig.1)	Ferromagnesian silicate minerals* (summed to 100%)					Opaques ² (%)	H.M. ³ (%)
		Hyp	Aug	Hbe	Cgt	Bio		
Kaharoa	1	42	3	17	2	36	28.5	1.3
Taupo	2	97	2	1	-	-	30.5	11.1
Mapara	3	84	13	3	-	-	11.3	0.5
Waimihia	4	88	10	2	-	-	19.5	1.0
Whakatane	5,6	21	1	15	63	-	22.1	1.1
Rotoma	10	9	1	9	81	-	21.8	0.4

1. Determined by point-count of the 2-4 ϕ size fraction of the heavy mineral assemblage ($\geq 2.95 \text{ g.cm}^{-3}$). Between 300 and 550 grains were counted in each sample.

2. Proportion of Fe-Ti oxides in the 2-4 ϕ heavy mineral fraction (point-count).

3. Abundance of heavy minerals in the total 2-4 ϕ size fraction (by weight).

* Additional minerals identified include zircon and apatite; a trace of olivine occurs in sample 1.

Hyp = Hypersthene; Aug = Augite; Hbe = Calcic Hornblende (mainly green-brown; sparse reddish-brown-brown); Cgt = Cumingtonite; Bio = Biotite; - = not observed.

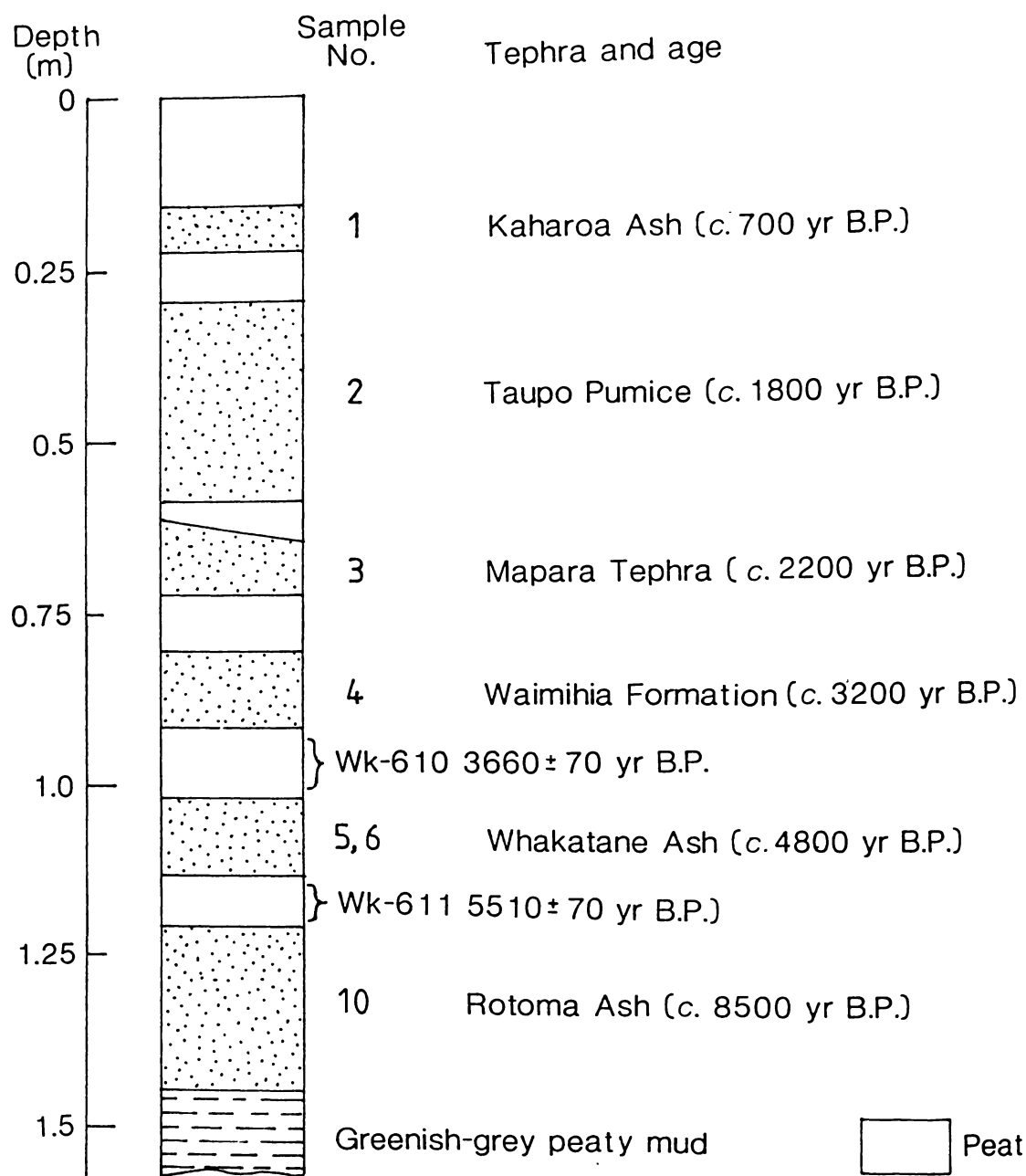


Fig.1. Tephrostratigraphy of Te Rangaakapua sub-alpine bog (Profile 1), Urewera National Park (G.R. NZMS260 W17/765894). Kaharoa, Whakatane, and Rotoma tephras are derived from the Okataina Volcanic Centre; Taupo, Mapara, and Waimihia tephras were erupted from the Taupo Volcanic Centre (Healy et al. 1964). Ages on old $T\frac{1}{2}$ basis; Wk- number is Waikato Radiocarbon Dating Laboratory number.

PAPER 6

Revision of the age and stratigraphic relationships of Hinemaiaia Tephra and Whakatane Ash, North Island, New Zealand, using distal occurrences in organic deposits.

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61-73 (1986).

Revision of the age and stratigraphic relationships of Hinemaiaia Tephra and Whakatane Ash, North Island, New Zealand, using distal occurrences in organic deposits

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Keywords Hinemaiaia Tephra Formation; Hinemaiaia Ash Formation; Whakatane Ash Formation; pyroclastics; Holocene; stratigraphy; tephrostratigraphy; organic matter; C-14; isopach maps; glasses; chemistry; electron probes; explosive eruptions

Abstract The stratigraphic and chronologic relationships of Hinemaiaia Tephra and Whakatane Ash are examined using distal tephras preserved in organic-rich deposits at five sites in eastern and northern North Island, New Zealand. A c. 10 mm thick, unnamed white rhyolitic ash layer described at two of the sites (Tiniroto and Poukawa), and previously of disputed stratigraphic significance, also occurs at the other three sites (Kaipo, Rotomanuka, and Okoroire) as a primary airfall tephra. The tephra is derived from the Taupo Volcanic Centre and is correlated with Hinemaiaia Tephra (definition of Froggatt) using similarity of stratigraphic position, composition (ferromagnesian mineralogy and glass chemistry), and radiocarbon age. It stratigraphically overlies Whakatane Ash. The tephra underlying Whakatane Ash, and previously identified as Hinemaiaia Ash (definition of Vucetich & Pullar), is probably Motutere Tephra.

Hinemaiaia Tephra has a mean age of (old T^{1/2}) c. 4500 years, Whakatane Ash c. 4800 years. New ¹⁴C dates, obtained on peat or gyttja adjacent to these tephras, are (old T^{1/2}, years B.P.): 4220 ± 60 (NZ3160A), 4490 ± 70 (Wk541) (above Hinemaiaia Tephra); 4470 ± 70 (Wk542) (below Hinemaiaia Tephra); 4800 ± 50 (NZ3161A), 4490 ± 60 (Wk496), 4530 ± 60 (Wk497), 4260 ± 140 (Wk662) (below Hinemaiaia Tephra and above Whakatane Ash); 5210 ± 80 (NZ3162A), 4860 ± 70 (Wk501), 4850 ± 80 (Wk660) (below Whakatane Ash).

Based on the distal occurrences described here, the Hinemaiaia Tephra has a much more widespread distribution than previously demonstrated, and may have been emplaced by a very powerful "above average" plinian eruption.

INTRODUCTION

Late Quaternary tephras erupted from rhyolitic and andesitic sources in the Taupo Volcanic Zone (Fig. 1), and from Mt Egmont and Mayor Island, cover large areas of the North Island (e.g., Pullar et al. 1973; Howorth et al. 1981). Following early reconnaissance mapping of these deposits, chiefly for soil survey purposes (e.g., Grange 1931), many studies in the past 20 years have concentrated on the stratigraphy, age, and distribution of the tephras near their source areas (e.g., Healy 1964; Vucetich & Pullar 1964; Howorth 1975). During this period it has been found that tephra deposits proximal to a particular source commonly contain interbedded distal deposits from outside centres, and a more complex tephrostratigraphy than originally described has ensued (e.g., Topping & Kohn 1973; Vucetich & Pullar 1973; Stewart et al. 1977; Howorth & Topping 1979). Largely because of their thinness in relation to the locally derived deposits, the distal tephras can be difficult to trace or identify with certainty in the field, especially where affected by weathering or soil-forming processes. Similar problems are evident in distal sequences consisting wholly of thinly bedded tephras (e.g., Vucetich & Pullar 1969; Pullar & Birrell 1973; Hodder & Wilson 1976).

Two approaches have been applied to circumvent this problem. The first has involved detailed laboratory-based tephra "fingerprinting" methods (e.g., Kohn 1970, 1979; Topping & Kohn 1973; Hogg & McCraw 1983); the second has been the utilisation of sections or sediment cores of muddy or organic-rich deposits within which discrete tephra layers are separated and preserved (e.g., Topping & Kohn 1973; Kohn & Glasby 1978; Howorth et al. 1980; Lowe et al. 1980). These latter studies have begun to provide not only an improved chronology for many of the tephras (through radi-

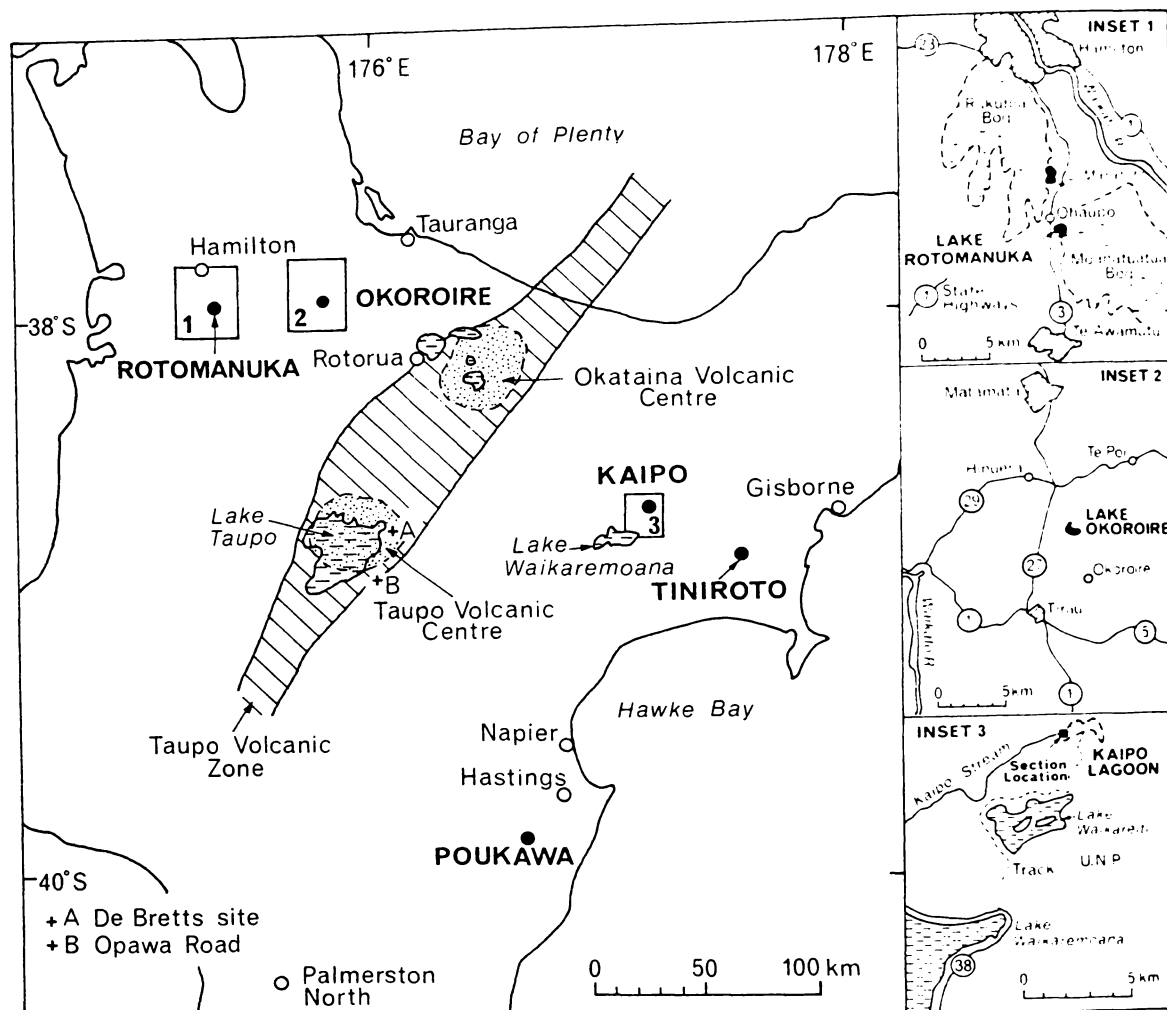


Fig. 1 Location map of the Poukawa, Tiniroto, Kaipō, Rotomanuka, and Okoroire sites in the North Island showing their distant positions peripheral to the Okataina and Taupo Volcanic Centres. The boundaries of the Taupo Volcanic Zone and volcanic centres are from Cole & Nairn (1975). Insets show detailed locations of Kaipō Lagoon, Lake Rotomanuka, and Lake Okoroire. U.N.P. = Urewera National Park.

ocarbon dating of the intervening organic sediments) but also a clearer record of the stratigraphic relationships of interbedded tephras derived from different volcanic centres.

In this paper, distal tephras contained within peat and organic lake sediments (gyttja) are investigated to determine the stratigraphic and chronologic relationships of two Holocene tephras, the Taupo-derived Hinemaiaia Tephra (defined by Froggatt 1981a) and the Okataina-derived Whakatane Ash (defined by Vucetich & Pullar 1964). From studies in the Taupo area, Vucetich & Pullar (1973) defined Hinemaiaia Ash and considered it to be stratigraphically overlain by Whakatane Ash. Froggatt

(1981a), in redefining Hinemaiaia Ash as Hinemaiaia Tephra, essentially followed the stratigraphy of Vucetich & Pullar (1973) which, until now, has been unquestioned. However, recent examination of the tephras in peat and gyttja deposits at Kaipō, Rotomanuka, and Okoroire, in eastern and northern North Island (Fig. 1), identified a thin rhyolitic ash layer which, with regard to its characteristics and stratigraphic position, could not be correlated with any known proximal eruptive. Moreover, such an "unnamed rhyolitic tephra" had previously been found in a similar stratigraphic position in organic sediments at Tiniroto and Poukawa (Fig. 1), although its stratigraphic significance

at these sites was disputed (Howorth & Ross 1981; Kohn et al. 1981). It is shown here that the unnamed rhyolitic tephra found at all of these distal sites is the same eruptive unit and that it is a correlative of Hinemaiaia Tephra. That Whakatane Ash stratigraphically underlies Hinemaiaia Tephra at the distal sites has meant revision of the stratigraphic and chronologic relationships previously described by Vucetich & Pullar (1973) and Froggatt (1981a) for these tephtras.

The revision includes 10 previously unpublished ^{14}C dates on the Hinemaiaia Tephra and the Whakatane Ash. Electron microprobe analyses of glass shards from the distal correlative of Hinemaiaia Tephra and from Whakatane Ash are given, and implications of the possible widespread distribution of Hinemaiaia Tephra in the North Island are examined.

STRATIGRAPHY AND CHRONOLOGY OF THE HINEMAIAIA AND ASSOCIATED TEPHRAS IN THE TAUPO AREA

In a revision of earlier work by Baumgart (1954) and Healy (1964), Vucetich & Pullar (1973) defined the Hinemaiaia Ash Formation (symbol Hm) at the De Bretts Hotel type section near Taupo (Fig. 1). The Hinemaiaia Ash, established as originating from the Taupo Volcanic Centre, was defined as lying conformably between the Whakatane Ash Formation and the Rotoma Ash Formation (these last two tephtras being derived from the Okataina Volcanic Centre; Fig. 1). It was dated at c. 6200 years old by correlation with a tephra at Tiniroto that had ^{14}C dates of 6390 ± 120 (NZ1137)* and 6190 ± 70 (NZ1247) years B.P. (Pullar & Heine 1971; Vucetich & Pullar 1973). Vucetich & Pullar (1973) noted that both Whakatane and Rotoma tephtras were infrequently exposed around Taupo and were difficult to distinguish with certainty. In many sections, Hinemaiaia Ash was sandwiched within a multiple paleosol with a blotchy appearance. Of the tephtras derived from Taupo, Hinemaiaia Ash lies between Waimihia Formation (above) and Opepe Tephra Formation (below).

Froggatt (1981a) redefined the Hinemaiaia Ash as the Hinemaiaia Tephra Formation (Hm) at a new type site in Opawa Road in Lake Taupo State Forest (Fig. 1). Recognising the difficulty of iden-

tifying the Whakatane and Rotoma tephtras as discrete units in the Taupo area (Whakatane Ash could not be found at Opawa Road), he purposely defined Hinemaiaia Tephra in relation to locally mappable Taupo-source tephtras only. It was thus defined as the rhyolitic tephra lying conformably between the Waimihia Lapilli Formation and the paleosol capping the Motutere Tephra Formation. The Motutere Tephra, a Taupo-derived tephra first recognised and described by Froggatt (1981a), and similarly defined without reference to Okataina-source tephtras, lies below the Hinemaiaia Tephra and overlies the paleosol on Opepe Tephra. Froggatt (1981a) considered that both Hinemaiaia Tephra and Motutere Tephra were wholly airfall deposits in the type area. The volume of the Hinemaiaia Tephra is c. 3 km^3 (Froggatt 1982a). New ^{14}C dates of 4650 ± 80 years B.P. (NZ4574) for the Hinemaiaia Tephra, and 5370 ± 90 years B.P. (NZ4846) for the Motutere Tephra, both determined on charcoal found in the type area, were published by Froggatt (1981a).

Other dates of possible relevance to these tephtras were collated in a summary diagram by Froggatt (1981a, p. 103). Whakatane Ash, with ages ranging from 4600 to 5180 years, is shown between Waimihia Lapilli and Hinemaiaia Tephra. This stratigraphy, based on Vucetich & Pullar (1973), tacitly implies that Hinemaiaia Tephra, like Hinemaiaia Ash, underlies Whakatane Ash. However, Froggatt's (1981a) definition does not preclude the possibility of Hinemaiaia Tephra occurring stratigraphically above Whakatane Ash. Motutere Tephra, significantly older than Hinemaiaia Tephra by about 700 radiocarbon years, therefore probably underlies Whakatane Ash (Froggatt 1981a), as discussed later.

Thus, at the time of publication of Froggatt's (1981a) paper, there was effectively no new information regarding the stratigraphic relationship of the Hinemaiaia and Whakatane tephtras beyond that of Vucetich & Pullar (1973). Moreover, Froggatt's caution regarding the identification of Whakatane Ash in the Taupo area indicates that Vucetich & Pullar's (1973) stratigraphy with respect to this tephra must be viewed as uncertain. In comparing the ages, and associated errors, of the Hinemaiaia and Whakatane tephtras, it is evident that the solitary ^{14}C date on the Hinemaiaia Tephra (Froggatt 1981a) is indistinguishable from most of those available for Whakatane Ash (a few are several hundred years older: Grant-Taylor & Rafter 1971; Howorth et al. 1980). Hence, in the absence of a definitive section containing both tephtras, a chronologic separation based on the published dates is unjustifiable.

*NZ = New Zealand Radiocarbon Dating Laboratory number. These and other ^{14}C ages discussed in the text are all conventional ages based on the old half-life of 5568 years. See also Table 2.

STRATIGRAPHY OF DISTAL TEPHRAS IN ORGANIC DEPOSITS IN EASTERN AND NORTHERN NORTH ISLAND

Previous studies at Tiniroto and Poukawa (Fig. 1) have reported the occurrence of an uncorrelated rhyolitic ash layer between the Waimihia and Whakatane tephtras, but its existence and stratigraphic significance have been disputed, and its identification is problematical. However, since this previous work was published, three further sections or sediment cores containing airfall tephtras intercalated with organic deposits have been investigated — at Kaipo Lagoon (Urewera National Park) and at Lake Rotomanuka and Lake Okoroire (both in the Waikato region). In these sections, which have a more comprehensive tephrostratigraphy than at Tiniroto and Poukawa, a rhyolitic tephtra also occurs between the Waimihia and Whakatane tephtras or within the general age range they span. The nature, stratigraphic position, and age of this tephtra, and those immediately adjacent to it, are specifically examined to establish its origin and possible correlation with Hinemaiaia Tephtra.

Tephrostratigraphy

Tiniroto

The sequence of tephtras preserved within muddy lacustrine sediments has been variably interpreted largely because of unreliable radiocarbon dating (Vucetich & Pullar 1964, 1973; Pullar & Heine 1971; Howorth & Ross 1981; Kohn et al. 1981). Most studies have noted the presence of a thin (c. 10–25 mm) rhyolitic tephtra, or “ashy horizon”, lying between the Waimihia and Whakatane tephtras (labelled Un in column 2, Fig. 2) that has been assigned several names. Kohn et al. (1981) called it an “unnamed rhyolitic tephtra” that “records an eruption from the Taupo Volcanic Zone which has not been previously recognised on the east coast of the North Island” (p. 65). This conclusion was based on its orthopyroxene-rich ferromagnesian mineralogy, its stratigraphic position above Whakatane Ash (considered to be aged between 4680 ± 100 years B.P. (NZ1358) and 5180 ± 80 years B.P. (NZ1066)), and the apparent lack of any known rhyolitic eruption in this time period (between Waimihia and Whakatane tephtras). The tephtra below Whakatane Ash at Tiniroto was correlated with Hinemaiaia Ash from its stratigraphic position and mineralogy, and its age was estimated at between 4680 ± 100 years B.P. (NZ1358) and 6345 ± 130 years B.P. (NZ427).

In contrast, Howorth & Ross (1981) dismissed the “ashy horizon” as being of no stratigraphic importance due to its occurrence in one core only and within sediments described as badly slumped. The tephtra below Whakatane Ash was identified

as Hinemaiaia Ash (column 1, Fig. 2) and assigned an age of c. 5500 years old (based on correlation with a tephtra in a similar stratigraphic position at Poukawa: Howorth et al. 1980).

Poukawa

The stratigraphy of the Holocene tephtras preserved in peats and lake sediments at Poukawa has been described by Pullar (1970), Howorth et al. (1980), and B. P. Kohn, V. E. Neall & R. B. Stewart (unpublished manuscript, V. E. Neall pers comm.). The last workers, as at Tiniroto, recorded at Poukawa a thin (c. 10 mm) “unnamed rhyolitic white coarse ash” lying below Waimihia Lapilli and just above Whakatane Ash (column 4, Fig. 2). It was ^{14}C dated from peat above at 4220 ± 60 years B.P. (NZ3160) and below at 4800 ± 50 years B.P. (NZ3161). The tephtra below Whakatane Ash was identified as Hinemaiaia Ash.

Howorth et al. (1980) did not record any tephtra layer between Waimihia and Whakatane tephtras at Poukawa. Whakatane Ash was dated between 4600 ± 90 (NZ3948) and 4640 ± 90 (NZ3949) years B.P.; the tephtra below was identified as Hinemaiaia Ash with ^{14}C dates of 5680 ± 130 (NZ3950) years B.P. (above) and 5370 ± 90 (NZ3951) years B.P. (below) (column 3, Fig. 2). However, Froggatt (1981a) concluded that this tephtra was probably a correlative of Motutere Tephtra (dated at 5370 ± 90 years B.P. (NZ4846) near the source), and this correlation presumably also applies to the tephtra identified as Hinemaiaia Ash by Kohn, Neall & Stewart at Poukawa.

Kaipo Lagoon

Kaipo Lagoon is a montane peat bog located near Lake Waikareiti, north of Lake Waikaremoana. Kaipo Stream, draining the bog, has exposed a 3 m section at its western end (Fig. 1) that shows interbedded tephtras and peats overlying material dated at about 11 000 years old (Lowe & Hogg 1986). At a depth of about 1 m is a 5–10 mm layer of white pumiceous ash (labelled HmT in Fig. 2). It underlies Waimihia Lapilli and overlies, within 2–3 cm, Whakatane Ash. It has a modal ferromagnesian mineralogy (2–4 ϕ fraction) of 95% orthopyroxene and 5% clinopyroxene (based on point count). This composition indicates a Taupo source (Froggatt 1981b). The Whakatane Ash was identified by its characteristic cummingtonite-dominated (65%) ferromagnesian mineralogy (Kohn & Glasby 1978; Howorth et al. 1980) and its age (Fig. 2). The difference in mineralogy indicates that the white ash layer cannot be a disturbed fragment derived from the Whakatane Ash. The Waimihia Lapilli was identified by its field characteristics, its

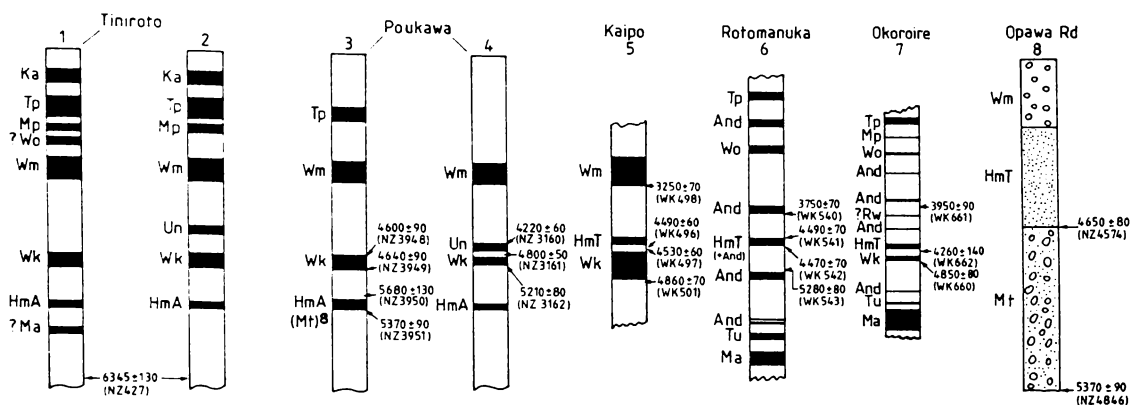


Fig. 2 Schematic stratigraphic columns of tephras and ^{14}C dates at Tiniroto, Poukawa, Kaipo, Rotomanuka, Okoroire, and Opawa Road (Taupo) sites; ages are in years B.P. (old $T\frac{1}{2}$) (see also Table 2). The "unnamed rhyolitic tephra" is labelled either Un or HmT (see below).

Ka, Kaharoa Ash; Tp, Taupo Pumice; Mp, Mapara Tephra; Wo, Whakaipo Tephra; Wm, Waimihia Lapilli; ?Rw, possibly Rotokawau Ash; Un, unnamed rhyolitic tephra (correlated with HmT in this study); HmT, Hinemaiaia Tephra (of Froggatt 1981a); Wk, Whakatane Ash; HmA, Hinemaiaia Ash (of Vucetich & Pullar 1973) (probably correlates with Mt); Mt, Motutere Tephra; Tu, Tuhua Tephra; Ma, Mamaku Ash; And, uncorrelated andesitic tephra. Sources, and specific locations of new sites (Fig. 1), are: 1, Howorth & Ross (1981); 2, Kohn et al. (1981); 3, Howorth et al. (1980); 4, B.P. Kohn, V. E. Neall & R. B. Stewart (V. E. Neall pers. comm.), section located on northern margin of Lake Poukawa at NZMS 260 map grid reference V22/281522; 5, this study, section located at W18/740720; 6, this study, core site at S15/136615; 7, this study, core site at T15/555611; 8, Froggatt (1981a).

orthopyroxene-dominated ferromagnesian mineralogy (100%), and a carbon date of 3250 ± 70 years B.P. (Wk498)* (Fig. 2; Lowe & Hogg 1986). It is most unlikely that the white ash has derived from reworking of the overlying Waimihia Lapilli, being separated from it by a generally uniform 25–30 cm thickness of peat.

The white ash layer can be traced as a discrete bed c. 20 m along the exposure of peat. The ^{14}C dates of 4490 ± 60 years B.P. (Wk496) and 4530 ± 60 years B.P. (Wk497) were obtained on samples c. 2 cm thick taken from beneath the tephra at two sites c. 10 m apart on the section face. These dates apply equally to the white ash and to Whakatane Ash because the samples spanned the entire layer of peat between the tephras. The date of 4860 ± 70 years B.P. (Wk501) here gives a maximum age of the Whakatane Ash (Fig. 2). The dates from Kaipo are consistent with minimal mixing in the section, further indicating that the white ash layer has not been reworked (Lowe & Hogg 1986).

Lake Rotomanuka

Lake Rotomanuka is a shallow (< 8 m) lake located adjacent to the Moanatuatua bog near Ohaupo about 15 km south of Hamilton (Fig. 1). It was

formed when a valley was dammed by alluvium (Hinuera Formation) at least 17 000 years ago (Green & Lowe 1985). A series of sediment cores was collected using a modified Livingstone piston corer. The cores, up to 3.5 m long, contain numerous thin, discrete tephra layers, derived from various volcanic sources, interbedded with gyttja. Such tephras have been described and correlated previously for nearby Lake Maratoto by Lowe et al. (1980) and Green & Lowe (1985). By virtue of its greater sedimentation rate, its less peaty character, and perhaps its slightly more southerly, nearer source location, Lake Rotomanuka contains a clearer and more detailed tephrostratigraphic record than Lake Maratoto, particularly in the upper one-third of the sediment column.

The tephrostratigraphy of part of a core from Lake Rotomanuka is shown in Fig. 2. A thin (3–5 mm) white, fine ash layer (HmT in Fig. 2) occurs at a depth of c. 0.5 m below Taupo Pumice. It is straddled by andesitic tephras, probably from a Mt Egmont source (D. J. Lowe in prep. "Stratigraphy, chronology, and correlation of late Quaternary distal rhyolitic and andesitic tephras interbedded with organic sediments in the Waikato region, North Island, New Zealand"), which are dated at 3750 ± 70 years B.P. (Wk540) and 5280 ± 80 years B.P. (Wk543) (Fig. 2); their ferromagnesian mineral assemblages are dominated by clinopyroxene

*Wk = University of Waikato Radiocarbon Dating Laboratory number (Hogg 1982).

(augite) and hornblende in approximately equal amounts. The white fine ash is found in five other cores taken from the lake. In some of these it is intermixed with a contemporary, slightly coarser ash derived from Mt Egmont additional to those noted above. Neither Waimihia nor Whakatane tephra were identified as megascopic layers, although the latter may be sparsely present as microscopic "dust" associated with the underlying andesitic tephra. Because of the thinness (ranging from only c. 1–5 mm) of the white ash, insufficient ferromagnesian minerals could be extracted from it for an accurate point count, but both orthopyroxene and clinopyroxene were present. Dates of 4490 ± 70 years B.P. (Wk541) and 4470 ± 70 years B.P. (Wk542) were obtained from 1–2 cm thick slices of gyttja taken from above and below the tephra, respectively (Fig. 2). A thin, white ash layer of similar age (as estimated from sedimentation rates) and stratigraphic position is known to occur in at least four other lakes (Rotokauri, Ngaroto, D, and Mangahia) in the Hamilton area.

Lake Okoroire

Lake Okoroire, located about 5 km north of Tirau (Fig. 1), is a shallow peaty lake similar to Lake Rotomanuka in origin and character. Three cores, up to 3 m long, were taken, as at Rotomanuka, revealing a similar tephrostratigraphy (Fig. 2). An unnamed white fine ash layer (HmT in Fig. 2) occurs c. 0.3 m below Taupo Pumice, and is underlain by Whakatane Ash and overlain by an Egmont-derived tephra, each within c. 1 cm of it in the core. The white fine ash layer, 8–10 mm thick, was found in each core taken. It has a ferromagnesian mineralogy (2–4 ϕ fraction) of 87% orthopyroxene with 13% clinopyroxene. The Whakatane Ash was identified by cummingtonite (81%). The andesitic tephra overlying the white ash contains clinopyroxene and hornblende in approximately equal amounts in the ferromagnesian mineral assemblage.

A 1 cm thick slice of gyttja between the white fine ash and the Whakatane Ash was dated at 4260 ± 140 years B.P. (Wk662); a 2 cm thick slice below Whakatane Ash was dated at 4850 ± 80 years B.P. (Wk660) (Fig. 2). The andesitic tephra immediately above the white ash layer is aged c. 4100 years based on the date 3950 ± 90 years B.P. (Wk661) obtained 3 cm above it in the core (Fig. 2).

Glass chemistry

Glass shards were extracted from three samples of the uncorrelated white ash from the Kaipo and Rotomanuka sites and analysed for nine major elements using an electron microprobe (Table 1). The results show that each of the tephra layers sampled

is homogeneous, as indicated by the generally low standard deviations (cf. Froggatt & Gosson 1982, p. 10); sample 1 shards have the smallest, and sample 3 shards the greatest, variance. The compositions are remarkably similar to one another (Fig. 3A), as demonstrated by the similarity coefficients of the sample-pair histograms (Fig. 3B) whose values, near 1.0, lie within the range that typically indicates an origin from a single emplacement unit (Borchardt et al. 1972; Sarna-Wojcicki et al. 1984; Davis 1985). The small coefficient of variation (CV) values (< 6.0) similarly indicate a close chemical match (Borchardt et al. 1971; Froggatt 1983).

The analyses confirm that the white ash is rhyolitic in composition, and favour an origin in the Taupo Volcanic Centre (Table 1, Fig. 4). All Taupo-derived tephra of Holocene age apparently have similar major element compositions (exemplified by Motutere Tephra in Table 1), and most appear chemically indistinguishable from one another on this basis (Froggatt 1981b, 1982b; see also glass analyses in Ewart 1963 and Froggatt 1983). However, they are quite distinct from many of the Okataina-derived tephra (e.g., Whakatane Ash, Table 1), as illustrated in Fig. 4 for CaO and FeO (see also glass analyses in Cole & Nairn 1975 and Kohn 1979). (The Holocene Taupo-derived tephra also contain more Al_2O_3 , TiO_2 , and MgO, but less K_2O , than the Okataina-derived tephra.)

CORRELATION OF THE UNNAMED RHYOLITIC TEPHRA WITH HINEMAIAIA TEPHRA AND STRATIGRAPHIC IMPLICATIONS

The occurrence of the unnamed rhyolitic tephra at Kaipo, Okoroire, and Rotomanuka as a distinct stratigraphic unit supports the arguments for its existence as a genuine primary tephra at Tiniroto and Poukawa. Moreover, in considering all sites, the tephra manifestly has many features in common.

- (1) It is white with comparable grain size (fine to coarse ash) and thickness (av. c. 10 mm) compatible with a distal location.
- (2) It has an orthopyroxene-dominated ferromagnesian mineralogy (demonstrated for four sites) indicative of a Taupo Volcanic Centre source.
- (3) It has a radiocarbon age of between c. 4200 and c. 4800 years (av. c. 4500 years: Table 2).
- (4) It occupies a similar stratigraphic position (Fig. 2): at Kaipo, Poukawa, and Tiniroto the tephra occurs stratigraphically below the Waimihia Lapilli and just above Whaka-

Low—Revision of Hinemaiaia Tephra Fm

Table 1 Chemical analyses of glass from the unnamed white ash, Motutere Tephra, and Whakatane Ash, as determined by electron microprobe*. The analyses are normalised to 100% loss free.

	White ash					
	1	2	3	4	5	6
SiO ₂	76.90 (0.23)	76.97 (0.57)	77.04 (0.77)	76.97 (0.52)	77.01 (0.22)	78.41 (0.24)
Al ₂ O ₃	12.99 (0.10)	13.01 (0.27)	12.75 (0.38)	12.92 (0.28)	13.18 (0.11)	12.41 (0.15)
TiO ₂	0.19 (0.03)	0.17 (0.04)	0.17 (0.02)	0.18 (0.03)	0.16 (0.01)	0.12 (0.03)
FeO†	1.60 (0.08)	1.75 (0.13)	1.61 (0.15)	1.65 (0.13)	1.62 (0.08)	0.78 (0.11)
MnO	n.d.	n.d.	n.d.	n.d.	0.08 (0.04)	0.12 (n.d.)
MgO	0.17 (0.02)	0.17 (0.04)	0.14 (0.06)	0.16 (0.05)	0.19 (0.03)	0.10 (0.01)
CaO	1.30 (0.07)	1.37 (0.16)	1.22 (0.17)	1.29 (0.15)	1.30 (0.04)	0.67 (0.05)
Na ₂ O	3.75 (0.12)	3.53 (0.11)	3.89 (0.22)	3.73 (0.20)	3.59 (0.08)	3.77 (0.08)
K ₂ O	2.99 (0.04)	2.92 (0.12)	3.08 (0.37)	2.99 (0.22)	2.88 (0.08)	3.62 (0.09)
Cl	0.11 (0.02)	0.11 (0.02)	0.10 (0.03)	0.10 (0.03)	n.d.	n.d.
Water‡	2.50 (0.96)	2.10 (3.23)	1.25 (0.71)	2.00 (1.93)	1.79 (1.66)	n.d.
n	13	10	10	33	9	20

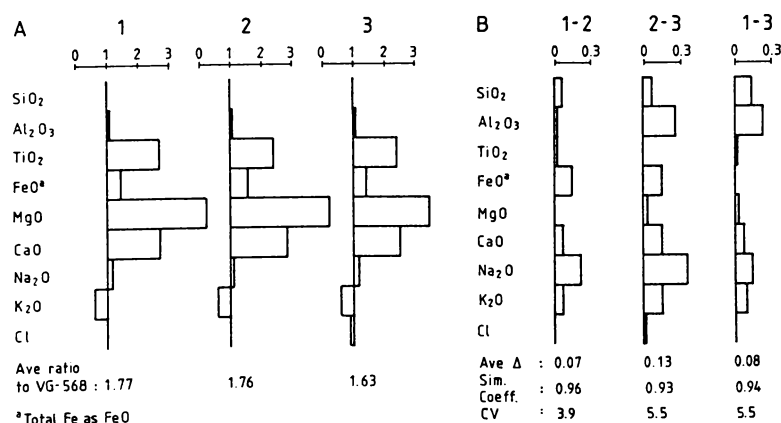
1 = white ash, Kaipō Lagoon; 2 = white ash, Lake Rotomanuka (core A); 3 = white ash, Lake Rotomanuka (core D); 4 = mean of all analyses 1-3 (=Hinemaiaia Tephra in this study); 5 = Motutere Tephra (lower unit, Opawa Rd; analyses from Froggatt 1982b, p. 320); 6 = Whakatane Ash (analyses from P. C. Froggatt pers. comm. 1984). n = number of analyses in mean (each analysis was done on a different shard); numbers in parentheses are 1 standard deviation. n.d. = not determined or unavailable. Note that analyses on Hinemaiaia Tephra from the Taupo area are not currently available.

*Glass shards in the 2-4 ϕ size fraction were analysed using a JEOL JXA-733 SUPERPROBE at Victoria University of Wellington (Froggatt & Gosson 1982). Analytical conditions were as described in Froggatt (1982b, 1983) including a 10 μ m beam diameter, an 8.0 nA beam current, and peak counts of 3 \times 10 s (meaned). Repeated analysis of glass standards (KN-18 comendite glass; VG-99 basaltic glass) gave a check on probe calibration and operation. Some samples showed slight Na loss (< 1 wt% oxide), probably due to volatilisation or electron-induced Na⁺ migration (Federman & Carey 1980; Froggatt 1983), and only moderate precision for SiO₂, as may occur in probing glasses (e.g., Smith & Westgate 1969).

†All Fe calculated as FeO.

‡Water by difference.

Fig. 3 Chemical composition of the "white ash" glass shown as arbitrary ratios to (A) Yellowstone rhyolitic glass standard VG-568, (B) histograms of absolute difference between sample pairs where the plot 1-2 compares samples 1 and 2, and so on.



Ave Δ = average difference in ratios; Sim. Coeff. = similarity coefficient for sample pair using all elements analysed (Borchardt et al. 1972); CV = coefficient of variation (Borchardt et al. 1971) (see text). Samples are: 1, Kaipō Lagoon; 2, Lake Rotomanuka (core A); 3, Lake Rotomanuka (core D). Note: The white ash-Whakatane Ash sample pair (analyses 4 & 6, Table 1) similarity coefficient = 0.75, CV = 18.4.

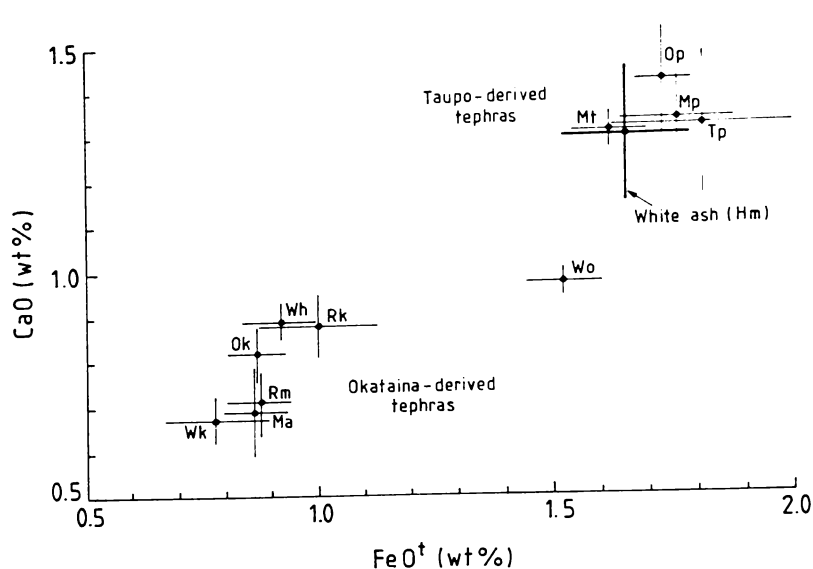


Fig. 4 Plot of CaO versus FeO (total) in glass of some late Quaternary tephtras derived from Taupo or Okataina sources. The "white ash" samples (Hm) from Kaipo and Rotomanuka have a Taupo rather than Okataina affinity, and are considered to be correlatives of Hinemaiaia Tephtra.

All analyses were by electron microprobe as described in Table 1; bars represent 1 standard deviation from the mean (dots). Tephtra abbreviations and sample details (lake and core, number of shards analysed) are: Tp, Taupo Pumice (Lake Rotomanuka core A, 10); Mp, Mapara Tephtra (Lake D core 2, 9) (NZMS 260 grid ref. S14/072893); Wo, Whakaipo Tephtra (L. Rotomanuka core A, 11); Hm, white ash (=Hinemaiaia Tephtra) (column 4, Table 1); Mt, Motutere Tephtra (column 5, Table 1); Op, Opepe Tephtra (L. Rotomanuka core A, 7) [all from Taupo Volcanic Centre]; Wk, Whakatane Ash (column 6, Table 1); Ma, Mamaku Ash (L. Rotomanuka core A, 14); Rm, Rotoma Ash (L. Rotomanuka core C, 10); Wh, Waiohau Ash (L. Rotomanuka core A, 10); Rk, Rerewhakaaitu Ash (L. Rotomanuka core A, 10); Ok, Okareka Ash (L. Rotomanuka core A, 9) [all from Okataina Volcanic Centre].

tane Ash; at Rotomanuka it is straddled by andesitic tephtras dated at 3750 years (above) and 5280 years (below); at Okoroire it underlies a c. 4100 year old andesitic tephtra and closely overlies Whakatane Ash.

- (5) The glass shards of samples from Rotomanuka and Kaipo are chemically indistinguishable from one another and have major element concentrations typical of Taupo-derived Holocene tephtras (Table 1, Fig. 4).

These stratigraphic, chronologic, and compositional similarities together indicate that at all five sites the unnamed rhyolitic tephtra is the equivalent eruptive unit, and, furthermore, that it is a distal correlative of Froggatt's (1981a) Hinemaiaia Tephtra. Based on this identification, and with both tephtras occurring together at four of the five distal sites, it becomes obvious that Hinemaiaia Tephtra stratigraphically overlies Whakatane Ash. The tephtra originally identified as Hinemaiaia Ash at Poukawa and Tiniroto, and underlying Whakatane Ash, is probably Motutere Tephtra. These previous

identifications as Hinemaiaia Ash, although strictly correct in terms of the definition of Vucetich & Pullar (1973), are now obsolete in view of Froggatt's (1981a) redefinition and the findings in this study.

The correlation of the unnamed rhyolitic tephtra with Hinemaiaia Tephtra allows revision of the radiocarbon dates pertaining to it and the closely associated Whakatane Ash, and a reconsideration of the distribution pattern of Hinemaiaia Tephtra in the North Island.

CHRONOLOGY OF THE HINEMAIAIA AND WHAKATANE TEPHTRAS

Radiocarbon dates relevant to the Hinemaiaia Tephtra and Whakatane Ash are summarised in Table 2 and Fig. 5. Four of the dates are deliberately listed in both parts of the table because they apply equally to both tephtras. This duality arises because the samples taken for dating bridged the

Table 2 Summary of radiocarbon dates relevant to Hinemaiaia Tephra or Whakatane Ash.

Dating laboratory number ¹	Age (years B.P.)		Sample material ²	Location and reference ³
	Old half-life	New half-life		
HINEMAIAIA TEPHRA				
<i>Above⁴ (mean = 4360)</i>				
NZ3160	4220 ± 60	4340 ± 70	P	Poukawa (a)
Wk541	4490 ± 70	4620 ± 70	G	Rotomanuka (b)
<i>Below (mean = 4530)</i>				
NZ3161	4800 ± 50	4940 ± 60	P	Poukawa (a)
NZ4574	4650 ± 80	4780 ± 90	C	Near Opawa Rd, Taupo (c)
Wk496	4490 ± 60	4620 ± 60	P	Kaipo (b)
Wk497	4530 ± 60	4660 ± 60	P	Kaipo (b)
Wk542	4470 ± 70	4600 ± 70	G	Rotomanuka (b)
Wk662	4260 ± 140	4390 ± 150	G	Okoroire (b)
Mean age for Hinemaiaia (n = 8): 4490 (std. error ± 140 at p 0.05)*				
WHAKATANE ASH				
<i>Above (mean = 4540)</i>				
NZ3161	4800 ± 50	4940 ± 60	P	Poukawa (a)
NZ3948	4600 ± 90	4740 ± 90	P	Poukawa (d)
Wk496	4490 ± 60	4620 ± 60	P	Kaipo (b)
Wk497	4530 ± 60	4660 ± 60	P	Kaipo (b)
Wk662	4260 ± 140	4390 ± 150	G	Okoroire (b)
<i>Below (mean = 4930)</i>				
NZ426	5085 ± 102	5240 ± 110	CW	Terraces pumice pit, Taupo (e)
NZ1066	5180 ± 80	5340 ± 80	C	Haumia Rd, Galatea (e)
NZ1358	4680 ± 100	4820 ± 100	C	Mt Haroharo (f)
NZ3162	5210 ± 80	5370 ± 90	P	Poukawa (a)
NZ3949	4640 ± 90	4770 ± 90	P	Poukawa (d)
Wk501	4860 ± 70	5000 ± 70	P	Kaipo (b)
Wk660	4850 ± 80	4990 ± 80	G	Okoroire (b)
Mean age for Whakatane (n = 12): 4770 (std. error ± 170 at p 0.05)*				

¹NZ = New Zealand Radiocarbon Dating Laboratory (Lower Hutt); Wk = University of Waikato Radiocarbon Dating Laboratory (Hamilton).

²C = charcoal; P = peat; G = gyttja (organic lake sediment); CW = charred wood.

³a = B. P. Kohn, V. E. Neall & R. B. Stewart (unpublished); b = this study; c = Froggatt (1981a); d = Howarth et al. (1980); e = Grant-Taylor & Rafter (1971); f = Goh & Pullar (1977).

⁴Sample position with respect to tephra (NZ1358 within deposit).

two closely spaced tephtras. That Whakatane Ash is older than Hinemaiaia Tephra is now unquestioned because of its established lower stratigraphic position. However, the magnitude of the age difference is less certain because of the various uncertainties in the radiocarbon dating method (Hogg 1982) and possible errors related to variations in sample thickness, position, or type of material being dated. Although there are variations amongst the dates in relation to each tephra, a *t*-test comparison of them nevertheless shows that the mean age for Hinemaiaia Tephra (4490 years) is significantly younger, at a 95% significance level, than that of Whakatane Ash (4770 years). The difference between the means is 280 years; the standard errors indicate that, at *p* = 0.05, the actual difference may

be several hundred years greater or less than this figure. A more precise estimate of age difference may be difficult to attain by the ¹⁴C method because the errors associated with the dates ultimately limit its resolution (Table 2, Fig. 5). However, more ¹⁴C dates from reliable samples may help to resolve some of the discrepancies evident in Fig. 5.*

Because Whakatane Ash consists of multiple eruptive units in the Rotorua area (Vucetich & Pullar 1964), it is conceivable that one or more of these units may yet be found to overlie Hinemaiaia Tephra, perhaps at sites proximal to their Okataina source. This possibility clearly requires that the uppermost Whakatane Ash eruptives are several hundred years younger than the lowermost ones.

* See Postscript to this paper

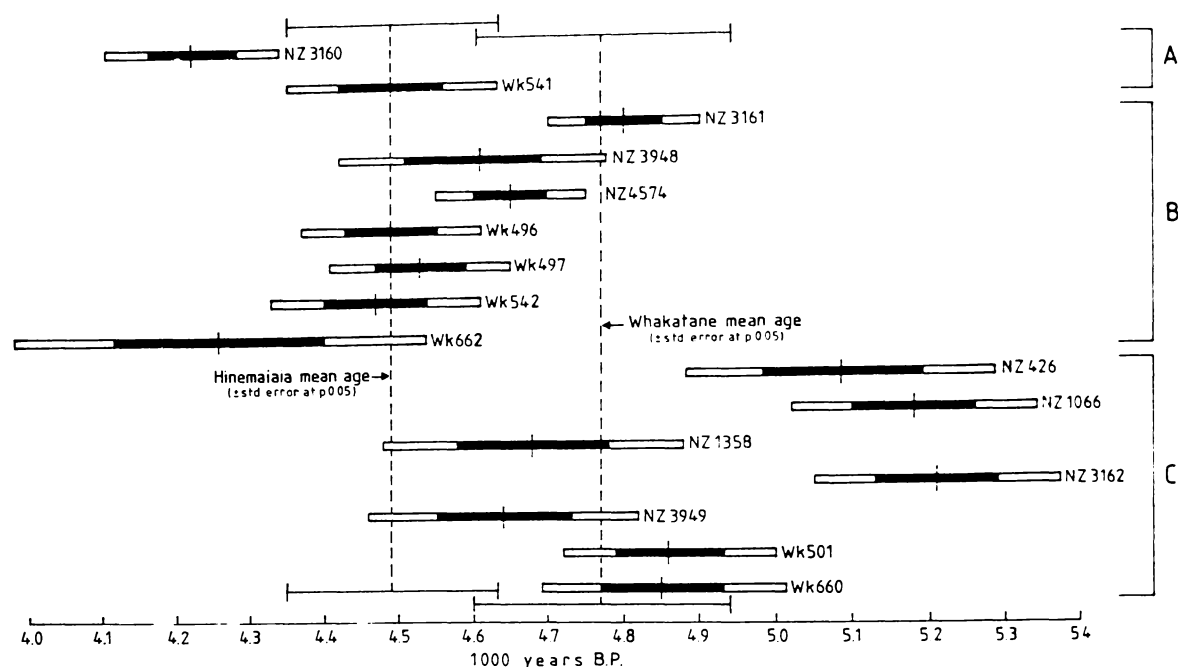


Fig. 5 Comparison of radiocarbon dates (old $T_{1/2}$) that apply to Hinemaiaia Tephra or Whakatane Ash (from Table 2). The dates show considerable variation when their error terms are considered. The solid bars represent 1 standard deviation, the open bars 2 standard deviations. The dates are arranged according to their sampling position relative to the Hinemaiaia or Whakatane tephras: A, samples above Hinemaiaia Tephra; B, samples below Hinemaiaia Tephra, or above Whakatane Ash, or both (NZ3948 applies to Whakatane only, NZ4574 and Wk542 to Hinemaiaia only; the rest apply to both tephras); C, samples below Whakatane Ash.

DISTRIBUTION OF THE HINEMAIAIA TEPHRA

The Hinemaiaia Tephra probably originated from the vicinity of a submerged dome-like feature in the southeastern part of Lake Taupo (Froggatt 1981a; Fig. 6). The tephra is about 65 cm thick at its type section (c. 10 km from the postulated vent), and probably has a near-source isopach distribution pattern very similar to that shown for Motutere Tephra (Froggatt 1981a, p. 102) or Hinemaiaia Ash (Vucetich & Pullar 1973, p. 761). However, its demonstrated occurrence at the five widely separated sites in Hawke's Bay, Gisborne, eastern Bay of Plenty, and the Waikato, between 110 and 155 km from the source, shows that it is a much more widespread tephra than previously mapped. This adds support to the studies on other plinian deposits that have indirectly deduced much larger dispersion areas than their isopachs indicated (e.g., Walker 1980, 1981b). Because the eruption of Hinemaiaia Tephra apparently lacked an ignimbritic component (Froggatt 1981a; cf. Vucetich & Pullar 1973), the distal deposits studied here pre-

sumably derive from plinian fallout rather than cognimbrite ash fallout. The occurrence of Hinemaiaia Tephra in the Waikato area, well upwind of the vent, and the roughly circular shape of the tentative 10 mm isopach in Fig. 6, suggests that it may also be found in suitable sediments in the Wanganui and Taranaki regions. Assuming an exponential decrease in thickness (Froggatt 1982a), the Hinemaiaia Tephra is likely to be only a few millimetres thick at distances of c. 200–250 km from Lake Taupo.

Dispersive power

The area, D, enclosed by the $0.01T_{MAX}$ isopach (where T_{MAX} is the maximum thickness of the deposit) is indicative of the dispersive power of an eruption (Walker 1973, 1980). Assuming that T_{MAX} for Hinemaiaia Tephra is similar to its type section thickness of c. 650 mm (it may be a little more or less than this, allowing for the uncertain vent position), then the c. 10 mm isopach in Fig. 6, admittedly based on sparse data, may be regarded as a crude approximation of the $0.01T_{MAX}$ isopach (i.e.,

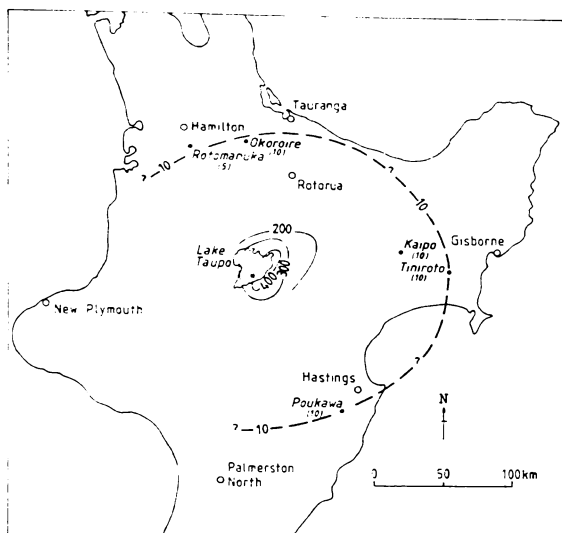


Fig. 6 Possible distal distribution of the Hinemaiaia Tephra. The dashed line is a tentative c. 10 mm isopach of Hinemaiaia Tephra based on its estimated thickness at the five sites as indicated. Isopachs (in millimetres) around Lake Taupo are of the Hinemaiaia Ash (Vucetich & Pullar 1973, p. 761). Hinemaiaia Tephra's probable source location in Lake Taupo is indicated by an asterisk (Froggatt 1981a).

c. 6.5 mm). On this basis, and using a circular distribution of radius 110 km, a D (dispersal index) value of about 40 000 km² is obtained. Even if this figure is overestimated by 25%, comparison with D values in the literature (Nairn 1980; Walker 1980, 1981b) suggests that the Hinemaiaia Tephra represents an "above average" plinian event of comparable ranking to the Waimihia Lapilli eruption ($D \approx 30\,000$ km²), being surpassed only by the Taupo Pumice ultraplinian eruption ($D \approx 100\,000$ km²). The Hatepe Lapilli eruption ($D \approx 10\,000$ km²) represents an "average" plinian event (Walker 1980), as presumably does the Rotorua Ash eruption ($D \geq 10\,000$ km²; Nairn 1980). The implication is that the Hinemaiaia Tephra eruption was extremely powerful and had a very high eruptive column (possibly between 30 and 50 km, and with an extensive plume) because the dispersal area is mainly a function of the column height and the atmospheric wind regime (Walker 1973, 1981a; Wilson et al. 1978). The generally fine ash size grade and the low phenocryst content of Hinemaiaia Tephra at its distal localities supports the deduction of such a high eruption column (Walker 1980, 1981a).

Walker (1981b, p. 323) commented that it was remarkable that the two latest major eruptions

(Taupo, Waimihia) from the Taupo Volcanic Centre produced exceptional plinian deposits. From the above inferences regarding the above average status of Hinemaiaia Tephra, it seems that such exceptional plinian eruptions are perhaps not so rare.

CONCLUSIONS

The stratigraphic and chronologic relationships of Hinemaiaia Tephra and Whakatane Ash, uncertain from prior studies in the Taupo area, have been resolved through the examination of distal tephra preserved within organic deposits at five sites in eastern and northern North Island. The existence of a disputed unnamed rhyolitic tephra, previously reported between the Waimihia and Whakatane tephra at two of the sites (Tiniroto and Poukawa), is confirmed by its unequivocal occurrence as a primary tephra deposit at the other three sites (Kaipo, Rotomanuka, and Okoroire). Based on its stratigraphic position, composition (ferromagnesian mineralogy and glass chemistry), and ¹⁴C chronology, this tephra, derived from the Taupo Volcanic Centre, is established as a distal correlative of Hinemaiaia Tephra (as defined by Froggatt 1981a). It stratigraphically overlies Whakatane Ash at all of the sites except Rotomanuka where the latter tephra is not evident as a megascopic layer. The tephra previously identified as Hinemaiaia Ash (following the definition of Vucetich & Pullar 1973) at Tiniroto and Poukawa, and underlying Whakatane Ash, is probably Motutere Tephra (Froggatt 1981a).

The 10 new ¹⁴C dates obtained on peat or gyttja associated with the Hinemaiaia and Whakatane tephra permit revision of their eruption ages: Hinemaiaia Tephra has a mean age of c. 4500 years, Whakatane Ash c. 4800 years, with standard errors near c. 150 years (Table 2). The Motutere Tephra has a mean age of c. 5400 years (Froggatt 1981a).

Based on the distal occurrences described here, the Hinemaiaia Tephra has a considerably more widespread distribution, probably from coast to coast across central North Island, than previously mapped. Such a large dispersal area for this tephra (perhaps of the order of 10⁴ km²) as a sheet-forming deposit suggests that it may have been deposited by a very powerful, above average plinian event (Walker 1980) with an eruption column probably exceeding 30 km in height.

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glass chemistry data on near-source Motutere Tephra and Whakatane Ash. I am grateful also to Messrs G. J. Gosson, K. Palmer, and J. Carter who, together with Dr Froggatt, greatly assisted me in obtaining and interpreting electron microprobe analyses at the Analytical Facility, Victoria University of Wellington. Dr V. E. Neall (Massey University) is thanked for willingly providing unpublished data, including three ^{14}C dates, on Poukawa. Mr N. B. Rogers and Drs A. G. Hogg, J. D. Green, C. H. Hendy, the late Professor H. S. Gibbs (University of Waikato), and Dr M. Ouellet (Université du Québec), assisted with sampling or interpretations at Rotomanuka, Okoroire, or Kaipō. Professor J. D. McCraw (University of Waikato) is thanked for commenting on the manuscript, Mrs V. L. Lockwood and Dr Hogg for rapidly dating the samples submitted to the Waikato Radiocarbon Dating Laboratory, and Mrs M. Griffin and Miss D. Bovill for their expert wordprocessing.

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Cross referencing to thesis papers

Green, J.D.; Lowe, D.J. 1985 = Paper 9

Lowe, D.J.; Hogg, A.G. 1986 = Paper 5

Lowe, D.J. *et al.* 1980 = Paper 1

Postscript to Paper 6

The mean ages calculated in Table 2 are arithmetic means of the old half-life ages. The standard errors (at 95% confidence limits) are derived from these means (e.g., Loveday 1968), i.e., the dating laboratory counting errors (± 1 standard deviation - see Paper 8) have not been taken into account.

Mean ages that incorporate these laboratory counting errors are "error weighted" or "pooled" means, and are calculated as shown on the next page (Gupta & Polach 1985). The mean dates given in Table 2 may be recalculated using this method as follows:

	Pooled mean (t_p)	Error (σt_p)
HINEMAIAIA TEPHRA		
Samples above tephra (n = 2)	4336	46
Samples below tephra (n = 6)	4596	27
<i>All samples</i> (n = 8)	4528	23
WHAKATANE ASH		
Samples above tephra (n = 5)	4612	30
Samples below tephra (n = 7)	4942	32
<i>All samples</i> (n = 12)	4766	22

The pooled mean ages for Hinemaiaia and Whakatane tephras are similar to those calculated in Table 2. The pooled mean errors generally decrease as n increases because of the better counting statistics. However, as exemplified in Fig. 5 (which incorporates the dating laboratory counting error terms), Chi-square tests on these means show very high T values (defined over page), hence the individual values differ significantly.

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Calculation of pooled means and errors (from Gupta & Polach 1985, p.141)

For the general case of more than two values we proceed as follows

Firstly calculate the pooled mean (t_p) and its error (σt_p) as below

$$t_p = \frac{\sum [t_i / (\sigma t_i)^2]}{\sum 1 / (\sigma t_i)^2} \quad \text{Eqn (6.7)}$$

$$\sigma t_p = \pm \sqrt{1 / \sum (1 / \sigma t_i)^2} \quad \text{Eqn (6.8)}$$

Where t_i , σt_i , t_p , σt_p are as defined before and summation is over the number of ages pooled (n).

Next we calculate the test statistic (T), and use the simplified formula as given by

$$T = \sum [(t_i - t_p)^2 / (\sigma t_i)^2] \quad \text{Eqn (6.9)}$$

(T) has a chi-squared distribution with ($n - 1$) degrees of freedom. If the value of (T) is less than the tabulated chi-square value at the chosen significance level then we accept the hypothesis that the results are statistically indistinguishable. The pooled mean (t_p) and its error (σt_p) can then be accepted as valid.

For example, we have four dates: (4900 \pm 100), (4700 \pm 90), (4800 \pm 70) and (5100 \pm 200).

$$t_p = \frac{[4900/100^2 + 4700/90^2 + 4800/70^2 + 5100/200^2]}{[1/100^2 + 1/90^2 + 1/70^2 + 1/200^2]}$$

$$= 4811 \text{ yr}$$

$$\sigma t = \pm \sqrt{\frac{1}{[1/100^2 + 1/90^2 + 1/70^2 + 1/200^2]}}$$

$$= \pm 47 \text{ yr}$$

degrees of freedom are 3 and the statistics

$$T = \frac{(4900-4811)^2}{100^2} + \frac{(4700-4811)^2}{90^2} + \frac{(4800-4811)^2}{70^2} + \frac{(5100-4811)^2}{200^2}$$

$$= 4.43$$

To test the hypothesis that the results are distinguishable from each other at 5% confidence level we look in table Chi-square (0.05, 3) = 7.82; since this is more than the computed value of statistics (T), we reject the postulated hypothesis and accept the hypothesis that the results are insignificantly different from each other at 95% confidence level and calculate a mean age of 4811 \pm 47.

PAPER 7

Notes on the stratigraphy, chronology, and correlation of tephras in Lake Waiatarua (Lake St. Johns), Auckland, and Lake Omapere, Northland.

This paper, in preliminary form, is divided into two parts: Part 1, Lake Waiatarua; Part 2, Lake Omapere. A location map for both sites is given in Fig. 1.

Part 1.

Tephrostratigraphy of a core from Lake Waiatarua (Lake St. Johns), Remuera, Auckland.

INTRODUCTION

Lake Waiatarua (also known as Lake St. Johns) was probably formed by damming of local drainage by a basaltic lava flow from Mt. Wellington volcano (Fig.1A) c.9000-9300 years ago (Searle 1962; Kermode 1983; Lowe & Green 1987). The lake has since been drained (drainage works began in the 1920s) and part of it is now used as a golf course. Dr M.S.McGlone (Botany Division, DSIR, Christchurch) took a core of the lake sediments in 1982 (core X82/11), and asked me to identify the thin tephra layers contained in the sediments (Fig.2).

TEPHRA CORRELATION AND AGES

The tephras are identified chiefly from their dominant ferromagnesian mineralogy (Table 1) and their stratigraphic relationships.

1. Tuhua Tephra (derived from Mayor Island; Hogg & McCraw 1983) is characterised by its unique aegirine-dominated ferromagnesian mineralogical assemblage, and has been dated at c.6200 years B.P. (old $T\frac{1}{2}$) (Lowe et al. 1980; Buck et al. 1981; Hogg & McCraw 1983).

2. Rotoma Ash (sample 2, Table 1) contains abundant cummingtonite, which is diagnostic of a source in the Haroharo Complex, Okataina Volcanic Centre (Ewart 1971). The occurrence of this tephra stratigraphically below the Tuhua Tephra shows that it cannot be Whakatane Ash, the only other Holocene tephra containing abundant cummingtonite (Lowe 1986). (The possible presence of Rotoehu Ash, aged c.50 000 years B.P., is untenable

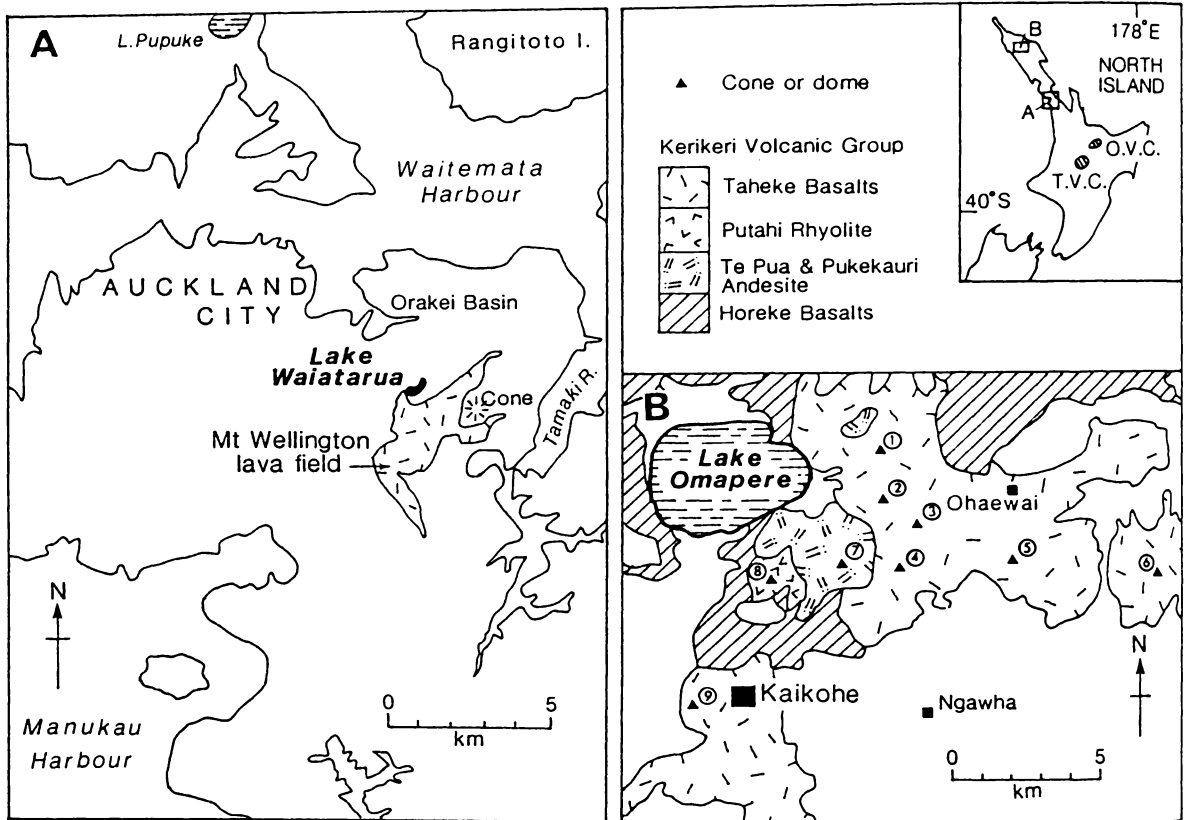
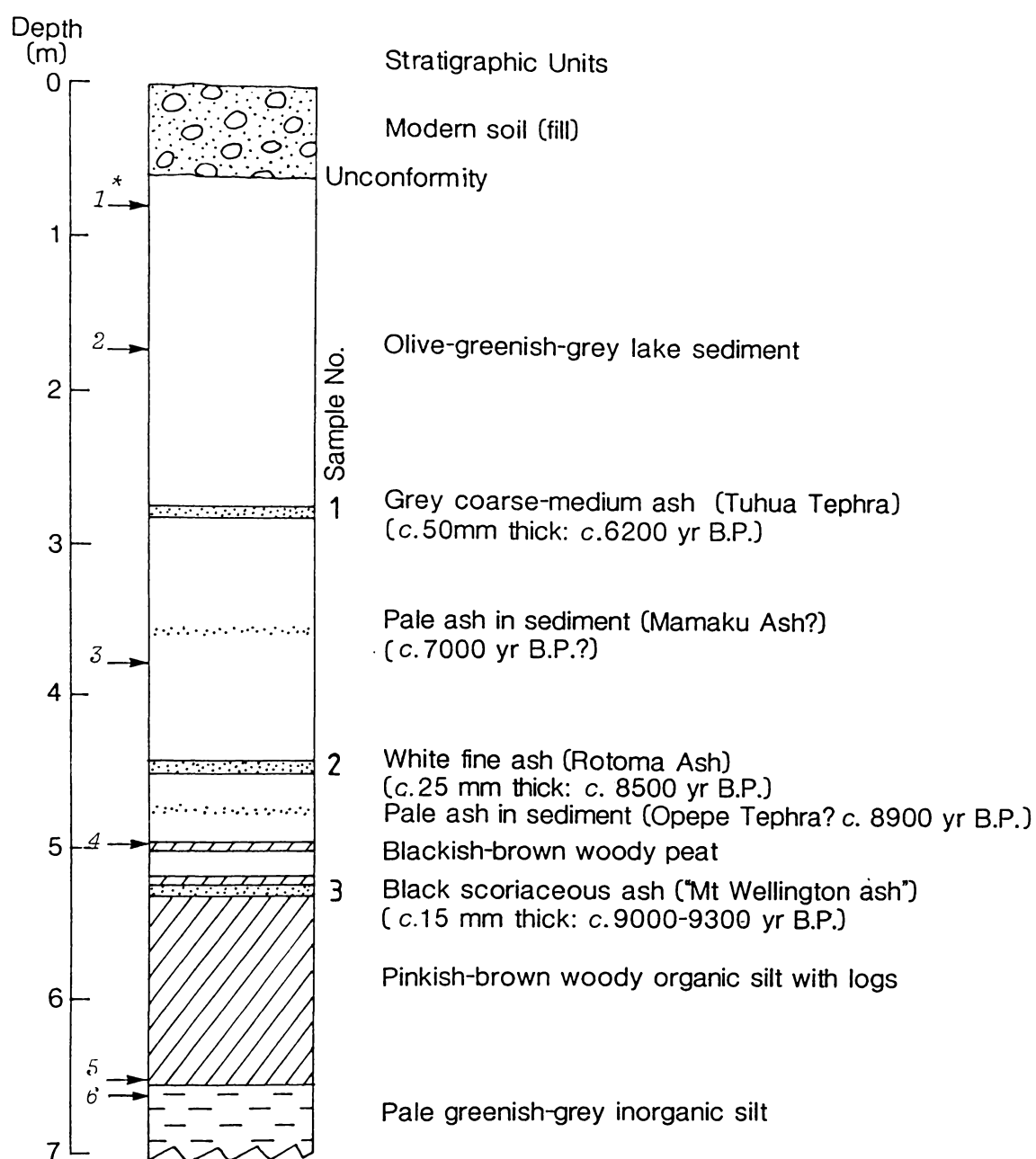


Fig.1. A. Location of (drained) Lake Waatarua in Auckland City in relation to Mt. Wellington volcano and lava flows (after Kermode 1983). B. Location of Lake Omapere in Northland in relation to volcanic rocks of the Kerikeri Volcanic Group (after Browne et al. 1981). Numbered volcanic cones or domes are: 1, Te Ahuahu; 2, Maungakawakawa; 3, Tarahi; 4, Waimimihi; 5, Maungaturoto; 6, Pouerua; 7, Te Pua; 8, Putahi; 9, Kaikohe (see also Kear 1961). Inset: O.V.C. = Okataina Volcanic Centre; T.V.C. = Taupo Volcanic Centre.



(* Wa-1, Wa-2 etc. are C-14 field sample numbers)

Fig. 2. Stratigraphy of core (X82/11) from Lake Waiatarua, Auckland (G.R. NZMS260 R11/732781). The tephra layers are shown in stipple. Estimated ages given on old $T\frac{1}{2}$ basis. Arrows indicate sampling positions for ^{14}C dating (not yet determined). The core description is based on notes by Dr M.S. McGlone (pers. comm. 1983).

Table 1. Dominant ferromagnesian mineral abundances¹ in tephras at Lake Waiatarua (core X82/11).

Tephra	Sample No. (Fig.2)	Ferromagnesian silicate minerals (summed to 100%)								Opagues ² (%)	H.M. ³ %
		Hyp	Aug	Hbe	Cgt	Aeg	Aen	Olv	Oth		
Tuhua	1	2	2?	3	-	73 ⁴	3	17	-	15.6	1.3
Rotoma	2	10	2	2	79	-	-	-	7	48.4	1.4
"Mt.Wellington"	3	2	10	-	-	-	-	22	66	12.0	54.3

1. Determined by point-count of the 2-4 ϕ size fraction of the heavy mineral assemblage ($\geq 2.95 \text{ g.cm}^{-3}$). Between 150 and 400 grains were counted in each sample.
2. Proportion of opaque minerals (mainly Fe-Ti oxides) in the 2-4 ϕ heavy mineral fraction (may include some v. dark aegirine crystals in Tuhua Tephra) (point-count).
3. Abundance of heavy minerals in the total 2-4 ϕ fraction (by weight). Hyp = Hypersthene; Aug = Augite; Hbe = Calcic Hornblende; Cgt = Cummingtonite; Aeg = Aegirine; Aen = Aenigmatite; Olv = Olivine; Oth = other minerals (includes zircon and apatite in sample 2; includes dark, partly altered, glassy, ferromagnesian-bearing scoriaceous grains in sample 3); - = not detected; ? = uncertain identification.
4. Includes many acicular grains with glassy rims.

given that the lake was formed by the Mt. Wellington lava in Holocene times.) Its age is around c.8500 years B.P. (Green & Lowe 1985). Electron microprobe analyses obtained on cummingtonite grains from Rotoma Ash are given in Table 2.

3. The dark scoriaceous nature and the presence of olivine (Table 1) in the lowest tephra in the core are both indicative of a basaltic origin. Searle (1962, fig.7) shows a thin ash cover, informally designated Mt. Wellington Ash, in the Remuera-Mt. Wellington district, and it is this ash that is likely to be represented in the core. The age is probably c.9000-9300 years based on three dates associated with the Mt. Wellington eruptions (NZ386 9315 \pm 145, NZ387 9330 \pm 150, NZ500 8970 \pm 130 years B.P.; Grant-Taylor & Rafter 1971).

Two further tephras occur in the core, at c.3.6 m and at c.4.8 m (Fig.2). These were not sampled, but based on their stratigraphic position and the assumption that they are rhyolitic, they are probably Mamaku Ash and Opepe Tephra, respectively. These two tephras occur in the Waikato lakes as prominent, c.2-3 cm-thick layers, so their postulated occurrence in Auckland is tenable (see also Part 2).

DISCUSSION

The occurrence of the rhyolitic tephras, derived from the Okataina (Mamaku, Rotoma), Taupo (Opepe), and Mayor Island (Tuhua) volcanoes (Fig.1, inset) in Auckland City has not previously been documented. The distal isopachs of Mamaku, Rotoma, and Opepe are extended well beyond those mapped previously for these tephras (Pullar & Birrell 1973; Vucetich & Pullar 1973). That the Tuhua Tephra is relatively thick (c.50 mm) is perhaps not surprising, however, because the lake site lies almost directly on an extension of the northwesterly-trending Axis-1 of the Tuhua Tephra eruption as shown in Hogg & McCraw (1983, p.182). Also, this tephra was identified

by Lowe (1981) from its aegirine mineralogy in a soil profile at a site in South Auckland (Kerns Road, Pukekohe).

Table 2. Electron microprobe analyses¹ of cummingtonite grains in Rotoma Ash in a core from Lake Waiaatarua, Auckland.

Analysis No. ²	1	2	3	4	5	6a	6b
SiO ₂	52.81	53.39	52.62	52.07	52.75	53.17	52.82
Al ₂ O ₃	1.71	1.32	1.97	1.95	1.73	1.53	1.48
TiO ₂	0.30	0.33	0.35	0.39	0.40	0.26	0.29
FeO*	19.26	19.97	19.81	19.56	20.15	20.26	19.64
MnO	1.60	1.57	1.57	1.72	1.73	1.60	1.39
MgO	18.63	19.00	18.20	17.80	18.23	18.53	18.51
CaO	2.22	1.55	2.30	2.05	1.79	1.67	1.66
Na ₂ O	0.53	0.38	0.59	0.52	0.44	0.47	0.43
K ₂ O	0.01	0.01	0.01	0.03	0.03	0.00	0.04
Total	97.07	97.52	97.42	96.09	97.25	97.49	96.26
Cations on the basis of 23 oxygens							
Si	7.720	7.767	7.691	7.714	7.727	7.760	7.781
Al	0.294	0.227	0.339	0.340	0.299	0.262	0.257
Ti	0.033	0.036	0.038	0.043	0.044	0.028	0.032
Fe	2.355	2.429	2.421	2.423	2.468	2.473	2.420
Mn	0.198	0.193	0.194	0.216	0.215	0.198	0.173
Mg	4.060	4.121	3.966	3.932	3.981	4.032	4.066
Ca	0.347	0.242	0.360	0.325	0.281	0.261	0.262
Na	0.150	0.108	0.168	0.148	0.125	0.132	0.122
K	0.002	0.002	0.001	0.006	0.005	0.000	0.007
Total	15.159	15.125	15.178	15.147	15.145	15.146	15.120

*Total Fe as FeO

- Analyses done with a Jeol 733 Superprobe at Victoria University of Wellington under conditions as described in Froggatt & Gosson (1982) (12 nA beam current at 15 kV and 3 μ m beam). Probe calibration checked using PSU 4-190 (Hornblende), PSU PX-1 (Augite), and element standards.
- Analyses on grain cores except 6b (rim of same grain as 6a).

Part 2.

Tephrostratigraphy of cores from Lake Omapere, Northland.

INTRODUCTION

Lake Omapere is an 11.6 km² shallow lake (maximum depth 1.9 m) near Kaikohe, Northland (Fig.1B). Bell & Clarke (1909) and Cotton (1958) suggested that the lake was formed through damming of the Waitangi River by basaltic lava flows (Taheke Basalts) at the eastern end of the lake basin, probably in the late Pleistocene or Holocene (Kear 1961). ¹⁴C dating of lake sediment in cores taken from the lake (Fig.3) indicate that the modern lake is very young (c.1000 years B.P.), but that earlier transitory lakes existed periodically in the Omapere basin. These were probably shallow and weedy, as at present (Harper 1987). Lowe & Green (1987) suggest that the modern lake may have originated by siltation (blockage) of the western outlet (the Uakura River) as a consequence of erosion induced by Polynesian deforestation (cf. McGlone 1983).

This prehistoric age supports local Maori legends. These record that Lake Omapere was once a "swampy plain on which five Maori villages stood until being flooded after a fire swept through the area" (e.g., see Buese 1977, p.190-193).

CORING AND TEPHRA CORRELATION

Nine cores were taken from 5 sites in the lake in December 1983 as part of a joint New Zealand-Japan project on palaeolimnology (see Lowe 1984; Lowe & Green 1987). A generalised description of the cores is given in summary form in Fig.3. Six macroscopic tephras were found. Only the top two of these have been provisionally identified (Mamaku Ash and Rotoehu Ash), based on sparse ferromagnesian mineralogy, glass chemistry, and age.

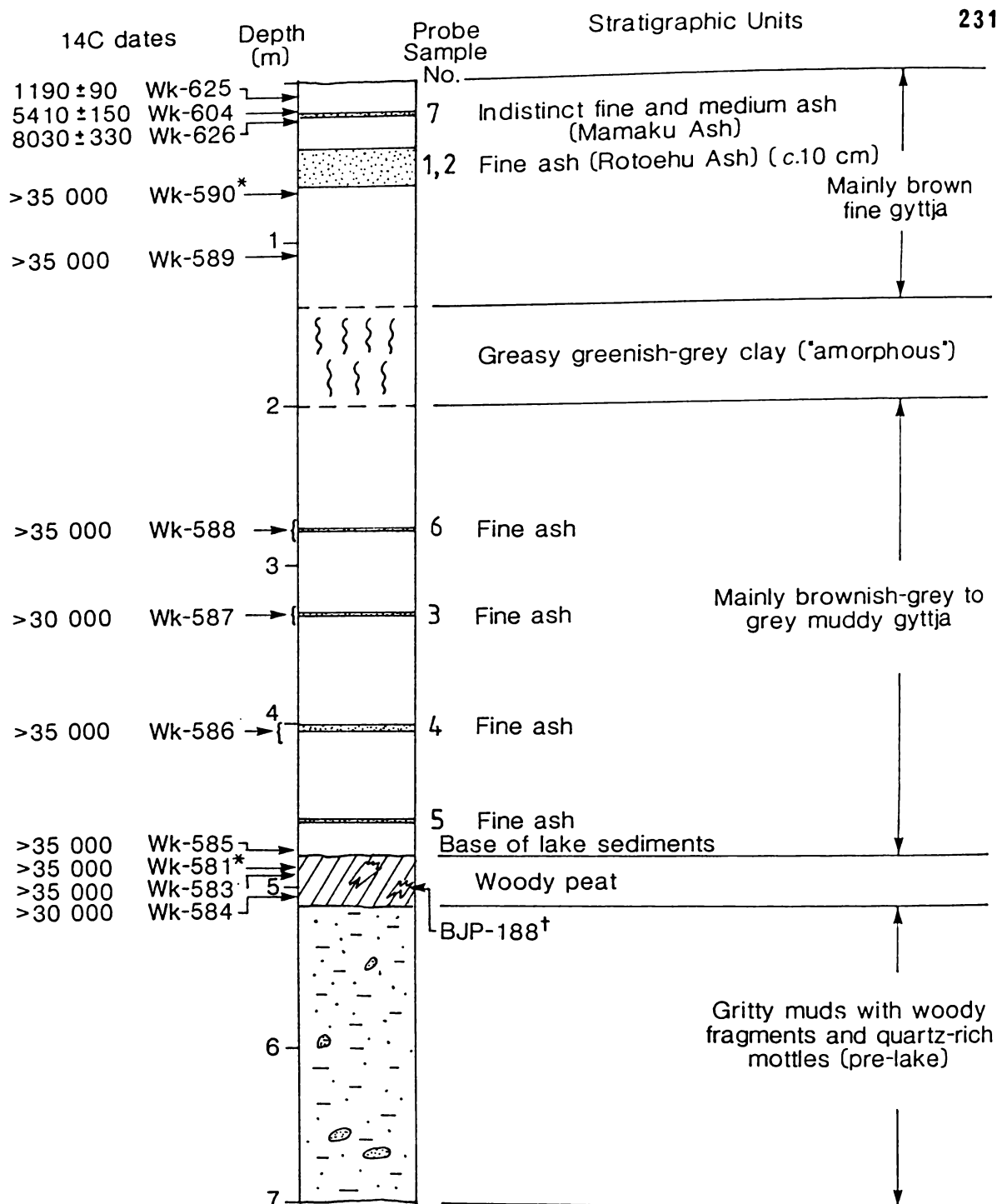


Fig.3. Generalised stratigraphy and chronology of cores from Lake Omapere, Northland. The ^{14}C dates (old $T_{1/2}$ basis) were all assayed from muddy lake sediment (low in C) except the lowest three which were wood samples (see Hogg et al. 1987 for details).

* Samples Wk-590, -581 have also been submitted (Jan 1987) for re-counting by Dr H.A.Polach, Radiocarbon Research Laboratory, Australian National University, Canberra. (A preliminary result (*provisional - not to be quoted*) of 46 900 + 1930 - 1550 years B.P. has been obtained for Wk-590 (ANU-5642).)

† Sample BJP-188 is a wood sample on which an amino acid racemisation date is being attempted (by Dr B.J.Pillans, Victoria University of Wellington).

Table 3. Electron microprobe analyses on glass shards in two tephtras from Lake Omapere, Northland, and comparative analyses on Mamaku Ash and Rotoehu Ash samples from central North Island.

Sample No. (see Fig.3)	7 (Ma?)	1 (Re?)	2 (Re?)	Ma ^a	Re ^b
SiO ₂	78.01 (0.58)	78.24 (0.24)	78.26 (0.37)	78.87 (0.50)	78.72 (0.48)
Al ₂ O ₃	12.42 (0.33)	12.32 (0.18)	12.36 (0.15)	12.05 (0.17)	12.16 (0.19)
TiO ₂	0.14 (0.04)	0.14 (0.03)	0.13 (0.02)	0.12 (0.02)	0.14 (0.03)
FeO*	1.11 (0.13)	0.88 (0.10)	0.89 (0.07)	0.87 (0.07)	0.90 (0.08)
MgO	0.11 (0.04)	0.15 (0.02)	0.13 (0.03)	0.10 (0.02)	0.13 (0.03)
CaO	0.98 (0.26)	0.87 (0.06)	0.87 (0.06)	0.69 (0.10)	0.82 (0.06)
Na ₂ O	3.61 (0.30)	4.07 (0.14)	3.99 (0.20)	3.80 (0.20)	3.84 (0.39)
K ₂ O	3.43 (0.55)	3.16 (0.12)	3.16 (0.41)	3.38 (0.43)	3.29 (0.21)
Cl	0.19 (0.03)	0.17 (0.06)	0.21 (0.03)	0.12 (0.02)	n.d.
Water†	6.41 (2.97)	4.36 (0.80)	5.41 (1.15)	1.13 (1.40)	n.d.
n	7	12	12	14	42

Analyses normalised to 100% loss free. n = number of analyses in mean (each analysis done on a different shard); numbers in parentheses are 1 standard deviation. Analyses by JEOL -733 Superprobe at Victoria University of Wellington, using 8 nA beam at 15 kV defocussed to 10 μ m or 20 μ m (see Froggatt & Gosson 1982; Froggatt 1983; Green & Lowe 1985).

Samples 7, 1, 2, and Re were analysed by Dr P.C.Froggatt, Victoria University of Wellington.

* All Fe as FeO

† Water by difference

a Mamaku Ash (sample from Lake Rotomanuka: Green & Lowe 1985)

b Rotoehu Ash (P.C.Froggatt, pers. comm. 1984).

n.d. = not determined or unavailable.

1. The tephra identified as Mamaku Ash (sample 7) contains Fe-Ti oxides, hypersthene, calcic hornblende, augite, and zircon in its heavy mineral assemblage, all indicative of an Okataina origin. Its glass chemistry, listed in Table 3, shows relatively high standard deviations but is generally consistent with an Okataina source (cf. Green & Lowe 1985; Lowe in press). The ^{14}C dates above and below the tephra have large error limits but constrain its age at between c.5500 and c.8000 years (Fig.3). Mamaku Ash has been dated elsewhere at c.7000 years B.P. (McCraw 1975; Green & Lowe 1985), so it appears to be the most probable correlative.

2. The tephra identified as Rotoehu Ash (samples 1.2) is c.100 mm thick, very compact and highly vitric. Cummingtonite predominates in the sparse heavy mineral suite, together with augite, Fe-Ti oxide, calcic hornblende, hypersthene, zircon, and apatite. The glass chemistry closely matches analyses on Rotoehu Ash glass samples obtained near source (Table 3; P.C.Froggatt, pers. comm. 1984). These results, together with the age of >c.35 000 years B.P. obtained on sediment immediately underlying the ash layer, suggest that it is Rotoehu Ash. (Rotoehu Ash is probably aged c.40 000 - 50 000 years: McGlone et al. 1984.) Isopachs of the Rotoehu Ash are given in Fig.4. Lake Omapere is about 400 km from the primary eruptive vent.

DISCUSSION

These are the first rhyolitic tephras, other than Kaharoa Ash and Taupo Pumice, to be identified with some surety in Northland. However, the presence in Northland of late Quaternary rhyolitic tephras from central North Island sources has been known for many years (e.g., Fieldes & Weatherhead 1968; J.E.Cox 1973 and pers. comm. 1984) (see also Rankin 1973, Self 1983, and Stewart et al. 1984). Kaharoa Ash and Taupo Pumice, both <c.5 cm thick, were positively identified and ^{14}C dated at various sites in Northland by Pullar et al. (1977), following Wellman (1962). The

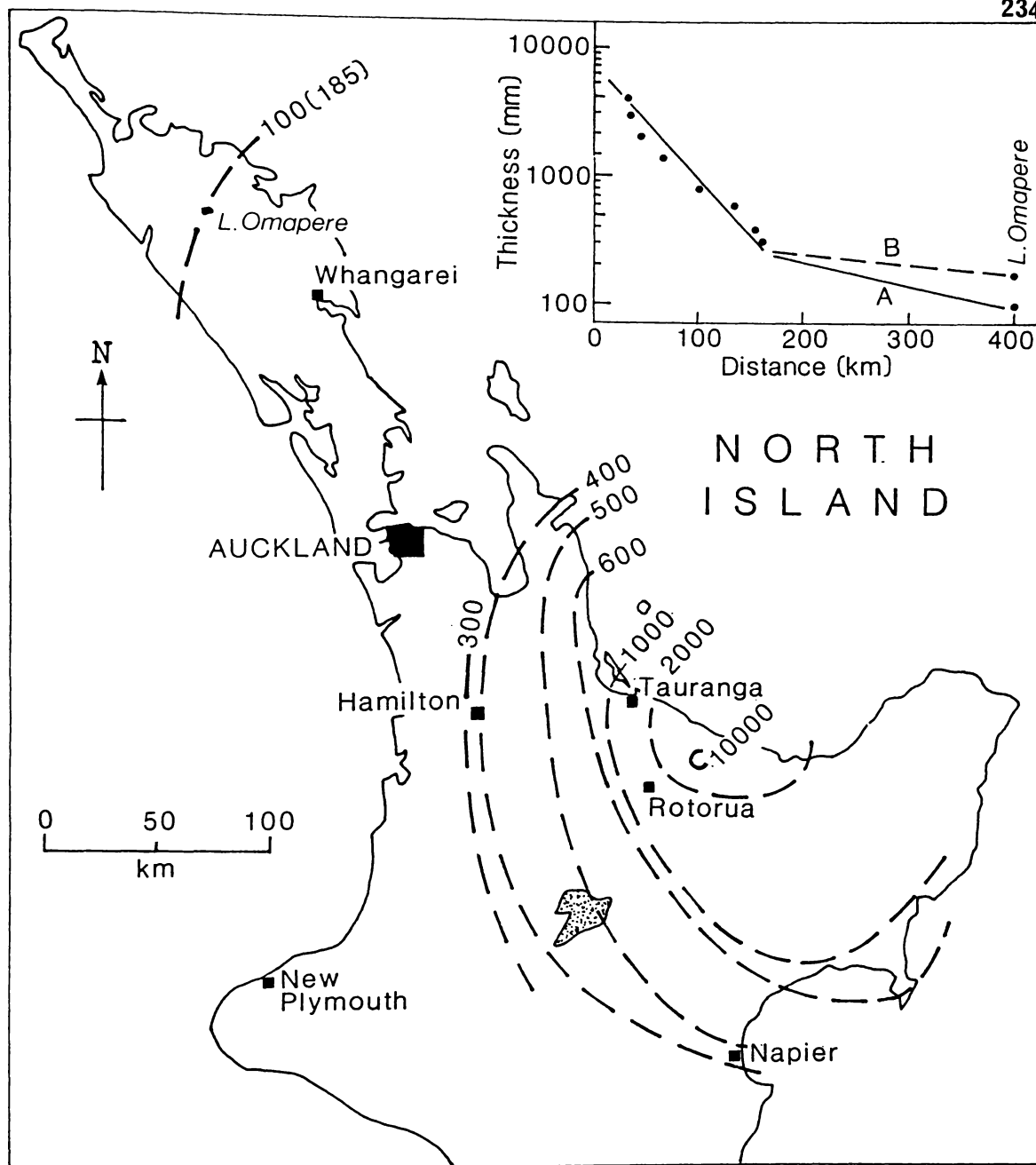


Fig.4. Isopach map of Rotoehu Ash, in mm (central North Island isopachs after Pullar & Birrell 1973). Tentative estimated dry land thickness for the Lake Omapere site is given in parentheses (adjusted for compaction and dissemination - see Table 2 in Paper 4). The inset shows a log-normal plot of isopach thickness against distance from isopach centre. Curve A = thickness as measured at L. Omapere; curve B = adjusted thickness. Whichever curve applies, the marked change in slope probably reflects a "fine tail" of "littoral cognimbrite ash-fall" generated by the Rotoehu eruption (see Walker 1979). Alternatively, it may relate to a change in dispersal mechanism (e.g., see Fisher & Schmincke 1984).

absence of these latter tephras from the Lake Omapere cores is presumably due to their non-preservation or erosion. Because of such hiatuses in the depositional record (shown also by pollen analysis, M.S.McGlone pers. comm. 1984), the cores provide only an incomplete record of tephra deposition in the area.

The four thin tephra layers older than Rotoehu Ash (samples 3-6, Fig.3) are uncorrelated as yet. They are rhyolitic and probably derived from central North Island caldera volcanoes. Similar relatively thin tephras aged between c.50 000 and c.80 000 years are recorded in sediments at Mahia Peninsula, East Coast (Berryman & Hull 1984, p.84). Further work is in progress (D.J. Lowe & P.C.Froggatt in prep).

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Cross referencing to thesis papers

Green, J.D.; Lowe, D.J. 1985 = Paper 9

Hogg, A.G.; Lowe, D.J.; Hendy, C.H. 1987 = Paper 8

Lowe, D.J. 1986 = Paper 6

Lowe, D.J. in press = Paper 12

Lowe, D.J.; Green, J.D. 1987 = Appendix B

Lowe, D.J. *et al.* 1980 = Paper 1

PAPER 8

University of Waikato radiocarbon dates 1: with emphasis on ages of late Quaternary tephras from limnic and peat deposits, North Island, New Zealand.

Published in: *Radiocarbon* 29(2) : in press (1987).

Note. The paper is presented here in manuscript form; reprints were not available at the time of thesis binding. Differences between the manuscript and final paper are minor and chiefly of an editorial nature. Where the dates are commented upon, the manuscript wording "provides max age of" (etc.) has, as appropriate, been modified to "date is max for" (etc.).

ABBREVIATIONS OFTEN USED IN *RADIOCARBON*

- abs — abstract
 acad — academy
 agric — agriculture, al
 alt — altitude
 Am — American
 ann — annual
 approx — approximate, ly
 archaeol — archaeologic, al
 asl — above sea level
 assoc — association
 atm — atmosphere, s
 bot — botanical
 bldg — building
 bull — bulletin
 bur — bureau
 ca — circa
 cf — compare
 chem — chemical
 cm — centimeter
 co — company, county
 coll — collected, college
 colln — collection, s
 comm — commission, committee
 commun — communication
 conf — conference
 cong — congress
 contr — contribution, s
 dept — department
 diam — diameter
 dir — director
 dissert — dissertation
 dist — district
 div — division
 ed, s — editor, s, edition
 eg — for example
et al — and others
 est — estimate, ed
 fac — faculty
 fig — figure
 fm — formation
 g — gram
 gen — general
 geog — geography, ic, al
 geol — geologic, al
 geophys — geophysical
 ref — reference
 rept — report
 rev — review
 rm — room
 rr — railroad
 rte — route
 sci — science, s
 sec — section, sector
 ser — series
 soc — society
 sq — square
 sta — station
 strat — stratigraphy, stratigraphic, al
 subm — submitted
 supp — supplement
 tech — technical
 technol — technology, technologic, al
 temp — temperature
 terr — territory
 govt — government
 hist — historic, al
 hr — hour
 hwy — highway
 i., is. — island, s
 id — identified
ie — *id est*, that is
 inf — information
 inst — institution
 internatl — international
 inv — investigation, s
 jour — journal
 kg — kilogram
 km — kilometer
 L — liter
 lab — laboratory
 loc — locality, location, locus
 lat — latitude
 long — longitude
 m — meter
 max — maximum
 mem — memoir
 min — minimum, mineral, minute
 misc — miscellaneous
 mon — monograph
 ms, mss — manuscript, s
 mt — mountain
 mtg — meeting
 mus — museum
 nat — natural
 natl — national
 no. — number
 p — page, s
 pers — personal
 phys — physical
 pl — plate
 proc — proceedings
 prof — professor, professional
 proj — project
 prov — province
 pt — part
 pub — publication, published
 quad — quadrangle, quadrant
 r — river
 rd — road
 tpk — turnpike
 trans — transaction
 tr — trench
 unid. — unidentified
 univ — university
 v — volume
 yr — year, s
 1st — first
 2nd — second etc
 N — north, northern
 E — east, eastern
 S — south, southern
 W — west, western
 NE — northeastern, etc
 S-central — south-central, etc
 Jan — January
 Feb — February etc

[RADIOCARBON, VOL 29, No. 2, 1987, P 00-00]

UNIVERSITY OF WAIKATO RADIOCARBON DATES I

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INTRODUCTION

The radiocarbon dating laboratory at Waikato was established in 1975, primarily as a research tool in the fields of geomorphology, volcanology, tephrostratigraphy, coastal studies and paleolimnology, to cope with the increasing supply of late Quaternary lake sediment, wood, peat, and shell samples submitted by University staff and postgraduate students undertaking research in the North Island of New Zealand. The method employed is scintillation counting of benzene using the procedures and vacuum systems designed by H A Polach for the Australian National University (ANU) Radiocarbon Dating Research Laboratory (Hogg, 1982). This date list reports on samples submitted by University of Waikato researchers and assayed in the Waikato laboratory mainly between 1979 and 1985. Other dates on material submitted by individuals working in other organisations in New Zealand, and overseas, are to be reported later.

When necessary, combustible samples are boiled in both dilute NaOH and dilute H_3PO_4 to remove humic acid contaminants and inorganic carbon. Carbonate samples are leached in dilute HCl, dried, crushed and analysed by XRD methods to determine the relative proportions of calcite and aragonite. Benzene is synthesised using the three well established chemical steps : oxidation of sample carbon to carbon dioxide, conversion to acetylene and catalytic trimerisation to benzene (eg Noakes, Kim & Stipp, 1965; Polach & Stipp, 1967; Polach, Gower & Fraser, 1972; Tamers, 1975). Carbon dioxide is generated by combustion in a silica combustion tube, and purified using a purification

train including AgNO_3 , hot CuO (600°C), KI in I_2 , $\text{Hg}(\text{NO}_3)_2$, and chromic acid. The CO_2 is desiccated by a series of ethanol slush traps (at -80°C) and a silica gel column and the CO_2 condensed by liquid N_2 traps. The CO_2 is converted to C_2H_2 using a stainless steel reaction vessel based on the design of Polach, Gower & Fraser (1972). Acetylene is trimerised to benzene using Noakes' catalyst, sealed in silica catalyst columns and cleaned between samples by flushing with air at 500°C . Undersized samples are diluted with dead CO_2 prior to C_2H_2 generation to standardise benzene synthesis reactions. The dead CO_2 is obtained from coal for combustible samples, or from ancient limestone for carbonates.

Synthesised benzene samples are transferred into 5ml, low-K glass vials (constructed after the design of Polach, 1969), into which 75mg of scintillator (t-butyl PBD) has been weighed. The vials are then sealed with teflon stoppers and the benzene weight (around 4.5g) accurately determined. Machined aluminium caps (black anodised) are then slid over the teflon stoppers and butted against the glass vials to reduce cross-talk between the counter photomultiplier tubes. Sample activities are determined in either an LKB 1211 scintillation counter, factory modified by Wallac ("Kangaroo Package") for low level ^{14}C determinations, or a Packard Tri-Carb, similarly modified for low level counting. Eight samples and two reference standards (sealed ANU sucrose and AR benzene) are interspersed in a chain and automatically cycled over a period of 14 days with a counting interval of 20 minutes, with each sample being counted for a minimum of 1980 minutes. Background levels vary between counters and vials and range from 0.72 cpm/gC to 0.96 cpm/gC. Modern activities (A_{on}) also vary, ranging from 8.11 cpm/gC to 9.80 cpm/gC. The laboratory working standard is ANU sucrose, with the

normalised oxalic activity calculated using the conversion factor determined from an international cross-calibration exercise conducted by H A Polach of ANU ($\delta^{14}\text{C} = 508.1 \pm 2.0\%$, Currie & Polach, 1980).

Radiocarbon dates presented are conventional radiocarbon ages as defined by Stuiver & Polach (1977) with ages expressed in years BP \pm 1 standard deviation. The counting error includes the statistical uncertainties of the sample, background, and reference standards and, in addition, errors in estimating the $\delta^{13}\text{C}$ (in the few samples where this was not measured), and in the ANU sucrose/oxalic acid conversion factor. Carbon-13 determinations for each sample were performed on a Micromass 602C mass spectrometer. Interlaboratory comparisons are reported in Table 1. Sample descriptions and interpretations are based upon information received from the submitters.

ACKNOWLEDGMENTS

We wish to thank H A Polach and his staff at the ANU Radiocarbon Research Laboratory, Canberra, for their valued assistance in the construction and operation of our laboratory. We are particularly grateful to H A Polach for helping to design the original vacuum systems, for providing the ANU sucrose standard, and for organising a fellowship to help in the training of one of the authors (AGH). We thank the University Grants Committee of New Zealand for contributing to the cost of the scintillation counters. J E Noakes of the University of Georgia willingly provided the catalyst and M Stuiver the international calibration standard ACT VII. For technical assistance in the laboratory between 1975 and 1985, we thank E Raynor, P Chevis, A Brennan, A Limmer, J Smeaton, M Lawrence and V Lockwood. Mass spectrometric determinations were carried out by A Thomas and W Schick. Finally, special thanks are due A T Wilson who founded the laboratory, and J D McCraw and K M Mackay who encouraged its development.

TABLE 1

Interlaboratory check samples

Wk-1. Benzene cross check # 24 19,925 ± 300
Est $\delta^{13}\text{C} = -25\%$
 ANU-1310 19,600 ± 300

Wk-526. Lab cross check (NPL-64) 9450 ± 100
 $\delta^{13}\text{C} = -31.7\%$
 ANU-03 9410 ± 100, 9800 ± 220

$$\frac{A_{\text{sn}}}{A_{\text{on}}} = 1.2444 \pm 0.0056\%$$

Wk-742. Lab cross check (ACT VII) $\delta^{13}\text{C} = -23.2\%$

Reported $\frac{A_{\text{sn}}}{A_{\text{on}}}$ values from participating labs (M Stuiver, pers commun, 1986):

Quaternary Isotope Lab (M Stuiver) : 1.2460 ± 0.0022%
 Participating laboratory A : 1.2506 ± 0.0019%
 Participating laboratory B : 1.2538 ± 0.0040%

GEOLOGIC SAMPLES

New Zealand

The majority of the dates reported here relate to the deposition of distal airfall tephras in lakes and peats in the central and northern North Island of New Zealand (Section 1). The tephras were erupted from rhyolitic and andesitic sources in the Taupo Volcanic Zone or from Mt Egmont or Mayor Island (Fig 1). They are useful as datable stratigraphic marker beds for a wide variety of purposes (eg Pullar, 1973; Self & Sparks, 1981; Howorth et al, 1981; Pillans et al, 1982; McGlone, Howorth & Pullar, 1984; Harper, Howorth & McLeod, 1986), and as a "window" into volcanological processes, volcanic history, and the composition and evolution of magmas (eg Walker, 1980, 1981a,b; Hodder, 1981, 1983; Froggatt, 1982; Wilson et al, 1984; Blake, Smith & Wilson, 1986). The preservation of tephra deposits in suitable organic sediments potentially allows their stratigraphic and chronologic relationships to be determined more accurately and possibly in much greater detail than might be obtained from subaerial exposures, particularly at distal localities where relatively thin tephras can be difficult to trace with certainty because of postdepositional mixing and weathering processes (eg Hodder & Wilson, 1976; Howorth, Froggatt, & Robertson, 1980; Lowe et al, 1980; Hogg & McCraw, 1983; Lowe, 1986a). Lakes and peat bogs of late Pleistocene and Holocene age in the North Island, particularly in the Waikato region (Fig 1), have proved ideal sites for preserving multiple tephra layers, including fine grained deposits of only a few millimetres thickness (Lowe, Hogg & Hendy, 1981; Green & Lowe, 1985; Lowe, 1986a; see illustration in Plate 1). Various ongoing paleoenvironmental studies on the Waikato lakes have utilised the time stratigraphic framework provided by the tephras, and include Green (1979), Boubée (ms), Green et al

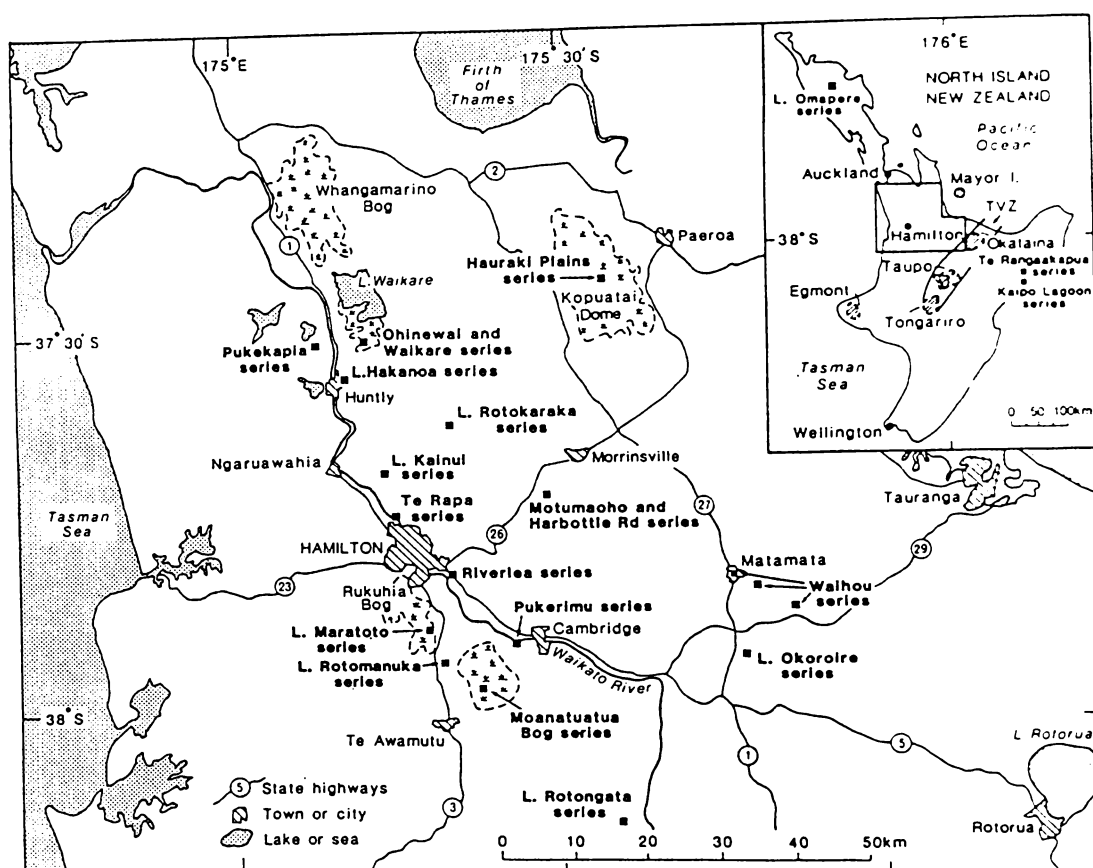


Fig 1. Locations of sample series in the Waikato region, New Zealand. Inset shows locations of other series and the main tephra-producing volcanoes (hatched) active in the late Quaternary period. TVZ = Taupo Volcanic Zone (after Cole & Nairn, 1975). Note: Mt Egmont is also known as Mt Taranaki.

(1984), McGlone, Nelson & Todd (1984), Lowe (1985, 1986b), McCabe (ms), Kellett (ms), and Green & Lowe (1985).

The dates in Section 1 were determined on lake sediment (dy or gyttja) and peat from cores obtained with a modified Livingstone piston corer (Rowley & Dahl, 1956; Green, 1979) and with a modified D-section Russian/Jowsey peat corer (Jowsey, 1966), except where noted. The samples are grouped into series named after the lake or peat bog cored (Fig 1), and arranged stratigraphically with samples closest to the surface listed first. Most samples came from five lakes, and stratigraphic columns showing the sampling positions with respect to the tephras identified in cores from these lakes are given in Fig 2. The majority of samples consist of slices of sediment (usually 1-2cm thick in the lake cores, 2-5cm or occasionally thicker in the peats) from above or below a tephra layer. Such slices of sediment, deliberately kept as thin as possible, represent an accumulation time and hence may reduce date accuracy (with respect to the age of deposition of the tephras). This possible reduction in accuracy is offset, however, by the tight stratigraphic control that the continuous cores provide, and by the availability of dates on many of the tephras in other environments (see below), thus acting as independent monitors of error (cf Mathewes & Westgate, 1980). To provide sufficient material for dating, slices of lake sediment from two or more suitable cores (taken within the same lake) were commonly combined into a composite sample (Green & Lowe, 1985). In some samples with very low carbon contents, the slices from above and below the tephra have been combined as a "straddle" sample, providing an average age for the tephra. Where tephras are closely spaced in the cores, the entire layer of sediment between two adjacent tephras (ie "bridging" the tephras) was occasionally sampled. The date thus obtained applies equally to both tephras, giving a maximum age for one, minimum for the other (eg see Lowe, 1986a).

Except for Lakes Purimu and Maungarataiti (Wk-426, Wk-842), none of the lakes sampled have calcareous rocks in their catchments, hence the "hard water effect" frequently encountered in such environments in Europe, Scandinavia, North America, and elsewhere (eg Ogden, 1967; Olsson, 1979; Mathewes & Westgate, 1980; Turner et al, 1983), does not arise.

Most of the tephras have been correlated with named eruptives elsewhere using diagnostic mineralogic and chemical criteria, together with stratigraphic and age relationships (Lowe et al, 1980; Green & Lowe, 1985; Lowe & Hogg, 1986; Lowe, 1986a, c, and work in progress). Although most of the rhyolitic tephras (from Taupo, Okataina, and Mayor Island sources; Fig 1) have been dated previously (Healy, 1964; Vucetich & Pullar, 1964, 1969, 1973; Grant-Taylor & Rafter, 1966; Pullar & Heine, 1971; Topping & Kohn, 1973; McCraw, 1975; Nairn, 1980; Froggatt, 1981a, b; Hogg & McCraw, 1983), many have only one or two dates. The andesitic tephras (from Tongariro and Egmont sources; Fig 1) have a rather complex stratigraphy with relatively few available dates (Topping, 1973; Neall, 1972, 1979; Neall & Geddes, 1981; Neall & Alloway, 1986). In the lake cores, many of the tephras derived from the Mt Egmont volcano have not yet been positively correlated with named near-source eruptives, so they are informally designated as "Eg-1", "Eg-2" etc in the date list (see Fig 2).

The dates listed in Section 2 have been obtained on carbonaceous material associated with the Hinuera Formation, an extensive low-angle fan of volcanogenic alluvium that was deposited in several phases in the Waikato and Hauraki basins before and during the last stadial (isotope stage 2) of the last glaciation (Fig 3; Schofield, 1965; Hume, Sherwood & Nelson, 1975; McGlone, Nelson & Hume, 1978; Cuthbertson, ms; Selby, 1982; Green & Lowe, 1985). The aggradation of the Hinuera Formation resulted in the formation of most of the lakes noted above (McCraw, 1967; Lowe & Green, 1987). Some of the dates obtained on material from the lower parts of cores from these lakes therefore provide information on the age of Hinuera Formation sedimentation.

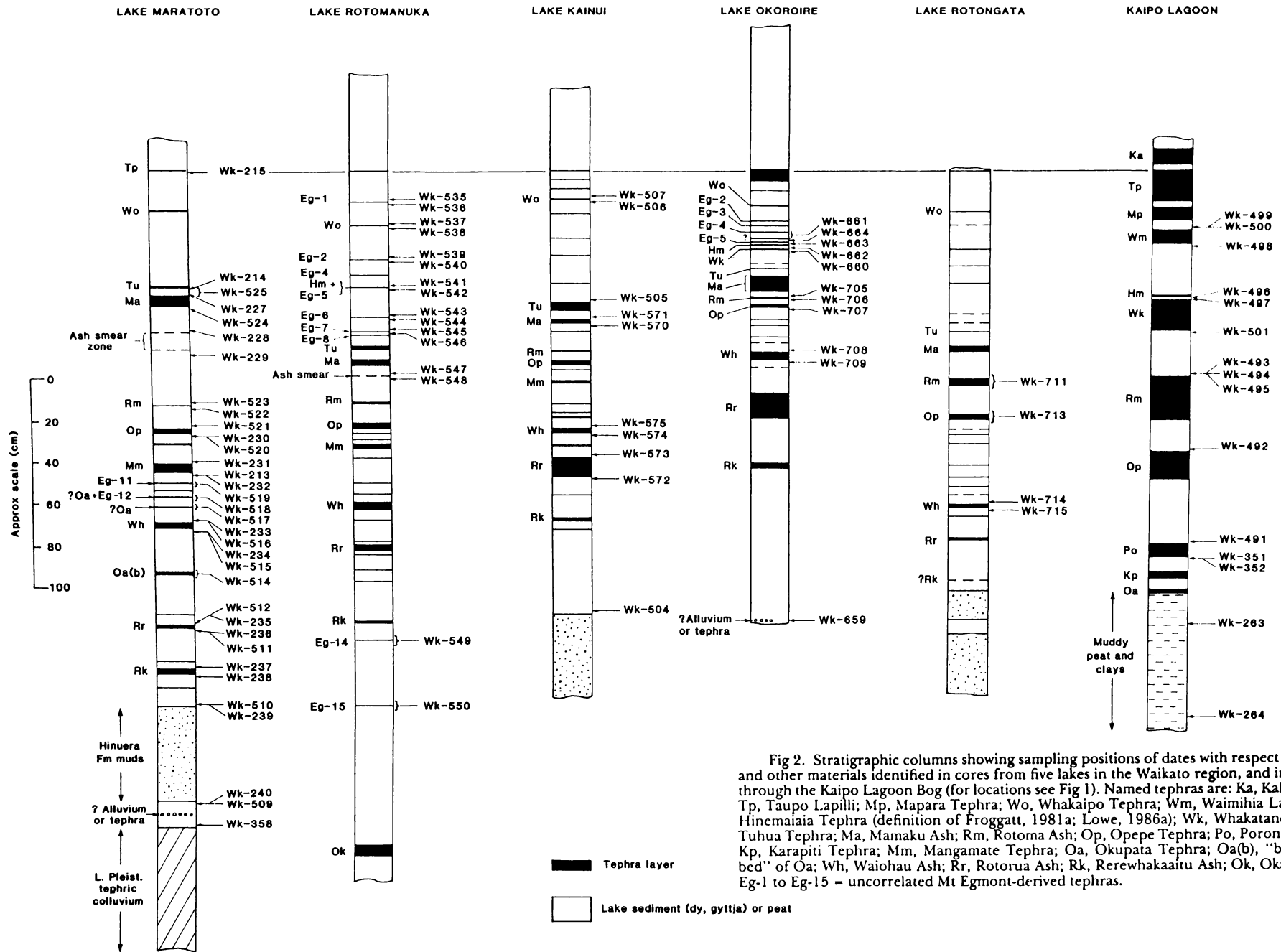


Fig 2. Stratigraphic columns showing sampling positions of dates with respect to tephras and other materials identified in cores from five lakes in the Waikato region, and in a section through the Kaipo Lagoon Bog (for locations see Fig 1). Named tephras are: Ka, Kaharoa Ash; Tp, Taupo Lapilli; Mp, Mapara Tephra; Wo, Whakaipo Tephra; Wm, Waimihia Lapilli; Hm, Hinemaiaia Tephra (definition of Froggatt, 1981a; Lowe, 1986a); Wk, Whakatane Ash; Tu, Tuhua Tephra; Ma, Mamaku Ash; Rm, Rotoma Ash; Op, Opepe Tephra; Po, Poronui Tephra; Kp, Karapiti Tephra; Mm, Mangamate Tephra; Oa, Okupata Tephra; Oa(b), "basal lapilli bed" of Oa; Wh, Waiohau Ash; Rr, Rotorua Ash; Rk, Rerewhakaaitu Ash; Ok, Okareka Ash. Eg-1 to Eg-15 = uncorrelated Mt Egmont-derived tephras.

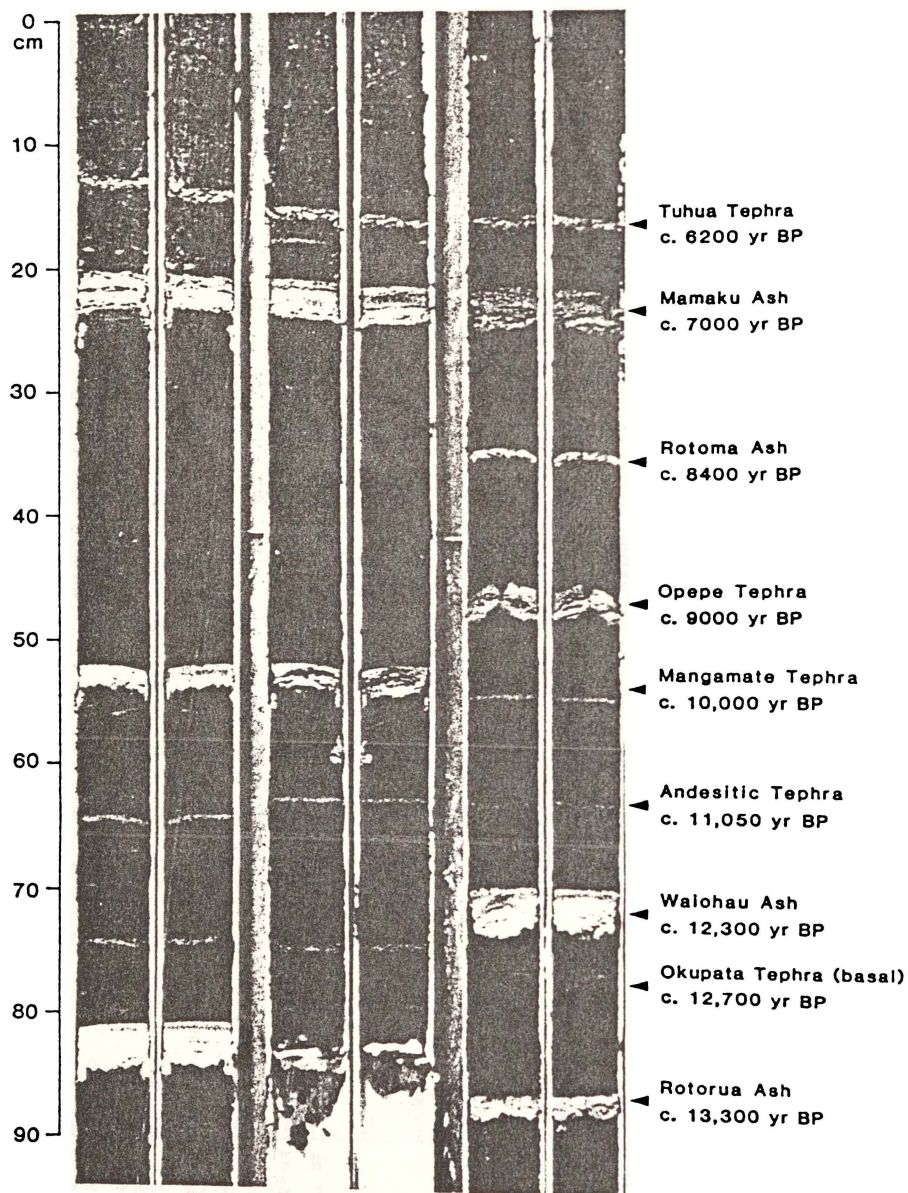


Plate 1. Three longitudinally sliced cores from Lake Rotomanuka, near Hamilton, showing ash-grade tephra layers preserved within dark, fine-grained organic lake sediment. The tephras are derived from five volcanic centers located 110 to 180km from Lake Rotomanuka (Fig 1). Photograph: RR Julian and W Forbes.

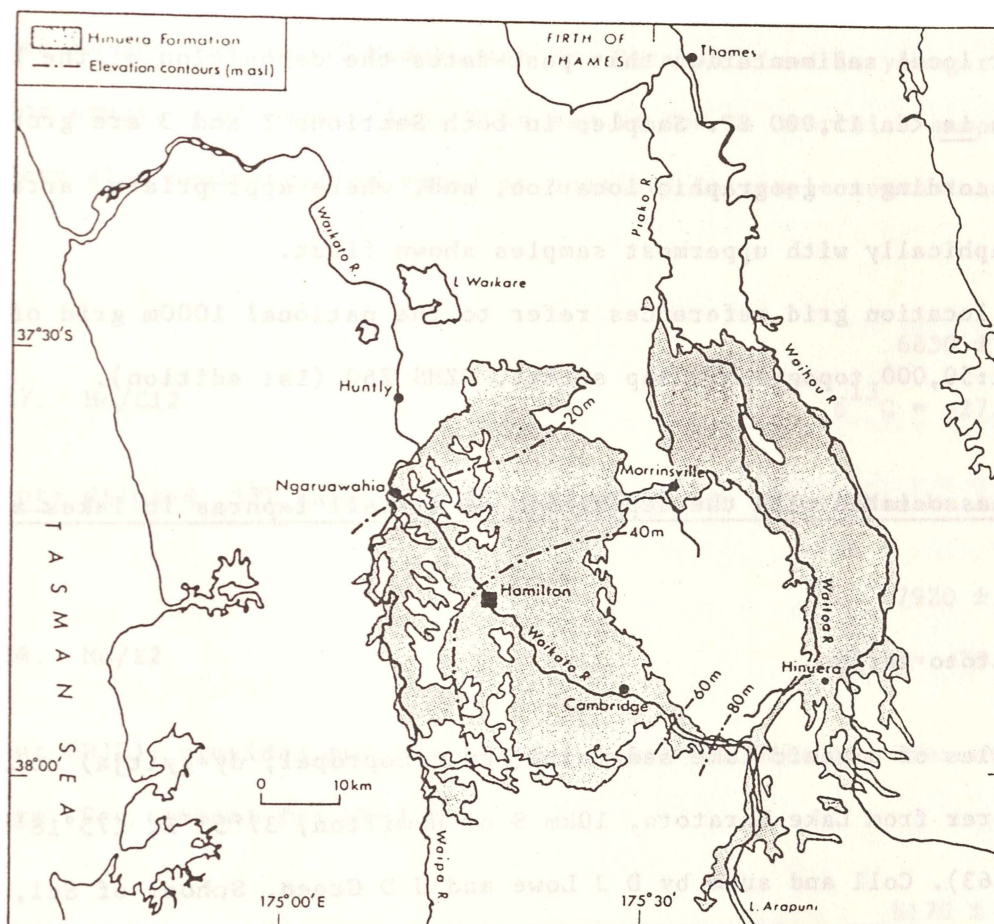


Fig 3. The distribution of the Hinuera Formation in the Hamilton Basin (left) and the Hauraki Basin. Contours show the alluvial fan form. From Selby (1982), based on Hume, Sherwood & Nelson (1975),

These dates could thus be grouped in Section 2, but have been retained in Section 1 because of their stratigraphic relationship to the overlying dates associated with the tephras.

In Section 3, the samples comprise materials associated with peat bog growth or local sedimentation that post-dates the deposition of the Hinuera Formation ie <ca 15,000 BP. Samples in both Sections 2 and 3 are grouped into series according to geographic location, and, where appropriate, arranged stratigraphically with uppermost samples shown first.

Map location grid references refer to the national 1000m grid of the New Zealand 1:50,000 topographic map series, NZMS 260 (1st edition).

1. Dates associated with the deposition of airfall tephras in lakes and peat bogs

Lake Maratoto series

Samples of organic lake sediment (humic copropel, dy-gyttja) coll by piston corer from Lake Maratoto, 10km S of Hamilton, 37°53'S, 175°18'E (S15/130663). Coll and subm by D J Lowe and J D Green, School of Sci, Univ of Waikato. Coll in 4 sampling sets in 1979 (Mo/A), 1980 (Mo/C), 1981 (Mo/D), and 1982 (Mo/E).

Wk-215. Mo/A5 1730 ± 60
Est $\delta^{13}\text{C} = -28\%$

Comment: diluted, 82% sample. (DJL): provides max age of Taupo Pumice Fm (Taupo Lapilli Member).

Wk-214. Mo/A4 6210 ± 70
 $\delta^{13}\text{C} = -28.4\%$

Comment (DJL): provides max age of Tuhua Tephra Fm.

Wk-525. Mo/E1 5800 ± 70
 $\delta^{13}\text{C} = -28.8\%$

Comment (DJL): sample bridges two tephra layers; provides max age of Tuhua Tephra Fm and min age of Mamaku Ash Fm. Date obtained is younger than expected for eruption of Mamaku Ash. This may be due to overthick sample (given a very slow sedimentation rate) or possibly to sample contamination in core.

Wk-227. Mo/C12 6830 ± 90
 $\delta^{13}\text{C} = -27.0\%$

Comment: diluted, 57% sample. (DJL): provides min age of Mamaku Ash Fm.

Wk-524. Mo/E2 7920 ± 80
 $\delta^{13}\text{C} = -29.8\%$

Comment (DJL): provides max age of Mamaku Ash Fm. Date may overestimate eruption age. See comment for Wk-228.

Wk-228. Mo/C11 8170 ± 90
 $\delta^{13}\text{C} = -29.7\%$

Comment: diluted, 72% sample. (DJL): provides max age of Mamaku Ash Fm. Date considered perhaps ca 1000 yr too old, with regard to eruption of Mamaku Ash, as mineralogical evidence shows sample contaminated by underlying Rotoma Ash Fm (Green & Lowe, 1985).

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Wk-229. Mo/C14 7650 ± 160
 $\delta^{13}\text{C} = -30.0\text{‰}$

Comment: diluted, 34% sample. (DJL): provides min age of Opepe Tephra Fm. Date younger than expected for eruption of Opepe Tephra (by ca 1000 to 1500 yr?), possibly due to compression of sediment in core between Mamaku and Opepe tephtras.

Wk-523. Mo/E3 8350 ± 100
 $\delta^{13}\text{C} = -30.7\text{‰}$

Comment: diluted, 72% sample. (DJL): provides min age of Rotoma Ash Fm. Date obtained differs from previous ones on eruption of this tephra, ca 7000 to 7300 BP (Pullar & Heine, 1971; Pullar, Birrell & Heine, 1973), but is closer to date of (NZ1945) 8860 ± 120 BP given by Nairn (1980). Dates 8000 to 9000 BP considered more reliable, but specific eruption age remains uncertain.

Wk-522. Mo/E4 8370 ± 90
 $\delta^{13}\text{C} = -31.3\text{‰}$

Comment: diluted, 78% sample. (DJL): provides max age of Rotoma Ash Fm. See comment for Wk-523.

Wk-521. Mo/E5 8670 ± 110
 $\delta^{13}\text{C} = -31.2\text{‰}$

Comment: diluted, 62% sample. (DJL): provides min age of Opepe Tephra Fm.

Wk-230. Mo/C13 9370 ± 210
 $\delta^{13}\text{C} = -31.6\text{‰}$

Comment: diluted, 33% sample. (DJL): provides max age of Opepe Tephra Fm.

Wk-520. Mo/E6 8930 ± 100
 $\delta^{13}\text{C} = -31.1\text{‰}$

Comment: diluted, 72% sample. (DJL): provides max age of Opepe Tephra Fm.

Wk-231. Mo/C10 9700 ± 140
 $\delta^{13}\text{C} = -30.9\text{‰}$

Comment: diluted, 52% sample. (DJL): provides min age of Mangamate Tephra Fm (?Te Rato Lapilli Member).

Wk-213. Mo/A3 $10,120 \pm 100$
Est $\delta^{13}\text{C} = -27\text{‰}$

Comment: diluted, 82% sample. (DJL): provides max age of Mangamate Tephra Fm (?Te Rato Lapilli Member).

Wk-232. Mo/C9 $10,000 \pm 120$
 $\delta^{13}\text{C} = -31.9\text{‰}$

Comment: diluted, 76% sample. (DJL): provides max age for Mangamate Tephra Fm (?Te Rato Lapilli Member).

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Wk-519. Mo/E7 10,100 ± 100
 $\delta^{13}\text{C} = -31.9\text{‰}$

Comment: diluted, 86% sample. (DJL): sample straddles tephra layer; provides average age for uncorrelated tephra from Egmont, Eg-11.

Wk-518. Mo/E8 11,050 ± 130
 $\delta^{13}\text{C} = -32.1\text{‰}$

Comment: diluted, 68% sample. (DJL): sample straddles two? intermixed andesitic tephra visible as a single "speckled" layer; provides average age for tephra tentatively identified as unnamed member of Okupata Tephra Fm (from Tongariro) and uncorrelated tephra from Egmont, Eg-12. Volcanoes apparently erupted approx contemporaneously.

Wk-517. Mo/E9 11,700 ± 180
 $\delta^{13}\text{C} = -34.6\text{‰}$

Comment: diluted, 47% sample. (DJL): sample straddles tephra layer; provides average age for unnamed Member of ?Okupata Tephra Fm.

Wk-233. Mo/C8 12,200 ± 230
 $\delta^{13}\text{C} = -35.0\text{‰}$

Comment: diluted, 42% sample. (DJL): provides min age of Waiohau Ash Fm. Date is older than previous dates obtained on charcoal from this tephra of between ca 11,100 to 11,800 BP (generally accepted age is ca 11,300 BP, Pullar & Heine, 1971; Pullar & Birrell, 1973). Sample conceivably contaminated by redeposited older organic material (eg see Olsson & Florin, 1980; Björck & Håkansson, 1982), but Green & Lowe (1985) and Lowe & Hogg (1986) suggest instead that the charcoal dates may underestimate the real age of the Waiohau eruption by several hundred yr at

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least, ie Waiohau Ash age probably closer to ca 12,000 BP than 11,000 BP. See dates in other ser below.

Wk-516. Mo/E10 12,300 ± 190
 $\delta^{13}\text{C} = -31.6\text{‰}$

Comment: diluted, 47% sample. (DJL): provides min age of Waiohau Ash Fm. See comment for Wk-233.

Wk-234. Mo/C7 12,500 ± 190
 $\delta^{13}\text{C} = -35.6\text{‰}$

Comment: diluted, 47% sample. (DJL): provides max age of Waiohau Ash Fm. See comment for Wk-233.

Wk-515. Mo/E11 12,450 ± 200
 $\delta^{13}\text{C} = -32.4\text{‰}$

Comment: diluted, 44% sample. (DJL): provides max age of Waiohau Ash Fm. See comment for Wk-233.

Wk-514. Mo/E12 12,700 ± 200
 $\delta^{13}\text{C} = -33.4\text{‰}$

Comment: diluted, 46% sample. (DJL): sample straddles tephra layer; provides average age of "basal lapilli" bed? of Okupata Tephra Fm (as denoted by Topping, 1973).

Wk-512. Mo/E14 12,800 ± 150
 $\delta^{13}\text{C} = -33.2\text{‰}$

Comment: diluted, 68% sample. (DJL): provides min age of Rotorua Ash Fm. Thick sample slice may reduce date reliability. See comment for Wk-511.

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Wk-235. Mo/C6 12,900 ± 310
 $\delta^{13}\text{C} = -32.5\text{‰}$

Comment: diluted, 26% sample. (DJL): provides min age of Rotorua Ash Fm.

Wk-236. Mo/C5 12,600 ± 230
 $\delta^{13}\text{C} = -35.6\text{‰}$

Comment: diluted, 33% sample. (DJL): provides max age of Rotorua Ash Fm.

Date is younger than expected. See comment for Wk-511.

Wk-511. Mo/E15 13,450 ± 120
 $\delta^{13}\text{C} = -31.9\text{‰}$

Comment (DJL): provides max age of Rotorua Ash Fm. Agrees closely with near-source date on this tephra of (NZ1615) 13,450 ± 250 BP (Nairn, 1980). Taking other dates on Rotorua Ash, and those on adjacent tephras (Waiohau, Rerewhakaaitu) into account, age of eruption thought to be near ca 13,300 BP.

Wk-237. Mo/C4 14,700 ± 220
 $\delta^{13}\text{C} = -31.6\text{‰}$

Comment: diluted, 55% sample. (DJL): provides min age of Rerewhakaaitu Ash Fm.

Wk-238. Mo/C3 14,700 ± 180
 $\delta^{13}\text{C} = -30.5\text{‰}$

Comment: diluted, 78% sample. (DJL): provides max age of Rerewhakaaitu Ash Fm.

Wk-510. Mo/E16 15,850 ± 130
 $\delta^{13}\text{C} = -28.5\%$

Comment (DJL): provides age of fm of present-day Lake Maratoto and dates cessation of final episode of deposition of Hinuera Fm at this locality.

Wk-239. Mo/C2 16,300 ± 250
 $\delta^{13}\text{C} = -29.7\%$

Comment: diluted, 52% sample. (DJL): dates fm of present-day Lake Maratoto and cessation of final episode Hinuera Fm deposition at this locality.

Wk-240. Mo/C1 16,900 ± 470
Est $\delta^{13}\text{C} = -30\%$

Comment: diluted, 28% sample. (DJL): dates beginning of final episode of Hinuera Fm deposition at this locality, which resulted in the fm of present-day Lake Maratoto. Sample is of gyttja deposited in relatively shortlived "proto-Lake Maratoto" formed by penultimate episode of Hinuera Fm sedimentation. This gyttja contains an indistinct band of greyish sandy mud with pumice lapilli that is most likely reworked volcanogenic alluvium. However, lapilli might represent an uncorrelated airfall tephra. If so, its stratigraphic position below Rerewhakaaitu Ash suggests ?Okareka Ash Fm (Fig 2; Vucetich & Pullar, 1969); hence date obtained (also Wk-509, Wk-358) would provide min age on it. Elsewhere, Okareka Ash is undated but thought to be ca 17,000 BP (Nairn, ms).

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+360

16,200

-340

 $\delta^{13}\text{C} = -25.9\text{‰}$

Wk-509. Mo/E17

Comment: diluted, 35% sample. (DJL): dates beginning of final episode of Hinuera Fm deposition at this locality that resulted in the fm of present-day Lake Maratoto. Sample is of gyttja deposited in relatively shortlived "proto-Lake Maratoto" formed by penultimate episode of Hinuera Fm sedimentation. See comment for Wk-240.

17,050 \pm 200 $\delta^{13}\text{C} = -29.9\text{‰}$

Wk-358. Mo/D1

Comment: diluted, 78% sample. (DJL): dates fm of "proto-Lake Maratoto" by penultimate episode of deposition of Hinuera Fm alluvium in this area. See comment for Wk-240.

General Comment (DJL): Wk-213, Wk-214, Wk-215 are first dates to be obtained on airfall tephras in the Hamilton Basin. Ages generally accord with stratigraphy (increase down core), and the dates on tephras closely match those on same tephras elsewhere, except as noted (Lowe et al, 1980; Hogg & McCraw, 1983; Green & Lowe, 1985). Dates on Okupata Tephra and uncorrelated Egmont tephras (Wk-517, Wk-518, Wk-519) are consistent with sparse dates on related eruptive sequences nearer source (Topping, 1973; Neall & Alloway, 1986). Deposition of Hinuera Fm at Lake Maratoto around 16,000 to 17,000 BP agrees with ages in McGlone, Nelson, & Hume (1978) and McGlone, Nelson, & Todd (1984). Dates also give rates of sedimentation during lake's developmental history (average ca 0.1 to 0.2mm/yr, Green & Lowe, 1985) - similar average rates are evident for most other Hinuera-dammed lakes (see below).

Lake Rotomanuka series

Samples of organic lake sediment (dy, gyttja or dy-gyttja) coll by piston corer (see Plate 1) from Lake Rotomanuka, 15km S of Hamilton, 37°55'S, 175°19'E (S15/136615). Coll (1983) by D J Lowe, J D Green and C H Hendy and subm by D J Lowe and J D Green.

2560 ± 80

Wk-535. Rot/D-1

 $\delta^{13}\text{C} = -29.9\text{‰}$

Comment: diluted, 57% sample. (DJL): provides min age of uncorrelated tephra from Egmont, Eg-1.

2350 ± 80

Wk-536. Rot/D-2

 $\delta^{13}\text{C} = -29.5\text{‰}$

Comment: diluted, 58% sample. (DJL): provides max age of uncorrelated tephra from Egmont, Eg-1.

2560 ± 60

Wk-537. Rot/D-3

 $\delta^{13}\text{C} = -29.5\text{‰}$

Comment: diluted, 77% sample. (DJL): provides min age of Whakaipo Tephra Fm. Date (and Wk-538) supports identification of this tephra as Whakaipo (based upon chem analysis of glass, Lowe, 1986a) rather than the older Waimihia Fm as reported by Lowe et al (1980).

2860 ± 60

Wk-538. Rot/D-4

 $\delta^{13}\text{C} = -29.9\text{‰}$

Comment: diluted, 88% sample. (DJL): provides max age of Whakaipo Tephra Fm. Date agrees closely with near source dates on this tephra (Vucetich & Pullar, 1973).

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Wk-539. Rot/D-5 3610 ± 60
 $\delta^{13}\text{C} = -28.8\text{‰}$

Comment (DJL): provides min age of uncorrelated tephra from Egmont, Eg-2.

Wk-540. Rot/D-6 3750 ± 70
Est $\delta^{13}\text{C} = -29.9\text{‰}$

Comment (DJL): provides max age of uncorrelated tephra from Egmont, Eg-2. Also provides upper age limit for indistinct tephra, Eg-4, which sporadically occurs below Eg-2 in some cores from lake.

Wk-541. Rot/D-7 4490 ± 70
 $\delta^{13}\text{C} = -29.4\text{‰}$

Comment (DJL): sample overlies layer of two? apparently admixed tephras; provides min age for Hinemaiaia Tephra (definition of Froggatt, 1981a; Lowe, 1986a), and for uncorrelated tephra from Egmont, Eg-5. Date also gives lower age limit to overlying Eg-4 tephra. Supports dates on Hinemaiaia Tephra reviewed in Lowe (1986a).

Wk-542. Rot/D-8 4470 ± 70
 $\delta^{13}\text{C} = -29.6\text{‰}$

Comment (DJL): sample underlies layer of two? apparently admixed tephras; provides max age for Hinemaiaia Tephra (definition of Froggatt, 1981a; Lowe, 1986a), and for uncorrelated tephra from Egmont, Eg-5. Supports dates on Hinemaiaia Tephra reviewed in Lowe (1986a).

Wk-543. Rot/D-9 5280 ± 80
 $\delta^{13}\text{C} = -30.2\%$

Comment: diluted, 77% sample. (DJL): provides min age of uncorrelated tephra from Egmont, Eg-6.

Wk-544. Rot/D-10 5210 ± 90
 $\delta^{13}\text{C} = -29.9\%$

Comment: diluted, 72% sample. (DJL): provides max age of uncorrelated tephra from Egmont, Eg-6.

Wk-545. Rot/D-11 5850 ± 80
 $\delta^{13}\text{C} = -30.3\%$

Comment: diluted, 84% sample. (DJL): provides min age of uncorrelated tephra from Egmont, Eg-7.

Wk-546. Rot/D-12 5850 ± 80
 $\delta^{13}\text{C} = -29.5\%$

Comment: diluted, 75% sample. (DJL): sample bridges two tephra layers; provides max age of uncorrelated tephra from Egmont, Eg-7 (overlies sample) and min age for uncorrelated Egmont tephra, Eg-8 (underlies sample).

Wk-547. Rot/D-13 7980 ± 150
 $\delta^{13}\text{C} = -31.1\%$

Comment: diluted, 36% sample. (DJL): sample occurs about midway between Mamaku Ash and Rotoma Ash and overlies (cf Wk-548 which underlies) an indistinct, discontinuous layer of tephric material. The indistinct layer was originally thought to represent a separate eruptive event but is now considered likely to be material reworked from adjacent Mamaku and/or Rotoma

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tephras (either naturally or in coring procedure). Date gives approx age limits for Mamaku Ash Fm (max) and Rotoma Ash Fm (min) - cf Wk-228.

Wk-548. Rot/D-14

8030 ± 200
 $\delta^{13}\text{C} = -30.8\text{‰}$

Comment: diluted, 29% sample. (DJL): date gives approx age limits for Mamaku Ash Fm (max) and Rotoma Ash Fm (min). See comment for Wk-547.

Wk-549. Rot/D-15

14,750 ± 130
 $\delta^{13}\text{C} = -22.7\text{‰}$

Comment (DJL): sample straddles tephra layer; provides average age of uncorrelated Egmont tephra, Eg-14, occurring 7cm below Rerewhakaaitu Ash Fm in core.

Wk-550. Rot/D-16

14,650 ± 240
 $\delta^{13}\text{C} = -24.7\text{‰}$

Comment: diluted, 47% sample. (DJL): provides max age of uncorrelated Egmont tephra, Eg-15, that occurs ca 30cm below Rerewhakaaitu Ash in core. Date younger than expected, being similar to reliable dates on Rerewhakaaitu Ash (14,700 BP, see Lake Maratoto ser); possibly due to contamination of sample by younger carbon in coring procedure or to relatively fast sedimentation rate in lake in this early post-glacial period (cf Green & Lowe, 1985).

General Comment (DJL): dates on distal Egmont-derived tephras in this ser contribute greatly to relatively few dates available nearer source, and may help to establish distribution patterns and correlations of eruptives from Egmont volcano.

Lake Kainui series

Samples of organic lake sediment coll by piston corer from Lake Kainui (also known as Lake D), 15km NW of Hamilton, 37°41'S, 175°14'E (S14/072892). Coll (1982) by D J Lowe, J D Green, and C H Hendy and subm by D J Lowe, Earth Sci, Univ of Waikato.

2010 ± 80

Wk-507. Lake D-12

Est $\delta^{13}\text{C} = -28\%$

Comment: diluted, 49% sample. (DJL): provides min age of Whakaipo Tephra Fm. Date younger than expected. See comment for Wk-538.

3030 ± 70

Wk-506. Lake D-11

 $\delta^{13}\text{C} = -28.0\%$

Comment: diluted, 53% sample. (DJL): provides max age of Whakaipo Tephra Fm.

5800 ± 90

Wk-505. Lake D-10

 $\delta^{13}\text{C} = -28.8\%$

Comment: diluted, 56% sample. (DJL): provides min age of Tuhua Tephra Fm.

7140 ± 110

Wk-571. Lake D-5

 $\delta^{13}\text{C} = -29.2\%$

Comment: diluted, 47% sample. (DJL): provides min age of Mamaku Ash Fm.

7200 ± 120

Wk-570. Lake D-4

 $\delta^{13}\text{C} = -29.1\%$

Comment: diluted, 40% sample. (DJL): provides max age of Mamaku Ash Fm.

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Wk-575. Lake D-9 11,800 ± 230
 $\delta^{13}\text{C} = -31.6\text{‰}$

Comment: diluted, 33% sample. (DJL): provides min age of Waiohau Ash Fm.

See comment for Wk-233.

Wk-574. Lake D-8 11,700 ± 270
 $\delta^{13}\text{C} = -32.3\text{‰}$

Comment: diluted, 29% sample. (DJL): provides max age of Waiohau Ash Fm.

See comment for Wk-233.

Wk-573. Lake D-7 12,350 ± 210
 $\delta^{13}\text{C} = -32.1\text{‰}$

Comment: diluted, 42% sample. (DJL): provides min age of Rotorua Ash Fm.

Date is younger than expected (by ca 1000 yr?); may be due to disturbed top and base of tephra (has in situ gas pockets, tephra-infilled cracks in gyttja). See comment for Wk-511.

Wk-572. Lake D-6 12,650 ± 230
 $\delta^{13}\text{C} = -31.1\text{‰}$

Comment: diluted, 37% sample. (DJL): provides max age of Rotorua Ash Fm.

Date is younger than expected. See comment for Wk-573.

Wk-504. Lake D-1 +680
15,150
-630
 $\delta^{13}\text{C} = -26.3\text{‰}$

Comment: diluted, 15% sample. (DJL): provides age of fm of Lake Kainui and dates cessation of deposition of Hinuera Fm sediments at this locality.

Age consistent with previous determinations elsewhere (McGlone, Nelson & Hume, 1973; Green & Lowe, 1985).

General Comment (DJL): ages generally accord well with previous determinations except those noted as younger than expected.

Lake Okoroire series

Samples of organic lake sediment coll by piston corer from Lake Okoroire, 5km N of Tirau, 37°55'S, 175°48'E (T15/555611). Coll (1984) by D J Lowe, C H Hendy and M Ouellet and subm by D J Lowe. Note: minimal sample material was available for this ser. Each of samples Wk-661 to Wk-664 bridges two closely spaced tephras, thus applying equally to both tephras (see Fig 2).

Wk-661. Ok-6 3950 ± 90
 $\delta^{13}\text{C} = -30.6\text{‰}$

Comment: diluted, 42% sample. (DJL): provides max age of uncorrelated tephra from Egmont, Eg-4, and min age for uncorrelated tephra of uncertain source.

Wk-664. Ok-5 3810 ± 140
 $\delta^{13}\text{C} = -30.6\text{‰}$

Comment: diluted, 20% sample. (DJL): provides max age of uncorrelated tephra of uncertain source and min age for uncorrelated tephra from Egmont, Eg-5.

Wk-663. Ok-4 3510 ± 150
 $\delta^{13}\text{C} = -30.2\text{‰}$

Comment: diluted, 21% sample. (DJL): provides max age of uncorrelated tephra from Egmont, Eg-5, and min age of Hinemaiaia Tephra Fm (definition of

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Froggatt, 1981a; Lowe, 1986a). Date younger than expected as discords with succession of dates on overlying and underlying sediments (Wk-660, Wk-661, Wk-664) and hence may be unreliable (contaminated by younger carbon?).

Wk-662. Ok-3

$$4260 \pm 140$$

$$\delta^{13}\text{C} = -31.7\text{‰}$$

Comment: diluted, 23% sample. (DJL): provides max age of Hinemaiaia Tephra Fm (definition of Froggatt, 1981a; Lowe, 1986a) and min age of Whakatane Ash Fm.

Wk-660. Ok-2

$$4850 \pm 80$$

$$\delta^{13}\text{C} = -32.1\text{‰}$$

Comment: diluted, 55% sample. (DJL): provides max age of Whakatane Ash Fm (Lowe, 1986a).

Wk-705. Ok-7

$$7520 \pm 130$$

$$\delta^{13}\text{C} = -31.5\text{‰}$$

Comment: diluted, 44% sample. (DJL): provides min age of Rotoma Ash Fm. Gives max limit to age of Mamaku Ash Fm as sample within a few cm of base of Mamaku Ash Fm (Fig 2). Date younger than expected for Rotoma Ash (probably aged ca 8000 to 9000 BP), but as expected for Mamaku Ash range (see comment for Wk-523). Appear to have very slow sedimentation rate in lake at this time so sample slice, although only 2cm thick, may span ca 1000 yr.

Wk-706. Ok-8

$$7920 \pm 130$$

$$\delta^{13}\text{C} = -31.5\text{‰}$$

Comment: diluted, 44% sample. (DJL): provides max age of Rotoma Ash Fm. Gives min limit to age of Opepe Tephra Fm as sample within a few cm of top of Opepe Tephra Fm (Fig 2). See comment for Wk-705.

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Wk-707. Ok-9 8700 ± 130
 $\delta^{13}\text{C} = -32.4\%$

Comment: diluted, 49% sample. (DJL): provides max age of Opepe Tephra Fm.

Wk-708. Ok-10 10,220 ± 160
 $\delta^{13}\text{C} = -27.0\%$

Comment: diluted, 47% sample. (DJL): provides min age of Waiohau Ash Fm.
 Age younger than expected for this tephra, dated between ca 11,000 BP to 12,500 BP elsewhere. See comment for Wk-233.

Wk-709. Ok-11 11,570 ± 130
 $\delta^{13}\text{C} = -27.3\%$

Comment: diluted, 68% sample. (DJL): provides max age of Waiohau Ash Fm.
 See comment for Wk-233.

Wk-659. Ok-1 15,850 ± 320
 $\delta^{13}\text{C} = -20.0\%$

Comment: diluted, 32% sample. (DJL): provides min age for fm of Lake Okoroire (base of lake sediments not seen) and upper limit to deposition of Hinuera Fm sediments in this area (see comment for Waihou ser). Sparse white pumice grains at base of sample may represent an uncorrelated tephra layer. If so, may be ?Okareka Ash Fm, based solely upon stratigraphic position relative to Rerewhakaaitu Ash Fm in core (Fig 2; Vucetich & Pullar, 1969), and thus could give upper age limit for this possible tephra. See comment for Wk-240.

General Comment (DJL): dates excepting Wk-663 accord with stratigraphy. With regard to dating tephra-producing eruptions, it is evident that the degree of resolution that can be achieved through dating the associated lake sediment is

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limited when sample material is restricted and sedimentation rates are slow (ie ca 0.1mm/yr or less).

Lake Rotongata series

Samples of organic lake sediment coll by piston corer from Lake Rotongata, Arapuni District, 38°08'S, 175°36'E (T16/380376). Coll (1985) by D J Lowe, C H Hendy and M Ouellet and subm by D J Lowe.

Wk-711. Rn-1/2 8000 ± 170
 $\delta^{13}\text{C} = -32.5\%$

Comment: diluted, 34% sample. (DJL): sample straddles tephra layer; provides average age of Rotoma Ash Fm. See comment for Wk-523.

Wk-713. Rn-3/4 8990 ± 220
 $\delta^{13}\text{C} = -33.0\%$

Comment: diluted, 28% sample. (DJL): sample straddles tephra layer; provides average age of Opepe Tephra Fm.

Wk-714. Rn-5 11,840 ± 340
 $\delta^{13}\text{C} = -24.1\%$

Comment: diluted, 22% sample. (DJL): provides min age of Waiohau Ash Fm. See comment for Wk-233.

Wk-715. Rn-6 11,990 ± 230
 $\delta^{13}\text{C} = -25.8\%$

Comment: diluted, 35% sample. (DJL): provides max age of Waiohau Ash Fm.

Lake Omapere series

Samples of organic lake sediment or wood fragments coll by piston corer from five sites in Lake Omapere, near Kaikohe, North Auckland, 35°21'S, 173°47'E, as part of joint New Zealand - Japan project in paleolimnology organised by S Horie, chairman of Special Working Group of Societas Internationalis Limnologiae (Lowe, 1984). Coll (1984) by D J Lowe, J D Green, S Bergin, J A T Boubée and S Horie and subm by D J Lowe and J D Green.

Wk-625. Om-4

1190 ± 90
 $\delta^{13}\text{C} = -27.4\%$

Lake sediment at loc P5/827494. Comment: diluted, 33% sample. (DJL): dates soft brown gyttja overlying greenish grey clay layer ca 20cm below surface of sediments in Lake Omapere. Grey clay seems to represent increased erosion in catchment, possibly forming the present-day lake by blockage of drainage (Lowe & Green, 1987). Such erosion is likely to reflect deforestation, either by natural causes or possibly in response to Polynesian activities (cf McGlone, 1983) as date obtained is around time of earliest known settlement of Polynesians in New Zealand (Davidson, 1981). See also general comment for Lake Hakanoa ser below.

Wk-604. Om/E1-30B

5410 ± 150
Est $\delta^{13}\text{C} = -25\%$

Lake sediment at loc P5/827494. Comment: diluted, 24% sample. (DJL): sample overlies diffuse tephra layer (lab no.7) tentatively identified as Mamaku Ash Fm; date provides min age. If tephra is Mamaku, age is younger than expected (see Wk-227) but could easily be explained by an excessively thick sample slice (5cm). See Wk-626.

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8030 ± 330
 Wk-626. Om/E1-40 $\delta^{13}\text{C} = -25.4\text{‰}$

Lake sediment at loc P5/827494. Comment: diluted, 14% sample. (DJL): sample underlies diffuse tephra layer (lab no.7) tentatively identified as Mamaku Ash Fm; date provides max age. Date obtained is consistent with range for this tephra in Waikato lakes (see ser above), and supports identification as Mamaku Ash.

>35,000
 Wk-590. Om-2 $\delta^{13}\text{C} = -25.5\text{‰}$

Lake sediment at loc P5/827494. Comment: diluted, 15% sample. (DJL): sample underlies 10cm-thick airfall tephra (lab nos.1, 2) provisionally identified as Rotoehu Ash (member of Rotoiti Breccia Fm, Nairn, 1972). Date obtained agrees with previous dates of ca 42,000 BP (Pullar & Heine, 1971) and est age of ca 50,000 BP (McGlone, Howorth & Pullar, 1984).

>35,000
 Wk-589. Om-3 Est $\delta^{13}\text{C} = -25\text{‰}$

Lake sediment at approx loc P5/821505. Comment: diluted, 26% sample. (DJL): sample at ca 1m depth in core. Dates thin, slightly gritty layer within greyish, muddy gyttja.

>35,000
 Wk-588. Om/D1-225 $\delta^{13}\text{C} = -28.6\text{‰}$

Lake sediment at loc P5/821505. Comment: diluted, 25% sample. (DJL): sample straddles thin, intermittently-occurring ?tephra layer (lab no.6) at ca 2.2m depth that marks change in sediments from greyish mud (above) to brownish gyttja (below).

Wk-587. Om/C2-247 >30,000
 $\delta^{13}\text{C} = -24.5\%$

Lake sediment at loc P5/827494. Comment: diluted, 24% sample. (DJL): sample straddles uncorrelated white rhyolitic ash layer (lab no.3) at ca 2.5m depth in core; gives average age for tephra.

Wk-586. Om-1 >35,000
 $\delta^{13}\text{C} = -24.3\%$

Lake sediment at loc P5/821505. Comment: diluted, 46% sample. (DJL): sample straddles uncorrelated white rhyolitic ash layer (lab no.4) at ca 4m depth in core; gives average age for tephra.

Wk-585. Om/C2-400 >35,000
 $\delta^{13}\text{C} = -21.7\%$

Basal lake sediment at loc P5/827494. Comment: diluted, 44% sample. (DJL): gives age of fm of initial "proto-Lake Omapere". As initial lake basin thought to be formed by lava flow blocking drainage (Bell & Clarke, 1909; Cotton, 1958), sample should date eruption of lava (from Te Ahuahu, Maungakawakawa or other volcano).

Wk-584. Om/C2-417 >30,000
 $\delta^{13}\text{C} = -22.5\%$

Small fragments of conifer wood (either Podocarpus totara / hallii or Dacrydium cupressinum or Libocedrus; R Patel, pers commun, 1984) and associated carbonaceous material in paleosol-like muds underlying basal lake sediments at loc P5/827494. Comment: diluted, 53% sample. (DJL): gives max age for inundation of pre-lake surface by proto-Lake Omapere at this site.

Wk-581. Om/E1-470 >35,000
 $\delta^{13}\text{C} = -26.3\text{‰}$

Wood fragments in peat underlying basal lake sediments at loc P5/821501.

Comment (DJL): gives max age for inundation by proto-Lake Omapere at this site, and age of sub-lake peat bog.

Wk-583. Om/A2-160 >35,000
 $\delta^{13}\text{C} = -26.2\text{‰}$

Wood (Agathis australis?) underlying basal lake sediments at loc P5/840502. Comment (DJL): gives max age for inundation of pre-lake surface by proto-Lake Omapere at this site.

General Comment (DJL): changes in nature of lake sediment, the range of ages obtained, and the sparse tephras preserved, suggest that the lake has existed only intermittently in Omapere basin with hiatuses in the depositional record. Modern lake was possibly formed only ca 1000 BP. Dates on ?Mamaku Ash, Rotoehu Ash, and the older tephras (probably all derived from Taupo Volcanic Zone) are the first to be obtained on rhyolitic tephras in Northland other than the late Holocene Kaharoa Ash and Taupo Pumice deposits (Pullar, Kohn & Cox, 1977; Stewart, Neall & Syers, 1984).

Kaipo Lagoon series

Samples of peat, containing abundant coarse roots, coll from two sites at the outlet of the Kaipo Stream, draining the Kaipo Lagoon, Urewera National Park, 38°41'S, 177°11'E (W18/740720). The Kaipo Lagoon is a 73ha ombrogenous shrub bog at 1100m altitude and surrounded by mature silver beech (Nothofagus menziesii) and red beech (N. fusca) (Lowe & Hogg, 1986). Coll and subm (1982) by N B Rogers, D J Lowe and A G Hogg, School of Sci, Univ of Waikato. Samples

are from site 1 unless noted. Some samples were split into coarse (handpicked roots) and fine (fine peat residual after root extraction) fractions, each being dated separately.

Wk-499. K-I1 2910 ± 60
 $\delta^{13}\text{C} = -25.7\text{‰}$

Coarse root fraction of K-I (for residual fine peat fraction, see Wk-500). Comment: diluted, 91% sample. (DJL): provides min age of Waimihia Lapilli Member of Waimihia Fm.

Wk-500. K-I2 3040 ± 50
 $\delta^{13}\text{C} = -26.4\text{‰}$

Residual fine peat fraction of K-I (for coarse root fraction, see Wk-499). Comment (DJL): provides min age of Waimihia Lapilli Member of Waimihia Fm. Similarity of date to Wk-499 indicates that material probably autochthonous.

Wk-498. K-H 3250 ± 70
 $\delta^{13}\text{C} = -26.4\text{‰}$

Bulk peat. Comment: diluted, 71% sample. (DJL): provides max age of Waimihia Lapilli Member of Waimihia Fm.

Wk-496. K-G 4490 ± 60
 $\delta^{13}\text{C} = -26.9\text{‰}$

Bulk peat. Comment (DJL): sample bridges two tephras; provides max age of Hinemaiaia Tephra Fm (definition of Froggatt, 1981a; Lowe, 1986a) and min age of Whakatane Ash Fm.

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Wk-497. K-Gg 4530 ± 60
δ¹³C = -26.4‰

Bulk peat from site 2, 10m S of site 1. Comment (DJL): provides max age of Hinemaiaia Tephra Fm (definition of Froggatt, 1981a; Lowe, 1986a) and min age of Whakatane Ash Fm.

Wk-501. K-J 4860 ± 70
δ¹³C = -26.4‰

Bulk peat from site 2, 10m S of site 1. Comment: diluted, 73% sample. (DJL): provides max age of Whakatane Ash Fm.

Wk-493. K-F1 5440 ± 170
δ¹³C = -25.8‰

Coarse root fraction of K-F (for residual fine peat fraction, see Wk-494). Comment: diluted, 23% sample. (DJL): provides min age of Rotoma Ash Fm. Date obtained is significantly younger than Wk-494, suggesting natural contamination of peat overlying tephra. Date thus unreliable for eruption of Rotoma Ash.

Wk-494. K-F2 7380 ± 80
δ¹³C = -26.8‰

Residual fine peat fraction of K-F (for coarse root fraction, see Wk-493). Comment (DJL): provides min age of Rotoma Ash Fm. Date obtained is nearer previous dates on this tephra but still appears anomalously young. See comment for Wk-523.

Wk-495. K-Ff 7560 ± 100
 $\delta^{13}\text{C} = -26.2\text{‰}$

Bulk peat from site 2, 10m S of site 1. Comment: diluted, 57% sample. (DJL): provides min age of Rotoma Ash Fm. Date obtained may be anomalously young for eruption of this tephra. See comment for Wk-523.

Wk-492. K-E 8710 ± 80
 $\delta^{13}\text{C} = -26.7\text{‰}$

Bulk peat. Comment (DJL): provides min age of Opepe Tephra Fm.

Wk-491. K-C 9560 ± 80
 $\delta^{13}\text{C} = -27.0\text{‰}$

Bulk peat. Comment (DJL): provides min age of Poronui Tephra Fm. First date to be obtained for this tephra (with Wk-351, Wk-352).

Wk-351. K-B1 10,160 ± 130
 $\delta^{13}\text{C} = -29.4\text{‰}$

Coarse root fraction of K-B (for residual fine peat fraction, see Wk-352). Comment: diluted, 61% sample. (DJL): provides max age of Poronui Tephra Fm (see comment for Wk-491). Also gives close estimate of min age of Karapiti Tephra Fm (ca 10,100 BP), which is only few cm below sample (see Figs 2 and 4). Date agrees with Wk-352 hence likely to be reliable.

Wk-352. K-B2 9960 ± 90
 $\delta^{13}\text{C} = -28.5\text{‰}$

Residual fine peat fraction of K-B (for coarse root fraction, see Wk-351). Comment (DJL): provides max age of Poronui Tephra Fm (see comment for

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Wk-491) and est of min age of underlying Karapiti Tephra Fm (see comment for Wk-351).

Wk-263. K-A

10,600 ± 90
 $\delta^{13}\text{C} = -29.6\text{‰}$

Bulk peat. Comment (DJL): provides max age of lowermost tephra, probably a member of the Okupata Tephra Fm, at 2.3m depth in section.

Wk-264. K-K

11,500 ± 80
 $\delta^{13}\text{C} = -29.1\text{‰}$

Bulk peat. Comment (DJL): sample at 2.7m depth in section; provides max age of inception of peat growth in Kaipo Lagoon.

General Comment (DJL): apart from the three dates associated with the deposition of Rotoma Ash (Wk-493, Wk-494, Wk-495), which are considered to be anomalously young, the dates on the other tephras generally accord with previous determinations (see Lowe & Hogg, 1986). The difference between Wk-493 (coarse root fraction) and Wk-494 (residual fine peat) suggests that where contamination is suspected in bogs, fine peat fractions may produce more reliable dates than roots or bulk samples. A plot of the peat accumulation rates (Fig 4) for Kaipo Lagoon bog shows slow rates overall (average 0.19mm/yr). However, the average rate between ca 11,500 BP and ca 8700 BP was 0.37mm/yr but from ca 8700 BP to the bog's surface (aged ca 700 BP) was a much slower 0.13mm/yr. Lowe & Hogg (1986) suggest that this pattern may relate to climatic change, but that variations in local conditions could also have been important influences.

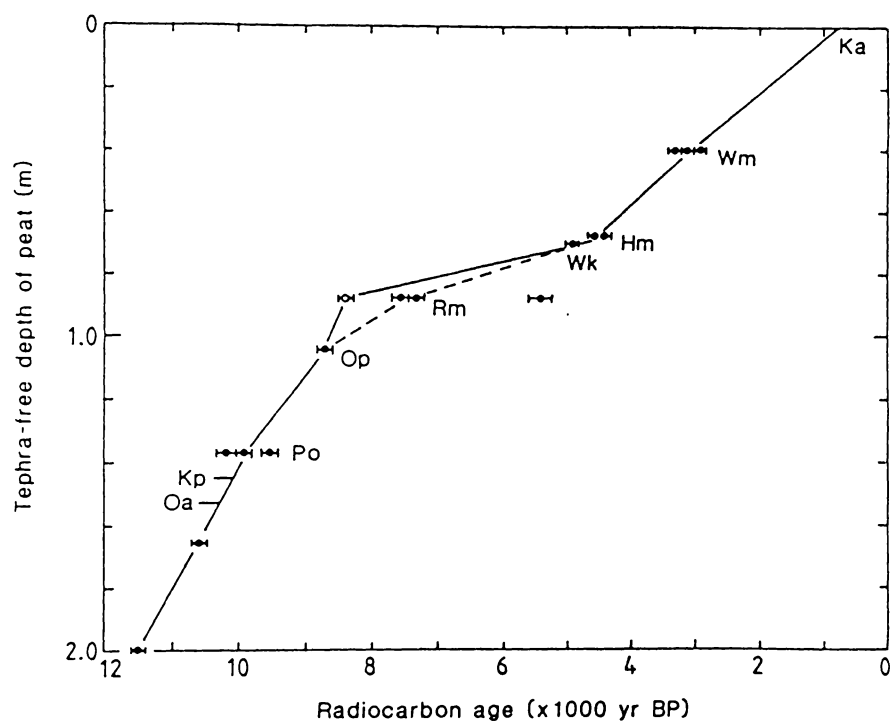


Fig 4. Peat accumulation rate curve for the Kaipo Lagoon Bog based on dates in the Kaipo Lagoon series (closed circles). Tephra abbreviations are given in Fig 2. The dates on Rotoma Ash (Rm) are considered anomalously young, hence the preferred sedimentation rate curve (solid line) is drawn through the dates obtained on this tephra in the Lake Maratoto series (open circle, Wk-522, Wk-523). After Lowe & Hogg (1986).

Moanatuatua Bog series

Samples of peat and wood fragments coll by Russian/Jowsey peat sampler from the Moanatuatua Peat Bog at Muir Rd near Ohaupo in the Hamilton Basin, 37°57'S, 175°22'E (S15/180581). Coll (1982) by D J Lowe, R S P Lane, and A G Hogg and subm by D J Lowe and A G Hogg. The Moanatuatua Bog is an oligotrophic, high moor, restiad bog with mesotrophic margins, is up to ca 12m in thickness, and covers ca 85km² (Davoren, 1978).

Wk-562. Muir-137 & 139 5850 ± 70
 $\delta^{13}\text{C} = -27.7\text{‰}$

Comment (DJL): sample between two tephra layers; provides min age of uncorrelated tephra (?Mamaku Ash Fm) at ca 6.2m depth and approx max age for uncorrelated tephra at ca 6.0m depth.

Wk-561. Muir-150 & 151 10,650 ± 140
 $\delta^{13}\text{C} = -28.0\text{‰}$

Comment (DJL): sample bridges two tephra layers; provides max age of uncorrelated tephra at ca 9.3m depth, min age of uncorrelated tephra at ca 9.4m depth. Base of bog at ca 10.8m.

Wk-531. Muir-168 & 170 12,800 ± 110
 $\delta^{13}\text{C} = -27.4\text{‰}$

Comment (DJL): sample straddles tephra layer tentatively identified as Waiohau Ash Fm at ca 10.7m depth; provides average age (see comment for Wk-233). Base of bog at ca 10.9m.

Wk-530. Muir-48 12,950 ± 110
 $\delta^{13}\text{C} = -28.0\text{‰}$

Comment (DJL): sample overlies tephra, probably Rotorua Ash Fm, at ca 10.9m depth; date obtained provides min age. Base of bog at ca 11.0m.

Wk-529. Muir-50 13,300 ± 110
 $\delta^{13}\text{C} = -28.6\text{‰}$

Comment (DJL): sample comprises muddy peat and underlies tephra, probably Rotorua Ash Fm, at ca 10.9m; date obtained provides max age. Also dates initiation of peat growth at this site (base of bog at ca 11.0m). See also Wk-116 (Waikato Swamp ser).

General Comment (DJL): dates first to be obtained on tephras in bogs in Hamilton Basin. Dates also indicate that average rate of peat growth of Moanatuatua bog at this site has been ca 1mm/yr (growth rate may not have been uniform, however).

Hauraki Plains series

Peat cored from the Kopuatai Peat Dome of the Hauraki Plains Swamp, Hauraki Plains, 37°25'S, 175°34'E (at three sites). Coll (1977 to 1980) by A G Hogg, D J Lowe and L Gaylor and subm by A G Hogg, Radiocarbon Lab, Univ of Waikato. The Kopuatai Dome is the largest raised (domed) bog in natural condition left in New Zealand (Irving, Skinner, & Thompson, 1984). Hauraki Plains Swamp is an oligotrophic, high moor restiad bog covering ca 240km² and is up to ca 12m in thickness (Davoren, 1978).

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Wk-106. HP2 6280 ± 70
 $\delta^{13}\text{C} = -27.6\text{‰}$

Coll (1977) from 6.0 to 6.3m below surface of bog at T13/377162. Comment:
diluted, 84% sample. (AGH): provides max age of Tuhua Tephra Fm.

Wk-241. HP3 6070 ± 80
 $\delta^{13}\text{C} = -28.0\text{‰}$

Coll (1980) from 5.9m below surface of bog at T13/373190. Comment:
diluted, 79% sample. (AGH): provides min age of Tuhua Tephra Fm.

Wk-242. HP4 6440 ± 80
 $\delta^{13}\text{C} = -28.2\text{‰}$

Coll (1980) from 6.0m below surface of bog at T13/373190. Comment:
diluted, 87% sample. (AGH): provides max age of Tuhua Tephra Fm.

Wk-244. HP5 6060 ± 80
 $\delta^{13}\text{C} = -27.3\text{‰}$

Coll (1980) from 5.9m below surface of bog at T13/366188. Comment (AGH):
provides min age of Tuhua Tephra Fm.

Wk-243. HP6 6710 ± 80
 $\delta^{13}\text{C} = -27.9\text{‰}$

Coll (1980) from 6.0m below surface of bog at T13/366188. Comment (AGH):
provides max age of Tuhua Tephra Fm. Date obtained probably overestimates age
of eruption because of excessive sample size.

Wk-102. HP1

9360 ± 100

 $\delta^{13}\text{C} = -27.6\text{‰}$

Coll (1977) from base of Hauraki bog (9.7 to 10.0m depth) at T13/377162.

Comment (AGH): marks the initial formation of the bog at this site.

General Comment (DJL): dates obtained agree with that on Tuhua Tephra at Lake Maratoto (Lowe et al, 1980; Hogg & McCraw, 1983). Dates indicate average growth rate for bog has been ca 1mm/yr.

Te Rangaakapua series

Peat coll from a pit dug into a sub-alpine bog containing tephra beds at Te Rangaakapua, Urewera National Park, 38°31'S, 177°12'E (W17/765894). Coll (1984) by W B Shaw and subm by W B Shaw and D J Lowe, School of Sci, Univ of Waikato. Each sample ca 4cm thick and separated from overlying and underlying tephra layers by ca 2 to 3cm of peat ie not immediately adjacent to either tephra.

Wk-610. TR1

3660 ± 70

 $\delta^{13}\text{C} = -25.4\text{‰}$

Comment: diluted, 72% sample. (DJL): provides max age limit for overlying Waimihia Lapilli Member of Waimihia Fm, and min age limit for underlying Whakatane Ash Fm.

Wk-611. TR2

5510 ± 70

 $\delta^{13}\text{C} = -26.0\text{‰}$

Comment: diluted, 80% sample. (DJL): provides max age limit of overlying Whakatane Ash Fm and min age of underlying Rotoma Ash Fm.

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General Comment (DJL): dates obtained are broadly consistent with previous obtained ages for these tephras (Lowe & Hogg, 1986; Lowe, 1986a), given position of samples with respect to tephras.

Wk-612. Mata-2/132-138 8560 ± 80
 $\delta^{13}\text{C} = -25.5\text{‰}$

Peat cored with motorised Giddings auger from a shallow peat bog at end of Pohlen Rd, Matamata, 37°47'S, 175°47'E (T14/562762). Coll (1984) by D J Lowe and M McLeod, and subm by D J Lowe. Comment (DJL): provides min age of ?Mamaku Ash Fm (possibly reworked) and dates inception of peat growth at this site.

Wk-425. Rotokare-1 1920 ± 110
 $\delta^{13}\text{C} = -31.6\text{‰}$

Greyish lake sediment cored from Lake Rotokare, near Eltham, Taranaki, 39°27'S, 174°24'E (V17/219904). Coll (1980) by C H Hendy and subm by D J Lowe and C H Hendy, School of Sci, Univ of Waikato. Comment: diluted, 26% sample. (DJL): provides min age for andesitic tephra at ca 1.3m depth (tentatively correlated with ?Mangatawai Tephra of Topping, 1973 or ?Kaupokonui tephra of Neall & Geddes, 1981); gives est of rate of sedimentation in lake (ca 1.5mm/yr), and min age of fm of lake (base of lake sediments not seen).

2. Dates Associated with Deposition of the Hinuera Formation Alluvium

Motumaoho series

Logs and peat from exposure on Hamilton to Morrinsville Rd (SH 26), 100m S of junction with Harbottle Rd, 37°42'S, 175°29'E. Coll (1975) and subm by H S Gibbs, Earth Sci Dept, Univ of Waikato. Samples occur either within the Hinuera Fm or overlying Hinuera Fm sediments at three sites (A,C,F). Peat 1

layer, 300 to 330cm below surface of terrain; peat 2 layer, 50cm below peat 1 layer (ie 380cm below terrain surface). See also Harbottle Rd ser.

Wk-65. A/2 16,630 ± 670
Est $\delta^{13}\text{C} = -25\%$

Peat in Hinuera sediments (upper 8cm of peat 1 layer) at site A,
 S14/276860. Comment: diluted, 69% sample.

Wk-66. A/3 16,600 ± 750
Est $\delta^{13}\text{C} = -25\%$

Peat in Hinuera sediments (8 to 15cm of peat 1 layer) at site A,
 S14/276860. Comment: diluted, 72% sample.

Wk-67. A/4 15,400 ± 1200
Est $\delta^{13}\text{C} = -25\%$

Peat in Hinuera sediments (20 to 30cm of peat 1 layer) at site A,
 S14/276860. Comment: diluted, 39% sample.

Wk-70. C/2 16,710 ± 480
Est $\delta^{13}\text{C} = -25\%$

Peat in Hinuera sediments (peat 1 layer) at site C, S14/275860 (50m W of site A).

Wk-74. Site F/1 17,050 ± 540
Est $\delta^{13}\text{C} = -25\%$

Log in peat layer 2 at site F, S14/276861 (70m NNW of site A).

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General Comment (HSG): dates are in broad agreement with one another and give approx date for last period of deposition of Hinuera-2 sediments by ancestral Waikato R in Morrinsville Gap.

Te Rapa series

Peat samples from Eastern Sanitary Interceptor, Te Rapa, Hamilton, 37°44'S, 175°15'E (S14/081826). Coll (1975) by C S Nelson and D Cope and subm by C S Nelson, Earth Sci Dept, Univ of Waikato.

+3300

39,900

-2400

Wk-37. CSN-1

Est $\delta^{13}\text{C} = -25\text{‰}$

Bore 2. (30m below Waikato R level on W bank).

>40,000

Wk-38. CSN-2

Est $\delta^{13}\text{C} = -25\text{‰}$

Bore 6. (30m below Waikato R level on W bank, 10m from bore 2).

General Comment (CSN): the first dates obtained for the Hinuera-1 alluvial deposits of the Hinuera Fm in the Hamilton Basin. Wk-37 also yielded a preliminary uranium-thorium age of <65,000 BP (C H Hendy in McGlone, Nelson & Hume, 1978).

Riverlea series

Carbonaceous mud and sand with occasional poorly preserved woody fragments from three carbonaceous strata within fluvial pumiceous silts, sands and gravelly sands of the Hinuera Fm at a site opposite Riverlea Wreckers near

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Hamilton on the Hamilton to Cambridge hwy, 37°49'S, 175°20'E (S14/162744).
Coll (1981) and subm by C S Nelson.

Wk-393. W3 18,250 ± 180
Est $\delta^{13}\text{C} = -25\%$

Carbonaceous mud 0.25m thick occurring 3.5 to 3.75m below Hinuera surface. Comment (CSN): dates the closing period of active aggradation of Hinuera sedimentation in Hamilton Basin.

Wk-392. W2 20,200 ± 210
Est $\delta^{13}\text{C} = -25\%$

Carbonaceous pumice sands 0.5m thick occurring 10.75 to 11.25m below Hinuera surface. Comment (CSN): dates active aggradation phase of Hinuera sedimentation in Hamilton Basin.

Wk-391. W1 21,300 ± 240
Est $\delta^{13}\text{C} = -25\%$

Woody, carbonaceous sands ca 0.7m thick occurring ca 14.5 to 15m below Hinuera surface. Comment (CSN): dates active aggradation phase of Hinuera sediments in Hamilton Basin.

General Comment (DJL): dates accord with stratigraphy and generally agree with previous determinations on Hinuera-2 sedimentation in Hamilton Basin (McGlone, Nelson & Hume, 1978).

Waihou series

Peat occurring as lenses within pumiceous silts, sands and gravels of the Hinuera Fm, exposed either within rd cuttings and quarries or obtained from

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drill cores. Sampled at four sites near Matamata in the Waihou R valley. Coll (1979) by A S Cuthbertson and subm by C S Nelson.

Wk-216. C3

19,400 ± 200
 $\delta^{13}\text{C} = -28.2\text{‰}$

Peat ca 2.5m below ground surface from quarry near Matamata on Matamata to Tauranga hwy, 37°49'S, 175°45'E (T14/572716). Comment (ASC): provides the upper age of Hinuera sedimentation in the Central Southern Hauraki Lowlands.

Wk-217. C2

18,400 ± 200
 $\delta^{13}\text{C} = -26.8\text{‰}$

Peat within layer 6.2 to 7.0m below ground surface from rd cutting near the Omahine Stream Bridge on Matamata to Tauranga hwy, 37°51'S, 175°52'E (T15/628677). Comment (ASC): provides the upper age of Hinuera sedimentation in the Central Southern Hauraki Lowlands.

Wk-218. Bore 37

23,900 ± 400
 $\delta^{13}\text{C} = -25.9\text{‰}$

Peat lens 0.8m thick occurring 28.1m below land surface, obtained from drill core in centre of Matamata Township, 37°48'S, 175°46'E (T14/542732). Comment (ASC): provides the lower age of Hinuera sedimentation in the Central Southern Hauraki Lowlands.

Wk-274. S36

>40,000
 $\delta^{13}\text{C} = -27.6\text{‰}$

Peat lens 2m thick occurring ca 20m below land surface, from a section exposed along the Waiomou Stream on the Matamata to Tauranga hwy, 37°51'S, 175°53'E (T15/621680). Comment (ASC): date may represent the boundary between the Hinuera-1 and Hinuera-2 depositional periods.

General Comment (DJL): dates indicate period when ancestral Waikato R debouched into Hauraki (Matamata) basin (Cuthbertson, ms).

Lake Rotokaraka series

Samples of lake sediment overlying or within sandy muds to muddy sands of Hinuera Fm obtained with piston corer from Lake Rotokaraka, Whitikahu, Hamilton Basin, 37°37'S, 175°20'E (S14/166965). Coll (1983) by D J Lowe, C H Hendy and L J Gaylor and subm by D J Lowe.

Wk-567. A/4-2.2

13,800 ± 370

$\delta^{13}\text{C} = -26.6\%$

Comment: diluted, 24% sample. (DJL): sample 20cm thick at base of lake sediment. Dates age of fm of modern Lake Rotokaraka, and provides age for the last depositional event of the Hinuera Fm at this site. Also provides est age for uncorrelated tephra ca 15cm above base of lake sediment column. Date obtained younger than expected as Rerewhakaaitu Ash (ca 14,700 BP) occurs in lake sediment 1.5m above sample.

Wk-568. A/4-2.8

15,900 ± 630

$\delta^{13}\text{C} = -25.5\%$

Comment: diluted, 18% sample. (DJL): gives age of proto-Lake Rotokaraka that existed between last and 2nd to last depositional episodes of Hinuera Fm deposition at this site.

Wk-569. A/4-3.7 16,600 ± 260
 $\delta^{13}\text{C} = -25.7\text{‰}$

Comment: diluted, 52% sample. (DJL): gives age of proto-Lake Rotokaraka that existed between 2nd to last and 3rd to last depositional episodes of Hinuera Fm at this site.

General Comment (DJL): dates provide chronology for succession of Hinuera-2 depositional episodes at this locality (see Lake Maratoto ser and Green & Lowe, 1985).

Wk-59. 17,500 ± 540
Est $\delta^{13}\text{C} = -25\text{‰}$

Sample is from peat layer 3 to 10cm thick, 5m below the top of the Hinuera Fm at the Hamilton Refuse site, Rototuna, Hamilton, 37°44'S, 175°16'E (S14/102830). Coll (1974) by T M Hume and C S Nelson and subm by C S Nelson.

Comment (CSN): date places a near upper age on the Hinuera Fm alluvial deposits (Hinuera-2) within the Hamilton Basin at this locality.

Wk-169. 17,790 ± 290
 $\delta^{13}\text{C} = -31.2\text{‰}$

Peat in layer occurring approx in the middle of Hinuera Fm silts and sands (total thickness varying from 7.3 to 11.5m), forming the highest of series of degradational terraces, at a site 3km SE of Karapiro Hall, Karapiro, 37°56'S, 175°35'E (T15/370593). Coll (1978) and subm by H S Gibbs. Comment (HSG): establishes the date the ancestral Waikato R broke through the Karapiro Gorge.

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Wk-566. LA/1-2.6

15,700 ± 200
 $\delta^{13}\text{C} = -23.9\%$

Lake sediment, ca 5.5 to 5.7m below sediment surface, cored from Leeson's Pond, Tauhei to Motumaoho Rd, Hamilton Basin, 37°39'S, 175°28'E (S14/287929). Coll (1983) by D J Lowe and L Gaylor and subm by D J Lowe. Comment: diluted, 61% sample. (DJL): base of lake sediment not seen. Date provides min age of fm of Leeson's Pond and est of age of last depositon of Hinuera Fm sediments in this part of the Hamilton Basin. Sedimentation rate for period between Wk-566 and Rerewhakaaitu Ash (ca 14,700 BP) at 4.5m depth is relatively fast, 0.7mm/yr, compared with later rates (see General Comment for Lake Maratoto ser).

Wk-614. Rototuna-1

17,600 ± 190
 $\delta^{13}\text{C} = -26.5\%$

Peat with twigs underlying lake sediment ca 6.6 to 6.8m below sediment surface, cored in drained "Rototuna lake" (Lake Tunawhakapeka) with motorised Giddings auger near Rototuna, Hamilton, 37°43'S, 175°17'E (S14/116853). Coll (1984) by D J Lowe and L Gaylor and subm by D J Lowe. Comment: diluted, 88% sample. (DJL): sample overlies gritty mud (Hinuera Fm). Dates age of fm of Lake Tunawhakapeka and min age for deposition of Hinuera Fm at this locality.

Waikare series

Carbonaceous mud and sand from drill cores at two sites (nos. 5, 13) in Ohinewai peatland near Lake Waikare, 37°30'S, 175°12'E. Coll (1979 to 80) by A J Todd and subm by C S Nelson.

Wk-280. P43

17,800 ± 200
 $\delta^{13}\text{C} = -28.3\text{‰}$

Sample from 10.9m depth at site 13 (S13/035109) in lacustrine mud.

Comments (AJT): dates late Pleistocene mud underlying modern surface peats and unconformably overlying Pleistocene fluvial gravelly sands. (DJL): mud unit found in proto-Lake Waikare formed by deposition of Hinuera Fm sediments (McGlone, Nelson & Todd, 1984).

Wk-226. P42

>40,000
 $\delta^{13}\text{C} = -29.8\text{‰}$

Sample from 25.7m depth at site 5 (S13/039097) in coarse volcanoclastic sands (alluvium) in either Karapiro or Puketoka Fm that predate Hinuera Fm sediments. Comments (AJT): dates Quaternary fluvial sequence in the Lower Waikato Basin. (DJL): gives max age for Hinuera Fm deposition at this site (McGlone, Nelson & Todd, 1984). See also Ohinewai Peatlands ser.

Pukerimu series

Peat and peaty mud samples in section through terrace at ca 40m asl, ca 10m above Waikato R, off* Cambridge to Ohaupo Rd, Pukerimu district, 37°54'S, 175°26'E (S15/241642). Higher terrace, at ca 60m asl, forms main Hinuera Surface. Coll (1985) by D J Lowe and M Lowe and subm by D J Lowe.

Wk-726. Pukerimu-4

22,900 ± 350
 $\delta^{13}\text{C} = -25.7\text{‰}$

Carbonaceous mud (gyttja-like) at top of ca 0.6m thick layer ca 2.2m below terrace surface. Layer underlies gravelly sand (Hinuera Fm) and overlies sticky blue clay (?overbank flood deposit, Hinuera Fm). Comment: diluted, 82%.

* Pukerimu Lane

sample. (DJL): gives max age for latest episode of Hinuera-2 sedimentation (overlying deposits) in Hamilton Basin.

Wk-725. Pukerimu-3 22,700 ± 290
 $\delta^{13}\text{C} = -27.0\%$

Carbonaceous mud (gyttja-like) at base of ca 0.6m thick layer ca 2.8m below terrace surface (see Wk-726). Comment (DJL): date supports Wk-726.

Wk-724. Pukerimu-2 >40,000
Est $\delta^{13}\text{C} = -25\%$

Peaty pumiceous mud layer ca 0.2m thick at ca 3.8m depth below terrace surface. Overlain by sticky blue clay, underlain by cross-bedded pumiceous sands and gravelly muds (Hinuera Fm). Comments: diluted, 25% sample. (DJL): date obtained indicates that underlying sediments represent Hinuera-1 (or earlier) deposits through which Waikato R has reentrenched.

Wk-723. Pukerimu-1 >40,000
Est $\delta^{13}\text{C} = -25\%$

Peat with small wood fragments at base of ca 1m thick peat layer ca 7.5m below terrace surface (at rd level). Peat layer underlies sands and muds of Hinuera Fm and overlies bluish ignimbrite (gleyed ?Puketoka Fm). Comment (DJL): date obtained suggests that overlying sediments up to Wk-725, Wk-726 represent Hinuera-1 deposits, in agreement with Wk-724.

General Comment (DJL): dates are in agreement with stratigraphy. Wk-723 and Wk-724 add to two previous dates on Hinuera-1 sediments in Hamilton Basin (see Te Rapa ser). Wk-725 and Wk-726 indicate that overlying sediments in this terrace (and higher terrace at 60m asl) represent Hinuera-2 sedimentation (McGlone, Nelson & Hume, 1978). Thus section apparently shows contact between Hinuera-1 (contd. next page)

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and Hinuera-2 sediments, the first such subaerial exposure known in Hamilton Basin.

3. Dates Associated with Peat Bog Growth or Local Sedimentation that Post-Dates Deposition of the Hinuera Formation ie <ca 15,000 BP

Lake Hakanoa series

Samples of wood or organic lake sediment coll by piston corer from Lake Hakanoa, Huntly, 37°33'S, 175°10'E (S13/018033). Coll (1982) (Hak-1) and 1984 (HK 1-3) and subm by B McCabe, D J Lowe and C H Hendy, School of Sci, Univ of Waikato. Hk 1-3 samples (coll BMcC) date a silt band within the organic sediment column and Hak-1 (coll DJL, BMcC, CHH) is derived from the base of the column.

Wk-608. HK-3 750 ± 50
 $\delta^{13}\text{C} = -29.0\text{‰}$

Lake sediment sample overlies silt layer. Comment: diluted, 75% sample.

Wk-607. HK-2 1020 ± 50
 $\delta^{13}\text{C} = -31.0\text{‰}$

Lake sediment sample obtained from within silt layer. Comment: diluted, 82% sample.

Wk-606. HK-1 1240 ± 60
 $\delta^{13}\text{C} = -32.3\text{‰}$

Lake sediment sample underlies silt layer. Comment: diluted, 55% sample.

General Comments (BMcC): dates the deposition of a silt band that accompanied deforestation in the catchment surrounding Lake Hakanoa and a change in the

$\delta^{13}\text{C}$ of the lake sediment. (DJL): postulated deforestation may relate to natural events or to Polynesian influence (cf McGlone, 1983). Polynesians inhabited many sites adjacent to such lakes in the Waikato district in last millenium (Pick, 1968; Shawcross, 1968; Bellwood, 1978; Lowe et al, 1984).

2040 \pm 50

Wk-424. Hak-1

 $\delta^{13}\text{C} = -26.9\%$

Wood (?kauri) within gritty muds overlain by ca 1m of Taupo Pumice Alluvium and ca 0.9m of lake sediments. Comment (DJL): provides approx age for deposition of Taupo Pumice Alluvium, and age of fm of Lake Hakanoa (Lowe & Green, 1987). Average sedimentation rate in lake, ca 2mm/yr, is approx 10 times faster than average rate in Hinuera-dammed lakes (see general comment for Lake Maratoto ser).

Pukekapia series

Peat from drained swamp E of Pukekapia Rd near Lake Rotongaro, Huntly District, 37°30'S, 175°8'E (S13/982089). Coll (1974) and subm by H S Gibbs. Peat ca 2.4m thick and overlies a silty base.

3760 \pm 110

Wk-61. S4

Est $\delta^{13}\text{C} = -25\%$

Sample from 2.07 to 2.17m below peat surface.

4040 \pm 120

Wk-60. S2

Est $\delta^{13}\text{C} = -25\%$

Sample from 2.27 to 2.34m below peat surface.

General Comment (HSG): ages provide approx date of commencement of peat fm at this location (see also Ohinewai Peatlands ser and McGlone, Nelson & Todd, 1984).

Ohinewai Peatlands series

Peat from drill cores at two sites (nos. 5, 9) in Ohinewai peatland, near Ohinewai, 37°30'S, 175°12'E. Coll (1981) by A J Todd and subm by C S Nelson. The Ohinewai Peatlands occur near Lake Waikare, cover 15km², and are mesotrophic with some oligotrophic characteristics (Davoren, 1978). The peat has an average thickness of 6 to 9m (max 11.5m) and overlies lacustrine mud deposited in a proto-Lake Waikare (McGlone, Nelson & Todd, 1984).

Wk-356. P87

2310 ± 60

$\delta^{13}\text{C} = -29.3\%$

Sample from 0.4m depth at site 9 (S13/044100). Comment (AJT): provides min age for surface peat fm in the Lower Waikato Basin.

Wk-359. P88

3290 ± 60

$\delta^{13}\text{C} = -27.9\%$

Sample from 3.4m depth at site 9 (S13/044100). Comment (AJT): improves age definition of surface peat in the Lower Waikato Basin.

Wk-281. P86

5820 ± 60

$\delta^{13}\text{C} = -27.7\%$

Sample from 6.5m depth at site 9 (S13/044100). Base of peat at 6.9m. Comment (AJT): dates base of surface peat of the Lower Waikato Basin.

Wk-224. P40 4950 ± 70
 $\delta^{13}\text{C} = -28.3\text{‰}$

Sample from 1.2m depth at site 5 (S13/039097). Comment (AJT): provides peat accumulation rate in the Ohinewai bog, Lower Waikato Basin.

Wk-225. P41 7100 ± 80
 $\delta^{13}\text{C} = -29.1\text{‰}$

Sample from 4.1m depth at site 5 (S13/039097). Comment (AJT): provides peat accumulation rate in the Ohinewai bog, Lower Waikato Basin.

General Comment (DJL): dates provide chronology for palynological study by McGlone, Nelson, & Todd (1984). See also Waikare ser.

Harbottle Rd series

Tree stumps in silty sands overlying peat layers on Hinuera Fm sediments in exposure on Hamilton to Morrinsville Rd (SH 26) at two sites (B, F), 37°42'S, 175°27'E (see also Motumaoho ser for additional stratigraphic details). Coll 1975 and subm by HS Gibbs.

Wk-68. B/1 6410 ± 290
Est $\delta^{13}\text{C} = -25\text{‰}$

Tree stump in silty sand 170cm below terrain surface and 130cm above peat layer 1, at site B (S14/276860), 8m W of site A. Comment: diluted, 49% sample.

Wk-73. E/1 7000 ± 170
Est $\delta^{13}\text{C} = -25\text{‰}$

Tree stump in silty sand at 300cm depth and lying above peat layer 1, at site E (S14/276861), 70m N of site A.

General Comment (HSG): dates obtained are much younger than dates on underlying peat and wood associated with Hinuera Fm sediments (see Motumaoho ser); this suggests that the silty sands are locally reworked deposits rather than from the ancestral Waikato R.

Waikato Swamps series

Basal peat or wood cored with Hiller corer from the Rukuhia and Moanatuatua Peat Swamps, near Hamilton (Fig 1). Wk-114, Wk-115, Wk-116 coll (1977) by A T Wilson and K Thompson and subm by A T Wilson, Chemistry Dept, Univ of Waikato; other samples coll (1982 to 1983) as noted. The Rukuhia bog, like Moanatuatua (see Moanatuatua ser) is an ombrogenous oligotrophic high moor bog with mesotrophic fringes, is up to 12m thick, and covers ca 64km² (Davoren, 1978).

Wk-114. 10,250 ± 90
Est $\delta^{13}\text{C} = -25\%$

Peat from base of Rukuhia bog (8.3m depth), 37°54'S, 175°18'E (S15/076694).

Wk-115. 10,750 ± 90
 $\delta^{13}\text{C} = -28.4\%$

Peat from base of Rukuhia bog (9m depth), 37°54'S, 175°18'E (S15/119691).

Wk-116. Moana #1 11,800 ± 120
 $\delta^{13}\text{C} = -28.6\%$

Peat from base of Moanatuatua bog (10m depth), 37°57'S, 175°22'E (S15/187608). See also Wk-529 (Moanatuatua bog ser).

General Comment (ATW): dates provide max age of peat fm at these sites.

Wk-553. GC1-1(RJ) 10,600 ± 90
 $\delta^{13}\text{C} = -28.5\%$

Basal peat cored by Russian/Jowsey corer from 7.5m below surface of the Rukuhia peat bog 400m W of Lake Maratoto, near Hamilton, 37°54'S, 175°18'E (S15/123660). Coll (1983) by D J Lowe and L Gaylor and subm by D J Lowe.

Comment (DJL): dates initiation of peat growth at this locality.

Wk-508. GC3-2 12,550 ± 110
 $\delta^{13}\text{C} = -25.9\%$

Rimu root wood (Dacrydium cupressinum, L Donaldson, pers commun, 1983) embedded in upper part of late Pleistocene colluvium underlying peat in arm of Rukuhia bog at N end of Lake Maratoto, near Hamilton, 37°54'S, 175°19'E (S15/663130). Wood at ca 6m below peat surface, ca 0.8m below base of peat (5.2m depth), and sampled with motorised Giddings auger. Coll (1983) by D J Lowe, J D Green and L Gaylor and subm by D J Lowe. Comment (DJL): gives approx age when growth of Rukuhia peat overwhelmed rimu tree (in situ?) at this site (Lowe, 1985).

Wk-534. RJ1-4 15,200 ± 130
 $\delta^{13}\text{C} = -27.7\%$

Basal woody peat (overlying Hinuera Fm sediments) cored by Russian/Jowsey corer from 7.2m below surface of the Rukuhia peat bog on the SW shoreline of Lake Maratoto, near Hamilton, 37°54'S, 175°19'E (S15/126657). Coll (1983) by D J Lowe, J D Green, M A Chapman and T G Northcote and subm by D J Lowe. Comment (DJL): dates initial development of marginal peat around Lake Maratoto shoreline soon after fm of lake basin by deposition of Hinuera Fm (see Lake Maratoto ser). Such growth may indicate that effective rainfall increased at this time (Green & Lowe, 1985).

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Cross referencing to thesis papers

- Green, J.D.; Lowe, D.J. 1985 = Paper 9
- Lowe, D.J. 1985 = Paper 2
- Lowe, D.J. 1986a = Paper 6
- Lowe, D.J. 1986b = Paper 11
- Lowe, D.J.; Green, J.D. 1987 = Appendix B
- Lowe, D.J.; Hogg, A.G. 1986 = Paper 5
- Lowe, D.J. *et al.* 1980 = Paper 1
- Lowe, D.J.; Hogg, A.G.; Hendy, C.H. 1981 = Paper 3

PAPER 9

Stratigraphy and development of c.17 000 year old Lake Maratoto, North Island, New Zealand, with some inferences about postglacial climatic change: a tephrochronological study.

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Stratigraphy and development of c. 17 000 year old Lake Maratoto, North Island, New Zealand, with some inferences about postglacial climatic change

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Abstract The stratigraphy and geomorphology of Lake Maratoto and its surrounds were investigated as part of a programme of paleolimnological studies based on sediment cores from lakes in northern North Island. Changes in the lake and catchment were inferred from variations in sediment character, the correlation and timing being determined from distinctive tephra layers in the sediments and by radiocarbon dating. Nineteen new C-14 dates, on gyttja or peat, are reported (old T½, years B.P.): 11 on tephra (Mamaku Ash 6830 ± 90, Wk227; Rotoma Ash 8370 ± 90, Wk522; 8350 ± 100, Wk523; Opepe Tephra 9370 ± 210, Wk230; Mangamate Tephra 9700 ± 140, Wk231; 10 000 ± 120, Wk232; Waiohau Ash 12 200 ± 230, Wk233; 12 500 ± 190, Wk234; 12 450 ± 200, Wk515; 12 300 ± 190, Wk516; Rotorua Ash 13 450 ± 120, Wk511); 5 on the deposition of Hinuera Formation alluvium (16 300 ± 250, Wk239; 16 900 ± 470, Wk240; 17 050 ± 200, Wk358; 16 200 + 360 – 340, Wk509; 15 850 ± 130, Wk510); and 3 on basal peat of the Rukuhia bog (10 250 ± 90, Wk114; 15 200 ± 130, Wk534; 10 600 ± 90, Wk553).

Lake Maratoto originated c. 17 000 years ago when a small valley was dammed by volcanogenic alluvium (Hinuera Formation). From c. 17 000 to c. 14 000 years ago the lake was about 2 m deep with clear water. Marginal peat first developed at c. 15 000 years ago, reducing the area of the lake by about one-half by c. 13 000 years ago. Lake area then expanded, possibly because of marginal erosion and/or oxidation of the peat, to its maximum size at the present day. The adjacent Rukuhia peat bog grew rapidly from c. 11 000 years ago and is now 8 m thick immediately to the west of the lake. As a result of this growth, the lake became dystrophic and deepened (3.5 m at c. 7000 years ago, 6.4 m at c. 2000 years ago, and 7.1 m today).

The developmental history suggests that net precipitation increased at c. 15 000 years ago, increased further at c. 11 000 years ago, remaining high to c. 7000 years ago at least, but with a decline at or before c. 2000 years ago. There may have been a distinctly wetter or windier period from c. 10 000 to 9000 years ago.

This interpretation is consistent with other reconstructions of postglacial climate in the Southern Hemisphere.

Keywords paleolimnology; lake sediments; drainage basins; peat; pyroclastics; tephrostratigraphy; tephrochronology; C-14; absolute age; ferromagnesian mineralogy; glass chemistry; late Quaternary; Holocene; climate; lake-level fluctuations; Hamilton Basin; Hinuera Formation; Lake Maratoto; Rukuhia; bogs

INTRODUCTION

Paleolimnology is a useful discipline for the investigation of Quaternary paleoecology and paleoclimate (e.g., Frey 1969; Birks & Birks 1980; Pennington 1981; Binford et al. 1983; Brugam 1984). Few such studies, none comprehensive, have been done in New Zealand (e.g., Deevey 1955; Kennedy et al. 1978; Boubée 1983; McGlone 1983), and hence we have begun a programme of paleolimnological studies based on sediment cores from lakes in the northern North Island.

One of the most promising areas for these studies is the Hamilton Basin (Fig. 1). Its major geomorphological features were developed in the late Quaternary, mainly by aggradation of the ancestral Waikato River (McCraw 1967; Hume et al. 1975), when a number of peat bogs and small lakes were formed. Exploratory corings of sediments on some of the lakes in 1979 verified that they are ideal sites for paleolimnological studies. The lakes are shallow with soft sediments and very low sedimentation rates. Particularly notable is a series of laterally continuous, thin, distinct volcanic ash layers. The stratigraphic sequence, thickness, lithology, and bedding characteristics of these layers is practically identical in all of the lakes examined, hence they are regarded as primary tephra (Lowe et al. 1980) and of great value as time-stratigraphic markers. Lake Maratoto, located about 10 km south of Hamilton City (Fig. 1), was chosen as the site

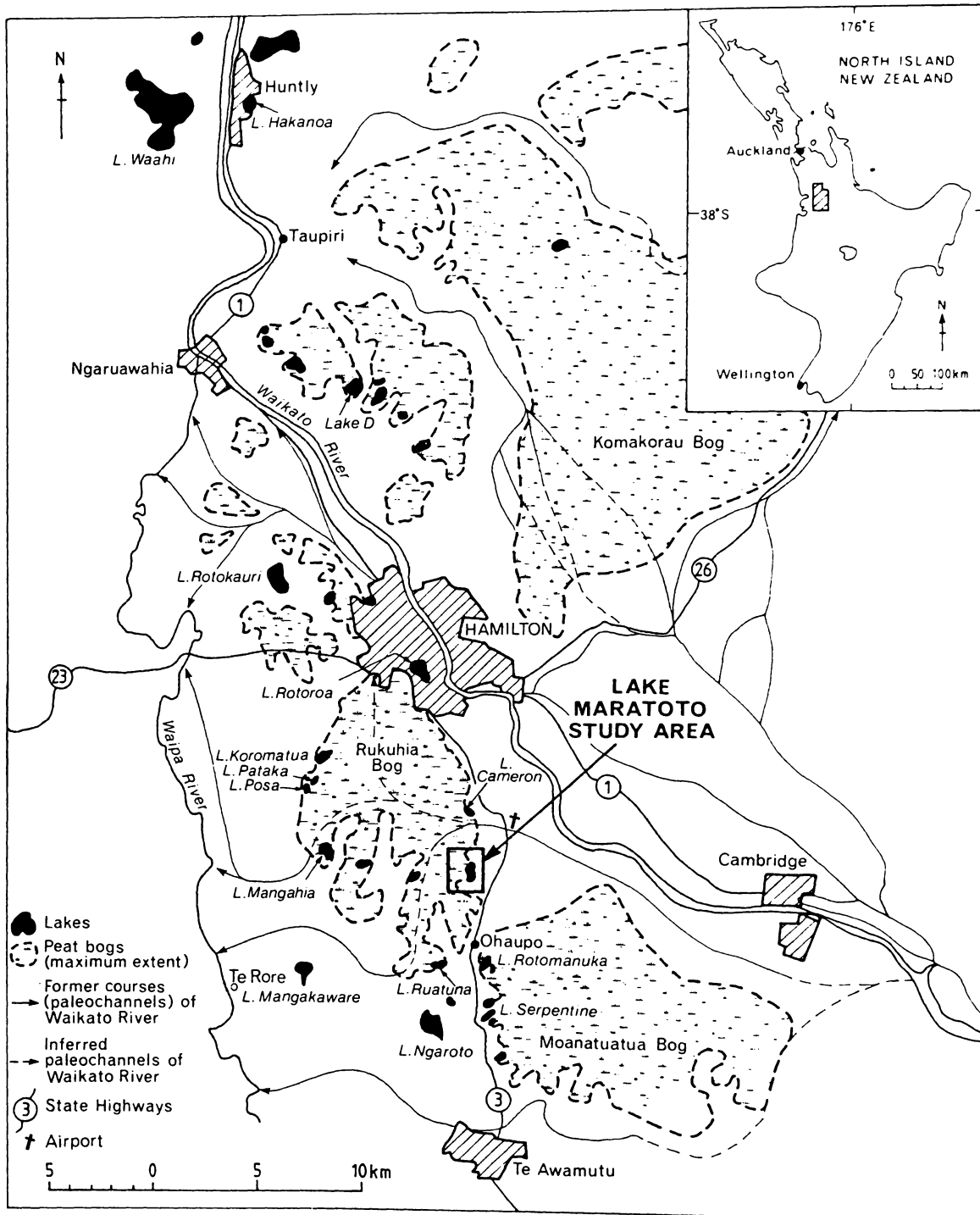


Fig. 1 The Hamilton Basin showing the location of Lake Maratoto and the distribution of other Waikato lakes, peat bogs, and the latest paleochannels of the Waikato River (after McCraw 1967).

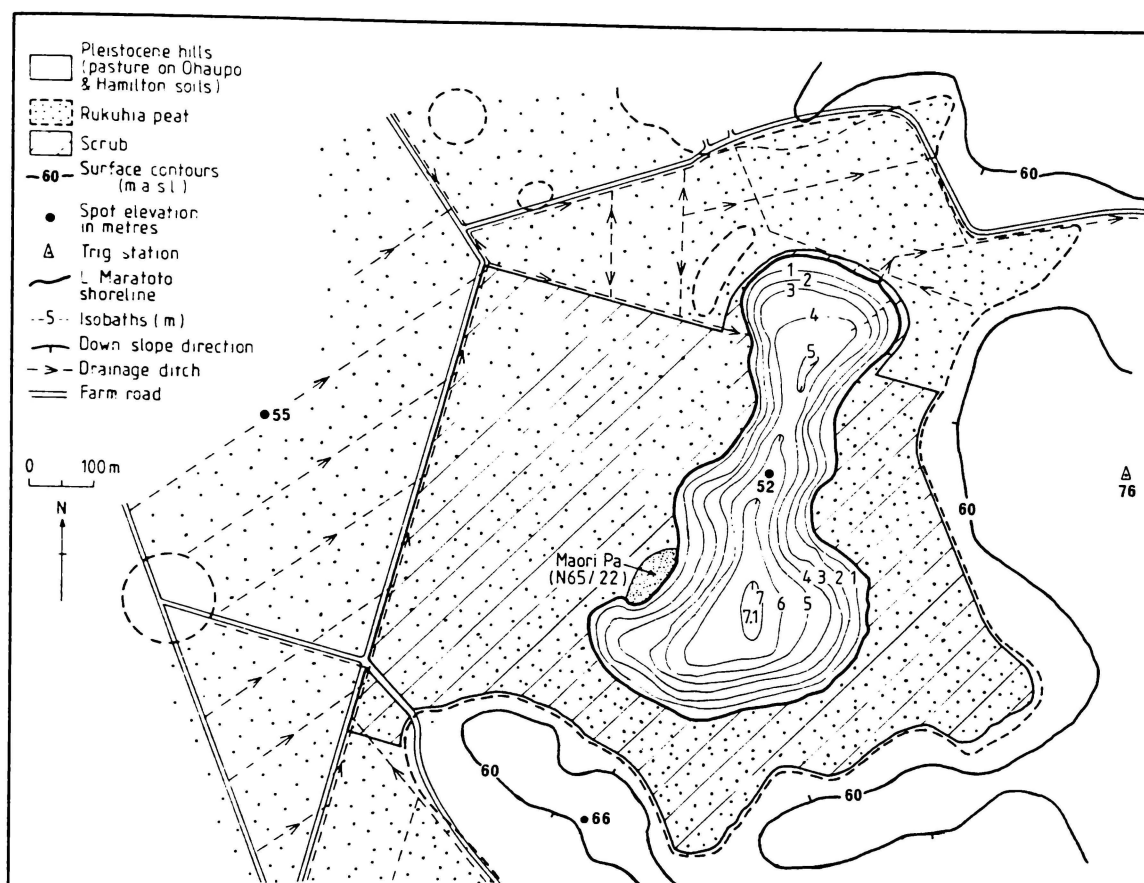


Fig. 2 The present-day Lake Maratoto area. The bathymetry is from Irwin (1982). The drainage ditches are modern, the lake having no outlet in pre-European times.

for initial paleolimnological studies. The purpose of this paper is to establish the age, origin, and developmental history of the lake basin.

Previous accounts of the origins of the lakes in the Hamilton Basin have been based on observations of lakes situated away from peat bogs (e.g., Lakes Rotokauri, Mangakaware, and Ngaroto; Fig. 1). Such lakes were formed when small valleys in low hills were blocked with alluvium (Hinuera Formation) deposited by the Waikato River at about the close of the last glaciation (McCraw 1967). Lakes on the margins of peat bogs, such as Lake Maratoto (and Lakes Cameron, Mangahia, Rotomanuka, and D; Fig. 1), are all situated within or near embayments in the hills, suggesting that they also lie in dammed valleys. However, this cannot be confirmed by observation of the local geomorphology as much of the older landscape in their vicinity is hidden by the blanket of younger peat. It is con-

ceivable that some of these lakes may have been formed by encroaching peat alone, backing up water draining from a valley (Grange et al. 1939). If the lakes did originate as valleys dammed by alluvium, it seems likely that later peat accumulation would have contributed to the form and depth of the present lake basins.

The age of the lakes is unknown, but they could have been formed at any time since the onset of deposition of the Hinuera Formation, which occurred in two phases: Hinuera-1 sedimentation (between c. 65 000 and 20 000 years ago) and Hinuera-2 sedimentation (between c. 20 000 and 12 000 years ago) (Schofield 1965; Hume et al. 1975; McGlone et al. 1978).

We have clarified the mode of origin of Lake Maratoto (and, by implication, other peat lakes in the area) by determining the topography, composition, and age of the surface lying below the lake

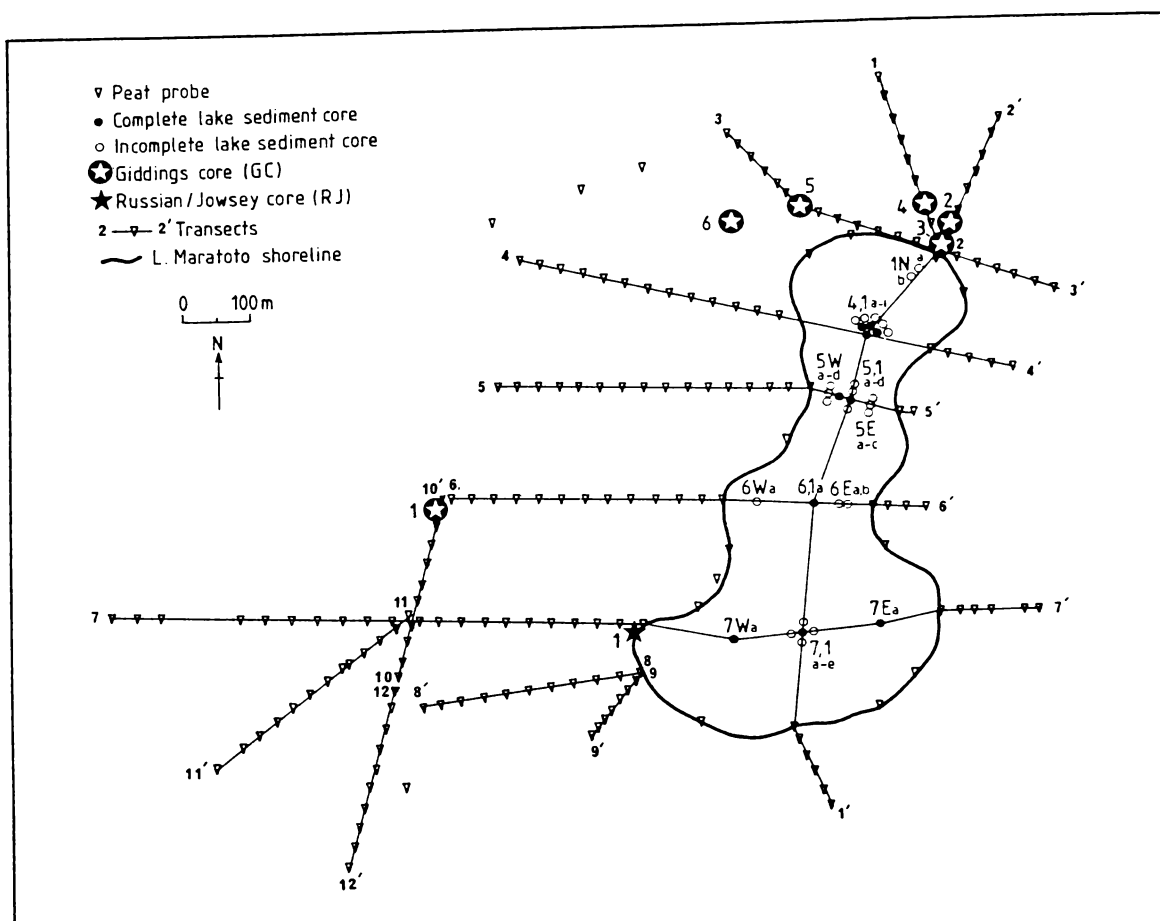


Fig. 3 Locations of transects and probing and coring sites. Lake sediment cores were labelled according to the transect they were on (a number) and their position in the lake (a letter) as follows: western cores (5W; 6W; 7W), eastern cores (5E; 6E; 7E), north cores (1N) and central cores (all on transect 1-1') (4,1; 5,1; 6,1; 7,1). The first core taken at each location was designated a (e.g., 5Wa), the second b (5Wb), and so on (see also Fig. 8).

sediments and surrounding peat. To find the age of the lake we have radiocarbon-dated the base of the lake sediments, and have estimated rates of sedimentation in the lake using the dated tephra in the sediments (Lowe et al. 1980). Utilising this tephrochronology, we also determined variations in the lake's area and depth, and the influence of peat development, from changes in the character of the lake sediment. The results have enabled us to make inferences about some aspects of postglacial climatic change.

Lake Maratoto and its surroundings

Lake Maratoto (37°53'S 175°18'E) lies on the eastern border of the domed ombrogenous Rukuhia

peat bog (23 000 ha) (Fig. 1). The lake, at an elevation of 52 m a.s.l., occupies an embayment in low hills that rise to 76 m a.s.l. immediately to the east of the lake with lower elevations to the north and south (Fig. 2). Such low hills in the Hamilton region consist of weathered Pleistocene tephra, ignimbrites, and volcanoclastic sediments that pre-date deposition of the volcanogenic Hinuera Formation (Kear & Schofield 1978). The lake is surrounded by peat, but to the west and northwest (Fig. 2) the tops of Pleistocene hills emerge above the peat, showing that the surface below is of varied relief. Some of this subpeat surface consists of Hinuera Formation sands and gravels since farm well-drilling showed "sand" 7-10 m below the present peat surface c. 400 m to the west of the lake (B. Davies pers. comm.).

The lake's bathymetry is shown in Fig. 2; its surface area is 16 ha, maximum depth 7.1 m, and volume 535 100 m³.

METHODS

Depths of peat and lake sediment were determined at regular distances along a series of transects (Fig. 3)*.

Surface contours of the peat along these transects were determined by standard levelling techniques with the lake surface (52 m a.s.l) as the datum. Peat depths were measured, usually at 30 m intervals along the transects, with a peat probe fitted with an auger for obtaining a bottom sample. An indication of the type of substrate below the peat was obtained by (1) examining the sample in the auger screw, which sampled clays and muds, and (2) listening to sound transmitted up the probe—gravels and sands were readily identified in this way.

Lake sediment was sampled along the transects (Fig. 3) with a modified Livingstone piston corer. The coring tube was 4 m of 50 mm internal diameter PVC pipe. The lake sediment was described and classified from its colour, consistency, texture, and organic content.

To positively identify substrate types noted during peat probing, seven cores were taken through the peat and into the underlying sediments (Fig. 3). Six of the cores (GC1–GC6) were taken with a Giddings motorised hydraulic drilling rig, and one (RJ1) with a modified Russian/Jowsey D-section manual corer. The particle-size distribution of substrate samples from these cores was analysed by sieve and pipette (Folk 1968), and sand-fraction (2–4 ϕ) compositions were determined by standard methods (see Table 3). Alluvial and colluvial muds and sands beneath the lake sediments were also sampled and particle-size distributions and sand-fraction compositions were similarly determined. Ashy horizons found in the peat column, and in the lake sediment cores below Rerewhakaaitu tephra (i.e., additional to the tephra described by Lowe et al. 1980), were correlated with known tephra mainly from their ferromagnesian mineralogy; the identification of one tephra (Waiohau Ash) was confirmed by electron microprobe analysis of its glass shards (see Table 2).

Sixteen samples of the lake sediment were collected to date the major tephra layers and other significant horizons in the core (e.g., the base of the lake sediment). These samples were composites of several 1 cm thick slices of sediment taken above and below the tephra in suitable cores from throughout the lake. The tephra, identified by Lowe et al. (1980), were correlated from core to core by their distinctive colour, thickness, lithology, and stratigraphic position. (Several of the tephra identifications of Lowe et al. (1980) were

*Some of these transects have also been profiled using subsurface interface radar in a separate study by Lowe (1985, this issue), evaluating the effectiveness of the radar method for this sort of work.

Table 1 Dominant ferromagnesian mineral abundances* in Mamaku Ash, Rotoma Ash, and Waiohau Ash at Lake Maratoto.

Tephra	Sample†	Ferromagnesian silicate minerals (summed to 100%)					Opagues (vol%)‡
		Hyp	Aug	Hbe	Cgt	Bio	
Mamaku Ash	1	75	8	17	tr	0	19
	2	56	10	34	0	0	32
Rotoma Ash	3	57	29	4	10	tr	25
	4	49	27	11	13	0	8
Waiohau Ash	5	73	2	24	0	1	34
	6	52	18	27	tr	3	27
	7	58	7	31	0	4	42

*Determined by point-count of the 2–4 ϕ (250–63 μ m) size fraction of the heavy mineral assemblage (≥ 2.95 g/cm³). Between 200 and 500 grains were counted.

†1 = peat core RJ1-2; 2 = Lake Maratoto core 4,1b; 3 = Lake Maratoto core 4,1b; 4 = Lake Maratoto core 4,1f; 5 = peat core RJ1-3; 6 = Lake Maratoto core 4,1b; 7 = Lake Maratoto core 4,1d.

‡Proportion of opaque minerals (mainly titanomagnetite) in 2–4 ϕ heavy mineral fraction.

Hyp = hypersthene; Aug = augite; Hbe = calcic hornblende; Cgt = cumingtonite; Bio = biotite; tr = trace (< 1%).

Table 2 Electron microprobe analyses* of glass from Mamaku Ash, Rotoma Ash, Waiohau Ash, and Rotorua Ash in peat and lake sediment cores from Lake Maratoto or Lake Rotomanuka. The analyses are presented on a normalised 100% loss free basis.

	1	2	3	4	5
SiO ₂	78.87 (0.50)	78.63 (0.16)	78.32 (0.33)	78.61 (0.30)	77.57 (0.58)
Al ₂ O ₃	12.05 (0.17)	12.33 (0.10)	12.38 (0.13)	12.35 (0.13)	12.68 (0.32)
TiO ₂	0.12 (0.02)	0.10 (0.05)	0.11 (0.05)	0.13 (0.03)	0.21 (0.05)
FeO†	0.87 (0.07)	0.87 (0.07)	0.87 (0.07)	0.92 (0.08)	1.26 (0.09)
MgO	0.10 (0.02)	0.12 (0.02)	0.10 (0.03)	0.14 (0.01)	0.20 (0.08)
CaO	0.69 (0.10)	0.71 (0.07)	0.82 (0.05)	0.89 (0.04)	1.20 (0.33)
Na ₂ O	3.80 (0.20)	3.76 (0.06)	3.55 (0.16)	3.60 (0.28)	3.55 (0.29)
K ₂ O	3.38 (0.43)	3.37 (0.09)	3.73 (0.41)	3.26 (0.10)	3.19 (0.44)
Cl	0.12 (0.02)	0.11 (0.05)	0.12 (0.01)	0.10 (0.03)	0.14 (0.03)
Water‡	1.13 (1.40)	0.70 (0.43)	3.05 (1.58)	4.99 (3.00)	7.07 (1.71)
n	14	10	11	10	10

1 = Mamaku Ash (Lake Rotomanuka, core A); 2 = Rotoma Ash (Lake Rotomanuka, core C); 3 = Waiohau Ash (peat core RJ1-3, Lake Maratoto); 4 = Waiohau Ash (Lake Rotomanuka, core A); 5 = Rotorua Ash (Lake Rotomanuka, core A).

n = number of analyses in mean (each analysis was done on a different shard); numbers in parentheses are 1 standard deviation. The location of Lake Rotomanuka is shown in Fig. 1; cores A & C were taken from near grid ref. (NZMS 260) S15/136615.

*Glass shards in the 2-4 ϕ size fractions were separated and purified using heavy liquids and Frantz electromagnetic methods, embedded in epoxy resin, polished, carbon coated, and analysed with a JEOL JXA-733 SUPERPROBE at the Analytical Facility, Victoria University of Wellington (Froggatt & Gosson 1982). All samples were analysed using an 8.0 nA beam current with either a 10 μ m or 20 μ m beam diameter, and peak counts of 3 \times 10⁵ s (measured). Repeated analysis of glass standards (KN-18 comendite glass; VG-99 basaltic glass; VG-568 rhyolite glass) gave a check on probe calibration and operation. There was probably some loss of Na and water by volatilisation (see also Froggatt 1983). Concentrations are given in oxide weight percent except Cl which is in atomic weight percent. Data are from D. J. Lowe (in prep.): "Stratigraphy, chronology, and correlation of late Quaternary rhyolitic and andesitic tephra interbedded with organic lake deposits in the Waikato region, North Island, New Zealand".

†All Fe calculated as FeO.

‡Difference between analytical total and 100.

provisional, and modifications based on new mineralogical and glass chemistry data (Table 1 and 2) are noted below.) Slices of peat 5 cm in thickness from the bottoms of cores RJ1 and GC1 were also collected. The samples were submitted for C-14 dating at the University of Waikato Radiocarbon Dating Laboratory (symbol Wk). All the dates presented and discussed in this paper are conventional and are based on the old (Libby) half-life of 5568 years (Hogg 1982).

STRATIGRAPHY

Peat and prepeat deposits

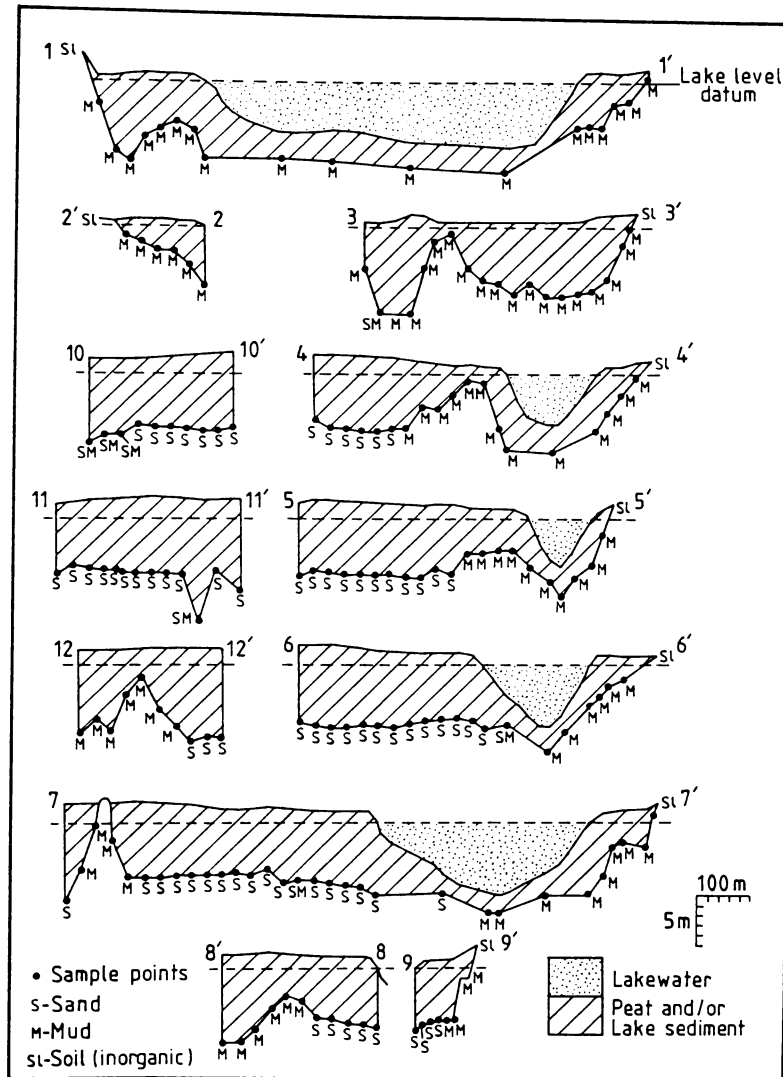
To the north and northwest of the lake (transects 1-1', 3-3', 4-4'; Fig. 4), peat depths are relatively shallow (1-4 m) and the subpeat deposits consist of greenish-blue to greyish-brown, sometimes gritty, muds. Further to the west and southwest, the peat deepens to 7-8 m and the subpeat materials are sands and gravels with a relatively flat surface (transects 5-5', 6-6', 7-7', 10-10', 11-11'; Fig. 4).

Between the lake and the hills to the east and south of the lake, the peat is less than 4 m thick. It shallows towards the hills and is underlain by muds similar to those beneath the peat to the north and west of the lake (transects 1-1', 2-2', 3-3', 4-4', 5-5', 6-6', 9-9'; Fig. 4).

Core GC1 (Fig. 5) shows that the subpeat materials to the west of the lake consist of at least 5.5 m of Hinuera Formation and are overlain by 8 m of fibrous peat. The base of the peat in GC1 has been dated (Wk553) at 10 600 \pm 90 years B.P. (see Fig. 9).

In core RJ1, at the southwestern lake edge, the subpeat sediments consist of a thin (10 cm) layer of greenish-grey mud passing down to sand of the Hinuera Formation (Fig. 5). There is more vertical variation in the texture of the peat in RJ1 than in GC1, but fine lake sediment is not present. Basal peat in RJ1 has been dated (Wk534) at 15 200 \pm 130 years B.P. Three diffuse ashy horizons, of about 10-20 mm thickness, were found in the RJ1 core. The top one (RJ1-1; Fig. 5) is identified as Taupo Pumice from its field character (vesicular, fine

Fig. 4 Transect profiles (vertical exaggeration $\times 20$) produced by combining the levelled lake sediment and peat probe depths. Lake sediment thickness was taken to be the thickness of sediment plus tephra layers between the top of the consolidated lake sediment above the Taupo tephra and the junction between the muds below the Rerewhakaaitu tephra (names and stratigraphy of the tephras are given in Fig. 8). Because of its sloppy nature, some of the sediment above the Taupo tephra was occasionally not sampled or was lost during coring, and sometimes the bottom alluvial mud layer was not quite reached. In these cases, total sediment thickness was obtained by adding estimated sediment thicknesses above the Taupo tephra and below the Rerewhakaaitu tephra. These estimates were calculated from sedimentation rates in the sediment immediately above and below these tephras respectively, provided the core included all the tephras between and including the Taupo and Rerewhakaaitu. The estimates were corroborated from sediment thicknesses in more complete nearby cores.



pumice lapilli) and persistent occurrence within a metre of the bog's surface. The middle (RJ1-2) and lowest (RJ1-3) ashy horizons both have a ferromagnesian mineralogy consistent with a source from the Okataina Volcanic Centre (Table 1; Lowe et al. 1980), and are probably Mamaku Ash and Waiohau Ash, respectively. The identification of the lowest tephra as Waiohau Ash was supported by the major element chemistry of its glass (Table 2). The only viable alternative, Rotorua Ash (c. 13 400 years), has distinctly more TiO_2 , FeO , MgO , and CaO than Waiohau Ash (Fig. 6) and hence is a less-likely correlative.

Cores GC2-5 to the north and northwest of the lake all showed similar features (Fig. 5). The peat column consists entirely of fibrous, sometimes woody, peat, occasionally with two diffuse ash layers. In GC2 these are identified as the Taupo (top) and the Mamaku tephras; in GC3 they are probably the Mamaku and Waiohau tephras. The sub-peat materials consist of about 1 m of moderately weathered gritty mud (upper unit) unconformably overlying at least 3 m of stongly weathered clay (lower unit) (Fig. 5). Upper unit samples (U-1 to U-4) are texturally similar (sandy mud or sandy silt; Fig. 7A). Their grading curves (Fig. 7B) closely

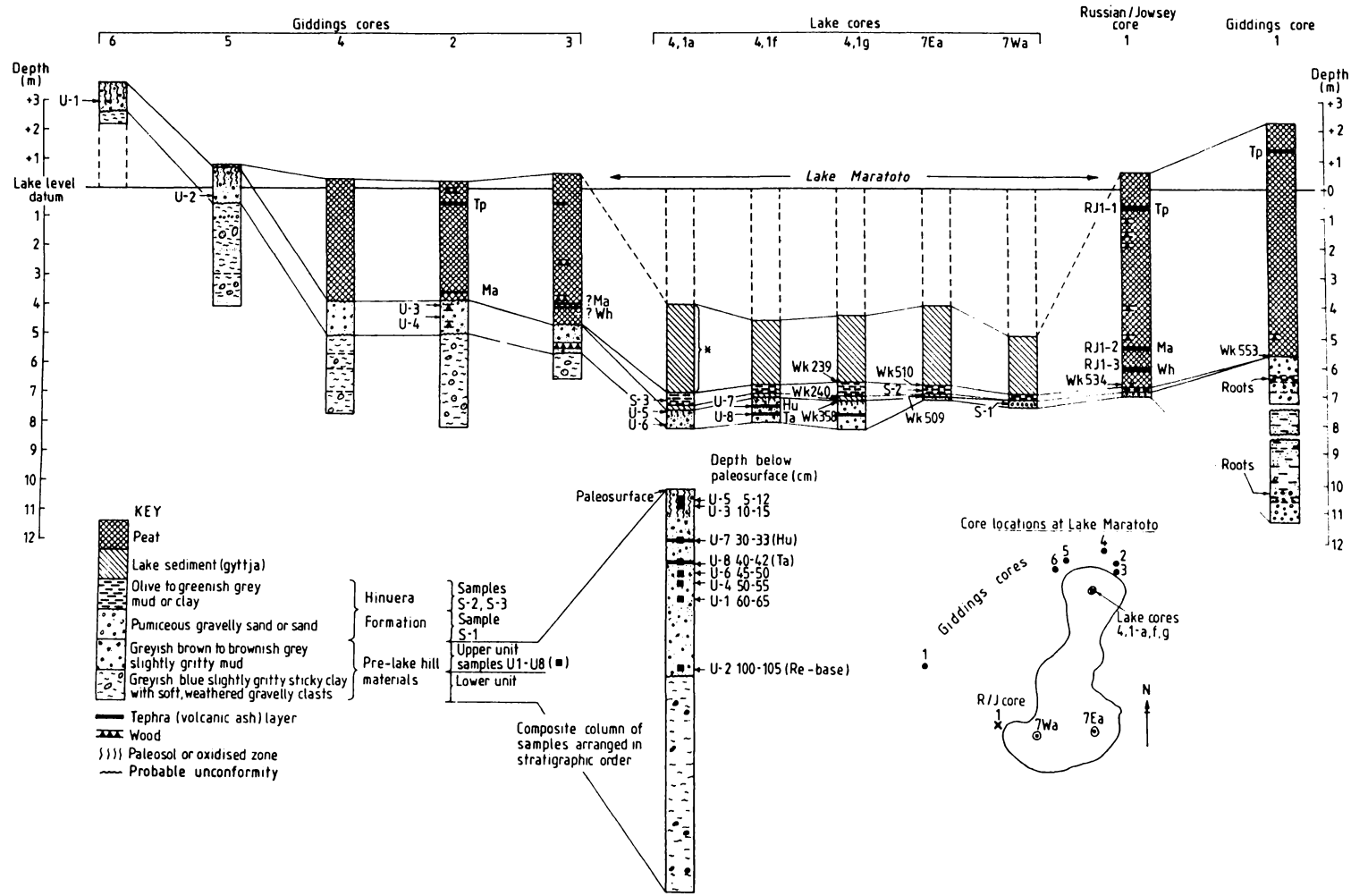


Fig. 5 Diagram showing the stratigraphy of the peat cores and correlation of the subpeat and subgyttja deposits, and the positions from which samples for C-14 assay (Wk) or compositional analysis (S-1 to S-3, U-1 to U-8, RJ1-3) were taken. Tephra symbols and names are: Tp, Taupo Pumice; Ma, Mamaku Ash; Wh, Waiohau Ash; Hu, Hauparu Tephra; Ta, Tahuna Tephra; Re, Rotoehu Ash.
 *The tephrostratigraphy of this part of the cores, based on Lowe et al. (1980), is shown in Fig. 8, and sampling positions for C-14 dates are shown in Fig. 9.

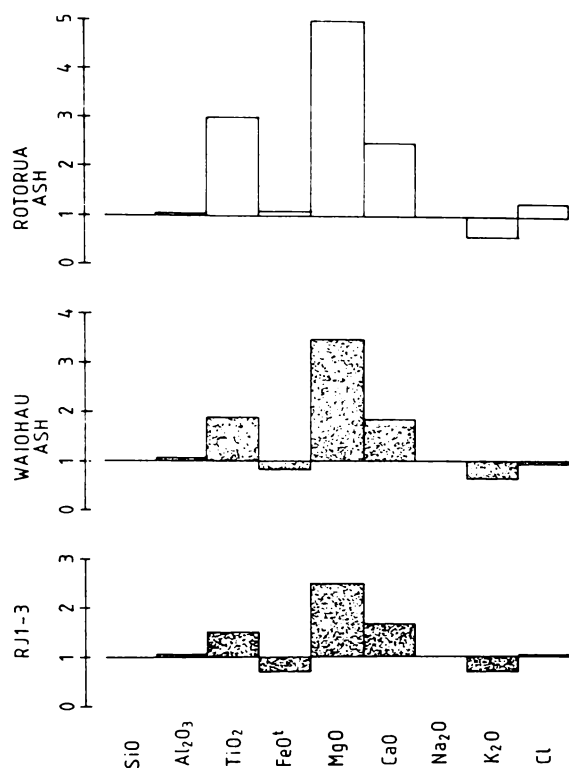


Fig. 6 Chemical composition of glass in peat core sample RJ1-3 compared with that in samples of Waiohau Ash and Rotorua Ash (data from columns 3, 4, and 5 in Table 2, respectively). The histograms are plots of ratios of element concentrations in the samples to concentrations of the same elements in Yellowstone Rhyolite Glass standard VG-568 (the method of plotting ratios is after Sarna-Wojcicki et al. 1984). RJ1-3 is better matched to Waiohau Ash, its probable correlative, than to Rotorua Ash.

match those of late Pleistocene tephtras that mantle the Pleistocene hills in the area. The sand mineralogical analyses (Table 3) confirm that the upper unit consists of late Pleistocene tephtras. The top part (U-3) is probably largely derived from (?)Hauparu tephtra; the middle to bottom parts (U-4, U-1, and U-2) are mainly derived from (?)Tahuna tephtra mixed with Rotoehu tephtra (Table 3; Fig. 7D). The lower unit consists of strongly weathered materials deposited considerably before Rotoehu tephtra, hence is not considered further.

Lake sediment and prelake-sediment deposits

The stratigraphy, lithology, and chronology of the cores are given in Fig. 8. Complete cores penetrated to sublake-sediment muds and sands; other

cores were incomplete but could be matched with the rest using the tephtras as stratigraphic markers.

Complete cores all have an upper part consisting of 2–3 m of lake sediment (mainly dy-gyttja and gyttja, or peat in shallow-water cores) containing a series of thin (1–40 mm) tephtra layers, and a lower part of either about 1 m of olive to greenish-grey fine mud (in middle and northern cores) or up to about 50 cm or less of alternating greyish-white mud and unweathered pumiceous sand layers (in cores from the southwest of the lake). The junction between the gyttja and the underlying muds and sands is taken as marking the origin of the present-day lake.

Particle-size analysis (Fig. 7A, C) of three samples (S-1 to S-3) of these subgyttja materials (sand, mud, and clay, respectively) show a fining trend eastward and northward in the lake basin (evidenced also in Fig. 8). There is thus a gradation in the subpeat and subgyttja deposits from coarse gravelly sands west of the lake at GC1, through sands at the base of RJ1 and the lake cores from the western side of the lake (cores 7W, 6W), to muds fining to clays in the eastern and northern parts of the lake. We interpret these muds and clays as a fine lithofacies of the Hinuera Formation deposited from suspension. This view is supported by the grading curves plotted in Fig. 7C that show that S-1 is similar to Hinuera lithofacies C2 (of Hume et al. 1975), while S-2 and S-3 apparently represent a finer variant of their lithofacies D. The C-14 dates straddling the Hinuera muds and clays (Wk239, 510; Wk240, 509; Fig. 9) show that these were deposited relatively rapidly between c. 16 000 and c. 17 000 years ago. This time is around that of the last stages of vigorous Hinuera-2 deposition in the Hamilton Basin (McGlone et al. 1978).

The 10 cores that penetrated beneath the Hinuera muds or sands have a thin layer (5–15 cm) of olive gyttja overlying up to 80 cm of gritty mud, usually with a dark 20 cm thick paleosol-like top containing two or three diffuse grey ashy layers (Fig. 8). We interpret the thin gyttja layer as having been deposited in a relatively shortlived proto-Lake Maratoto (see "Developmental history").

The composition of the gritty muds (samples U-5 to U-8; Fig. 5) below the proto-Lake Maratoto gyttja matches that of the subpeat upper unit materials (Fig. 7A, B, D; Table 3). Hence they are also Pleistocene hill materials and are contiguous with the subpeat materials.

All these Pleistocene hill material samples (U-1 to U-8) thus appear to consist chiefly of Hauparu, Tahuna, and Rotoehu tephtras, which are aged between c. 37 000 and c. 40 000–50 000 years (Fig. 7D, 8). Neither Okareka Ash, aged between c. 17 000 and c. 20 000 years (Vucetich & Pullar 1969;

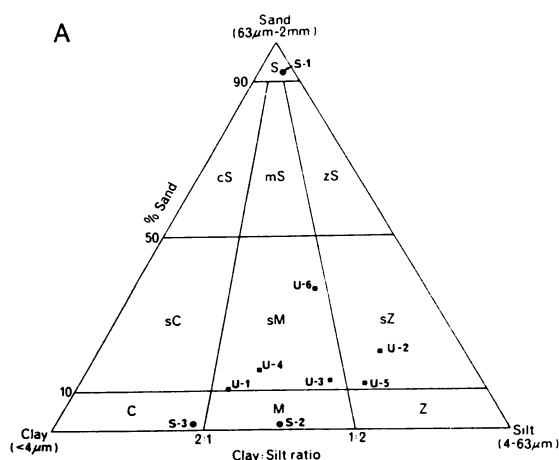
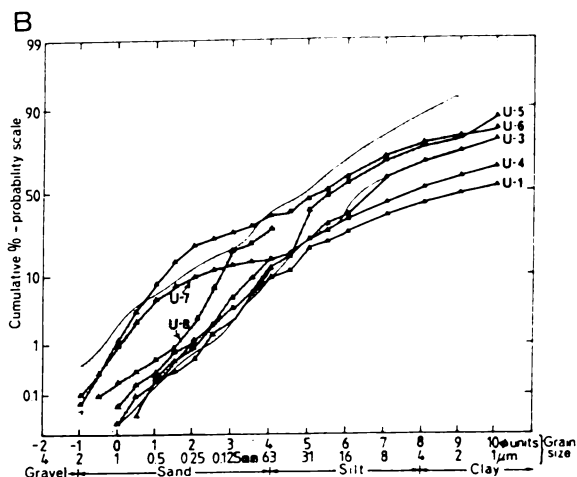


Fig. 7 Compositional analyses of the subpeat and sublake materials.

A Triangular textural plot for samples S-1 to S-3 (Hinuera Formation) and U-1 to U-6 (subpeat and subgyttja Pleistocene hill materials). Textural classes (from Folk 1968) are: S, sand; s, sandy; Z, silt; z, silty; M, mud; m, muddy; C, clay; c, clayey. Sample S-1 is a slightly gravelly sand.



B Comparison of the particle-size distributions of upper unit materials (U-1, U-3 to U-8) with those of late Pleistocene tephra from the Waikato region (stippled band). The latter Waikato samples (30) comprise tephra aged from c. 17 000 to c. 40 000–50 000 years (see Table 3; data from Lowe 1981).

Pullar et al. 1973), nor Kawakawa Tephra, aged c. 20 000 years (Vucetich & Howorth 1976a), are recognised (Table 3; Fig. 7D), although both are known to have been deposited in the region (Pullar & Birrell 1973; Lowe 1981). So it seems that there is a disconformity, possibly of up to about 20 000 years duration, between the proto-Lake Maratoto gyttja and the Pleistocene paleosurface, a suggestion supported by the moderately weathered and paleosol-like character of the paleosurface.

Lowe et al. (1980) identified the series of tephra layers above the Hinuera mud in core 4,1b. The tephra that were provisionally identified as ?Rotoma Ash and Unnamed ash by Lowe et al. (p. 483) are reidentified here as Mamaku Ash and Rotoma Ash, respectively. Mamaku Ash, dated at (Wk227) 6830 ± 90 years B.P. (Fig. 9), is characterised by its Okataina-derived ferromagnesian mineralogy (Table 1) and glass chemistry (Table 2; cf. analyses in Cole & Nairn 1975 and Kohn 1979). Rotoma Ash, with dates of (Wk522) 8370 ± 90 years B.P. and (Wk523) 8350 ± 100 years B.P. (Fig. 9), contains the diagnostic amphibole, cummingtonite (Table 1; Hogg & McCraw 1983). Its glass chemistry is listed in Table 2.

The Taupo, Tuhua, Mamaku, Opepe, Mangamate, Waiohau, Rotorua, and Rerewhakaaitu tephra were readily discernible in cores from throughout the lake (Fig. 8) and were used to calculate sedimentation rates during the lake's his-

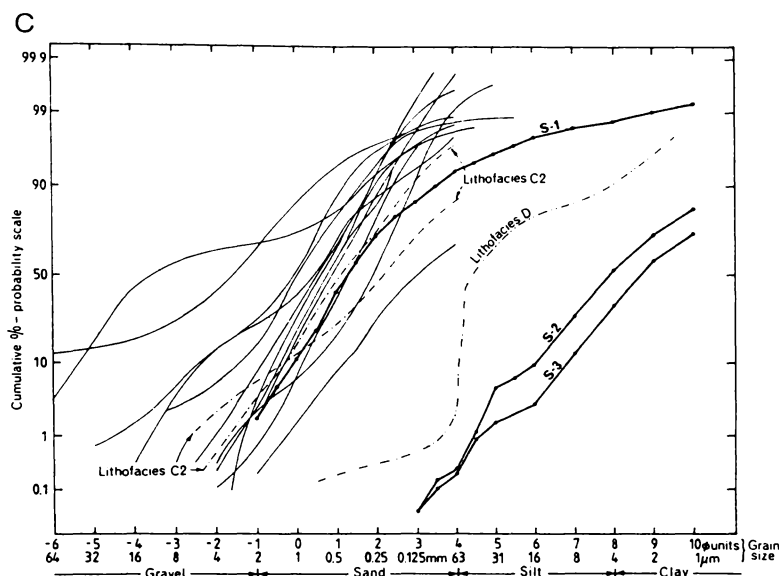
tory. Dates on gyttja associated with all these tephra, including 11 dates not published in Lowe et al. (1980), are given in Fig. 9. Dates on the gyttja above and below the Hinuera muds, and on the proto-Lake Maratoto gyttja, are given also.

The C-14 dates obtained on the tephra used as markers, apart from those for the Waiohau Ash, closely match dates on the same tephra elsewhere (Topping 1973; Pullar et al. 1973; Nairn 1980; Hogg & McCraw 1983)*. This agreement indicates that the chronology for the lake's developmental history may be regarded in large part as reliable, as the independently dated tephra provide a check on the accuracy of the radiocarbon dates (an important consideration for projected paleoecological and paleolimnological studies; Mathewes & Westgate 1980). The Waiohau Ash has been previously dated at (NZ568) $11\,250 \pm 200$ years B.P., (NZ878) $11\,100 \pm 210$ years B.P., and (NZ1135) $11\,800 \pm 150$ years B.P. (Pullar & Heine 1971) and has a generally accepted age of c. 11 300 years (Pul-

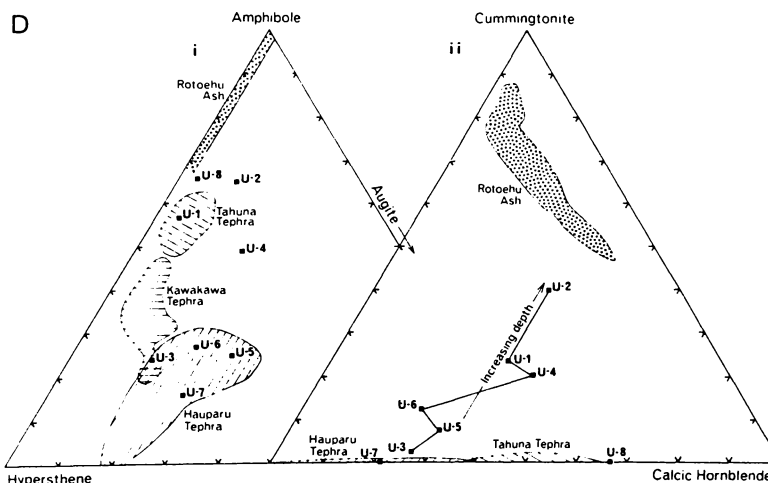
*The dates obtained on Rotoma Ash (which was not used as a stratigraphic marker) differ markedly from previous age estimates of c. 7000–7300 years by Pullar & Heine (1971) and Pullar et al. (1973), but are better matched with the date of (NZ1945) 8860 ± 120 years B.P. given by Nairn (1980). This latter date is significantly older than our dates, however, hence the specific age of the Rotoma Ash eruption is uncertain.

Fig. 7 (continued).

C Particle-size distribution of subgyttja alluvial samples S-1 to S-3. Grading curves of various lithofacies of Hinuera Formation sediments are shown for comparison (mainly after Hume et al. 1975; the majority of the unlabelled curves represent lithofacies A1 or C1).



D Ternary diagrams comparing relative abundances of ferromagnesian minerals (summed to 100%, see also Table 3) of upper unit tephric materials (U-1 to U-8) with those of some late Pleistocene tephras that are their possible correlatives. On this basis, the bulk of the upper unit is probably derived from Hauparu Tephra, aged c. 37 000 years; Tahuna Tephra, aged c. 38 000 years; and Rotoehu Ash, aged c. 40 000–50 000 years (McGlone et al. 1984b; see C-14 dates in Fig. 8). In diagram i, amphibole consists of calcic hornblende plus cummingtonite. Rotoehu Ash is characterised by a high cummingtonite content (diagram ii—Lowe 1981; Hogg & McCraw 1983). Data sources for the mineralogies of the late Pleistocene tephras are given in note (d) of Table 3.



lar & Birrell 1973). The average age of 12 400 years we obtained for Waiohau Ash in Lake Maratoto is significantly older than this. This difference in age may result from an "error" in the Lake Maratoto dates due to contamination by redeposited organic material (cf. Björck & Håkansson 1982). Alternatively, the previous ages on the Waiohau Ash, all determined on charcoal which is very susceptible to contamination (Hogg 1982), may be underestimates. We prefer the older age (12 400 years), but the age discrepancy nevertheless signifies that the chronology in this zone of the cores is less certain than in the others.

LAKE SEDIMENT CHARACTERISTICS AND SEDIMENTATION RATES

The characteristics of the four types of lake sediment described are summarised in Table 4. Since the bulk of the sediment probably originates in the catchment, as in other small lakes (e.g., Mackereth 1966), we have made broad inferences about conditions in the catchment using this classification. In addition, we use sedimentation rates to indicate rates of erosion in the catchment.

Sediment type 1 (T1), largely inorganic, suggests that catchment soils had a low organic content with

Table 3 Mineralogical composition of the sand fractions of subpeat and subgyttja samples at Lake Maratoto*. Compositions of some widespread late Pleistocene tephras (note d below) and Hinuera Formation sediments are included for comparison with upper unit (U-1 to U-8) and Hinuera (S-1) samples, respectively. Some of the ferromagnesian mineralogical data is plotted in Fig. 7D.

Samples	Heavy minerals ^a					Accessory minerals (as % of heavy minerals)		Light minerals ^b (relative abundances)
	Ferromagnesian silicate minerals (summed to 100%)					Zir	Mag	
	Hyp	Aug	Hbe	Cgt	Bio			
Hinuera^c								
S-1	65	17	17	0	1	tr	12	$g \geq f > q$
Hinuera Formation ^d	75	8	14	0	3	0	38	$g \geq f \geq q \gg l$
Upper unit (cm)[†]								
U-5 (5-12)	45	30	20	5	0	2	5	$g \geq f \geq q$
U-3 (10-15)	60	15	21	2	2	1	18	$g \geq f \geq q$
U-7‡ (30-33)	59	25	16	0	0	2	6	$g \geq f > q$
U-8‡ (40-42)	31	3	65	1	0	3	17	$g \geq f > q$
U-6 (45-50)	51	22	18	9	0	2	9	$g \geq f \geq q$
U-4 (50-55)	31	20	33	16	0	2	7	$g \geq f \geq q$
U-1 (60-65)	40	4	34	22	0	1	18	$g \geq f \geq q$
U-2 (100-105)	24	11	30	35	0	tr	14	$g \geq f \geq q$
Tephra^d								
Okareka Ash ^{2, 3}	16-23	1-9	20-61	0-1	19-49	5	30	$g \geq f \geq q$
Kawakawa Tephra ^{3, 4}	41-62	2-20	23-53	0	0-2	1-2	33-38	$g \geq f > q$
Hauparu Tephra ^{5, 6}	38-83	15-38	0-32	0-1	0	nd	nd	nd
Tahuna Tephra ^{3, 4, 7}	32-60	tr-12	26-65	0-2	0-2	1-3	47-54	$g \geq f \geq q$
Rotoehu Ash ^{4, 5, 7}	7-16	0-2	1-44	47-91	0-2	1-3	28-51	$g \geq f > q$
"Composite" ^{e, 4}	30-39	11-21	24-29	16-31	0-2	1-2	32-67	$g \geq f > q$

a = S.G. > 2.9 g/cm³: Hyp = hypersthene; Aug = augite; Hbe = calcic hornblende; Cgt = cummingtonite; Bio = biotite; Zir = zircon; Mag = predominantly titanomagnetite.

b = S. G. < 2.9 g/cm³: g = glass (and rare pumice); f = feldspars (mainly plagioclase); q = quartz; l = lithics.

c = Hinuera Formation sediments are volcanogenic with diverse mineralogy. Data source: 1 = Hume et al. (1975).

d = Widespread rhyolitic tephras of c. 17 000 - c. 50 000 years age range that are predicted to be the most likely constituents of the Upper unit. Values show the characteristic range of mineral abundances in each tephra from various localities in the North Island. Data sources and locations are: 2 = D. J. Lowe, unpublished data (Lake Rotomanuka, Fig. 1); 3 = Howorth et al. (1980) (Poukawa; Gavin Road; Whangamata Road; Okataina area); 4 = Lowe (1981) (Waikato); 5 = Hogg & McCraw (1983) (Coromandel); 6 = McGlone et al. (1984b) (Bay of Plenty-Gisborne); 7 = Vucetich & Howorth (1976b) (Taupo). Data in the "Accessory minerals" and "Light minerals" columns are derived wholly from references 2 and 4 above.

e = "Composite" refers to a composite of pedogenically mixed late Pleistocene and Holocene tephras that occur as c. 50-150 cm thick cover bed deposit on the low hills in the Hamilton City-Lake Maratoto area (Lowe 1981).

*Sands (2-4φ) were fractionated by sieve and heavy liquid separation methods and analysed by standard petrological microscope (point-count) and X-ray diffraction procedures.

†Depth of sample below base of peat or paleosurface.

‡U-7 and U-8 occur as discrete, apparently pure tephra layers and probably represent the Hauparu Tephra and Tahuna Tephra, respectively (see text).

tr = trace amount (< 1%); nd = not determined.

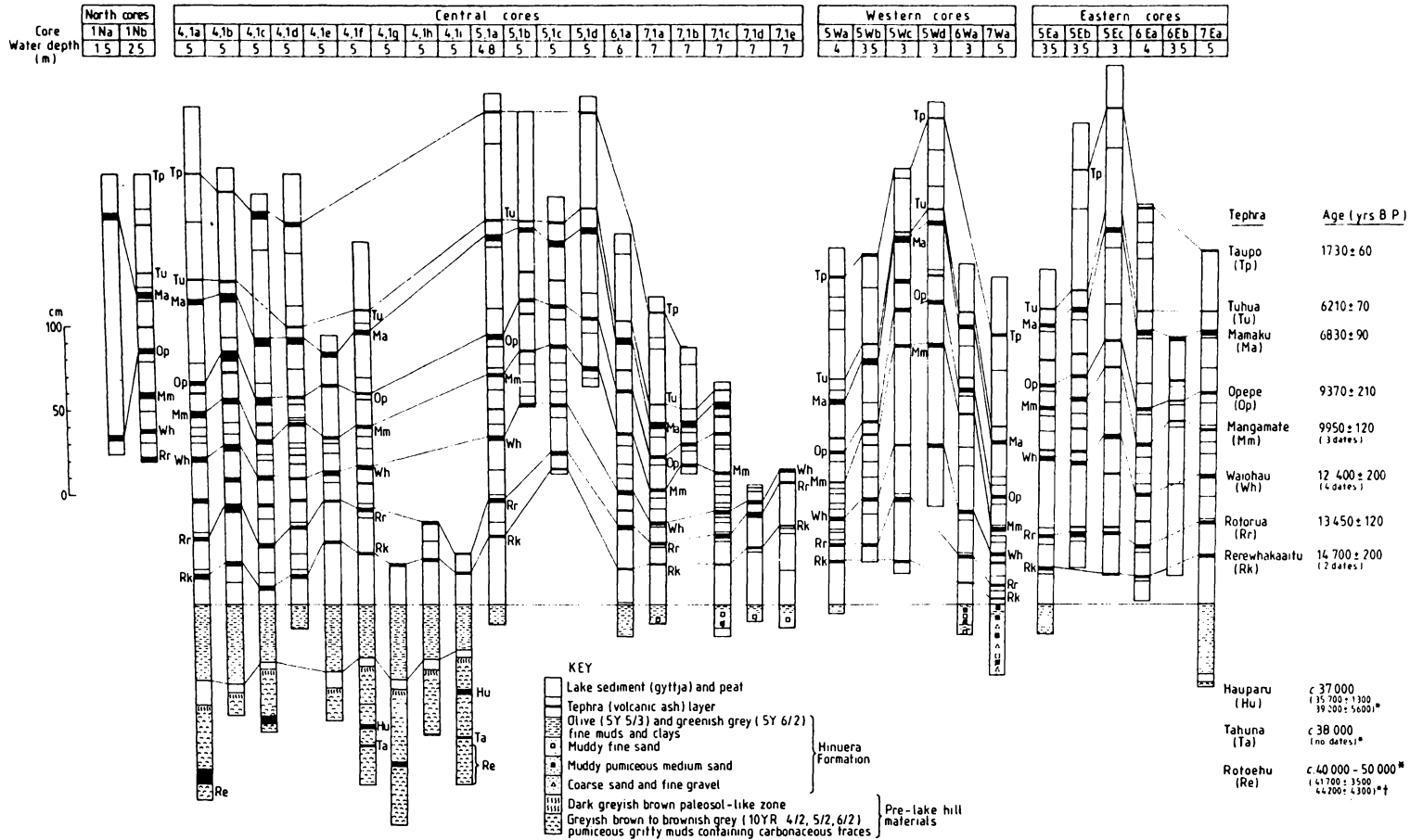


Fig. 8 Stratigraphy, lithology, and chronology of the lake sediment cores. Coring locations are shown in Fig. 3. Tephra identifications are based on Lowe et al. (1980) and work currently in progress (see text and Tables 1-3). The majority of the tephras are derived from the Okataina and Taupo Volcanic Centres; others originate from Mayor Island, Tongariro, and probably Mount Egmont sources. Ages of the distinctive tephras used throughout the lake as time planes (right-hand column) are from Fig. 9. Sediment descriptions generally follow Folk's (1968) nomenclature. The colours are based on Munsell notation.

*Ages from McGlone et al. (1984b, table 1, p. 333). †Ages from Pullar & Heine (1971) and McGlone et al. (1984b).

Tephra	Waikato Radiocarbon Dating Laboratory No	Age (years B.P.) ¹		Sample ²
		T _{1/2} OLD	T _{1/2} NEW	
Taupo Pumice	Wk 215 [#]	1730 ± 60	1750 ± 60	g
Tuhua Tephra	Wk 214 [#]	6210 ± 70	6420 ± 70	g
Mamaku Ash	Wk 227	6830 ± 90	7050 ± 100	g
Rotoma Ash	Wk 523 Wk 522	8350 ± 100 8370 ± 90	8600 ± 100 8620 ± 100	g g
Opepe Tephra	Wk 230	9370 ± 210	9680 ± 220	g
Mangamate Tephra	Wk 231 Wk 232 Wk 213 [#] Wk 553 [†]	9700 ± 140 10000 ± 120 10120 ± 100 10600 ± 90	10000 ± 140 10400 ± 120 10440 ± 100 10950 ± 90	g g g p
Waiohau Ash	Wk 516 Wk 233 Wk 234 Wk 515	12300 ± 190 12200 ± 230 12500 ± 190 12450 ± 200	12700 ± 190 12600 ± 240 12900 ± 200 12810 ± 200	g g g g
Rotorua Ash	Wk 511	13450 ± 120	13850 ± 120	g
Rerewhakaaitu Ash	Wk 237 [#] Wk 238 [#] Wk 534 [†]	14700 ± 220 14700 ± 180 15200 ± 130	15200 ± 230 15200 ± 190 15650 ± 140	g g p
	Wk 239 Wk 510	16300 ± 250 15850 ± 130	16800 ± 270 16300 ± 130	g g
Hinuera Formation (overbank mud deposits)				
	Wk 509	16200 ⁺³⁶⁰ -340	16650 ⁺³⁷⁰ -350	g
Proto-Lake Maratoto gyttja	Wk 240	16900 ± 470	17500 ± 490	g
Paleosol	Wk 358	17050 ± 200	17620 ± 210	g
Pre-lake hill materials				

Fig. 9 Summary of radiocarbon dates on gyttja and peat deposits in the Lake Maratoto area.

¹All ages discussed in the text are old half-life dates.

²g = gyttja; p = peat.

*Dates published by Lowe et al. (1980).

[†]Samples of basal peat in cores GC1 and RJ1 (Fig. 5) — stratigraphic positions inferred from ages. Peat sample Wk114 (10 250 ± 90 years B.P.) was collected from the base of the Rukuhia bog at 8.3 m depth about 6 km northwest of Lake Maratoto (near grid ref. S15/076694); sample Wk115 (10 750 ± 90 years B.P.; McGlone et al. 1978) was collected at 9 m depth about 3 km north of Lake Maratoto (near S15/119691) (A. G. Hogg pers. comm. 1983). Grid references are based on the national 1000 m grid of the topographical map series (NZMS 260).

Table 4 General descriptions of four classes of lake sediment in Lake Maratoto.

Type	Sediment description	Munsell colour notation (range)	Organic matter %*	Occurrence in present-day Lake Maratoto [†]
T4	Black fibrous soft peaty sediment containing plant fragments > 2 mm	10YR 2/1	54.2	Around lake margins to depths of 1 m
T3	Black to very dark brown fine soft dy-gyttja. Particles < 1 mm	10YR 2/1 10YR 2/2	42.7	Water depths > 1 m
T2	Very dark grey to very dark greyish-brown firm fine gyttja. Particles < 1 mm	10YR 3/1 10YR 3/2 2.5Y 3/2	18.9	Not found in surficial sediments
T1	Olive to very dark grey, firm slightly sticky fine gyttja. Particles < 1 mm	5Y 3/1 5Y 3/2 5Y 4/3	9.1	Not found in surficial sediments

*Loss on ignition determined on at least two samples of dried sediment by combusting at 550°C for 30 min.

[†]From Boubée (1983).

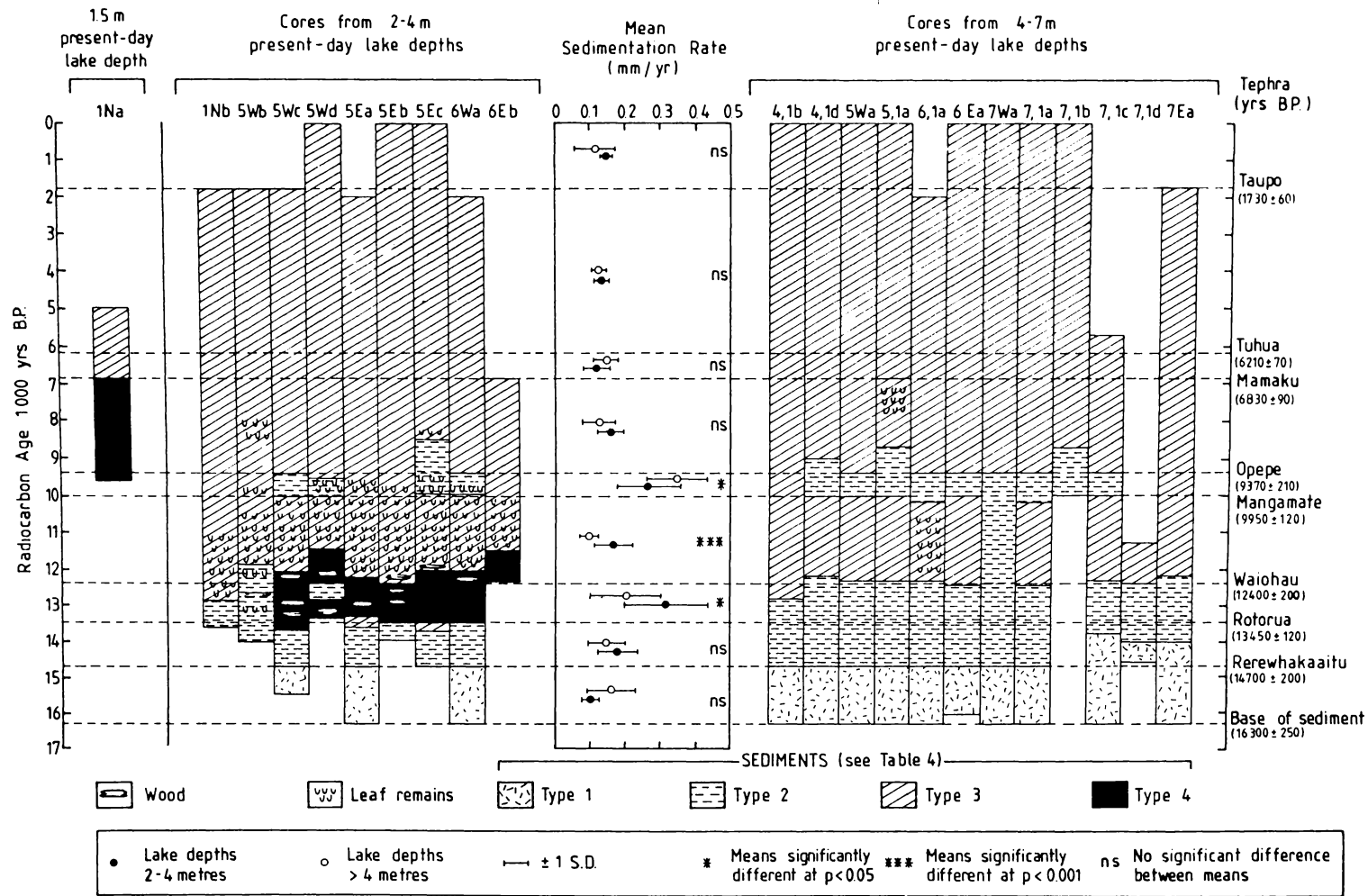


Fig. 10 Changes in lake sediment type over time in cores grouped into shallow-water and deep-water cores. Mean sedimentation rates for each time period (denoted by horizontal dashed lines) in both deep and shallow water cores, and the results of a *t*-test of the significance of their difference, are also given. Coring locations are shown in Fig. 3.

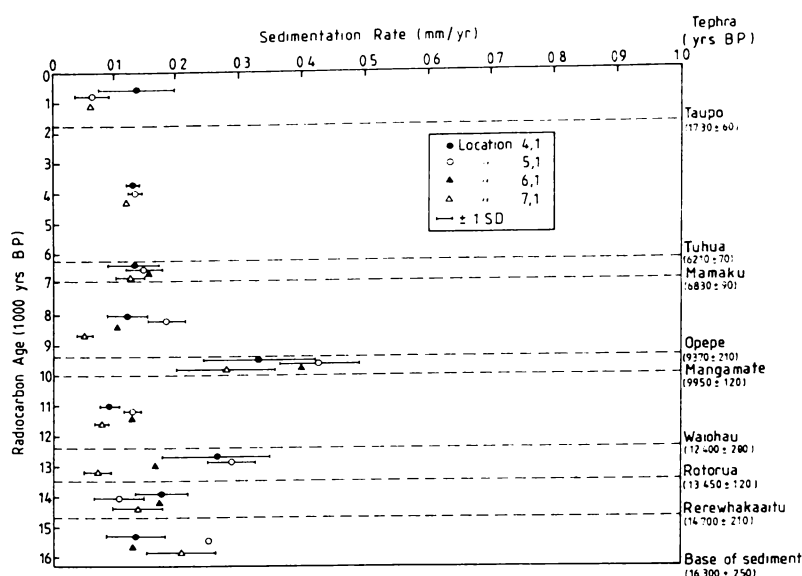


Fig. 11 Sedimentation rates in cores taken from central locations (along transect 1-1' in Fig. 3) and averaged for each designated time period (denoted by horizontal dashed lines).

little vegetational cover. The greenish tinge of this sediment is due largely to secondary chlorophyll degradation products, possibly produced within the lake itself. The lack of brown staining implies that the lake water was clear. The browner T2, with higher organic content, suggests more vegetation in the catchment and soils with greater organic content. Marginal vegetation may have contributed also to its darker colour. The very dark peaty T3 consists of decomposing remains of aquatic plants and animals, faecal pellets of aquatic animals, and fine plant remains from surrounding terrestrial vegetation (Boubée 1983), and is stained with humic material extractable with 10% KOH. Such sediment, often described as dy-gyttja (e.g., Hansen in Berg & Petersen 1956), shows dystrophic conditions in the lake and considerable peat development around it. Leafy fragments occur in T3 sediment within and around beds of the sedge *Eleocharis sphacelata*. T4 sediment is fibrous and woody and is similar to peat from the Rukuhia bog. It is found around the margins of the present-day lake (Table 4).

Changes in sediment type and sedimentation rates were examined in two groups of the lake sediment cores—those taken from modern lake depths shallower than 4 m (shallow-water cores) and those taken from depths deeper than 4 m (deep-water cores) (Fig. 10).

The temporal sequence is similar in most of the deep-water cores (Fig. 10, right panel). Sediment T1 occurs from c. 16 300 to 14 700 years ago, T2 from 14 700 to c. 12 400 years ago, and T3 thereafter, except for a brief period of T2 deposition from

10 000 to c. 9 000 years ago. No T4 or wood was found in the deep-water cores, and leaf remains are rare. Most of the shallow-water cores (Fig. 10, left panel) differ from the deep-water cores in having a band of woody T4 from c. 13 500 to c. 12 000 years ago, leafy T3 from c. 12 000 to 10 000 years ago, and a less-obvious zone of T2 from c. 10 000 to 9 000 years ago.

For most of the lake's history (c. 16 300–13 500 years ago, c. 12 400–10 000 years ago, and c. 9 000 years ago to present) (Fig. 10), mean sedimentation rates were slow (0.10–0.20 mm/year). For two brief periods, from c. 13 500 to 12 400 years ago, and from c. 10 000 to 9 000 years ago, the sedimentation rate was faster (0.20–0.35 mm/year).

There was no significant difference in sedimentation rate between shallow and deep water cores early (c. 16 300–13 500 years ago) and late (from c. 9 000 years ago to present) in the lake's history. However, from c. 13 500 to 10 000 years ago, sedimentation rates in shallow water were significantly faster than in deep water. During this period, sediment types T4 and leafy T3 were deposited in shallow water. In contrast, from c. 10 000 to 9 000 years ago, sedimentation rate was significantly faster in deep water, coinciding with T2 deposition. This was the only period of sediment focussing (i.e., greater accumulation of sediment in the deepest part of a lake basin; Davis & Ford 1982) in the lake's history.

In central locations (along transect 1-1'; Fig. 3), between c. 16 300 and 12 400 years ago, sedimentation rates declined in the south of the lake (location 7,1) but increased in the northern (4,1) and middle (5,1) locations (Fig. 11). Thereafter,

Table 5 Total lake sediment thickness in central locations.*

Location	No. of cores used in calculation	Sediment thickness (cm)
4.1	4	259
5.1	1	310
6.1	1	251
7.1	2	201

*Data also plotted in transect 1-1', Fig. 4.

from c. 13 500 to 7000 years ago, sedimentation rate was consistently slowest in the south and fastest in the middle (narrow) area of the lake. The faster sedimentation rates in location 5.1 from c. 13 500 to 7000 years ago account for the greater total sediment thickness there (Table 5). From c. 7000 to 2000 years ago, sedimentation rate was similar in all central locations. Sedimentation rates were faster in the northern basin (4.1) from c. 2000 years ago to the present.

In the central locations (transect 1-1'), sedimentation rates were inversely proportional to the distance from the shoreline (e.g., station 7.1 is 150 m, and station 5.1 is 50 m, from the shore), suggesting that input of littoral and terrestrial material is the major factor determining the sedimentation rates in Lake Maratoto.

DEVELOPMENTAL HISTORY

Origin of the lake basin

Beneath the lake is a shallow, elongated, northeast-southwest-orientated depression. This is an embayment in the Pleistocene hills which is dammed to the southwest by Hinuera sands and gravels and flooded by Hinuera muds and clays (Fig. 12). The southwest margin of the paleosurface depression, made up of these Hinuera sands and gravels, is lower lying than the low ridges and Pleistocene hills around its other sides. The lake is thus held at its present level mainly by the 8 m depth of peat overlying the sands and gravels to the southwest.

The Hinuera sediments blocking the embayment were laid down in two main episodes (Fig. 13), the first of which occurred c. 17 000 years ago forming a proto-Lake Maratoto in which the thin layer of gyttja lying beneath the Hinuera muds was deposited. The proto-Lake Maratoto gyttja lies directly on the Pleistocene hill derived materials in the valley floor with no intervening layer of Hinuera muds, at least in the northern part of the lake basin. This suggests either that there was no extensive flooding

by mud-laden river water, possibly because the major course of the Waikato River moved some distance away from the mouth of the valley after deposition of the dam materials, or that the basin was too shallow to hold enough water to produce an appreciable thickness of mud. Whichever, this proto-Lake Maratoto sediment was laid down in what may have been a swampy hollow with only shallow water. The duration of the proto-lake was between 150 and 800 years (Fig. 9).

The second episode of Hinuera deposition, that produced the initial modern lake basin, was more extensive and rapid. There must have been a considerable depth of floodwater ponded in the valley to act as a buffer to the river current to produce the sorted nature of Hinuera deposits in the embayment (Fig. 13). The alternating sand and mud layers found in the base of the cores from the southwest of the lake and in GC1 (Fig. 5, 8) suggest that the ponded mud-laden water was renewed in a series of floods. This is consistent with what is inferred about Hinuera Formation deposition by Hume et al. (1975) who deduced that the river formed an extensive braided channel system with high flow-rates and subject to periodic flooding and channel movements. Hume et al. (1975) identified several lithofacies related to flow regimes, and their lithofacies C2, formed by plane bed movements on the surface of longitudinal bars at higher discharges, is very similar to the gravelly sands in core 7Wa (Fig. 7C, 8). The presence of such deposits at this site shows that, at least during periods of high flow, the main channel system of the river flowed near the mouth of the valley. The river may have flowed in a north-south direction broadly along the course shown in Fig. 1 from the site of the present-day Hamilton Airport, past the lake, and then west into the Waipa River near Te Rore. Lakes Cameron, Ruatuna, Ngaroto, and Mangakaware, which lie adjacent to this paleochannel, are thus likely to have been formed at the same time, and in the same way, as Lake Maratoto.

Development of the lake basin and catchment

Initially, the lake was probably no larger than it is today because fine gyttja does not occur in the RJ1 core at the southwestern edge of the lake nor in GC3 only 10 m from the northern lake shore. At c. 16 300 years ago, the shoreline probably lay between the 7 and 8 m paleobasin contours (Fig. 12). The RJ1 core site lies on the 7 m contour and was clearly either above water or close enough to the shoreline for wave action to remove any gyttja to deeper water. The 8 m contour, however, seems to have been under water from the start of the lake's development, and cores from sites 5W, 6W, and 7W, that are on or close to this contour line, have

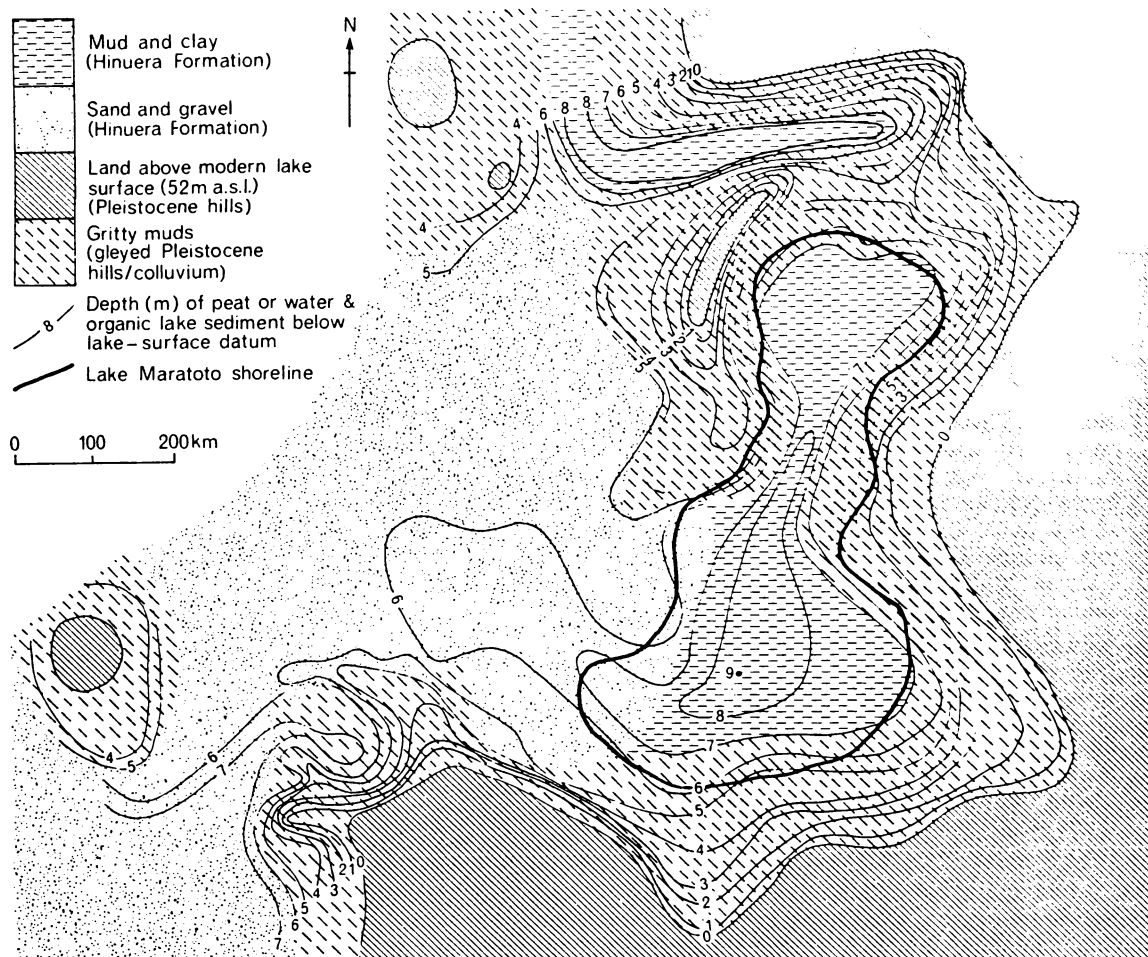


Fig. 12 Subsurface materials and topography of the Lake Maratoto area, derived from the transect profiles in Fig. 4. The 0 m contour is the lake-surface datum (52 m altitude). The map shows the northeast-southwest-orientated depression in which the modern lake (heavy line) lies. A separate, narrow, east-west-orientated paleovalley occurs to the north of Lake Maratoto. See also Fig. 13.

a considerable thickness of gyttja between the Hinuera overbank muds and the Rerewhakaaitu tephra. The lake would thus have been about 2 m deep in its early stages.

The subsequent development of the lake has been largely governed by the massive growth of peat around its margins and in the adjacent Rukuhia bog, as well as by the accumulation of gyttja. Peat growth has modified the basin configuration (area and depth) and water chemistry.

There was little or no peat development during the first 1000 years or so of the lake's history. The type of sediment deposited shows that lake water was clear and that, in the catchment, soils were low

in organic matter, with probably little vegetational cover. From pollen analyses of peat lenses, McGlone et al. (1978) and McGlone et al. (1984a) concluded that there was sparse vegetation in the Hamilton region at this time.

Peat began to accumulate around the lake about 15 000 years ago, as shown by the date (Wk534) of 15 200 \pm 130 years ago at the base of RJ1. The appearance of darker coloured T2 in the lake may have resulted from such peat development although other factors, such as increasing vegetational cover in the catchment, may have been important. Elsewhere in the central North Island, 14 700 years B.P. marked the beginning of major podocarp forest expansion (e.g., McGlone & Topping 1977; Flem-

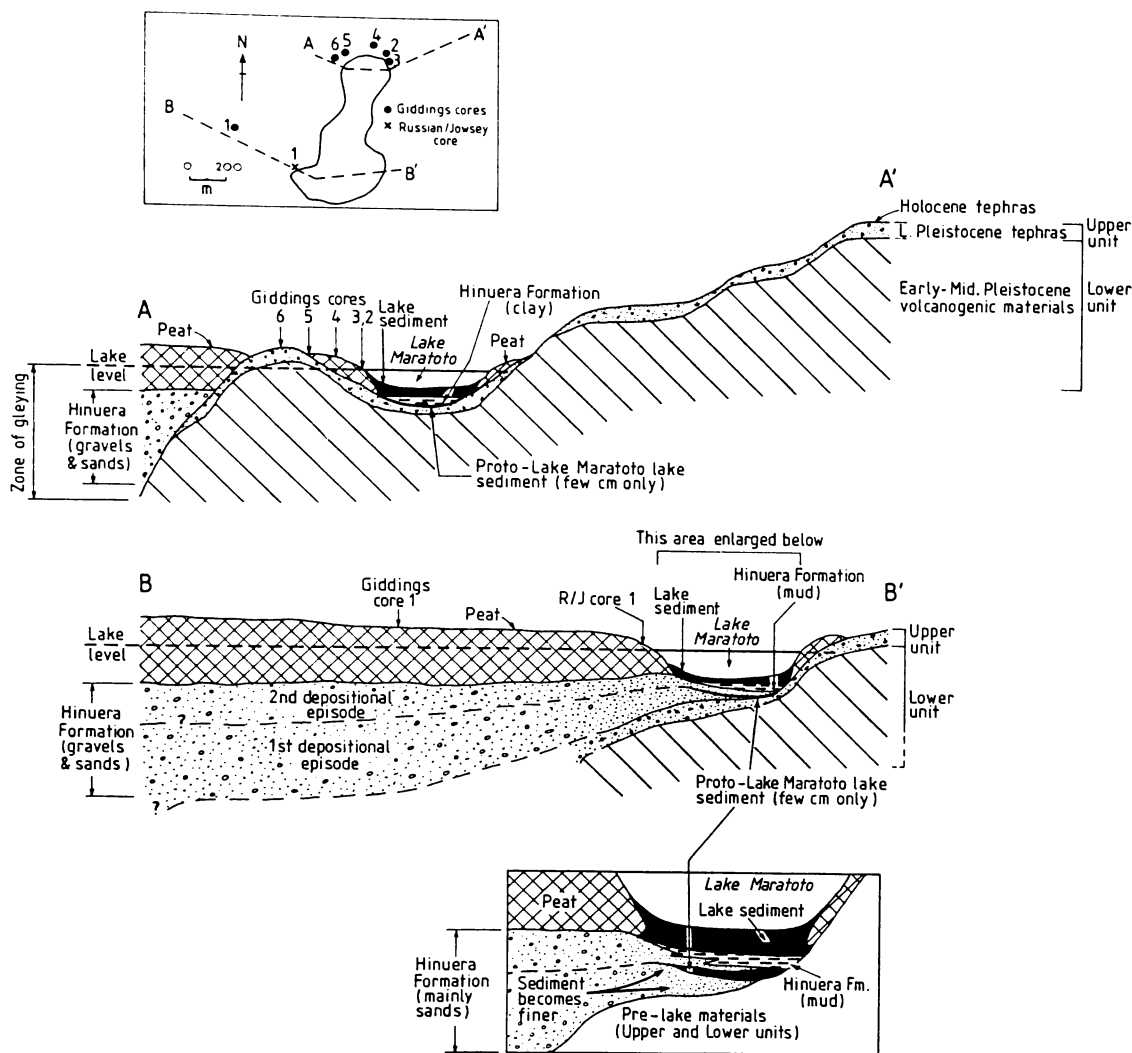
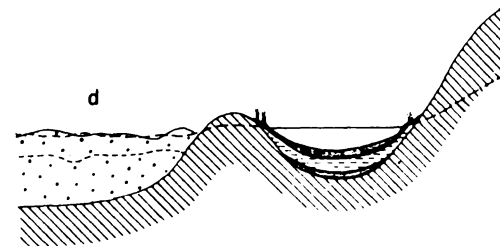
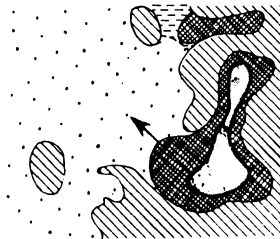
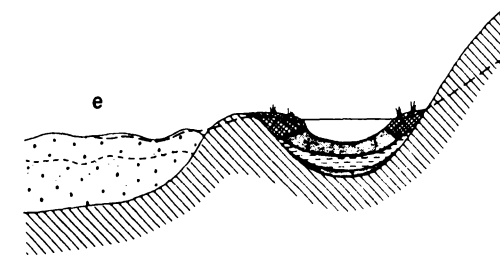
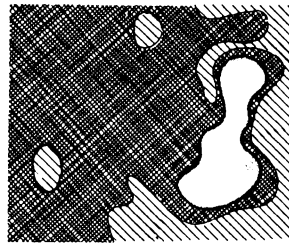
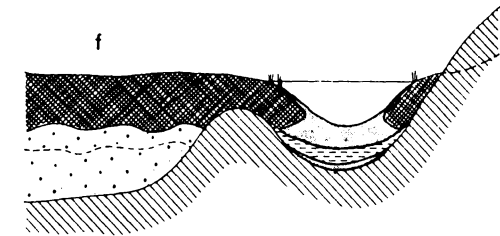
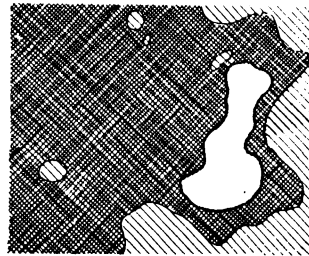
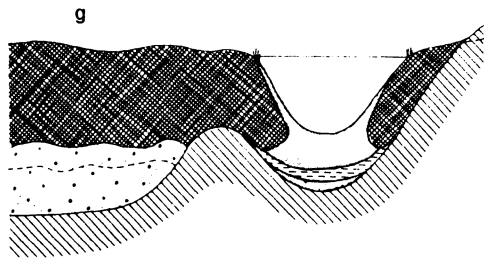


Fig. 13 Schematic cross sections summarising the stratigraphic units and their relationship to one another in the Lake Maratoto area, showing especially the differences between the northern and southern parts of the lake basin. There is a time gap of a few hundred years between the Hinuera depositional episodes shown in B-B', but note that both occurred within the Hinuera-2 sedimentation phase of McGlone et al. (1978).

ing 1979) and an increase in rates of soil formation (e.g., Vucetich & Pullar 1969; Birrell & Pullar 1973). This early peat development must have been fairly localised because the change to T3, marking the onset of dystrophy, did not occur until c. 12 400 years ago, and peat did not appear at the GC1 site, only 400 m from the lake, until (Wk553) 10 600 \pm 90 years ago. Thus it seems peat first developed near the lake and then spread outwards.

Dates from peat at the base of the main body of the Rukuhia bog (10 750 \pm 90 years B.P. (Wk115)

McGlone et al. 1978; 10 250 \pm 90 years B.P. (Wk114) unpublished) (Fig. 9) are similar to that for GC1, showing that most bog development occurred after c. 11 000 years ago. Peat bogs began developing at other sites in the Waikato region (e.g., Hauraki and Moanatuatua bogs—Schofield 1965; McGlone et al. 1978; Hogg & McCraw 1983) and elsewhere in the North Island (McGlone & Topping 1977; Lowe & Hogg in press) at about this time also, which suggests that climatic change resulting in an increase in net precipitation, and

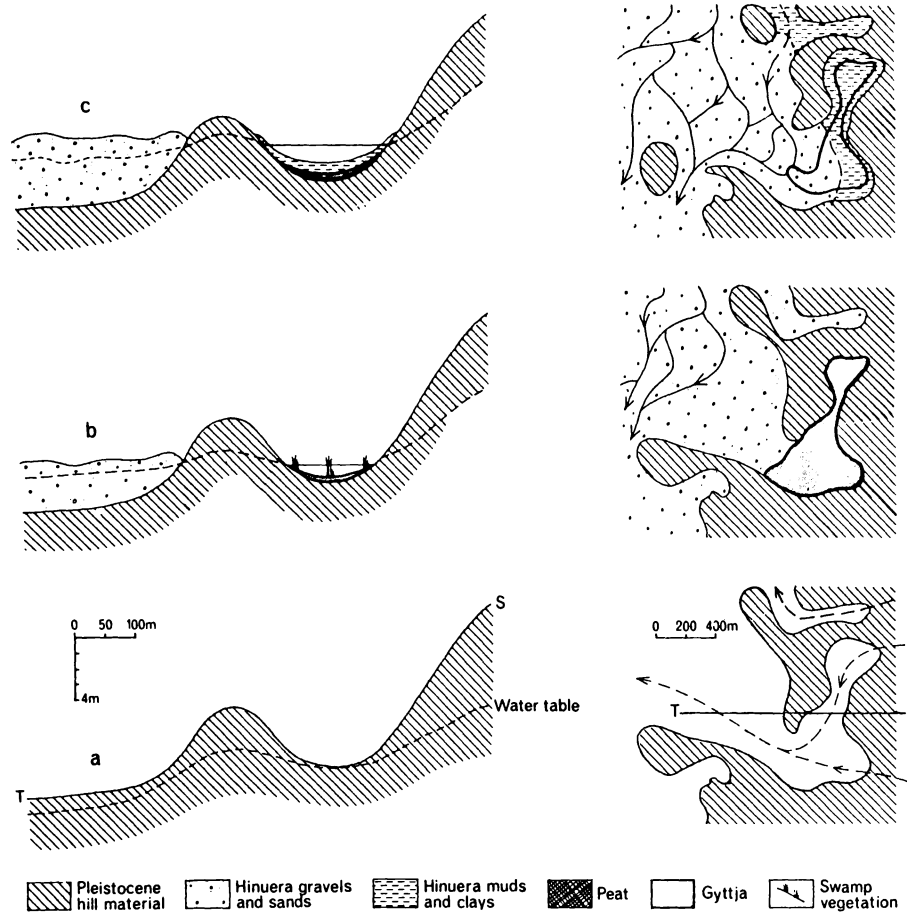


Present day The lake basin is formed in the surrounding peat, perched above and divorced from the initial lake basin in the valley floor. Area and depth of lake at maximum. Other lakes similar to present-day Lake Maratoto, and thus possibly of a similar ontogenetic stage, include Cameron, Pataka, Posa, and D.

10 000 years ago to present Rukuhia peat bog expands, most rapidly after c. 7000 years ago. Water deepens as rate of peat growth is much greater than gytja sedimentation rate in the lake. Water depth perhaps 3.5 m at 7000 years ago, 6.5 m at 2000 years ago. Lake area gradually expands but is never larger than at present. Lake dystrophic. A sequence of modern lakes possibly illustrating the development in the first part of this period is Lakes Mangahia, Rotoroa, Ruatuna, and Serpentine.

14 000 to 10 000 years ago Marginal peat and swamp vegetation encroaches into lake and reduces its surface area by half at c. 13 000 years ago. From 13 000 to 10 000 years ago, lake area expands again and water deepens. Main body of Rukuhia bog begins growth at c. 11 000 years ago, and the peat growing westward (arrow) from the lake contributes to this development. Dark brown-black gytja of high organic content because of peat growth and extensive catchment vegetation. Lake becomes dystrophic. Water 2.5 m deep at 10 600 years ago. Modern analogues include Lakes Rotomanuka, Rotokauri, Mangakaware, and Ngaroto.

16 300 to 14 000 years ago Initial lake development. Gytja olive-grey, low in organic matter. Gytja darkens later in the period because of development of marginal peat (at 15 200 years ago) and possibly catchment vegetation. Water clear, still c. 2 m deep. Modern analogues are Lakes Waahi and Hakanoa.



16 300 years ago Second phase of Hinuera deposition in the area. Coarse sediment deposited in valley mouth, fining to muds and clays at the end of the valley. Lake Maratoto forms, c. 2 m deep, with its shoreline approximating the 7 m contour in Fig. 12. Lake water clear. No peat, and sparse vegetation in catchment.

17 000 years ago First phase of Hinuera-2 deposition in the area. Proto-Lake Maratoto forms by damming of the valley by alluvium. Basin swampy or with only very shallow water.

Before c. 17 000 years ago Valley in Pleistocene hills draining to the southwest and west. Clear area represents land below c. 40 m contour.

Fig. 14 (above and facing page) Summary of the developmental history of Lake Maratoto (bold outline). Cross sections have a vertical exaggeration of $\times 25$. Possible modern analogues (see Fig. 1) of the major development stages are given also.

not local changes in drainage patterns, initiated the development of the bog.

The dystrophic conditions induced in the lake by the development of the Rukuhia bog have continued to the present, except for the brief period of T2 deposition from c. 10 000 to 9000 years ago. This was probably a time of increased input of material derived from erosion of surrounding soils because T2 has a higher inorganic content than T3. Possible explanations include sustained high rainfall, or disruption of catchment vegetation by events such as fire, drought, or increased storminess. Sediment focussing also occurred during this period, with greater transport of littoral material to the centre of the lake by (presumably) increased wave erosion at the shoreline. Such focussing is consistent with wetter or windier weather at this time.

The vertical distance between the bases of cores RJ1 and GC1 is 1.1 m and their respective ages are 15 200 and 10 600 years, so 1.1 m of peat accumulated in this time interval (4600 years), a net peat accumulation rate of 0.03 cm/year. This peat growth would not have greatly affected the lake depth because in this period about 65 cm of lake sediment was deposited. The net change of lake depth was thus 45 cm and the rate of increase in water depth was 0.01 cm/year. The lake would thus have been about 2.5 m deep at 10 600 years ago. The main body of the Rukuhia bog developed after c. 10 600 years ago, and with a much greater net peat accumulation rate (e.g., at GC1, 8 m of peat has accumulated since then, giving a net peat accumulation rate of 0.08 cm/year, treble the rate between 15 200 and 10 600 years ago). Similar rates of 0.10, 0.06, and 0.08 cm/year (average 0.08 cm/year) were estimated from peat depths between Mamaku tephra and Taupo tephra in cores RJ1, GC2, and GC3, respectively (Fig. 5).

This rapid peat growth around Lake Maratoto resulted in rapid deepening of the water. From 10 600 years ago to the present, the rate of peat growth was much greater than the rate of accumulation of lake sediment, and lake depth increased by 4.6 m, a change of 0.04 cm/year, four times the rate before 10 600 years ago. Assuming that the positions of the Mamaku and Taupo tephra in the peat cores mark the approximate level of the lake surface when they were deposited, and that the peat has not been compressed, we estimate that lake depth was 3.5 m c. 7000 years ago and 6.4 m c. 1800 years ago. Thus, between 10 600 and 7000 years ago, the rate of change of lake water depth was 0.03 cm/year; between 7000 and 1800 years ago, 0.06 cm/year; and from 1800 years ago to the present, 0.04 cm/year. Thus, lake depth has increased markedly in the last 11 000 years, but particularly since 7000 years ago.

Variations in the spatial pattern of the deposition of lake sediment have resulted in minor modifications to the bathymetry. Early in the lake's history, lake depth gradually increased from north to south, but because sedimentation rates were fastest in the region of core location 5.1 (because of nearness to the shoreline), there is now a shallower zone in the narrow waist of the lake (Fig. 2).

Although the area of the lake in its early stages was probably similar to that of today, the band of woody T4 sediment in the shallow-water cores between c. 13 500 and 12 400 years ago (Fig. 10) shows that during this period the lake margin moved inward to lie near the position of these coring sites, between the 3 m and 4 m water depth contours. The change to leafy T3 sediment between c. 12 400 to 10 000 years ago at these sites shows that the shoreline moved outward again, but was still close to the 3 m and 4 m depth contours. The faster rates of sedimentation in shallow-water cores from 13 500 to 10 000 years ago reflect this proximity of the shoreline to the coring sites and also suggest little movement of littoral material into deeper water. The disappearance of leafy T3 sediment from the shallow-water cores after about 10 000 years ago shows that lake area continued to expand. The shoreline reached the present 1.5 m water depth contour at about 7000 years ago, as shown by the abrupt transition from T4 to T3 sediment at this time in core 1Na (Fig. 10). Thereafter, expansion continued to the present day. This shoreline expansion in the last 10 000 years occurred together with the increase in water depth.

Throughout its history, the lake has never been larger than it is now, while at its minimum at c. 13 000 years ago, the area of open water was only about one-half that of today (7.6 ha using the 3.5 m depth contour).

Most lakes occupying basins in which peat development is occurring are gradually reduced in area and depth by centripetal peat growth that eventually develops into zones of "quaking bog", made of floating mats of encroaching peat vegetation and often supporting large trees (Moss 1980). The final result of this process is extinction of the lake. The complete process from lake origin to extinction can take less than about 12 000 years in the Northern Hemisphere (e.g., Pigott & Pigott 1963; Walker 1970). The only lake we know of which has a similar developmental history to Lake Maratoto is Myrtle Lake, in the Agassiz peatland area of Minnesota (Heinselman 1970). This lake originated as an embayment blocked by alluvium c. 10 000 years ago and, like Lake Maratoto, has maintained its area and increased its depth despite massive peat growth in the catchment during the last 3000–5000 years. Heinselman (1970) suggested

that because of Myrtle Lake's location adjacent to higher areas of mineral soil, it would have continually received minerotrophic water that has enhanced microbial breakdown of the encroaching peat. This explanation may apply to Lake Maratoto as well because there is only a narrow zone of peat between the lake water and the Pleistocene hills to the east (Fig. 2, 4). Also, these hills rise considerably above the lake's surface which would encourage greater flow rates of minerogenic ground and surface water into the lake during heavy rainfall.

Other mechanisms may also be involved in the expansion of Lake Maratoto's area. Wells & Boyce (1953) and Frey (1954) suggested that erosion of peat margins by wave action may have been a factor in the development of the Carolina Bays (North Carolina). This almost certainly occurs in Lake Maratoto. In the present-day lake, a vertical 50 cm high bank is maintained around the lake margins, particularly at the north and south ends, by wave action produced by the prevailing southwest and northerly winds. Wind-induced currents stir and aerate the lake waters for most of the year. The lake develops thermal stratification and deoxygenated bottom waters for only a few months in the summer (Boubée 1983), hence the lake waters are usually saturated or supersaturated with oxygen which will enhance organic breakdown.

Our interpretation of the development of the lake basin in summarised in Fig. 14, along with possible modern analogues of the major developmental stages.

CLIMATIC INFERENCES

Between c. 17 000 and 15 000 years ago, there seemed to be no peat development near the lake. The first appearance of peat at c. 15 000 years ago may indicate that effective rainfall increased at this time. Subsequently, net peat accumulation rate, regional water tables, and lake level rose continually until c. 2000 years ago. The major part of the Rukuhia peat bog developed after c. 11 000 years ago, but the fastest growth rates, and thus highest net precipitation rates, were apparently not until after c. 7000 years ago. Regional postglacial climatic warming, reaching a maximum at c. 9000 years ago (Hendy & Wilson 1968), may also have contributed to the peat growth.

In summary, there was a sudden increase in net precipitation at c. 15 000 years ago followed by further increases at c. 11 000 years ago continuing to c. 7000 years ago at least, but with a decline at or before c. 2000 years ago. The period from c. 10 000–9000 years ago may have been distinctly wetter or windier, or both. These inferences are consistent

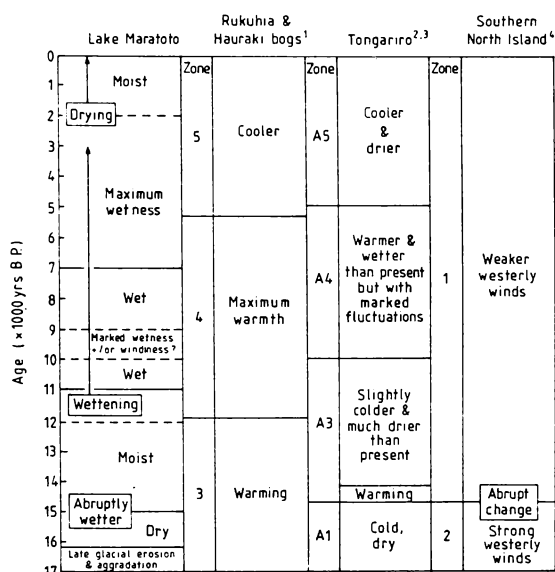


Fig. 15 Inferred changes in climate in the Lake Maratoto area compared with interpretations from some other North Island sites. References are: 1, Harris (1963); 2, McGlone & Topping (1977); 3, McGlone & Topping (1983); 4, Stewart & Neall (1984).

with late-glacial and postglacial climatic interpretations from other studies in the North Island of New Zealand (Fig. 15) (McGlone 1983; McGlone et al. 1984a) and elsewhere in the Southern Hemisphere (e.g., Burrows 1979; Street & Grove 1979; Heusser & Streeter 1980; Colhoun et al. 1982).

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- Lowe, D.J. 1985 = Paper 2
- Lowe, D.J.; Hogg, A.G. in press = Paper 5
- Lowe, D.J. *et al.* 1980 = Paper 1

PAPER 10

Late Quaternary tephras in the Hamilton Basin, North Island, New Zealand.

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LATE QUATERNARY TEPHRAS IN THE HAMILTON
BASIN, NORTH ISLAND, NEW ZEALAND.

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ABSTRACT

This paper summarises the occurrence and distribution of late Quaternary tephtras in the Hamilton (Middle Waikato) Basin and outlines a model to explain the pattern of soils formed from them. The collaborative work currently in progress on paleoecological aspects of the late Otiran-Aranuanian history of the area is also reported.

BACKGROUND AND PREVIOUS WORK IN THE WAIKATO REGION

Isopach maps showing the distribution of late Quaternary tephtras in New Zealand have been largely determined from field studies which are restricted to sites where the tephtras are more than several centimetres thick: Pullar (1967), Vucetich & Pullar (1969), Pullar & Birrell (1973a), and Pullar *et al.* (1977). Tephtra deposits in the Waikato generally thin north-westward away from the main source area in central North Island, well to the southeast (Fig. 1), and are difficult to differentiate in the field because of regional variations in original deposition, erosion, and mixing and weathering in the soil forming environment. Detailed examinations at reference sites (e.g., N.Z. Soil Bureau 1968a; Vucetich 1968; Pullar & Birrell 1973b; Jessen 1977; Hodder & Wilson 1976; Hodder 1978) have re-emphasised the composite rhyolitic and andesitic nature of these thin tephtras and the soils formed from them. However, they have not been successful in identifying all of the constituent tephtras. Only a few late Quaternary tephtras have been mapped either close to, or to the northwest of Hamilton City (Fig. 1; see also Table 1).

In the Hamilton Basin, the late Quaternary cover bed deposits which overlie Hamilton Ash have been ascribed a loessic origin by McCraw (1967, 1975), Vucetich (1968), and Cowie & Milne (1973). Other workers have alternatively proposed that the deposits consist either of differently weathered forms of Hamilton Ash (Ward 1967), or of unnamed ash younger than Hamilton Ash (N.Z. Soil Bureau 1968a: 90). A combination of tephtra and loess is also possible (Lowe 1981).

OCCURRENCE AND DISTRIBUTION OF TEPHRAS

The recent identification of numerous (>12) unweathered and unmixed thin, discrete airfall tephtras in piston cores from shallow (<8m) peaty lakes near

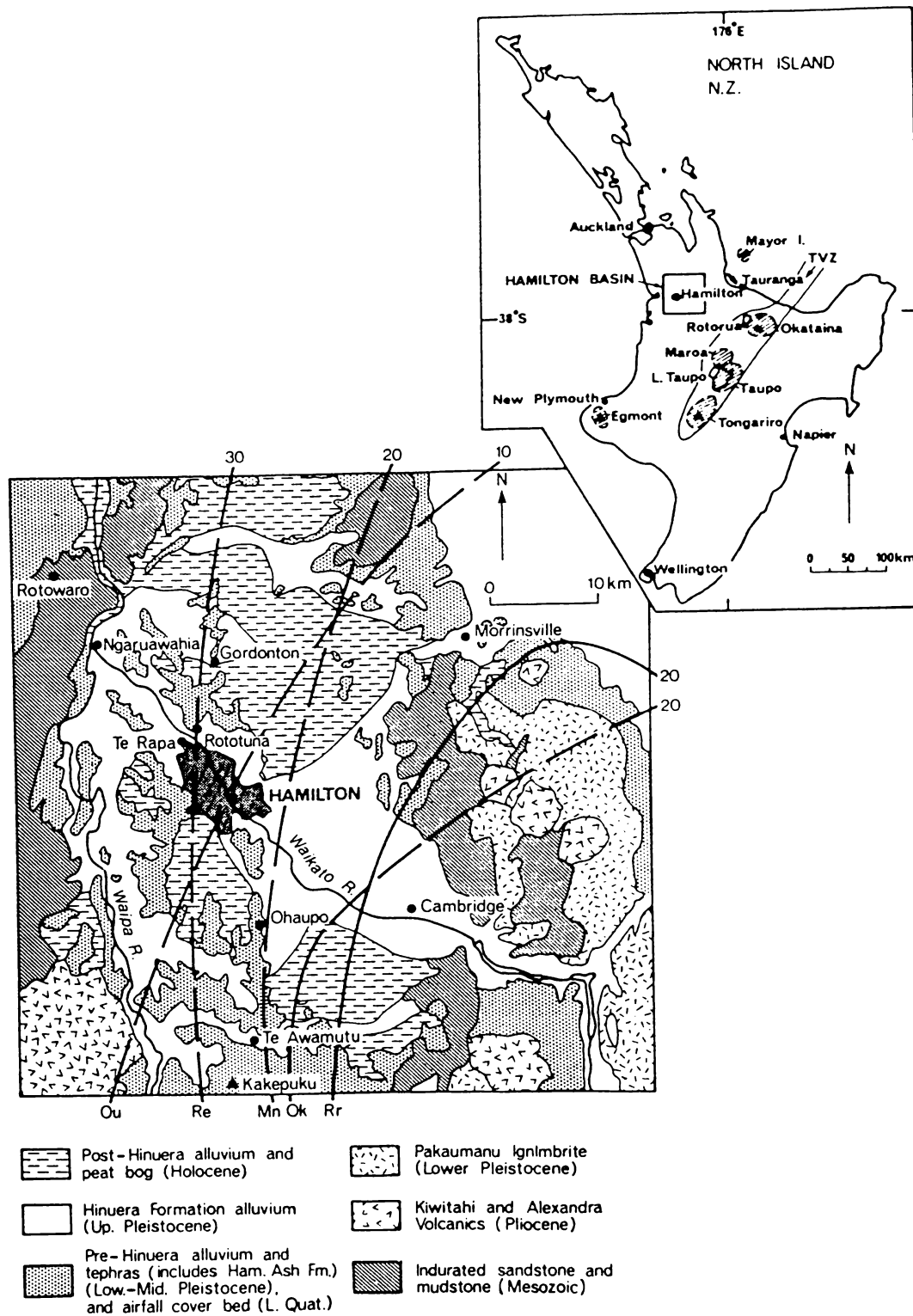


FIG. 1 - Simplified geological map of the Hamilton Basin (after Hume et al., 1975: 424), with distal-most tephra isopachs (cm) superimposed (from Pullar & Birrell, 1973a). Re = Rotoehu Ash; Mn = Mangaone Lapilli; Ok = Okareka Ash; Ou = Oruanui Ash; Rr = Rotorua Ash. Dashed line indicates isopach uncertain. Inset shows Hamilton Basin in relation to volcanic centres which were the most important sources of tephra, and Taupo Volcanic Zone (TVZ) (after McCraw, 1975; Mayor Island centre after Hogg, 1979). Note: "L.Quat." = Late Quaternary.

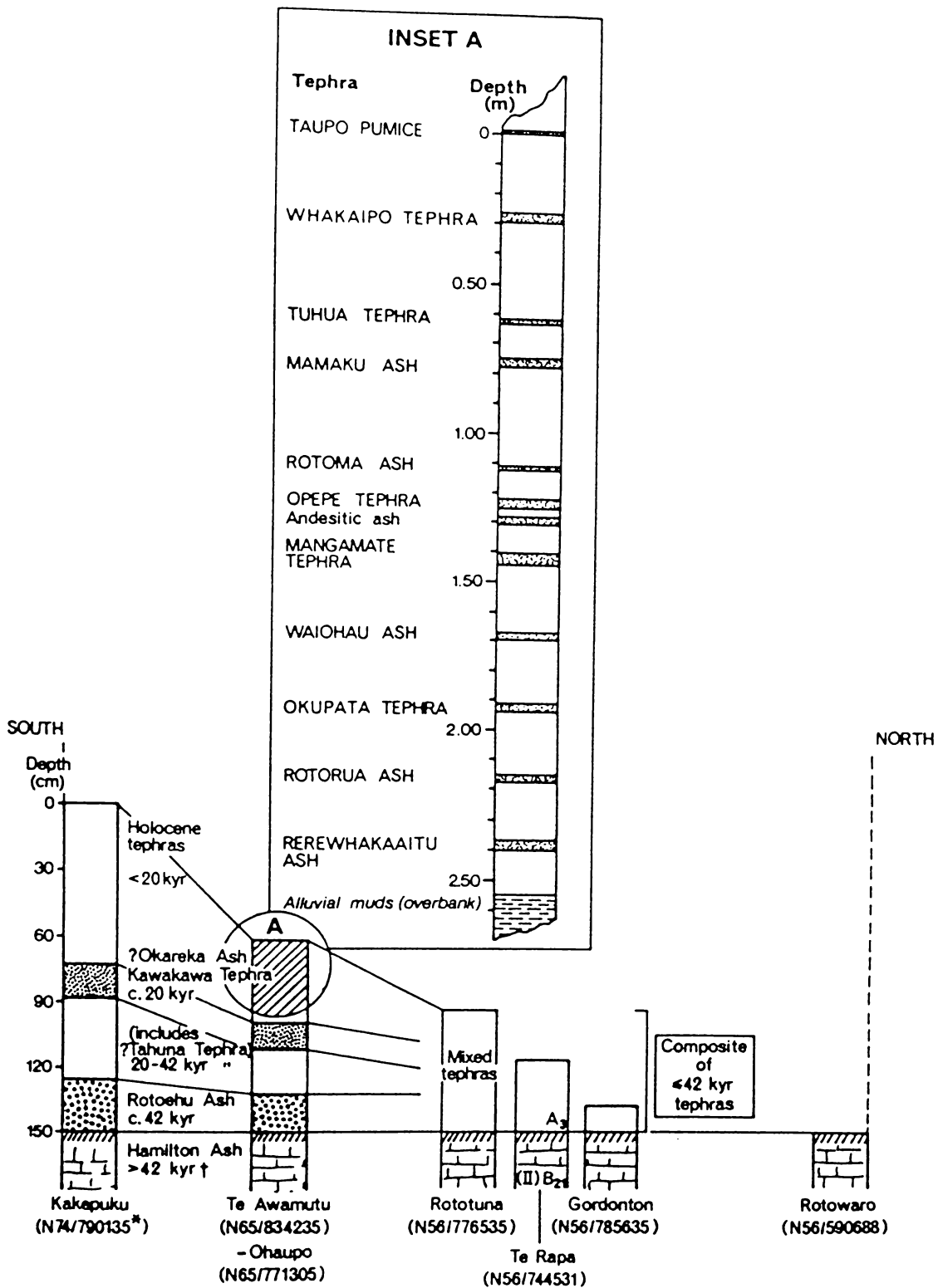


FIG. 2 - Correlation line apportioning relative thickness of late Quaternary deposits (soils) to proportionate thicknesses of Holocene and late Pleistocene tephras - illustrated at Te Awamutu-Ohaupo from Lake Maratoto core Inset A. In this transect, from south to north through Hamilton City, the changes in thickness of the late Quaternary deposits relate directly to the thinning of constituent tephras with increasing distance from source(s), and to erosion. Virtually all of the < 42,000 years B.P. tephras have been removed from the Rotowaro site, but late Quaternary tephras are present further north near Auckland City. Site locations are indicated in Fig. 1.

INSET A Thin airfall tephras preserved in organic lake sediments in Lake Maratoto, a peaty lake about 8km south of Hamilton City. Rerewhakaaitu Ash at the base of the core has been radiocarbon dated at 14,700 years B.P. (Lowe et al., 1980). The inset indicates potential contributions of specific tephras as probable parent materials in the soil profile.

† kyr = 1,000 years B.P.

* Grid reference based on national thousand-yard grid of the 1:63360 topographical map series (NZMS 1).

TABLE 1 - Names, sources, approximate ages and thicknesses of known distal late Quaternary airfall tephtras which have been deposited in the Hamilton City area. Unnamed tephtras in addition to those listed also occur.

Tephtra Formation or member	Source (volcanic centre)	Age (years B.P.) ¹	Approximate thickness (cm) (this study)	Previous references which report or predict the occurrence of the named tephtra (? indicates uncertainty)
Ngauruhoe Tephtra	Tongariro	Historical	<1	Nelson 1975; Nairn 1976 Pullar 1967; Tonkin 1967; Pullar and Birrell 1973a; Pullar <i>et al.</i> 1977; Lowe <i>et al.</i> 1980 Lowe <i>et al.</i> 1980; Hogg and McCraw 1983 Lowe <i>et al.</i> 1980 Lowe <i>et al.</i> 1980 Lowe <i>et al.</i> 1980 Lowe <i>et al.</i> 1980 Lowe <i>et al.</i> 1980 Lowe <i>et al.</i> 1980 Lowe <i>et al.</i> 1980 Lowe <i>et al.</i> 1980 Lowe <i>et al.</i> 1980 Pullar and Birrell 1973a(?); Howorth in McGlone <i>et al.</i> 1978; Lowe <i>et al.</i> 1980 Lowe <i>et al.</i> 1980 Pullar and Birrell 1973a(?); Pullar <i>et al.</i> 1973(?); Lowe 1981(?) ³ Vucetich 1968(?); ⁴ Vucetich and Pullar 1969; ³ Pullar and Birrell 1973a; ³ Pain 1975; ³ Lowe 1981 ⁴ Vucetich and Pullar 1969; ⁴ Pullar and Birrell 1973a; Lowe 1981 Vucetich and Pullar 1969; Pullar and Birrell 1973a; Pullar <i>et al.</i> 1973; Lowe 1976.
Taupo Pumice	Taupo	1800	1-2	
Whakaipo Tephtra	Taupo	2700	1	
Tuhua Tephtra	Mayor Island	6300	1	
Mamaku Ash	Okataina	c.7000-8000	2-3	
Rotoma Ash	Okataina	c.7000-9000	2-3	
Opepe Tephtra	Taupo	8800	2	
Andesitic Ash	Tongariro or Egmont	9000	1-2	
Manganate Tephtra	Tongariro	10000	3-4	
Waiohau Ash	Okataina	11300	2-3	
Okupata Tephtra	Tongariro	12500	1	
Rotorua Ash	Okataina	13500	2 [<c.20] ²	
Rotoaira Lapilli	Tongariro	13800	<1	
Rerewhakaaitu Ash	Okataina	14700	2-3	
Okareku Ash	Okataina	c.19000	75 [<c.20] ²	
Kawakawa Tephtra	Taupo	c.20000	710-15 [c.10] ²	
Tahuna Tephtra	Okataina	c.30100	710-15 [c.20] ²	
Rotoehu Ash	Okataina	c.42000	720-30 [c.30-40] ²	
Hamilton Ash	Unknown	>42000		Ward 1967; N.Z. Soil Bureau 1954, 1968b; Pain 1975; Lowe 1981

¹ Old (Libby) half-life basis

² Values according to previously published isopach thickness

³ Reported as *Oruanui Ash*

⁴ Reported as (undifferentiated) *Mangaoni Lapilli*

Hamilton City has confirmed the presence and provided a stratigraphic record of late Pleistocene (post-Kawakawa Tephra) and Holocene tephras in the Waikato (Lowe *et al.* 1980). Field studies, plus detailed mineralogical, textural, and chemical analyses of samples from representative sections in the Waikato have added complementary stratigraphic and pedological data from which the occurrence and general distribution of late Quaternary ($\leq 42,000$ years B.P.) tephras has been determined (Lowe 1981).

Eruptive sources within Okataina and Taupo Volcanic Centres provided the bulk of the tephras, with much smaller contributions from Tongariro, Mount Egmont and Mayor Island sources. The source, age and approximate thickness of each named tephra identified near Hamilton is summarised in Table 1.

Late Quaternary deposits in this area are thus established as a composite of airfall tephras aged $\leq 42,000$ years B.P., and are clearly not loess derived from Hinuera Formation alluvial deposits (Fig. 1).

Fig. 2 summarises the distribution of tephras in the Hamilton Basin, and the parent materials of the composite soils formed from them.

TEPHRA-SOIL PATTERN

Soil formation from the tephra deposits is a function of relative proportion of each tephra within the solum, and the soil climatic regime (Lowe 1979). With increasing distance from the tephra source areas, the age span of tephras in the solum increases (Fig. 2). The pattern of soils in the Waikato can be explained by a model of intermittent accumulation, with subsequent or concomitant mixing, of thinly bedded primary airfall late Quaternary tephras (Lowe & Gibbs 1981). North of Hamilton City, the thin increments of distal tephras have been more or less continuously modified by pedogenic mixing and weathering processes, producing silt-rich, compact and weakly structured deposits with characteristics commonly associated with loess.

COLLABORATIVE WORK

The tepthrostratigraphy and radiocarbon dates determined from the lake cores also provide a geochronological framework for paleoclimatic, paleoecological and sedimentological investigations in the Waikato Basin. Paleolimnological studies (Green 1979) and palynological studies (McGlone *et al.* 1978) are currently in progress.

ACKNOWLEDGEMENTS

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DISCUSSION

1. Can you explain the so-called "loess balls" which occur in the firmer post-Kawakawa material? - R. Parfitt.

The so-called "loess balls" found in post-Kawakawa Tephra deposits also occur (often as "eggshells") in the paleosol on Tahuna Tephra and Rotoehu Ash which underlies Kawakawa Tephra in the eastern Waikato.

Kennedy (1980) suggests that the "balls" originate as an accretion of fine ash which accumulates in a snowball fashion while rolling along the ground. An alternative explanation is that the "balls" are accretionary lapilli, sometimes described as chalazoidites or volcanic "hailstones" (Vucetich & Pullar 1969), and essentially of primary origin. Self & Sparks (1978, 1979) outline two common circumstances for their formation:

- (a) the explosive interaction of magma and water;
- (b) the flushing out of fine ash from eruption clouds by rain, or by formation of clumps of ash by flocculation in a steam-rich eruption column (as was reported for the recent Mount St. Helens' eruptions).

In the Hamilton Basin, small (1-2cm) "birds eyes" are occasionally present in the late Quaternary cover bed deposits - these may be weathered accretionary lapilli or merely discontinuous fine-grained clasts remnant from the original tephra mantle.

2. In the slide of the core of the various tephtras, could the "alluvium" at the base of the core be tephtric loess that has fallen in the water? - N. Kennedy.

The 50cm-thick greenish-grey mud at the base of the Lake Maratoto core is thought to be an overbank flood deposit related to Hinuera-2 sedimentation (as described in Hume *et al.* 1975). The deposit contains ~63% clay (<4 µm) and ~36% silt (4-63 µm). Unpublished ¹⁴C dates recently obtained from above and below the deposit are virtually identical, both being near 15,800 years B.P. This indicates a rapid depositional event, which argues against a relatively slow loess accumulation. Further, the dates place the deposit almost into the post-glacial period which is characteristically devoid of loess (post c. 15,000 years: Kennedy 1980).

3. Do you recognise much in the way of tephtric loess - Post-Kawakawa in the Hamilton area?

The late Quaternary cover bed deposits in the Hamilton area are considered to be predominantly primary airfall distal tephtras (see Lowe 1981). The loess-like appearance of the composite deposit is explained by a model of incremental accumulation of fine-grained tephtras with subsequent or concomitant pedogenic (biological) mixing. The deposits are currently

weathering in a wetting and drying environment. Weathering is intensified by the inclusion of the buried clay-rich Hamilton Ash beds in the solum (see also Lowe 1980).

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Cross referencing to thesis paper

Postscript to Paper 10.

Because this paper was written early in the course of the research leading to the thesis, several of the tephra identifications were provisional. Modifications to the tephrostratigraphy arising from subsequent work have been incorporated in Fig. 2 and Table 1 of Paper 10 (see also Postscript to Paper 1).

PAPER 11

Controls on the rates of weathering and clay mineral genesis in
airfall tephras: a review and New Zealand case study.

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CHAPTER 12

Controls on the Rates of Weathering and Clay Mineral Genesis in Airfall Tephra: a Review and New Zealand Case Study

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I. Introduction

Airfall tephra deposits of rhyolitic, dacitic, and andesitic composition form widespread, surficial deposits in many parts of the world. Consequently, they are of prime importance as soil parent materials. Clay fractions (less than 2 μm) of these tephra consist mainly of authigenic clay minerals along with smaller amounts of residual or accessory minerals. The outstanding feature of almost all tephra-derived clay fractions is the occurrence of short-range-order clay minerals in addition to well-ordered or crystalline species (Brindley, 1977). Short-range-order minerals can also occur in non-volcanic and nonvolcanic materials [e.g., Wada and Harward (1974), Young *et*

al. (1980), Farmer (1982), and Childs *et al.* (1983)]. A key characteristic of the short-range-order minerals is the presence of abundant “active” aluminum in various mineralogical forms (Shoji and Ono, 1978; Wada and Gungjigake, 1979; Wada, 1980; Shoji and Fujiwara, 1984).

The aim of this chapter is to demonstrate the relative importance of various influences on the rates of formation and transformation of clay minerals in tephra deposits of predominantly acid to intermediate composition. This is done in two parts. First, controls on the rates of weathering and the genesis of clay minerals in tephra are identified, and their degree of influence examined, in the review section (Section II). Second, the findings of a study on tephra weathering sequences in the Waikato region, New Zealand, are presented and interpreted with respect to the findings of the review (Section III). This New Zealand case study is based on the examination of distal, interbedded rhyolitic and andesitic tephra aged $< \sim 50,000$ years, and has been greatly facilitated by a complementary project investigating the stratigraphy, composition, and pattern of distribution of the same tephra—but in unweathered condition—preserved in organic-rich deposits in adjacent lakes and peats of late Pleistocene and Holocene age. Thus the study, with unequivocal tephrostratigraphic and chronologic control, clarifies the concept that rates of weathering and clay mineral transformations in tephra materials are strongly influenced by composition and environmental factors, especially microenvironmental factors, rather than a tephra age-dependent factor. It also helps explain the occurrence and persistence of various clays in tephra deposits elsewhere of widely differing ages.

II. Controls on the Weathering of Tephra and Clay Mineral Formation and Transformation

A. CONSTITUENTS OF THE CLAY FRACTION

The most common secondary minerals in the clay fraction of tephra deposits are allophane and halloysite. Allophane is a series of naturally occurring hydrated aluminosilicates characterized by short-range order and the predominance of Si–O–Al bonds (van Olphen, 1971). There are two main forms in the series, one having an Al:Si molar ratio of ~ 1.0 and another with a ratio of ~ 2.0 . The latter form seems to predominate and has been informally termed “proto-imogolite” allophane because of its imogolite structure on the atomic scale (Parfitt and Henmi, 1980; Parfitt *et al.*, 1980; Theng *et al.*, 1982). Both these and other forms in the series consist of nonrepetitive “structural units” made of hollow, spherically shaped particles with diameters of 35 to 55 Å. These forms probably have a defect gibbsitic Al-octahedral sheet framework (Henmi and Wada, 1976; Wada and Wada, 1977; Wada, 1979; Parfitt *et al.*, 1980). The recognition in the last few years

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of this structural series, with its Si-rich (kaolinitic) and Al-rich (gibbsitic or imogolitic) end members, has been of major importance in allowing new models of genesis to be advanced (Vucetich, 1983).

Halloysite is a kaolinite subgroup 1:1 layer silicate mineral that occurs in hydrated (10 Å) and dehydrated (7 Å) phases (Dixon, 1977; Brown *et al.*, 1978). Imogolite, similar to allophane of Al:Si molar ratio ~2.0 but with a fine tubular structure (Cradwick *et al.*, 1972), occurs with allophane but commonly in only small amounts (Wada, 1977). Subordinate amounts of various iron and aluminum oxides and hydroxides (mostly with short-range order and including gibbsite), secondary silica polymorphs of cristobalite, tridymite, and opaline silica (the last in various forms), humus and humus complexes, 14-Å vermiculite, and rare kaolinite have been reported in tephra deposits [e.g., Sudo and Shimoda (1978), Wada (1980), and Lowe and Nelson, (1983)]. Other 2:1 and 2:1:1 layer lattice silicates and their intergrades may occur in substantial amounts, particularly in Japan (Sudo and Shimoda, 1978; Wada, 1980) but also elsewhere [e.g., Pevear *et al.* (1982)]. Allophane-like constituents (defined by method of extraction) are reported in the Japanese literature (Wada, 1977, 1980). Residual (primary) quartz, feldspar, cristobalite, and volcanic glass may occur in the clay fraction of tephra.

Numerous studies have been made of the character, distribution, behavior, and genesis of clay minerals in tephra [e.g., reviews by Mitchell *et al.* (1964), Fieldes (1968), Gibbs (1968), Wada and Harward (1974), Fieldes and Claridge (1975), Kirkman (1975, 1978), Wada (1977, 1978, 1980), Brown *et al.* (1978), Shoji and Ono (1978), Sudo and Shimoda (1978), Ugolini and Zasoski (1979), Parfitt *et al.* (1982a), and Lowe and Nelson (1983)]. From these studies, and also others on the weathering of volcanic rock materials [e.g., Sieffermann and Millot (1969), Millot (1970), Eswaran and De Coninck (1971), Colman (1982), and Glassmann (1982)], weathering sequences that depict the formation and transformation of clay minerals in tephra can be grouped under one of the following controls:

- (1) Length of time of weathering (tephra age or effective weathering time);
- (2) Chemical and physical composition of the tephra deposit, particularly its vitric component and primary mineralogy; and
- (3) Postdepositional weathering environments.

B. WEATHERING SEQUENCES AND FACTORS THAT INFLUENCE CLAY MINERAL GENESIS

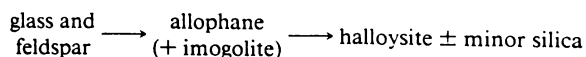
1. *Effect of Length of Time of Weathering*

The length of time of weathering of a tephra deposit is related to (1) its age (time since deposition), and (2) the period over which weathering processes

are able to operate effectively (e.g., time at land surface). A major problem in accurately evaluating the effect of the time factor is that other factors must remain relatively constant (Jenny, 1941) or else have negligible influence. This requirement is not easy to meet since factors such as macroclimate and microclimate, vegetation, tephra thickness or depth of burial, and the periodicity of tephra eruptions vary in both space and time. Hence, although an independent variable in the sense of Jenny (1941), the time function attains a new "time zero" status when one or more of these conditions change sufficiently so that the rate of weathering and clay mineral formation and transformation is significantly altered.

a. Clay Transformation Rates and Tephra Age. With increasing age the amount of clay-sized material in tephtras generally increases as glassy and other components are broken down and transformed to clay minerals. For example, tephtras in New Zealand weathering under currently temperate humid conditions and less than about 3,000 yr old have $< \sim 5\%$ clay; tephtras 3,000 to 10,000 yr old contain 5–10% clay, whereas those 10,000 to 50,000 yr old contain 15–30% clay; tephtras older than about 50,000 yr have $> 60\%$ clay (Table I; Lowe and Nelson, 1983). The amounts of clay formed in these deposits are thus broadly correlated with tephtra age. This general relationship applies only where the tephtras are weathering under similar conditions, however, as the rates of clay formation (hence amounts) differ according to environment (Jenny, 1941) (discussed further in Section II, B, 3).

A weathering sequence proposed by Fieldes (1955) for mainly rhyolitic tephtras has been modified and widely adopted by many workers since then (Fieldes and Furkert, 1966; Masui and Shoji, 1969; Cortes and Franzmeier, 1972a; Wada and Harward, 1974; Dudas and Harward, 1975a; Kirkman, 1975, 1976b, 1980a, 1981a; Fieldes and Claridge, 1975; Kirkman and Pullar, 1978; Rankin and Churchman, 1981). This sequence is essentially as follows:



The transition from glass to allophane in New Zealand was estimated to take about 3,000 yr, and from allophane to halloysite about 10,000 to 15,000 yr (Vucetich, 1968; Birrell and Pullar, 1973; Pullar *et al.*, 1973; Kirkman, 1975, 1976b, 1981a). Under humid temperate conditions in Japan, the allophane–halloysite transformation occurs after about 6,000 yr [Fig. 1, Wada (1977) and Nagasawa (1978)]. With time, the halloysite crystals enlarge and become better-ordered, attaining a diameter of up to $1 \mu\text{m}$ in 250,000 yr or so [Kirkman (1981a), see also Wada (1980), p. 96].

TABLE I
RELATIONSHIP BETWEEN TEPHRA AGE AND CLAY CONTENT OF SOME TEPHRAS
FROM NEW ZEALAND

Tephra name	Approximate age (yr BP) ^a	Average percentage of clay (< 2 μm) in tephra ^b	(n) ^c
Kaharoa Ash	900	6	(1)
Taupo Pumice	1,800	5	(7)
Waimihia Formation	3,400	5	(2)
Whakatane Ash	5,200	7	(4)
Mamaku Ash	7,000	8	(8)
Waiohau Ash	11,300	18	(3)
Rerewhakaaitu Ash	14,700	9	(7)
Okareka Ash and Te Rere Ash	19,000	15	(7)
Kawakawa Tephra	20,000	18	(11)
Tahuna Tephra and others	30,000	16	(10)
Rotoehu Ash	42,000	25	(9)
Hamilton Ash	100,000–400,000	65	(10)
Kauroa Ash	500,000–1,000,000	85	(43)

^a Ages from Pullar *et al.* (1973), Gibbs (1980), and Pullar (1980).

^b Tephtras are mainly rhyolitic but contain small proportions of admixed andesitic material at some sites. Hamilton and Kauroa tephtra sequences may contain some largely andesitic beds. Data after Birrell and Pullar (1973), Hogg (1974), Davoren (1976), Salter (1979), Lowe (1981a), and D. J. Lowe (unpublished).

^c n = number of samples analyzed.

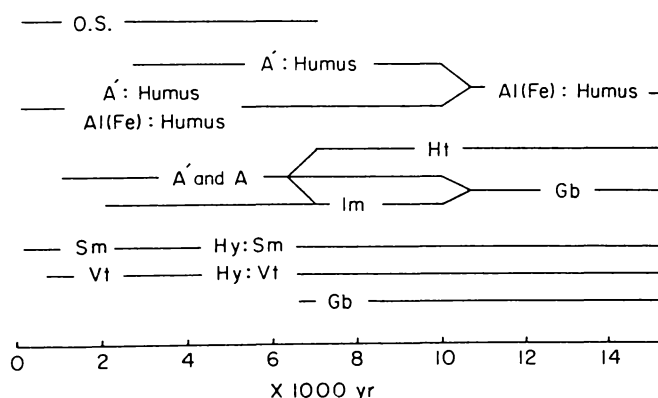


FIG. 1. Formation and transformation of clay minerals and their organic complexes in soils developed from tephras in humid temperate climatic zones in Japan. Abbreviations: A, allophane; A', allophane-like constituents; Al (Fe), sesquioxides; Ch, chlorite; Gb, gibbsite; Ht, halloysite; Im, imogolite; Sm, smectite; Hy:Sm, hydroxy interlayered smectite; O.S., opaline silica; Vt, vermiculite; Hy:Vt, hydroxy interlayered vermiculite. Horizontal lines represent approximate duration of the respective constituents. [Reproduced from "Minerals in Soil Environments," (1977, p. 620), by permission of the Soil Science Society of America and the author, K. Wada (1977).]

Thus, allophane and imogolite were shown to have a relatively short residence time due to their transformation to either halloysite or gibbsite, depending on environmental factors [Fig. 1 and Wada (1977)]. However, allophane and imogolite evidently persist for long time periods at some locations, such as in the strongly weathered Hamilton Ash Formation and Kauroa Ash Formation in New Zealand (Ward, 1967; Tonkin, 1970; Hogg, 1974; Salter, 1979; Kirkman, 1980b). They coexist with authigenic halloysite in very young (<2,500 yr) deposits such as Taupo Pumice and Mapara Tephra formations in New Zealand (McIntosh, 1979), and in a 2,000-yr-old lahar from Mount St. Helens, Washington (Mullineaux and Crandell, 1962). This implies that tephra composition and site weathering conditions frequently may have been underestimated in favor of the assumed tephra age-based weathering sequence. The relatively rapid rate of halloysite formation (in 300 to 4,000 yr) noted for deposits in humid tropical areas [e.g., Hay (1960), Cortes and Franzmeier (1972b), Bleeker and Parfitt (1974), Parfitt (1975)] further supports the view that the apparent transformation of allophane into halloysite cannot be expressed as a simple function of time [Nagasawa (1978), p. 118].

The above findings do not invalidate clay mineral transformation diagrams such as Fig. 1 because these represent measurements of real compositions at particular locations. The possibly misleading aspect of such weathering sequences, however, is that the transition rates are frequently construed as a direct function of the tephra age scale whereas factors other than time or aging actually dictate the rates of transformation.

b. Relict Transformation Rates and Effective Period of Weathering. Various studies have related the amounts and types of weathering products in tephra-derived paleosols to the effective period of weathering in order to explain the common coexistence of allophane and halloysite. Ugolini and Zasoski (1979) suggested that the occurrence of allophane and imogolite, together with halloysite, in a buried soil was related to its (relict) leaching when at the land surface. In New Zealand, Vucetich (1968), Birrell and Pullar (1973), and Birrell *et al.* (1977) attributed apparent changes in rates and products of weathering to changes in climate during the Quaternary — i.e., a residual or “memory” effect of paleoclimate. Kirkman (1976b), working on similar tephra sequences, suggested that the time between the burials of successive paleosols was insufficient to “register” the effect of changes in climate. Further uncertainty arises due to sparse unequivocal information on changes in the rates and conditions of weathering after burial (Gibbs, 1971, 1980; Mausbach *et al.*, 1982; Stevens and Vucetich, 1984). However, some of the differences in clay mineralogy observed in modern and buried tephra soils are directly attributable to the supply of organic matter (Mizota,

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1978) (see also Section II, B, 3). Hodder (1978) examined the hydration of rhyolitic glasses from buried Holocene tephras in New Zealand and demonstrated an Arrhenian relationship between temperature history and effective time for weathering. He suggested that the degree of weathering of the glass or the formation of allophane may be related to the effective weathering time but is likely to be more dependent on climatic factors.

In conclusion, it is evident that in many studies the length of time of weathering was viewed as the governing factor in clay mineral transformations and hence in the distribution and coexistence of allophane and halloysite in particular. However, other interpretations now tend to place more emphasis on separate genetic pathways for tephra-derived clay minerals. The pathways are influenced by both primary mineral composition and site weathering conditions, past and present [e.g., Yoshinaga *et al.* (1973a), Wada and Harward (1974), Birrell *et al.* (1977), Wada (1977, 1980), McIntosh (1980a), and Parfitt *et al.* (1982a)]. Furthermore, as demonstrated below, short-range-order minerals such as proto-imogolite allophane and imogolite are not just short-lived transition products but sometimes are metastable reaction end points. Conversely, halloysite and gibbsite, typically regarded as reaction end points derived from short-range-order precursor minerals, can apparently form rapidly and directly by precipitation of dissolution products of either primary or secondary minerals, or both.

2. Compositional Controls

Composition-dependent weathering sequences indicate that chemical and structural characteristics of the parent glass, together with the proportions and compositions of the various other primary minerals making up the parent assemblage, determine in part the composition, type, and morphology of resultant clays. Some may include mineral transformation rate factors. The actual kinetic mechanisms associated with the weathering of glass and similar materials are covered by White and Claassen (1980), White (1983), and Hodder (1985).

a. Andesitic versus Rhyolitic Composition. Unweathered andesitic and rhyolitic tephras differ mineralogically and chemically—the less siliceous andesitic eruptives are typically relatively enriched in mafic minerals, contain less glass, and may be dominated by Al- and Ca-rich plagioclase feldspars; in bulk chemistry they tend to have more Al, Ti, Fe, Mg, and Ca than rhyolitic eruptives [e.g., see Ewart (1969), Cole (1979), Inoue and Yoshida (1980), Kirkman and McHardy (1980), and Izett (1981)]. A study by Stevens and Vucetich (1984) in North Island, New Zealand, indicated that these chemical differences are generally maintained after weathering (weathered andesitic tephras having more Fe and Ti than weathered rhyolitic tephras)

[see also Kirkman and McHardy (1980)]. Where this relationship had apparently broken down, Stevens and Vucetich (1984) invoked changes in the leaching regime or topographic effects related to rates of tephra accretion.

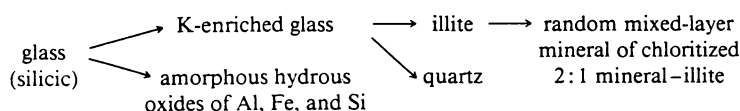
Andesitic glass ($\text{SiO}_2:\text{Al}_2\text{O}_3 = \text{less than } 2$) has an intrinsically smaller molar Si:Al ratio and a "soft," porous structure that favors weathering at a much higher rate than rhyolitic glass ($\text{SiO}_2:\text{Al}_2\text{O}_3 = 5 \text{ or } 6$) [Kirkman (1981a), p. 169], and with a marked loss of silica and mobile cations (Mizota and Aomine, 1975; Neall, 1977; Kirkman and McHardy, 1980; Kirkman, 1981a; White, 1983) (see also Table II in Section III). Kirkman and McHardy (1980) and Kirkman (1981a) concluded that the structure and chemical composition of allophane, hence its behavior and persistence, are governed chiefly by these glass chemical and bonding characteristics. This conclusion supports an earlier study by Trichet (1969) that involved laboratory leaching of glasses of differing compositions, and a study by Hamblin and Greenland (1972) on basaltic tephra deposits. Tokashiki and Wada (1975) found that allophane and imogolite predominated in andesitic tephtras, which contained only sparse quartz, and layer silicates in quartz-rich dacitic tephtras from Japan. They concluded that this compositional effect outweighed other possible factors such as environmental conditions and time since deposition. An investigation by Mizota (1976) led to similar conclusions.

Studies on the clay minerals formed in mainly andesitic tephtras weathered under humid tropical (e.g., Papua New Guinea) or temperate (e.g., Japan and New Zealand) climatic conditions found that: (1) halloysite is normally absent or only sparsely present (Parfitt, 1975; Parfitt *et al.*, 1982a); (2) stable allophane and imogolite form rapidly (in 300 yr) from the weathering of glass or pumice, and persist for long periods (Parfitt, 1975; Kirkman, 1978, 1980a,b, 1981a; Kirkman and McHardy, 1980; Russell *et al.*, 1981; Violante and Wilson, 1983); (3) gibbsite can form rapidly, coexisting with allophane and imogolite in deposits as young as 3,000 yr, but is generally more common in older deposits [Fig. 1, Wada and Matsubara (1968), Yoshinaga *et al.* (1973a), Parfitt (1975), Mizota (1976), and Wada (1977)]; and (4) gibbsite evidently forms through desilication of allophane and imogolite, sometimes only after a long time period (100,000 yr or more) [references in (2) above], but its formation is not dependent upon humid tropical climatic conditions (Wilson, 1975; Macias Vazquez, 1981; Shah Singh, 1982); its occurrence has also been associated specifically with lithic fragments or feldspar in the primary tephra deposit (Wada and Matsubara, 1968; Loi *et al.*, 1982). In New Zealand, relatively low concentrations of gibbsite in clays derived from andesitic tephtras, even in those that are strongly weathered (Taylor, 1933; Fieldes and Taylor, 1961; Tonkin, 1970; Yoshinaga *et al.*, 1973b; Salter, 1979; Kirkman, 1980a,b; Stevens and Vucetich, 1984), have been explained

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either by unfavorable site conditions that minimize desilication [e.g., Schwertmann (1979), Farmer *et al.* (1979), Kirkman (1980a)], or by the presence of iron oxide gel inhibitors (Kirkman and McHardy, 1980). Clearly, for New Zealand conditions, neither Al-rich glass and Al-rich feldspar and mafic-rich mineralogy nor the length of weathering time has been sufficient to produce gibbsite in other than small amounts or localized concentrations. Rather, allophane predominates (Kirkman, 1980b), hence environmental controls must be more dominant than time or composition in the weathering process, except where an unequivocal parent material effect can be demonstrated.

b. Origin of 2:1 and 2:1:1 Type Minerals. The genesis of 2:1 and 2:1:1 type clay material in tephra is controversial (Lowe and Nelson, 1983). A minority of workers, mainly in Japan, favor a "pedogenic" origin and suggest that the 2:1 clays derive from volcanic glass in a solid-state reaction that is related to the mobilities of SiO₂, MgO, and K₂O. The 2:1 clays may form coevally with opaline silica or quartz under conditions characterized by excess silica, low allophane, and low pH (Chichester *et al.*, 1969; Trichet, 1969; Wada and Aomine, 1973; Tokashiki and Wada, 1975; Hetier *et al.*, 1977; Shoji and Saigusa, 1977; Nagasawa, 1978; Yamada *et al.*, 1978; Kurashima *et al.*, 1981; Shoji *et al.*, 1981, 1982). Shoji *et al.* (1981, p. 344) proposed the following weathering sequence:



The preferential retention of potassium in volcanic glass has been demonstrated by Yamada and Shoji (1982).

Other workers favor the transformation of ferromagnesian minerals (principally micas, amphiboles, and pyroxenes), which are derived from either the primary tephra deposit [e.g., Calhoun *et al.* (1972), Cortes and Franzmeier (1972a), Pettapiece and Pawluk (1972), Wada and Aomine (1973), Tokashiki and Wada (1975), Mizota (1976), and Violante and Wilson (1983)] or postdepositional contamination by eolian accessions [e.g., Jackson *et al.* (1971), Mokma *et al.* (1972), Mizota (1982), and Mizota and Takahashi (1982)]. Evidence for the latter is based on distinctive ¹⁸O:¹⁶O ratios of silt-sized quartz particles isolated from soils in various countries [e.g., Stewart *et al.* (1984)]. The ratios show that the quartz, possibly together with 2:1 clay minerals, derives from continental dusts carried by tropospheric winds. Other sources of 2:1 type clays include "exotic" (or hydrothermally altered) layer silicates incorporated into the tephra during eruption [e.g., Kirkman (1976a), Dudas and Harward (1975b), Self and Sparks

(1978), Wada (1980), Dethier *et al.* (1981), and Pevear *et al.* (1982)], and detrital 2:1 clays in underlying materials that are subsequently mixed into the tephra deposit by processes such as tree fall [e.g., Dudas and Harward (1975b)]. Smectites may form from plagioclase under conditions of restrictive drainage (Borchardt, 1977; Glassmann, 1982).

In New Zealand, 2:1 minerals are rarely reported in "pure" volcanic ash deposits but they are relatively common in soils formed on loess derived from mica-bearing, quartzo-feldspathic sedimentary rocks and alluvium that also contains admixed volcanic ash (Cowie and Milne, 1973; McCraw, 1975). Thus, most New Zealand workers are suspicious of the pedogenic pathways explaining the 2:1 clays in tephtras in Japan, and prefer a "loessic contamination" explanation for their occurrence [e.g., Mokma *et al.* (1972), Stewart *et al.* (1977), Rankin and Churchman (1981), Russell *et al.* (1981)]. Ugolini and Zasoski (1979) similarly reject the pedogenic model.

c. Morphologies of Halloysite and Parent Mineralogies. Halloysite occurs in tephra-derived clays as spherical, roughly concentrically banded particles, or as tubes, scrolls, or curled flakes (Dixon, 1977; Kirkman, 1981b). Platy, tabular, and disk-shaped halloysite has also been reported (Kirkman, 1977). Evidence suggests that these morphological forms are directly related to primary mineralogy. Spherical halloysite may originate from rhyolitic glass, tubular halloysite from feldspar (mostly in rhyolitic rather than andesitic tephtras), and by various possible mechanisms [e.g., Parham (1969), Eswaran and De Coninck (1971), Dixon and McKee (1974), Nagasawa and Miyazaki (1976), Kirkman (1977, 1981b), Sudo and Yotsu-moto (1977), Violante and Violante (1977), Wada *et al.* (1977), Kirkman and Pullar (1978), Kohyama *et al.* (1978), Tazaki (1979), Rankin and Churchman (1981)]. Wada (1980) suggests that because the greatest amounts of allophane and imogolite coexist with the smallest particles of halloysite, the halloysite may be a recrystallization product of resilication of the allophane and imogolite.

It is concluded that the primary composition of parent tephra materials plays an important role, at least initially and in some cases persistently, in the types and composition of materials and clays produced by weathering. In general, halloysite is largely associated with rhyolitic tephtras, crystallizing directly from the dissolution products of feldspar or glass, and without a transitional allophane phase. Busenberg (1978) reports from dissolution experiments on feldspars that a "microcrystalline gibbsite" phase apparently precedes the rapid formation of halloysite. Allophane (Al:Si \approx 2:0), imogolite, and gibbsite predominate in andesitic tephtras and are able to form rapidly and to persist for long periods. Some 2:1 and 2:1:1 type minerals may form because of specific primary mineralogies. However, to explain the

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presence or absence of these various clay minerals at many sites, special conditions, special pedogenic pathways, and length of time have each been invoked. Apparently, the influence of environmental conditions does not just complement that of composition—it is ultimately of perhaps paramount importance in clay mineral genesis.

3. *Environmental Controls*

Environmental factors that affect the site weathering conditions include temperature, rainfall, degree of leaching, drainage, tephra thickness and depth of burial, and vegetation and other organic cycle factors. The chief effect of these factors, together with the composition of the inorganic phase, is in governing the proportions and availabilities of the main chemical constituents, SiO_2 and Al_2O_3 , in the tephra sequence [e.g., Aomine and Wada (1962), Jackson (1968), Kanno *et al.* (1968), Pedro *et al.* (1969), Millot (1970), Aomine and Mizota (1973), Rodrique *et al.* (1973), Yoshinaga *et al.* (1973a), Wada and Harward (1974), and Wada (1977, 1980)]. Generally, the environmental factors, some of which are interdependent, control the site conditions, which in turn favor either resilication or desilication and control the opportunity for coprecipitation of Al and Si gels. Some factors are regional or macroenvironmental (e.g., rainfall and temperature in a district), whereas others are local or microenvironmental (e.g., drainage conditions or the pH of percolating water at one site) (Hay, 1959; Eswaran and De Coninck, 1971; Glassmann, 1982). It is often difficult to determine which of these macro- or microfactors is more important [e.g., Stevens and Vucetich (1984)]. Consequently, it is not surprising that a tephra weathering sequence of universal application has been difficult to identify, especially since the rates and types of transformations in adjacent tephra sequences or within one sequence may differ markedly.

a. Temperature Effect. It is well known that higher temperatures promote higher rates of reaction in various geochemical systems [e.g., Curtis (1977)]. Climosequence studies have shown that an increase in the degree of weathering of tephra (e.g., an increase in clay content) is related to an increase in mean temperature (Calhoun *et al.*, 1972; Cortes and Franzmeier, 1972b; Birrell *et al.*, 1977; Lulli and Bidini, 1980). However, variations in rainfall, vegetation, depth of overburden, and tephra distribution usually coincide with the temperature variations. In New Guinea, Ruxton (1968) demonstrated that the rate of weathering of dacitic glass was limited by rainfall and ground water control (i.e., leaching potential), not temperature [see Hutton (1974), Hodder (1978)]. In comparison, a lower rate of weathering of andesitic glass from tephra in Taranaki, New Zealand, was attributed

to differences in drainage, composition, and rates of tephra accretion and lahar deposition, rather than to differences in temperature (Neall, 1977).

On an experimental thermodynamic basis, Farmer *et al.* (1979) showed that temperature as well as silica concentration affects the stability of various equilibria of silica and alumina, and that while imogolite, halloysite, and gibbsite can coexist over a range of temperatures, imogolite tends to be metastable relative to either halloysite or gibbsite in the long term. Above 25°C, imogolite and proto-imogolite become more stable relative to halloysite over a wide range of silica concentrations. Thus, although halloysite formation (stability) is theoretically favored by lower temperatures, an overriding requirement in its formation is a sufficient concentration of silica ($> \sim 20 \mu\text{g}/\text{cm}^3$) in solution (Farmer *et al.*, 1979, Parfitt *et al.*, 1983). In the North Island of New Zealand, present soil temperatures over a depth range of 1 m rarely exceed 20°C and normally average 10 to 15°C for a calendar year (Cowie, 1978; Wilson, 1980). Ambient temperatures during late Pleistocene glacial stages in the central North Island were about 4 to 6°C lower than present (Hendy and Wilson, 1968; Fleming, 1979). However, conditions were drier or more drought-prone (McGlone and Topping, 1977; McGlone *et al.*, 1978), hence rates of leaching of silica were probably reduced. Because this temperature drop coincides with reduced rainfall and leaching regimes, the possible contributory role of paleotemperature in clay mineral formation and transformation cannot be evaluated with certainty [see also Morrison (1978), Singer (1980), Retallack, (1981), and Ross *et al.* (1983)].

b. Rainfall and Leaching Effects. Rainfall may be regarded as a reliable indicator of leaching (Jenny, 1941), although this relationship is not always valid (e.g., where drainage is restricted). A relationship between rainfall distribution and degree of leaching, and the occurrence of various mineral types in tephra, was noted in New Zealand by Taylor (1933). Later, Fieldes (1966) correlated the occurrence of allophane with a high, seasonally well-distributed rainfall. He proposed that halloysite formed by the "crystallization" of random aluminosilicate "gels" (allophane) through Si-O-Al cross-linkage and seasonal dehydration over time. This hypothesis is in hindsight largely misleading as it is now known that allophane and related minerals have short-range order and that halloysite may crystallize directly from the dissolution products of primary minerals. However, rainfall and the leaching regime normally play a dominant role in the weathering of tephra and in determining the composition and stability of the clay product.

Allophane (Al:Si = 2:0), allophane-like constituents, imogolite, and proto-imogolite allophane generally occur where rainfall (and usually leaching, depending on drainage conditions) is moderate to high; allophane

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(Al:Si = 1.0), halloysite (especially the 7-Å phase), and possibly silica precipitates tend to occur where rainfall is low (Ruxton, 1968; Nagasawa, 1969; Wada and Harward, 1974; Nagasawa and Miyazaki, 1976; Neall, 1977; Lulli and Bidini, 1980; Wada, 1980; Kirkman, 1981a; Lowe and Gibbs, 1981; Miehl, 1981; Parfitt *et al.*, 1982a, 1983). Under a moderate to high rainfall, and low pH, SiO₂ and mobile cations are rapidly lost; hence the formation of allophane and imogolite, with an Al:Si ratio of around 2 or more, is preferred to the formation of halloysite or allophane with an Al:Si ratio nearer 1 [Fig. 2; see also Parfitt *et al.* (1984)]. Similarly, gibbsite may form if Si in solution is very low (< 1 ppm) in order to prevent Al-silicate formation, as in highly leached sequences, and possibly together with an Al-rich parent mineral composition (e.g., andesitic glass or abundant calcic plagioclase) (Parfitt, 1975; Aomine and Mizota, 1973; Schwertmann, 1979; Violante and Tait, 1979).

The effect of past rainfall amounts may be reflected in the present-day clays: Parfitt *et al.* (1983) inferred that some of the halloysite (and, presumably, allophane of Al:Si = 1.0 composition) in tephras they examined may be relict from a late Pleistocene glacial period when rainfall, hence leaching of Si, was lower, and temperatures were cooler than present.

Allophane and other aluminosilicates of short-range order may transform, via solution, to halloysite or gibbsite, largely depending on whether the

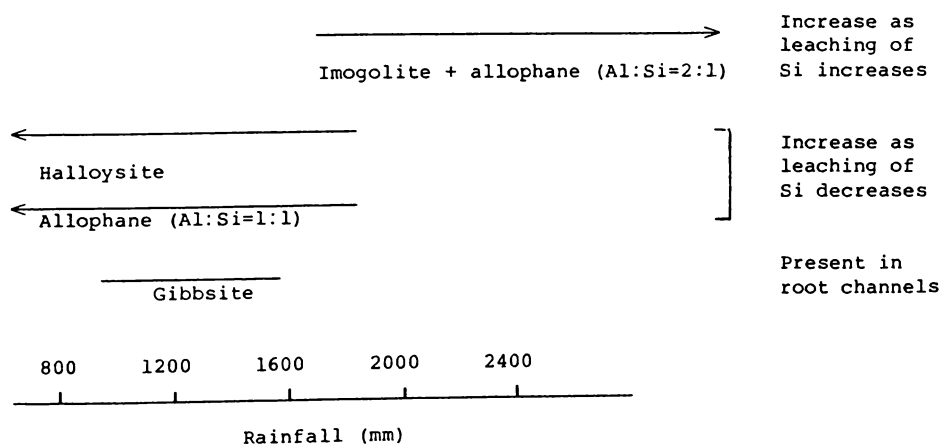


FIG. 2. Weathering scheme proposed for rhyolitic tephras in New Zealand aged between 2,000 and 100,000 yr. The amounts of the various clay minerals increase or decrease according to the degree of leaching of Si as a function of mean annual rainfall. A parallel weathering sequence for humus-rich horizons of tephras in northeastern Japan has been given by Shoji and Fujiwara (1984), based on pH and leaching. [Modified after "Weathering sequence of soils from volcanic ash involving allophane and halloysite, New Zealand," (1983, p. 54), of *Geoderma* 29, 41-57, by permission of Elsevier Scientific Publishing Co. and R. L. Parfitt *et al.* (1983).]

environmental conditions, in addition to the rainfall factor, favor resilication or desilication (Aomine and Mizota, 1973; Parfitt, 1975; Wada, 1977; Saigusa *et al.*, 1978; Miehllich, 1981; Rankin and Churchman, 1981; Violante and Wilson, 1983). Parfitt *et al.* (1982a) report that Al-rich allophane (with the proto-imogolite structure) cannot alter to halloysite since Si tetrahedra occur on the interior surface of the hollow allophane spherules as isolated SiO_3OH groups with their apices directed away from outer gibbsitic units, the reverse of the kaolinite structure (Cradwick *et al.*, 1972; Brown *et al.*, 1978; Farmer and Fraser, 1979; Wada, 1979; Parfitt, 1980). Thus, alteration to halloysite would necessitate the allophane effectively turning "inside out" by passing through a solution phase (decomposing) with concomitant enrichment with polymerized silica. Wada and Inoue (1974) measured concentrations of absorbed monomeric silica in ambient solutions associated with different clay species in tephras in Japan as follows: allophane and imogolite (Al:Si = 2.0), 11–12 $\mu\text{g cm}^{-3}$; allophane (Al:Si = 1.0), 22 $\mu\text{g cm}^{-3}$; and halloysite, 26 $\mu\text{g cm}^{-3}$. These values, and those given in McIntosh (1980a) and Parfitt *et al.* (1983), support the above results [also see Farmer *et al.* (1979)]. Wada (1977) noted that these concentrations may have a two-way effect on clay mineral formation. Similarly, Busenberg (1978) showed experimentally that the poorly ordered clay mineral phases (notably halloysite) that formed from the dissolution of feldspars controlled in part the activities of Al and silicic acid in the aqueous solution.

The study of synthetic aluminosilicates of short-range order has shown that allophane forms inside weathered glass or pumice fragments (or feldspar) where Si concentration and pH are relatively high [Wada (1980), p. 95]. Imogolite forms outside, possibly by alteration of allophane exposed to external solutions of lower Si concentration and lower pH (< 5), or by precipitation from such solutions whereby Al and Si form a soluble and mobile complex of proto-imogolite that is stable at pH less than 5 (Wada and Matsubara, 1968; Aomine and Mizota, 1973; Yoshinaga *et al.*, 1973a; Henmi and Wada, 1976; Brown *et al.*, 1978; Farmer and Fraser, 1979; Farmer *et al.*, 1979, 1980; Wada, 1980). Allophane requires a neutral or alkaline pH to give maximum Al in 4-fold coordination, whereas imogolite requires an acid pH, and high Al:Si ratio, to maintain Al in 6-fold coordination with monomeric silica (Brown *et al.*, 1978). The importance of pH in influencing the formation of allophane and imogolite is emphasized as it largely controls the types and amounts of Al species and their potential for coprecipitation with Si. It also plays a part in the rate of glass and feldspar dissolution (Busenberg, 1978; White and Claassen, 1980). Shoji *et al.* (1982) consider that the supply of H^+ ions (dissociated from organic acids) and the depletion of bases by leaching are the dominant controls in pH determination, and that these controls in turn are related to climate (especially intensity of leaching) and vegetation factors (see also Shoji and Fujiwara, 1984).

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c. Drainage Effect. The leaching regime in a tephra sequence is controlled in part by the site drainage conditions. Impeded or slow drainage and a "stagnant" (i.e., silica-rich) moisture regime (e.g., due to an impermeable buried paleosol) would tend to minimize the rate of loss of soluble Si and other cations and thus favor the formation of halloysite and silica-rich allophane (Al:Si = 1.0) (also smectites) (Kanno, 1959; Aomine and Wada, 1962; Yoshinaga *et al.*, 1973a; Wada and Harward, 1974; Dudas and Harward, 1975a; Wada, 1977, 1980; Lowe, 1981a; Violante and Wilson, 1983). Conversely, other conditions being equal, good drainage would promote the loss of silica and the formation of allophane (Al:Si = 2.0) and imogolite [e.g., Neall (1977)]. Between these drainage extremes an intermediate form of allophane is predicted to occur (Vucetich, 1983)—and shown by Parfitt *et al.* (1984).

An example of the effect of drainage is evident in the Waikato region in New Zealand (see Section III). Late Pleistocene rhyolitic volcanogenic and tephra-rich alluvium, with an ~0.3-m covering of largely admixed Holocene tephra deposits (Lowe *et al.*, 1980), was deposited about 17,000 yr ago by a braided river system (McCraw, 1967; Hume *et al.*, 1975; Green and Lowe, 1986). These deposits are weathering in either well-drained sites on low ridges of coarse material (sands), or poorly drained sites in shallow depressions (swales) of fine material (silts) adjacent to the ridges and with evidence of gleying. The clay fraction of the well-drained deposits is dominated by allophane with traces of gibbsite, whereas that of the poorly drained deposits is dominated by halloysite (McQueen, 1975; Pollok *et al.*, 1981). Clearly, as the deposits are geologically contemporaneous, occur close together in the same climatic regime, and have similar primary mineralogies, but contrasting textures, the different drainage conditions and ground water levels must be responsible for the different clay minerals present.

d. Tephra Thickness and Depth-of-Burial Effect. Deep burial alters the rate and opportunity for weathering and pedogenesis, especially as regards the organic cycle and clay mineral transformation (Ruxton, 1968; Gibbs, 1971). For example, burial of a surface horizon reduces the organic input, hence in time allows previously humus-bound Al to be released by weathering and to ultimately coprecipitate with Si to form allophane or imogolite (Mizota, 1978). A thick sequence (> 2 m) potentially provides a silica-rich environment for a buried tephra and hence favors the formation of halloysite in it by resilication (Aomine and Wada, 1962; Masui and Shoji, 1969; Calhoun *et al.*, 1972; Shoji and Saigusa, 1977; Wada, 1977; Nagasawa, 1978; Saigusa *et al.*, 1978; Sudo and Shimoda, 1978; Ugolini and Zasoski, 1979; McIntosh, 1980a; Violante and Wilson, 1983). Regular accretions of fresh silica-rich tephras, or poor drainage, would tend to enhance this effect [e.g., Calhoun *et al.* (1972), Yoshinaga *et al.* (1973a), Dudas and Harward

(1975a), Shoji and Saigusa (1977), and Lowe and Gibbs (1981)]. The rate of tephra accumulation and burial may also have a significant effect on site conditions, such as topography, and hence lateral drainage (Taylor, 1933; Gibbs, 1968; Stevens and Vucetich, 1984).

Halloysite occurs rarely in tephra horizons at or near the land surface (Masui and Shoji, 1969; Mizota and Wada, 1980; Rankin and Churchman, 1981; Parfitt *et al.*, 1983; Violante and Wilson, 1983; Shoji and Fujiwara, 1984). Where it does, the horizons are usually strongly weathered and possibly exhumed [e.g., New Zealand Soil Bureau (1968), Wada (1980)] with relict halloysite derived either from formation at depth due to a burial or aging effect, or from changes in surface weathering conditions [e.g., Masui and Shoji (1969), Gibbs (1971), Kirkman (1980b), Vucetich (1983), and Stevens and Vucetich (1984)]. McIntosh (1979), however, showed that authigenic halloysite (both spheroidal and tubular) can form by modern processes in tephra deposits aged as young as 1,800 yr and buried (by highly siliceous pumice materials) at a depth of 2 to 2.5 m. He demonstrated that the halloysite formation at this depth was due to resilication from a silica-rich solution (McIntosh, 1980a). The resilication was indicated by $\text{SiO}_2:\text{Al}_2\text{O}_3$ mole ratio values of ~ 2.0 at depths of 2 m or more, in contrast to values of ≤ 1.0 in surface horizons, and by lysimeter leachate compositions.

McIntosh's evidence, together with that from elsewhere (notably Japan), emphasizes the marked effect of tephra overburden in determining the availability of silica in solution. The overburden (and leaching) effect has previously been difficult to positively separate from an age effect because most studies on successions of tephra deposits and paleosols [e.g., Masui and Shoji (1969), Kirkman (1975, 1980a), and Nagasawa (1978)] showed that the content of halloysite and its degree of crystallinity increased with increasing depth, and therefore with increasing age. These depth trends hence implied an allophane-halloysite transition based on an age factor. Nevertheless, where halloysite occurs in a buried tephra or paleosol, and is due to resilication from the overburden, its formation is an indirect consequence of age because time is required to bury the tephra with a relatively thick cover deposit. The length of this period depends on the nature and eruptive frequency of the contributing volcanoes, and on the rate of addition of possible "tephric loess" to the tephra sequence.

e. Organic Cycle Effects. The deep accumulation of black humus in tephra-derived soils, especially in Japan, is usually associated with warm and humid, well-drained conditions and a grass (often pampas) vegetation (Wada and Harward, 1974; Shoji and Ono, 1978). The humus frequently coexists with stable Al- and Al/Fe-humus complexes and opaline silica in A_1 horizons, but with allophane and imogolite absent (Fig. 1; Wada, 1977).

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This relationship is generally explained with the suggestion that Al ion activity is suppressed by the formation of stable Al–humus complexes that are resistant to biological breakdown and leaching. Consequently, opaline silica and possibly other silica polymorphs form instead of allophane or imogolite because the Al–humus bonding reduces the potential for coprecipitation of Al and Si (Shoji and Masui, 1971; Wada and Harward, 1974; Tokashiki and Wada, 1975; Wada and Higashi, 1976; Wada, 1977; Mizota, 1978; Shoji and Saigusa, 1978; Henmi and Parfitt, 1980; Mizota and Wada, 1980). The Al–humus complexes undergo changes with age and burial (Mizota, 1978; Higashi and Shinagawa, 1981). This conclusion suggests a balance between the release rate of Al (and Fe) and the supply rate of organic matter (hence organic acids) (Wada, 1977; Huang and Keller 1971; Antweiler and Drever, 1983), which, together with silica availability, governs the formation rate of allophane and imogolite. The rate of alteration of glass (or clay minerals) is greatest in the A horizons of tephra-derived soils (Antweiler and Drever, 1983).

Living plants affect monosilicic acid concentration and biogenic opal and opaline silica formation [e.g., Wilding and Drees (1971), Wilding *et al.* (1977), Claridge and Weatherhead (1978), Shoji and Saigusa (1978), Henmi and Parfitt (1980), and Shoji *et al.* (1982)]. Biogenic opal forms through uptake of Si in solution by living plant cells. Most studies contend that opaline silica forms only in the early stages of weathering of tephtras. An alternative view is that it simply forms in near-surface tephtras (which are usually young and relatively unweathered). Opaline silica formation is favored by the supersaturation of silica by surface evaporation or plant evapotranspiration and the suppression of Al activity by humus accumulation, together with an abundant supply of soluble silica [e.g., Shoji and Saigusa (1978)]. The removal of Si in solution by plant roots [increased by cropping; Mizota and Wada (1980)] may also promote the formation of allophane (Al:Si = 2.0), imogolite, and possibly gibbsite [the last, for example, as root pseudomorphs; Wada and Matsubara (1968), Hogg (1974)] (Parfitt *et al.*, 1983). Alternatively, biogenic opal may be redissolved and either leached or precipitated with available Al to form allophane (Al:Si = 1.0) (Parfitt, 1975). The redissolved silica may form another polymorph such as cristobalite [Fig. 3; Shoji and Masui (1969), Wilding *et al.* (1977), and Lowe (1981a)]. Both primary and secondary origins for such silica polymorphs have been proposed, with some evidence controversial [e.g., Hardjosoestro (1956), Breese (1960), McKeague and Cline (1963), Henderson *et al.* (1971, 1972), Cortes and Franzmeier (1972a), Güven and Grim (1972), Jones and Segnit (1972), Jackson *et al.* (1977), and Wilding *et al.* (1977)].

Different types of vegetation may affect the types and rates of clays formed in tephtras. Leaching regimes, hence soil solution compositions, vary with vegetation types (Taylor, 1933; McIntosh, 1980a; Parfitt *et al.*, 1983). McIn-

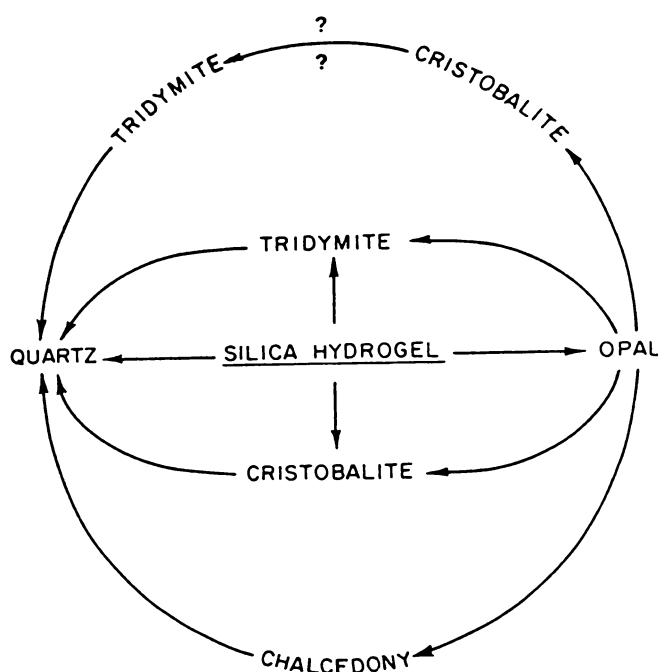


FIG. 3. Proposed pathways for conversion of silica hydrogel to various silica polymorphs. [Reproduced from "Minerals in Soil Environments," (1977, p. 516), by permission of the Soil Science Society of America and L. P. Wilding *et al.* (1977).]

tosh (1980b) showed that the replacement (in 1935) of native manuka trees by radiata pine on rhyolitic tephras in New Zealand produced changes in pH, titratable Al, exchangeable cation, total N, and organic P values of the deposits. Solution pH and Al and Fe mobility control the formation of imogolite and allophane (via precursory proto-imogolite) (Farmer *et al.*, 1980; Farmer, 1982), and are apparently important in the chloritization of 2:1 layer silicates also (Shoji *et al.*, 1982). Acid litter gives low pH values (<5) [McIntosh (1980b), Shoji *et al.* (1982), also studies on nontephric materials], which allow soluble proto-imogolite to form (Wada, 1980; Anderson *et al.*, 1982; Farmer, 1982). The effect of long-term vegetation change has rarely been considered in clay mineral genesis. In view of the findings above, it is clear that vegetation change may have influenced the types of clays occurring in a particular tephra bed. The vegetation change is likely to be difficult to separate from, for instance, a change in climate or an increase in depth of burial, however.

Pedoturbation by floral and faunal processes [e.g., Mueller and Cline (1959), Buntley and Papendick (1960), Hole (1961, 1981), Armson and

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Fessenden (1973), Dudas and Harward (1975b), Brown (1977), and Mizota and Wada (1980)] has its greatest influence in surface deposits. However, pedogenic mixing to depths of about 1 to 2 m in composite tephra deposits is reported by Lowe (1981a,b) and Hogg and McCraw (1983). A potentially important effect of this mixing is the masking of the tephra stratigraphy, especially where deposits are thinly bedded [e.g., Hodder and Wilson (1976)], thus complicating and possibly invalidating parent material-clay mineral genesis correlations. Another effect is the "contamination" of a particular deposit with detrital or exotic clay or other minerals from another bed [e.g., Dudas and Harward (1975b)].

C. CONCLUSIONS

The types and rates of formation and transformation of clay minerals derived from tephra deposits of acid to intermediate composition are determined chiefly by macro- and microenvironmental factors together with the mineralogical and physicochemical composition of the parent deposits. The length of time of weathering in clay mineral genesis is indirect and subordinate in its effect, in that weathering rates, and weathering products and their alteration, are largely dictated by other controls. The amounts of clay formed normally reflect the site weathering conditions. However, where tephras of different ages and weathering under broadly similar conditions are compared, a general correlation of increasing clay content with increasing age is found.

The environmental conditions that are the most important are those that affect the concentration of silica in solution, the movement and availability of alumina, and the opportunity for their coprecipitation. The pH of the solution, especially at a microscopic level, also plays an important role. The leaching regime and the organic cycle and vegetation type are probably the predominant controlling factors and are themselves conditioned by or dependent upon climate (chiefly rainfall and temperature), drainage, tephra thickness and depth of burial, and the frequency and amount of fresh tephra or "tephric loess" accessions. The specific role of these environmental controls, each of which may alter significantly through time, is difficult to assess accurately and to distinguish unequivocally from compositional controls. More studies at good sites are needed. Because of the importance of environmental controls in clay mineral genesis, some residual effects of paleoenvironmental conditions are to be expected in the clay fractions of weathered tephra deposits due to changes in climate and vegetation during the Quaternary. The rate of transformation, the duration, or the enhancement of any such relict clay would depend largely on the nature of the environmental changes. The interpretation of paleoclimate from clay mineral data alone is

inherently unreliable. Changes in climate must generally be deduced from other evidence.

Short-range-order minerals such as allophane and imogolite are possibly reaction end points rather than short-lived transition products, and persist for long periods of time (and in coexistence with halloysite and gibbsite) if conditions are favorable. Other clay minerals such as halloysite and gibbsite, generally envisaged as age-dependent transformation products of precursory allophane and imogolite, may form directly and rapidly from the dissolution products of certain primary or secondary minerals. Their formation and persistence depend on whether the conditions favor resilication (for halloysite) or desilication (for gibbsite). Experimental thermodynamic evidence suggests that, in the long term, imogolite and proto-imogolite allophane are metastable compared with halloysite (particularly at temperatures below 25°C) or gibbsite, but that all these minerals can coexist, depending chiefly on the concentration of silica in solution. Halloysite formation may be favored by lower temperatures, but depends more on a sufficient concentration of silica in solution and pH. Halloysite is rare in tephtras that are of recent age and at the land surface.

The occurrence of various authigenic silica polymorphs attests to resilication due to special site conditions, and their relationship to halloysite and allophane (Al:Si = 1.0) formation and transformation warrants further investigation. Similarly, the reason for the erratic occurrence of 2:1 and 2:1:1 type clay minerals in tephtras is uncertain. There is evidence for both the pedogenic weathering model and that involving the weathering of layer silicates, either inherent or derived from contamination by eolian additions or other mechanisms. The latter model apparently has the greater support.

III. Controls of Weathering and Clay Mineral Genesis in Late Quaternary Tephtras in the Waikato Region, New Zealand

A. INTRODUCTION, SETTING, AND METHODS

1. *Introduction*

The Waikato region (Fig. 4) has received airfall tephtra deposits of late Quaternary age (younger than about 50,000 yr) from five or six volcanic centers (Grange, 1931; New Zealand Soil Bureau, 1954; Pullar, 1967; Vucetich and Pullar, 1969; Pullar and Birrell, 1973a; Lowe, 1981b). The tephtras generally thin away from the centers and become increasingly difficult to differentiate toward the distal (100 to 200 km from source) Waikato region (Fig. 4). Some investigations at particular sites on the low rolling hills in the Waikato area [e.g., New Zealand Soil Bureau (1968), Pullar and Birrell

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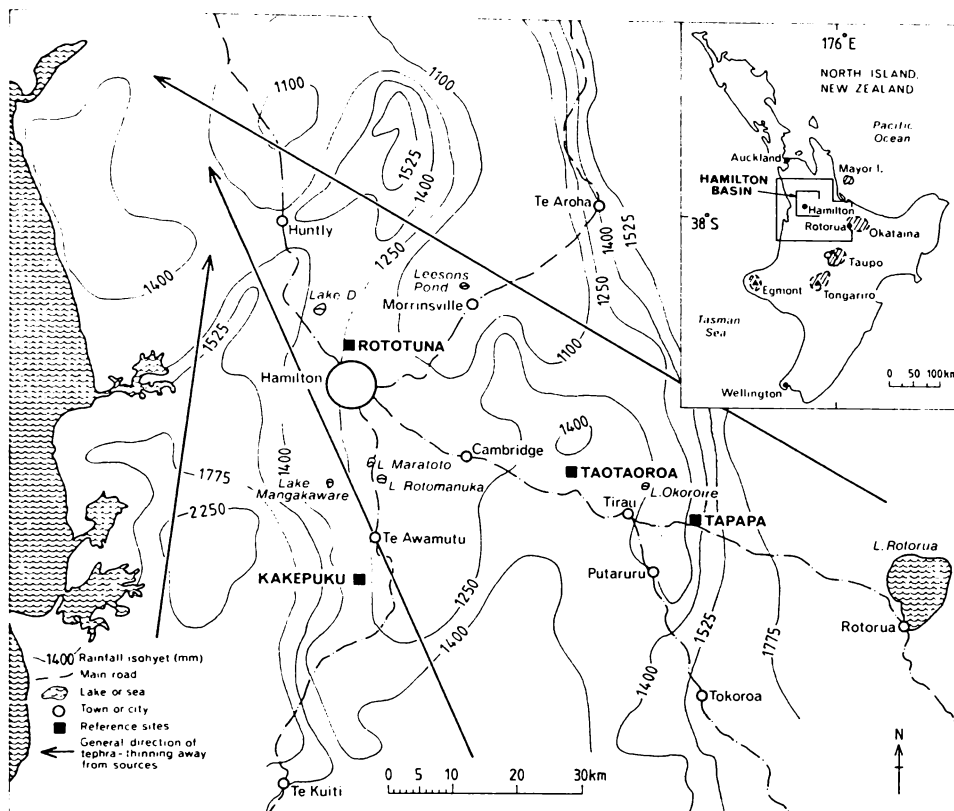


FIG. 4. Map of the Waikato region showing the general direction of tephra thinning, rainfall isohyets, and the Tapapa, Taotaoroa, Kakepuku, and Rototuna reference sample sites. Locations of some lake coring sites (see Fig. 6b) are also shown. The inset shows the Waikato region and the Hamilton Basin within it in relation to volcanic centers (hatched) which were the main sources of the late Quaternary (i.e., last circa 50,000 yr) tephras: Okataina, Taupo, and Mayor Island centers are rhyolitic while Tongariro and Egmont centers (black triangles) are andesitic (after McCraw, 1975; Lowe, 1981b). [The rainfall data are modified after "Climate and Climatic Resources of the Waikato Coromandel King Country Region," (1974, p. 10) (Maunder, 1974), by permission of the Director, New Zealand Meteorological Service].

(1973b), Hodder (1978), Hodder and Wilson (1976), and Parfitt *et al.* (1982b)] have identified few tephras with certainty, but emphasized the composite, interdigitating rhyolitic and andesitic nature of the thinly bedded deposits. Parfitt *et al.* (1982b) considered the proportion of andesitic tephras to be effectively insignificant. A more certain model of tephra occurrence, chronology, and distribution has been derived more recently, however (Lowe, 1981b; Lowe and Gibbs, 1981). This model is based on the identifi-

cation and C-14 dating of discrete and unmixed tephra layers preserved in very fine-grained organic lake sediments (gyttja) in peaty lakes in the Hamilton Basin (Lowe *et al.*, 1980). The model was established by detailed studies on sediment cores from the lakes using mineralogical assemblages and chemical "fingerprinting" methods such as electron microprobe analysis of glass shards and titanomagnetites in the tephtras [e.g., as in Westgate and Gorton (1981), Froggatt (1983), Hogg and McCraw (1983), see also Table II]. The cores have been exceptionally valuable for determining an accurate stratigraphy and distribution pattern of the late Quaternary tephtras in the region, and in providing a compositional reference for the parent materials of the adjacent subaerial tephtra deposits and soils under study [c.f. studies by Borchardt *et al.* (1973), and Stewart *et al.* (1977)]. Using this refined tephrochronology, a complementary study on the weathering and clay mineral genesis in the late Quaternary tephtras at four reference sites — Tapapa, Taotaoroa, Kakepuku, and Rototuna (Fig. 4) — in the Waikato region was done. The results of this study are reported and discussed here with specific reference to the findings of the previous review section.

2. General Setting of the Study Area

a. Physical Features and Paleoenvironment. The study area (Fig. 4) comprises low ridges and rolling hills of Mid to Late Pleistocene volcanogenic materials surrounded and partly buried by an alluvial fan (known as the Hinuera Formation) deposited by an ancestral Waikato River about 20,000 years ago (McCraw, 1967; McGlone *et al.*, 1978). The small, shallow lakes (up to ~8 m deep) used to elaborate the tephrostratigraphy in the area were formed about 17,000 years ago by the deposition of the Hinuera Formation (Green and Lowe, 1985). Extensive peat bogs, about 10,000 years old, overlie the alluvium and partly or fully enclose many of the lakes. Ranges or plateaux up to 300 m high virtually surround the area. The region has warm humid summers, mild winters, and a moderate rainfall with a winter maximum [Fig. 4; de Lisle (1967), and Maunder (1974)]. Mean annual rainfalls at the sample sites are: Tapapa, 1500 mm; Taotaoroa, 1250 mm; Kakepuku, 1300 mm; Rototuna, 1200 mm. Water balance data indicate a net annual moisture surplus in the Hamilton Basin; a short but frequent seasonal moisture deficiency occurs in late summer (de Lisle, 1967; Cox, in New Zealand Soil Bureau, 1968), generally most pronounced north of Hamilton city as at the Rototuna site. Mean annual air temperatures in the region range from 13 to 15°C with means of 18 to 20°C in summer and 8 to 11°C in winter (Maunder, 1974). Mean annual soil temperatures at 1 m depth are 15 to 16°C (Wilson, 1980). Winds in the region are predominantly westerlies (de Lisle, 1967).

Between about 36,000 and 28,000 yr ago the central North Island climate

was drier and temperatures slightly cooler but within about 2°C of present, with a mixed forest, grassland, and shrub vegetation (Hendy and Wilson, 1968; Birrell *et al.*, 1977; Fleming, 1979; McGlone and Topping, 1983). Various studies have determined that between about 20,000 and 18,000 yr ago, temperatures were probably 4 to 6°C lower than present with small areas of forest [*Nothofagus (menziesii)* and *fusca*] and *Libocedrus* preserved on the low hills in the Waikato area (McGlone *et al.*, 1978). The climate was probably dry and/or drought-prone, possibly with high-intensity rainstorms and seasonally wet periods (Hume *et al.*, 1975; McGlone *et al.*, 1978). Climatic amelioration began about 16,000 yr ago with marked warming 14,700 yr ago (Stewart and Neall, 1984; Green and Lowe, 1985). Much of the postglacial period was characterized by warming with a wetter and milder climate than present between about 10,000 and 5,000 yr ago (Harris, 1963; McGlone and Topping, 1977; Fleming, 1979; Green, 1979), and with an apparent increase in the rate of tephra weathering and soil formation (Vucetich, 1968; Vucetich and Pullar, 1969; Birrell and Pullar, 1973; Birrell *et al.*, 1977). Since 5,000 yr ago the climate has fluctuated from slightly drier and cooler to slightly warmer and wetter than present (Green, 1979). Vegetation consisted of mixed broadleaf–podocarp forest dominated by rimu (*Dacrydium cupressinum*) and tawa (*Beilschmiedia tawa*). At the time of European settlement (mid-1800s) most of the low rolling hills were covered with manuka (*Leptospermum* spp.) and fern (Cranwell, in Grange *et al.*, 1939), the original vegetation presumably being destroyed by Polynesian deforestation (McGlone, 1983). Most of the area is now covered by grass–clover pasture. Vegetation at the sample sites consists of bracken fern, scrub, and roadside pasture.

b. Tephrostratigraphy. The base of the late Quaternary tephra sequence is marked by Rotoehu Ash, a distinctive circa 42,000-yr-old marker bed that unconformably overlies older materials (normally Hamilton Ash Formation) (Fig. 5). Another widespread marker bed, Kawakawa Tephra, also known as Aokautere Ash or Oruanui Ash (Vucetich and Howorth, 1976), is about 20,000 yr old and occurs approximately midway in the stratigraphic sequence. The whole tephra column is thickest (about 3 m) in the southeastern part of the region and thinnest (about 0.25 to 0.60 m) in the northwest (Fig. 5). Details of the stratigraphy and chronology of the four reference sampling sites are given in Fig. 6a. The late Quaternary tephras at the Roto-tuna site are mixed and form a shallow, composite cover deposit (Fig. 5c). This profile comprises about 50% post-Kawakawa Tephra materials (predominant in the upper part) and 50% Kawakawa Tephra to Rotoehu Ash materials (predominant in the lower part) (Fig. 6a). That these cover deposits consist almost entirely of multiple, thin (< 100 mm) primary airfall tephras has been demonstrated by Lowe (1981a, pp. 314–322). This conclu-



FIG. 5. Photographs of sections of late Quaternary tephras in the Waikato region, including three (a–c) of the sites sampled (refer to Fig. 6). At each site illustrated, the late Quaternary tephra column is underlain (with an unconformity) by a dark brown, blocky, [Nomenclature here and in the text is after Taylor and Pohlen (1970).] and clay-rich paleosol formed on Hamilton Ash. The Rotoehu Ash and Kawakawa Tephra marker beds (pale and sandy) are readily visible in sections in the east and southeast part of the Waikato region, but become less distinct toward the northwest. Their upper boundaries are especially difficult to determine accurately because of reworking and mixing with later deposits (cf. Hodder and Wilson, 1976). Abbreviations: Kk, Kawakawa Tephra (circa 20,000 yr old); Re, Rotoehu Ash (circa 42,000 yr old); Hm, Hamilton Ash (circa 100,000 yr old); pal, paleosol; I. Quat., late Quaternary. (a) Tapapa site. Note the well-developed paleosols underlying the Kk bed in this 3-m-thick section. (b) Taotaoroa site. The weakly structured to massive Kk and Re beds (Kk protrudes from the section face) contrast with the dark, blocky paleosols underlying each of them. The total thickness of late Quaternary tephras is ~2 m. (c) Rototuna site. Certain identification in the field of the Re and Kk beds here is virtually impossible apart from occasional lenses of white Re

sion is confirmed by the results of studies on the tephra preserved in the lake deposits in the Hamilton Basin (Lowe *et al.*, 1980; Green and Lowe, 1986; see also Fig. 6b and Section III, B, 2). [It was previously postulated that the cover deposits were possibly loess derived from the aggrading Waikato fan surface—e.g., McCraw (1967), Vucetich (1968), and Cowie and Milne (1973).] Marked differences in physical properties and composition of the cover bed tephra and the Hamilton Ash at the Rototuna site indicate that mixing between these materials by such processes as tree fall is negligible (Lowe, 1981a). Occasionally “mounds” of exposed Hamilton Ash protrude through the cover deposits elsewhere in the northern Hamilton Basin and probably represent deep-seated tree fall as described in Denny and Goodlett (1956) and Lyford and MacLean (1966).

3. *Samples and Analytical Methods*

Channel samples were taken from each stratigraphic layer or horizon in the reference sections (Fig. 6a). At Rototuna samples were taken continuously at 50-mm intervals in the late Quaternary tephra cover bed; two samples from the underlying Hamilton Ash were taken. All samples were sealed in plastic bags and refrigerated (4°C) prior to analysis.

a. Size Fractionation and Treatment of Samples. Field moist samples were dispersed in distilled water by gentle crushing and ultrasonic vibrations at 20 kHz and 50 W output for 5 min. Some samples were treated with Calgon (pH 8), or NaOH (pH 9), or $Zr(NO_3)_4 \cdot 5H_2O$ (pH 2) to attain good dispersion and adequate clay yields. Standard particle size analysis and size fractionation were done by using sieve, pipet, photoextinction (hydrophotometer), and centrifuge methods (Lowe, 1981a). Clay fractions ($< 2 \mu m$) were separated by centrifuging and saturated with $MgCl_2$. These fractions were variously mounted and treated in standard fashion (Lowe and Nelson, 1983), except that oriented paste mounts were dried slowly over water to minimize artificial dehydration of halloysite from 10 to 7 Å (Nagasawa and Miyazaki, 1976; Kirkman and Pullar, 1978). Sand fractions ($> 63 \mu m$) (from both the reference sections and lake cores) were sieved and the minerals in the 250–63- μm (2–4 ϕ) size range density separated with 1,1,2,2-tetrabro-

at the base of the column, as indicated. The many constituent tephra in this composite, 0.6-m-thick cover bed have been pedogenically mixed, and markedly altered by weathering, so that they are quite indistinguishable in the field (see Fig. 6a). The tephra are compact, concretionary, and weakly structured to massive (protuberant) in place. (d) An overthickened composite tephra deposit infilling a hollow in the Hamilton Ash paleosurface (probably a tree overturn site). This section is located about 20 m north of the Rototuna site in (c), and many of its properties contrast with those of the latter site. The upper 0.75 m or so consists of soft, fluffy, well-structured, nonconcretionary, intermixed tephra that overlie inwashed Re at the base of the deposits (indicated).

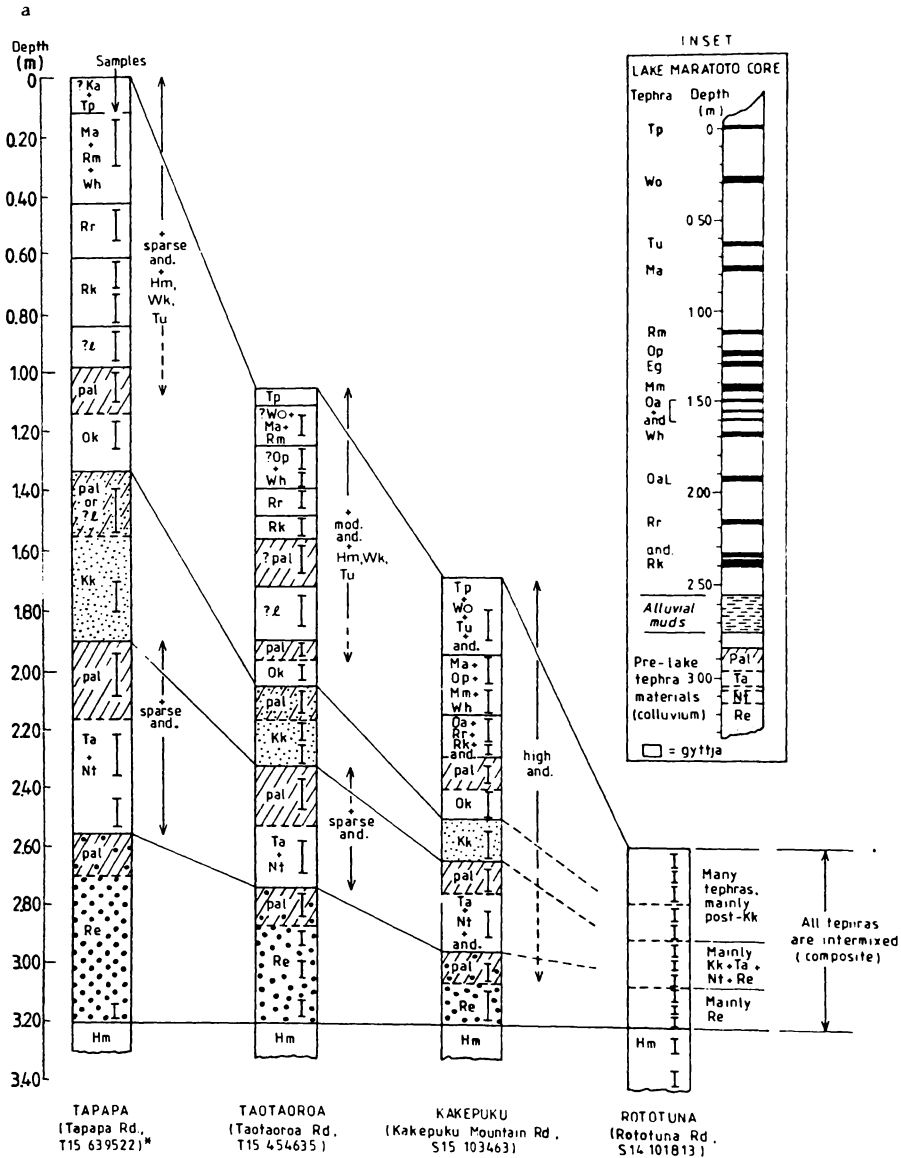


FIG. 6a

FIG. 6. (a) Late Quaternary tephrostratigraphy, chronology, and correlation of the reference sites, and sampling depths. Each site is situated on a flat-topped low hill where postdepositional erosion or accumulation was likely to have been minimal (Fig. 5a-c). Other tephras in addition to those named here were deposited in the region (from lake sediment core data as in inset and Fig. 6b). The certain identity and exact stratigraphic position of many of the tephras at each site are unclear because of possible reworking, intermixing, and soil formation. Stratig- (continues)

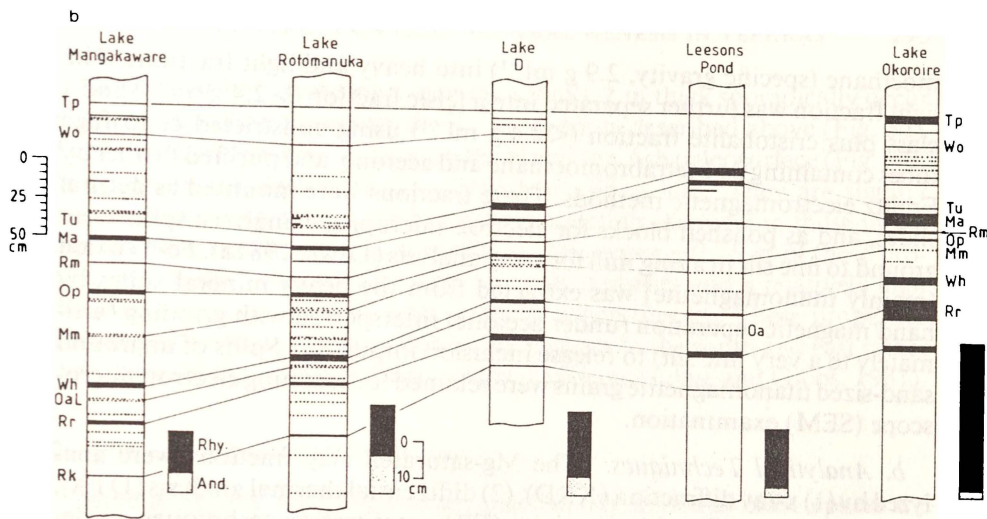


FIG. 6b

raphy after Pullar and Birrell (1973b) (Tapapa site), Hodder and Wilson (1976) (Tapapa and Kakepuku sites), and Lowe (1981a,b), Lowe *et al.* (1980), and D. J. Lowe (unpublished data). (Detailed descriptions of the sites are given in an appendix which is available from the author on request.) The inset shows the stratigraphy of thin airfall tephras preserved in gyttja in a piston core from Lake Maratoto, a small peaty lake located about midway between the Rototuna and Kakepuku sites (Fig. 4). It indicates potential contributions of specific tephras to these sections [after Lowe *et al.* (1980) and Green and Lowe (1985)]. Abbreviations and tephra ages (in old half-life years BP) are [after Healy *et al.* (1964), Pullar *et al.* (1973), Cole and Nairn (1975), Howorth (1975), Pullar (1980), Lowe *et al.* (1980), Froggatt (1981), Hogg and McCraw (1983), and Green and Lowe (1985)]: Ka, Kaharoa Ash (900); Tp, Taupo Pumice (1,800); Wo, Whakaipo Tephra (2,800); Hm, Hinemaiaia Tephra (4,650); Whakatane Ash (4,800); Tu, Tuhua Tephra (6,200); Ma, Mamaku Ash (7,000); Rm, Rotoma Ash (8,500); Op, Opepe Tephra (8,800); Eg, unnamed Egmont-derived tephra (9,000); Mm, Mangamate Tephra (10,000); Wh, Waiohau Ash (12,000); Oa, Okupata Tephra (10,000–12,500); OaL, basal lapilli unit of Oa (12,500); Rr, Rotorua Ash (13,500); Rk, Rerewhakaaitu Ash (14,700); Ok, Okareka Ash (circa 18,000); Kk, Kawakawa Tephra (circa 20,000); Ta, Tahuna Tephra (circa 38,000); Nt, Ngamotu Tephra (circa 38,500); Re, Rotoehu Ash (circa 42,000); Hm, Hamilton Ash (or Hm-like materials) (\geq circa 100,000); and, unnamed andesitic tephras; l, "tephric loess;" pal, paleosol (hatched); mod., moderate amounts; high, relatively high amounts. Grid reference* based on 1,000-m grid of the 1:50,000 topographic map series (NZMS 260, edition 1). (b) Correlation line of post-circa 17,000 yr BP tephras across the Waikato region based solely on lake sediment cores. Lakes Mangakaware and Rotomanuka occur south of Hamilton, Lake D and Leesons Pond to the north, and Lake Okoroire to the east (Fig. 4). Andesitic tephras (stippled) occur most frequently in the southern lakes, decreasing in proportion to the thicker rhyolitic tephras (solid black) to the east. The andesitic component also diminishes northward. Small histogram bars represent the total accumulated thickness of tephra material in the core [probably a conservative estimate of the equivalent thickness of dry tephra on land because of compaction: Borchardt *et al.* (1973)]. The chemical compositions of the dominant constituents (glass and plagioclase) in many of the tephras are illustrated in Table II. Tephra abbreviations are as in Fig. 6a.

moethane (specific gravity, 2.9 g ml^{-1}) into heavy and light fractions. The light fraction was further separated into a felsic fraction ($> 2.4 \text{ g ml}^{-1}$) and a glass plus cristobalite fraction ($< 2.4 \text{ g ml}^{-1}$) using constricted centrifuge tubes containing 3:1 tetrabromoethane and acetone, and purified further by Frantz electromagnetic methods. These fractions were mounted as detrital slides, and as polished blocks for electron microprobe analysis; splits were ground to fine silt in a ring mill for x-ray analysis (Lowe, 1981a). Fe-Ti oxide (mainly titanomagnetite) was extracted from the heavy mineral suites by hand magnetic separation (under acetone) interspersed with grinding (ultimately to a very fine silt) to release inclusion impurities. Splits of unground sand-sized titanomagnetite grains were retained for scanning electron microscope (SEM) examination.

b. Analytical Techniques. The Mg-saturated clay fractions were analyzed by (1) x-ray diffraction (XRD), (2) differential thermal analysis (DTA), (3) SEM, and (4) fluoride reactivity (FR) autotitration techniques, as described in Lowe and Nelson (1983). Sand fraction mineralogy was determined by petrological microscope (point count) and XRD methods (Lowe, 1981a; Hume and Nelson, 1982). The titanomagnetite fractions were analyzed with energy dispersive x-ray fluorescence (XRF) and SEM (with attached electron microprobe) apparatus and methodology as described in Lowe (1981a) and Lowe and Nelson (1983). Polished glass and feldspar grains were analyzed for major elements by electron microprobe (Table II).

B. FIELD PROPERTIES, COMPOSITION, AND WEATHERING

1. *Field Properties in Relation to Tephra Thicknesses*

At Tapapa, Taotaoroa, and Kakepuku (i.e., east and south of Hamilton city), the late Quaternary tephra column is $> 1 \text{ m}$ thick (Figs. 5a, b, and 6a). The modern soils are well-drained and have properties typical of Andepts (cf. Soil Survey Staff, 1975): yellowish-brown colors, sandy loam to silt loam textures, well-developed crumb and nut structures, very friable and "fluffy" consistencies with low bulk densities ($< 0.8 \text{ g cm}^{-3}$), and strong Fieldes and Perrott (1966) fluoride reactivities. At the Rototuna site and elsewhere north and northwest of Hamilton the late Quaternary tephra are usually $< 1 \text{ m}$ thick and poorly drained and partly gleyed because of the buried impermeable Hamilton Ash paleosol in the solum (Fig. 5c). Abundant Fe-Mn concretions and some mottles occur in the deposits, and the soils characteristically have Ochrept rather than Andept properties: pale brown to buff colors, silt loam to silty clay loam textures, weak structures (massive *in situ*), and firm (hard and brittle when dry), compact consistencies with a high bulk density ($> 1.0 \text{ g cm}^{-3}$) (Fig. 5c). Fieldes and Perrott (1966) fluoride reactivities are typically weak. $\text{pH}(\text{H}_2\text{O})$ values are usually 5.1–5.9.

12. CONTROLS ON CLAY MINERAL GENESIS IN TEPHRAS 293

Deposits of late Quaternary tephra 1.0 to 1.2 m thick sporadically occur north of Hamilton alongside the < 1 m deposits described above (Fig. 5d). They usually fill shallow hollows in the Hamilton Ash paleosurface (Fig. 5d), or occur on downslope flanks of the low rolling hills. They are slightly overthickened but contain tephra parent materials identical to those in the thinner adjacent deposits (Lowe 1981a). The upper ~0.75 m of these profiles are "fluffy," very friable, have low bulk densities and a relatively high fluoride reactivity, and are only sparsely concretionary. These properties thus resemble those of the well-drained Andepts to the south and east rather than those of the poorly drained nearby Ochrepts (Lowe and Gibbs, 1981).

2. Primary Mineral Composition

Mineralogically, all of the sites are qualitatively similar as most tephra are common to each site (Fig. 6a). Volcanic glass (rhyolitic and andesitic), pumice, feldspar (mainly andesine-oligoclase with rare labradorite plagioclase and very rare K-feldspar), quartz, sparse lithics, and occasional traces of cristobalite make up the light mineral fractions. Similar proportions of glass (~80%), feldspar (~15–20%), and quartz (~5%) occur at each of the Tapapa, Taotaoroa, and Kakepuku sites. With increasing depth the feldspar and quartz content increases and glass content generally decreases. At Rototuna, the late Quaternary tephra (cover bed) samples on the average contain less glass (~65%) and a little more feldspar (~25%) and quartz (~10%) than at the other three sites. These proportions at Rototuna are similar to those in pre-Kawakawa Tephra samples at the other sites, however. Abundant Fe-Mn concretions (secondary) occur only at the Rototuna site.

The heavy-mineral fractions, which generally account for 3–5% (by weight) of the sand fraction at Tapapa, Taotaoroa, and Kakepuku, and 10% at Rototuna, contain variable amounts of opaques (mainly titanomagnetite and occasionally magnetite, ilmenite, and rare goethite and haematite), pyroxenes (hypersthene, augite, and occasionally rare aegirine), amphiboles (calcic or green hornblende, sparse basaltic or brown hornblende, and occasionally rare to dominant cummingtonite), and small amounts of biotite and zircon (Lowe, 1981a).

The results of the ferromagnesian sand mineralogical analyses and titanomagnetite chemical analyses show that rhyolitic tephra predominate at each of the sites. Andesitic tephra also occur in appreciable amounts with the greatest proportion at Kakepuku and lowest at Tapapa. At Kakepuku and to a lesser extent at Taotaoroa the post-Kawakawa tephra materials are particularly enriched in andesitic constituents (Fig. 6a). This compositional trend is illustrated in Figs. 7 and 8. In Fig. 7, the Kakepuku samples contain the highest proportion of augite, a ferromagnesian mineral that is abundant in the eruptives from Tongariro (with hypersthene and olivine) and Egmont

(with hornblendes) volcanic centers (Clark, 1960; Gow, 1968). Normally, only minor amounts are associated with the rhyolitic volcanic centers [e.g., Kohn and Glasby (1978), Lowe *et al.* (1980), and Lowe (1981a)]. In Fig. 8, V/Mn (relative intensity counts per second) ratios are plotted with respect to sample depth. The maxima relate to a significant andesitic character and the minima to a significant rhyolitic character. This compositional relationship was derived from *t*-test comparison of the V contents of titanomagnetites of rhyolitic and andesitic tephtras in New Zealand (Kohn, 1970; Kohn and Neall, 1973; Topping and Kohn, 1973; Kohn and Topping, 1978): at a 95% significance level, V is higher in andesitic tephtras than in rhyolitic tephtras (Lowe, 1981a). The V/Mn ratio reflects this andesitic character of V since there is no significant difference between the rhyolitic and andesitic tephtras for Mn. Figure 8 shows that Kakepuku samples are more andesitic than those from Tapapa and Taotaoroa, with Rototuna samples having an andesitic affinity generally between that of Taotaoroa and Kakepuku. The results

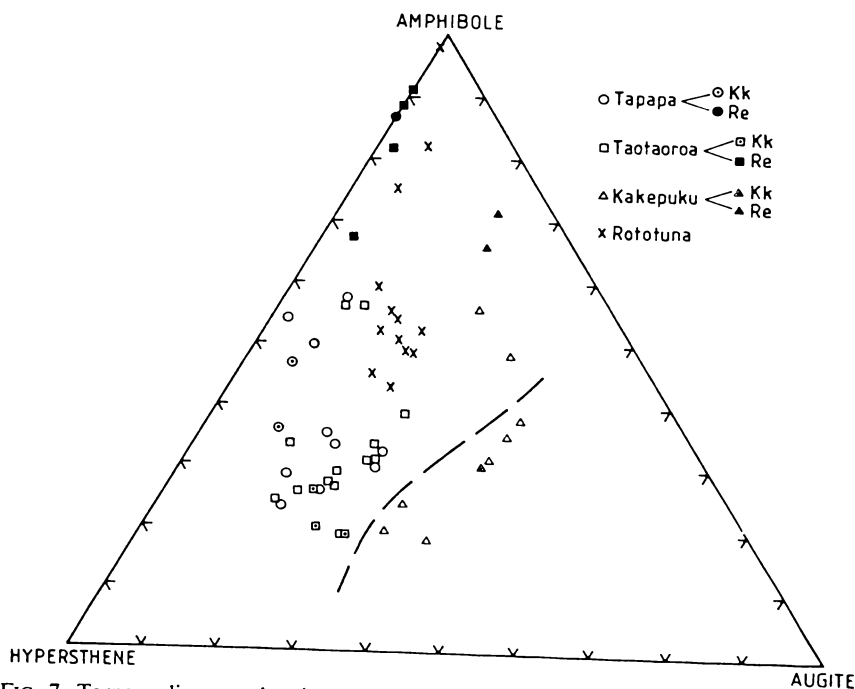


FIG. 7. Ternary diagram showing relative abundances of amphibole (calcic and basaltic hornblende, cummingtonite), augite (clinopyroxene), and hypersthene (orthopyroxene) in the heavy mineral assemblages of the 2–4 ϕ (250–63 μ m) size fractions (summed to 100%) in the samples from the four reference sites. The diagram illustrates that the Kakepuku site (with highest proportions of augite) has a greater component of andesitic tephtras than the other sites, particularly in the post-Kawakawa Tephra deposits (separated by the dashed line) (cf. Fig. 8). Kk, Kawakawa Tephra; Re, Rotoehu Ash.

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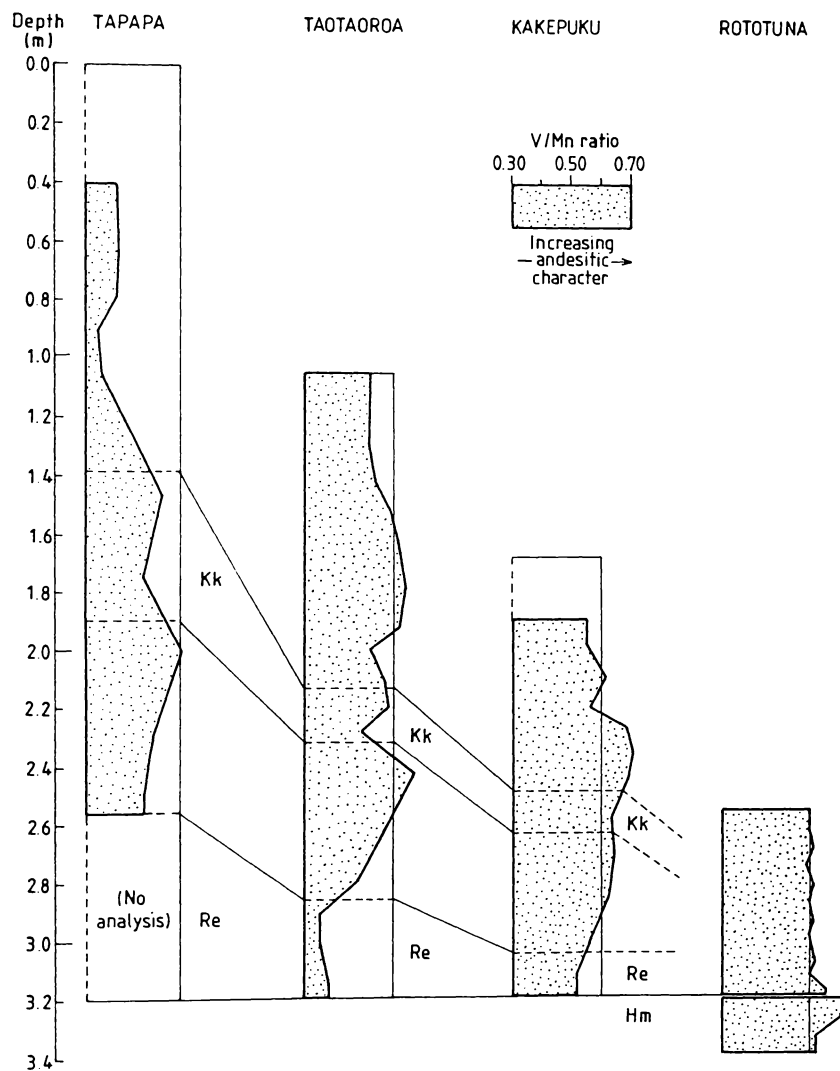


FIG. 8. Relative V/Mn ratios of titanomagnetites (from XRF analysis) and their distribution with depth at the reference sites. Maxima relate to a significant andesitic character, minima to a significant rhyolitic character. Kk, Kawakawa Tephra; Re, Rotoehu Ash; Hm, Hamilton Ash.

also demonstrate considerable mixing of the tephra components throughout the composite Rototuna profile, and also of the Kawakawa Tephra and younger tephra at Kakepuku.

a. Comparison with Composition of Tephra in Lake Cores. These compositional differences between the reference sites are corroborated by the

work on the tephtras in the lake sediment cores, even though the lakes are less widely distributed (Fig. 4). The mineralogy and the chemistry of the dominant components of the tephtras in the cores clearly shows their rhyolitic or andesitic origin [Table II; Lowe *et al.* (1980) and D. J. Lowe, unpublished data]; the distribution of the lake core sites illustrates how the relative proportions of these tephtra affinities alter regionally (Fig. 6b), and in accord with the changes noted above (Figs. 7 and 8). Electron microprobe analyses of some glass shards and plagioclase from lake core samples are given in Table II. The analyses contrast pre-weathering compositional differences between the rhyolitic and andesitic tephtras from which the subaerial deposits under investigation have weathered. The andesitic glasses (mean $\text{SiO}_2:\text{Al}_2\text{O}_3 = 3.8$ in Table II) contain less Si and more Al, Ti, Fe, Mg, and Ca than the rhyolitic glasses ($\text{SiO}_2:\text{Al}_2\text{O}_3 = 6.4$). Labradorite or bytownite ($\text{SiO}_2:\text{Al}_2\text{O}_3 = 1.74$) predominate in the andesitic, and andesine or oligoclase ($\text{SiO}_2:\text{Al}_2\text{O}_3 = 2.4$) in the rhyolitic tephtras. [Heavy mineral suites associated with the andesitic and rhyolitic tephtras in the lakes are summarized in Lowe *et al.* (1980) and Green and Lowe (1985)].

The degree of influence attributable to the differences in composition depends on both the proportion of rhyolitic to andesitic tephtras at each site, and the abundance of, in particular, glass, plagioclase, and heavy minerals in the tephtras. In the andesitic tephtras in the lakes, plagioclase and glass (generally in the ratio $\sim 2:1$ to $\sim 5:1$) make up 80–90%, and heavy minerals 10–20%, of the whole sample; in the rhyolitic tephtras, plagioclase and glass (in the ratio $\sim 1:4$) and quartz comprise 95–99%, and heavy minerals 1–5%. Combining these compositional differences with the proportions of rhyolitic to andesitic tephtras contained in the lake columns (Fig. 6b—bar graphs) adds support to the compositional “gradient” deduced from the analyses on the subaerial deposits at the reference sections.

All these results are consistent with the findings of Birrell and Pullar (1973), Pullar and Birrell (1973b), Hodder and Wilson (1976), and Hodder (1978), but contrast with the conclusions of Parfitt *et al.* (1982b) who discount an appreciable andesitic–rhyolitic tephtra “gradient” across the Waikato region (see further discussion in Section C below).

3. Mineralogy of Clay Fractions

Allophane and/or halloysite are the most abundant clays at all sites (Table III). Together they account for virtually all of the clay fractions at Tapapa, Taotaoroa, and Kakepuku. Traces of gibbsite were identified in some samples, mostly from lower horizons (pre-Kawakawa Tephtra) at Kakepuku and Taotaoroa. At Rototuna, allophane plus halloysite make up 60–70% of the clay fraction, the remainder consisting of cristobalite, 14-Å vermiculite (trioctahedral), humus and/or hydrous iron oxide complexes, and traces of quartz and feldspar.

TABLE II
AVERAGE MICROPROBE ANALYSES^a OF GLASS AND PLAGIOCLASE FROM SOME
RHYOLITIC AND ANDESITIC TEPHRAS IN LAKE DEPOSITS, WAIKATO REGION

	Glass			Plagioclase ^b	
	Rhyolitic ^c	Andesitic ^d		Rhyolitic ^e	Andesitic ^f
SiO ₂	78.61 (0.30)	61.78 (1.17)	SiO ₂	59.72 (1.68)	51.39 (1.22)
Al ₂ O ₃	12.35 (0.13)	16.18 (1.36)	Al ₂ O ₃	24.69 (0.85)	29.51 (0.96)
TiO ₂	0.13 (0.03)	0.98 (0.10)	TiO ₂	0.02 (0.02)	0.04 (0.03)
FeO ^g	0.92 (0.08)	6.41 (0.51)	FeO ^g	0.26 (0.09)	0.56 (0.15)
MgO	0.14 (0.01)	2.71 (0.50)	MgO	0.01 (0.01)	0.07 (0.03)
CaO	0.89 (0.04)	6.44 (0.94)	CaO	6.70 (0.94)	13.25 (1.03)
Na ₂ O	3.60 (0.28)	3.52 (0.21)	Na ₂ O	7.51 (0.44)	3.84 (0.58)
K ₂ O	3.26 (0.10)	1.89 (0.23)	K ₂ O	0.43 (0.13)	0.15 (0.07)
Cl	0.10 (0.03)	0.09 (0.05)	Sum	99.34 (1.56)	98.81 (0.53)
Water ^h	4.99 (3.00)	1.97 (0.82)	An range	23–37	58–75
<i>n</i>	10	10	<i>n</i>	8	8

^a Glass shards and plagioclase feldspar grains in the 2–4 ϕ size fraction were mounted in araldite, polished, carbon coated, and analysed using a JEOL JXA-733 SUPERPROBE at Victoria University of Wellington. Reference standards used included KN-18 (comenditic glass), VG-568 (Yellowstone rhyolitic glass), VG-99 (basaltic glass), and Or-1A (orthoclase). Glasses were probed with a 10 μ m beam diameter and 8 nA beam current, plagioclases a 10 μ m diameter and 12 nA current. Other analytical conditions were as described in Froggatt (1983). Concentrations are given in oxide weight percent except Cl which is in atomic weight percent. The glass analyses are presented on a normalized 100% loss-free basis; some of the andesitic glasses may contain tiny microlites (chiefly of plagioclase). *n* = number of analyses in mean; numbers in parentheses are 1 S.D. Each analysis was done on a separate grain.

^b Plagioclases may exhibit relatively wide compositional ranges within individual tephra beds, but in New Zealand there are generally marked differences between grouped rhyolitic and andesitic tephtras, as exemplified here [cf. Cole and Nairn (1975) and Cole (1979)]. Grain cores were probed.

^c Samples from Waiohau Ash, Lake Rotomanuka (tephra source: Okataina v.c.—refer Figs. 4 and 6).

^d Samples from Okupata Tephra (basal lapilli unit), Lake Maratoto (Tongariro v.c.).

^e Samples from Whakaipo (1), Rotoma (2), Waiohau (1), Rerewhakaaitu (4) tephtras, Lake Rotomanuka (Taupo and Okataina v.c.) [andesine and oligoclase].

^f Samples from Mangamate Tephra (4), Okupata Tephra (basal lapilli unit) (4), (Tongariro v.c.) [labradorite and bytownite].

^g All Fe calculated as FeO.

^h Difference between original analytical total and 100.

a. Allophane and Halloysite. Allophane is dominant (> 80%) in all the samples that overlie Kawakawa Tephra at Tapapa, Taotaoroa, and Kakepuku sites, as illustrated in Fig. 9a. Allophane decreases in abundance

(~40–60%) at or below the Kawakawa Tephra bed at Tapapa and Taotaoroa, but predominates (~80–90%) throughout the Kakepuku profile. Concomitantly, halloysite is absent or is present in only small amounts (~1–2%) in the post-Kawakawa samples (above 0.8 to 1.4 m). It increases in abundance at and below Kawakawa Tephra, markedly so at Tapapa (~30–60%) and to a lesser extent at Taotaoroa (~10–50%), but to only a small degree at Kakepuku (~2–10%) (Table III).

Rototuna differs from the other sections in that halloysite and allophane occur together in all parts of the profile, halloysite increasing from small quantities at the surface (~5–10%) to dominant quantities (~50%) at the base of the late Quaternary tephra profile (Table III). Figure 9b shows a mixture of stubby halloysite tubes (spherules were rarely observed in any Rototuna samples) mantled with some (?) allophanic material in a sample from 0.32 to 0.37 m depth at Rototuna. A significant portion of the halloysite may thus have originated from feldspar. The samples of Hamilton Ash from Rototuna are, in contrast, almost wholly dominated by halloysite (tubular) (Figs. 9c, d), again possibly formed from feldspar. Comparative analyses (not reported here) of the “fluffy,” overthickened cover deposits (e.g., Fig. 5d) show that allophane, with traces of halloysite, predominates in the upper (above ~0.75 m) part of the profile, whereas halloysite with subordinate allophane is dominant in the lower (below ~0.75 m) part (Lowe, 1981a).

Slope ratios (Bramao *et al.*, 1952) of the ~500°C halloysite DTA endotherms averaged about 1.5 for most samples from Tapapa, Taotaoroa, and Kakepuku but were considerably lower (≤ 1.0) for the Rototuna-derived halloysite. The latter values probably reflect the relatively high abundance of humus complex material in the Rototuna samples (Table III and below), which produced an exotherm near 500°C (Satoh, 1976) and thereby tended to “oversteepen” the descendant (dehydroxylation) side of the halloysite endotherms (Lowe, 1981a).

Typically, halloysite in the cover deposits at Rototuna consists of mixed 7- and 10-Å phases with an intermediary “plateau” of variably dehydrated 10-Å halloysite between the two end-member diffractogram peaks. The 7-Å phase is dominant in upper samples and the 10-Å phase dominant in lower samples (Table III). Only three other samples, each of Kawakawa Tephra and from Tapapa (especially), Taotaoroa, and Kakepuku sites, exhibited a similar 7–10-Å hydration range. Because all samples were prepared in a same manner (i.e., dried at 100% relative humidity), this 7- to 10-Å range is considered a function of *in situ* dehydration and not an artifact of laboratory drying. The interlayer water in the Rototuna halloysite was estimated from XRD peak height–area relationships (Nagasawa and Miyazaki, 1976) to be relatively unstable (hence giving the high proportion of 7-Å halloysite throughout). The interlayer water becomes more stable with depth because

TABLE III
CLAY CONTENT AND RELATIVE ABUNDANCES^a OF MINERALS IDENTIFIED IN THE CLAY FRACTIONS

Depth (m)	Clay (wt. %) ($< 2 \mu\text{m}$)	Allophane	Halloysite ^b	Gibbsite	Vermiculite	Cristobalite	Quartz	Feldspar	Humus complexes etc. ^c
Tapapa site									
0.15-0.30	—	4	0	0	0	0	0	0	—
0.45-0.55	6	4	0	0	0	0	0	0	—
0.61-0.71	10	4	?	0	0	?	0	1	s
0.73-0.83	5	4	0	0	0	0	0	0	—
0.86-0.96	4	4	?(7 Å)	0	0	1	?	0	—
1.00-1.10	4	4	0	0	0	0	0	?	—
1.16-1.26	7	4	0	0	0	0	0	?	—
1.40-1.56 ^d	18	2	4(10 Å)	0	0	0	1	?	—
1.70-1.80 ^d	19	2	4(10 Å + 7 Å)	0	0	0	1	0	vs
1.95-2.08	14	2	4(10 Å)	0	0	0	?	0	—
2.22-2.36	13	3	3(10 Å)	0	0	0	?	0	vs
2.44-2.54	13	3	3(10 Å)	0	0	0	0	0	—
3.14-3.19 ^e	10	—	—	—	—	—	—	—	—

(continues)

TABLE III (Continued)

Depth (m)	Clay (wt. %) ($< 2 \mu\text{m}$)	Allophane	Halloysite ^b	Gibbsite	Vermiculite	Cristobalite	Quartz	Feldspar	Humus complexes etc. ^c
Taotaoroa site									
0.10-0.16	8	4	0	0	0	0	?	0	—
0.21-0.27	5	4	0	0	0	0	?	?	—
0.29-0.34	18	4	0	0	0	0	0	0	—
0.34-0.42	5	4	0	0	0	0	?	0	s
0.45-0.50	5	4	?(10 Å)	?	0	0	0	0	—
0.54-0.63	5	4	?(10 Å)	0	0	0	0	0	—
0.70-0.80	10	4	1(10 Å)	1	0	1	?	0	—
0.86-0.90	15	4	1(10 Å)	0	0	0	0	0	—
0.93-0.98	15	4	?(10 Å)	0	0	0	0	0	—
1.02-1.09	19	4	?(10 Å)	0	0	0	?	?	—
1.12-1.18 ^d	16	4	0	0	0	0	1	1	—
1.20-1.26 ^d	13	4	1(10 Å + 7 Å)	0	0	0	0	0	—
1.31-1.42	28	2	3(10 Å)	1	0	?	1	0	s
1.53-1.63	21	3	2(10 Å)	?	0	0	1	1	—
1.70-1.78	24	3	2(10 Å)	0	0	0	1	0	—
1.83-1.88 ^e	14	3	3(10 Å)	0	0	0	2	0	—
1.93-1.99 ^e	10	3	3(10 Å)	0	0	0	2	1	—
2.05-2.13 ^e	14	2	4(10 Å)	0	0	0	1	?	s
Kakepuku site									
0.10-0.20	—	4	0	0	0	0	0	0	—
0.25-0.35	11	4	0	0	0	?	0	0	—
0.35-0.45	7	4	0	0	0	0	0	0	—
0.45-0.55	20	4	0	0	0	0	0	0	s
0.55-0.59	29	4	0	0	0	0	0	0	—
0.62-0.68	20	4	0	0	0	0	1	0	—

0.70–0.80	18	4	?	0	0	0	1	0	—
0.84–9.94 ^d	22	4	1(7 Å + 10 Å)	?	0	0	1	0	—
0.97–1.05	14	4	2(10 Å)	1	0	0	1	0	—
1.11–1.20	11	4	2(10 Å)	0	0	0	1	1	—
1.29–1.35	14	4	2(10 Å)	1	0	0	1	0	vs
1.38–1.48 ^e	16	4	1(10 Å)	1	0	0	?	0	vs

Rototuna site

0.02–0.07	20	2	2(7 Å + 10 Å)	0	1	2	1	0	l
0.07–0.12	18	2	3(7 Å + 10 Å)	0	2	2	1	?	l
0.13–0.19	17	2	3(7 Å + 10 Å)	0	2	1	1	?	l
0.20–0.25	17	2	3(7 Å + 10 Å)	0	2	3	1	0	m
0.25–0.30	18	2	3(10 Å + 7 Å)	0	1	2	1	0	m
0.32–0.37	16	2	4(10 Å + 7 Å)	0	1	2	2	0	m
0.37–0.41	22	2	3(10 Å + 7 Å)	0	1	2	1	?	m
0.42–0.46	23	2	4(10 Å + 7 Å)	0	1	2	1	1	m
0.47–0.51 ^e	18	2	4(10 Å + 7 Å)	0	2	2	2	?	s
0.51–0.55 ^e	16	2	4(10 Å + 7 Å)	0	1	1	1	0	s
0.56–0.60 ^e	30	1	4(10 Å + 7 Å)	0	?	2	2	?	vs
0.63–0.68 ^f	54	1	4(10 Å + 7 Å)	0	0	1	2	0	vs
0.75–0.80 ^f	58	1	4(10 Å + 7 Å)	0	0	2	2	0	vs

^a Relative amounts estimated as follows: 4 = present in dominant amounts (>50%), 3 = present in moderate amounts (25–50%), 2 = present in small amounts (5–25%), 1 = present in trace amounts (<5%), ? = possibly present in trace amounts (<1%), 0 = not detected, — = not determined.

^b Halloysite hydration phase is indicated in parentheses; if both are present, the dominant one is given first.

^c Small proportions of hydrous Fe oxides probably present as well (see Fieldes, 1968; Satoh, 1976). Peak heights and areas of DTA exotherms 200–400°C abbreviated as follows: l = large, m = moderate, s = small, vs = very small.

^d Kawakawa Tephra.

^e Rotoehu Ash (at Rototuna these samples contain a small portion of other admixed tephtras).

^f Hamilton Ash.

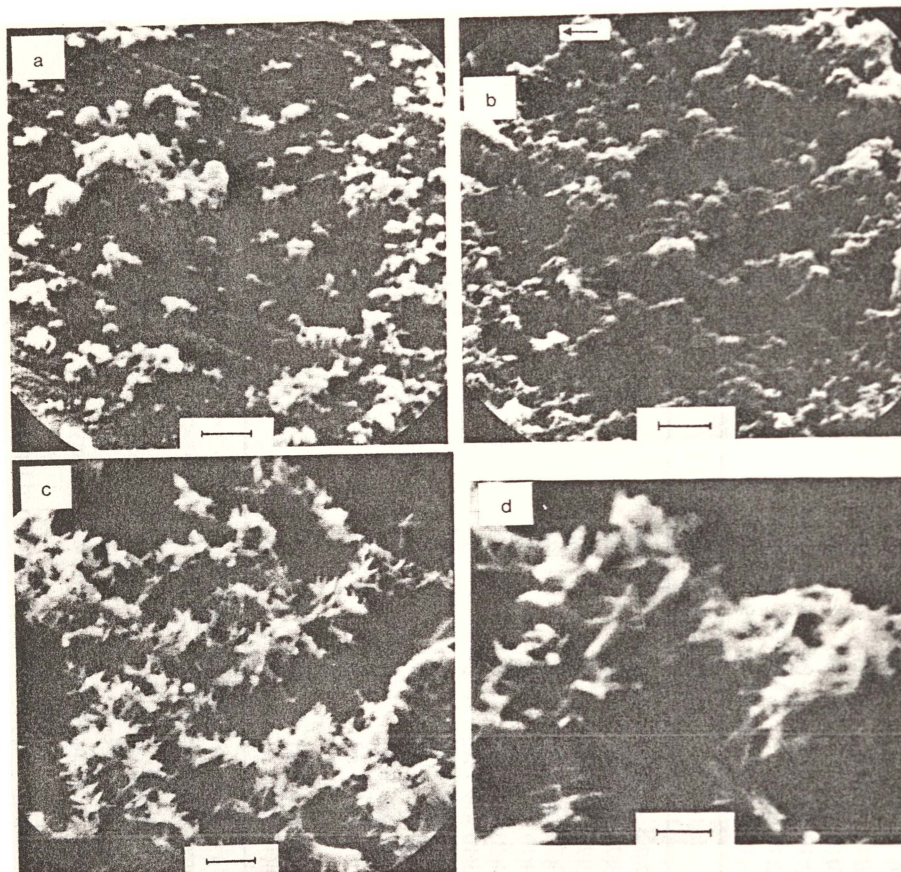


FIG. 9. Scanning electron micrographs of tephra-derived clay minerals. (a) Micrograph showing typical spongelike aggregates of allophane in a sample from 0.45–0.55 m depth at the Kakepuku site. $\times 6,930$; bar represents $0.9 \mu\text{m}$. (b) Micrograph of intermixed mainly tubular halloysite and subordinate allophane, with a silica-rich plate (arrow, top left), characteristic of the Rototuna site tephra clay fractions. This sample was from 0.32–0.37 m depth at the Rototuna site. $\times 6,300$; bar represents $1.0 \mu\text{m}$. (c) Micrograph of clays dominated by interlaced halloysite tubes or laths, some of which appear to be split. The tubes average $0.07 \times 0.3 \mu\text{m}$ in size. This sample was from 0.75–0.80 m depth (Hamilton Ash) at the Rototuna site. $\times 7560$; bar represents $0.8 \mu\text{m}$. (d) Enlarged micrograph of sample in (c); $\times 13,860$; bar represents $0.5 \mu\text{m}$.

of reduced dehydration (hence giving the increasing proportion of 10-Å halloysite with depth).

The halloysite XRD peaks for most Rototuna and Kakepuku samples were only moderately well defined, indicating relatively poor crystallinity (Millot, 1970; Kirkman, 1975). Peaks for Tapapa and Taotaoroa samples tended to be sharper and to become better defined with increasing depth, being sharpest in samples of Rotoehu Ash at Taotaoroa. Halloysite from the

lowermost samples of the cover bed tephra at Rototuna was better ordered than in the upper samples. The XRD evidence of possible changes in degree of ordering within halloysite crystals is supported by differences in the dehydroxylation temperature as shown in DTA curves. These curves indicated a low degree of crystallinity, which may be related to small particle size and shape and to the presence of short-range-order material (Bramao *et al.*, 1952; Hay, 1959; Mackenzie, 1970; Dudas and Harward, 1975a). Samples from Rototuna (cover deposits) and Kakepuku all had peaks between 460 and 490°C; those from Tapapa and Taotaoroa were between 480 and 510°C.

b. Other Minerals. Cristobalite occurred in significant quantities in all Rototuna samples (up to ~30%) but was rarely detected in any samples from the other three sites (Table III). Identical results were obtained from analyses of the silt (2–63- μm) fractions (Lowe, 1981a). This occurrence and abundance of cristobalite at only the Rototuna site indicates that it is probably secondary. If primary, it would be expected to occur at all four sample sites since most of the constituent tephra are common to each (Fig. 6a). Similarly, if it had originated as fine aerosolic dust (c.f. Stewart *et al.*, 1984), it would presumably have occurred at all sites, perhaps in greater amounts at Kakepuku and Rototuna which are west (upwind) of Tapapa and Taotaoroa (Fig. 4). The distribution of cristobalite with respect to other mineral components in the silt fraction in the Rototuna cover deposits showed that as its abundance increases, the glass content decreases (correlation coefficient $r = -0.800$) and the feldspar (total) to quartz ratio decreases ($r = -0.833$). These relationships imply that most of the cristobalite at Rototuna in the cover tephra is authigenic and probably originates from dissolution of glass and possibly feldspar. The concentration of authigenic cristobalite at the Rototuna site suggests some difference in weathering or biological transfer effectively not operative at the other sites.

Vermiculite was detected at only the Rototuna site, where it occurred in most of the cover bed samples but not in those of the underlying Hamilton Ash. The 14-Å peaks were low but usually moderately well defined. This occurrence in tephra materials is unusual for New Zealand (noted previously in Section II) and its persistence at Rototuna is indicative, as with the cristobalite, of peculiar site weathering conditions. That the vermiculite is trioctahedral attests to a micaceous origin (Weaver, 1958; Douglas, 1977; Hume and Nelson, 1982), probably biotite, which is present in small amounts in most of the ferromagnesian mineralogical assemblages. Several of the well-preserved tephra that occur in the lake cores taken near Rototuna are biotite-rich (~40% of 2–4 ϕ fraction: Lowe *et al.*, 1980; Fig. 6) and together total about 100-mm thickness. This amount of biotite is enough to account for the percentage of vermiculite in the Rototuna clay fractions; an alternative origin of locally derived loess is untenable (Lowe, 1981a). The lack of

TABLE IV
FLUORIDE REACTIVITY VALUES^a

<i>Tapapa site</i>				<i>Taotaoroa site</i>			
Depth (m)	Whole sample	Clay ($< 2 \mu\text{m}$)	Field test ^b	Depth (m)	Whole sample	Clay ($< 2 \mu\text{m}$)	Field test ^b
	mmol OH ⁻ /100 g				mmol OH ⁻ /100 g		
0.15-0.30	—	—	s	0.10-0.16	528	—	m
0.45-0.55	529	832	s	0.21-0.27	604	—	m
0.61-0.71	531	—	m	0.29-0.34	657	—	m
0.73-0.83	540	543	s	0.34-0.42	679	832	m
0.86-0.96	522	620	s	0.45-0.50	653	—	m
1.00-1.10	547	797	s	0.54-0.63	685	—	m-s
1.16-1.26	594	870	m	0.70-0.80	595	772	m-s
1.40-1.56 ^c	82	—	w-vw	0.86-0.90	577	—	w
1.70-1.80 ^c	75	185	w-vw	0.93-0.98	549	720	m
1.95-2.08	115	242	w	1.02-1.09	556	—	m
2.22-2.36	295	361	w	1.12-1.18 ^c	550	—	m
2.44-2.54	321	302	m	1.20-1.26 ^c	536	1152	m
3.14-3.19 ^d	—	—	—	1.31-1.42	290	440	w
<i>Kakepuku site</i>				1.53-1.63	353	428	w
				1.70-1.78	338	—	vw
				1.83-1.88 ^d	298	448	vw
				1.93-1.99 ^d	247	772	vw
				2.05-2.13 ^d	210	452	vw
<i>Rototuna site</i>							
				Depth (m)	Whole sample	Clay ($< 2 \mu\text{m}$)	Field test ^b
					mmol OH ⁻ /100 g		
0.10-0.20	—	—	vs	0.02-0.07	81	—	vw
0.25-0.35	660	684	vs	0.07-0.12	94	214	vw
0.35-0.45	696	—	vs	0.13-0.19	91	272	w
0.45-0.55	674	818	m-s	0.20-0.25	122	—	w
0.55-0.59	717	—	m-s	0.25-0.30	138	263	w
0.62-0.68	733	—	m-s	0.32-0.37	130	275	vw
0.70-0.80	780	764	m	0.37-0.41	124	347	w
0.84-0.94 ^c	763	—	m	0.42-0.46	97	295	vw
0.97-1.05	609	624	m	0.47-0.51 ^d	77	227	vw
1.11-1.20	540	536	w	0.51-0.55 ^d	49	204	nr
1.29-1.35	603	—	vw	0.56-0.60 ^d	79	195	nr
1.38-1.48 ^d	659	741	vw	0.63-0.68 ^e	169	249	nr
				0.75-0.80 ^e	118	211	nr

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vermiculite at the other reference sites must be related to site weathering conditions since the biotite-rich tephra occur there also.

Humus complexes, possibly together with small, subordinate quantities of hydrous iron oxides, occur in most Rototuna cover bed samples throughout the profile (Table III), with the greatest amount (as indicated by DTA exotherms) being in the modern A horizon. Proportionally much smaller amounts occur at the other sites, although the data are sparse. The XRD patterns of quartz and feldspar for Tapapa, Taotaoroa, and Kakepuku samples are weak and restricted mostly to samples taken from Kawakawa Tephra or below. In contrast, quartz occurs in all Rototuna samples and in similar or greater quantities than at the other sites. A few Rototuna samples also display very low feldspar peaks.

c. Sodium Fluoride Reactivity. The FR values for the clays are generally slightly higher than for the whole samples, but both sets of data show similar trends (Table IV). In post-Kawakawa Tephra materials, the Kakepuku, Taotaoroa, and Tapapa samples all had relatively high FR values, with those from Kakepuku, then Taotaoroa, generally being slightly greater than those from Tapapa. In Kawakawa Tephra, the FR values decrease markedly to very low values at Tapapa, but at Kakepuku and Taotaoroa this sudden decrease does not occur. Below Kawakawa Tephra, moderately high FR values persist at the Kakepuku site, but moderate to relatively low values are evident at Taotaoroa and Tapapa. The FR values for Rototuna samples, in contrast, are consistently low throughout the profile. The clay FR values are of the same order as the samples from Kawakawa Tephra and underlying tephra at Tapapa.

As a measure of Al—OH activity (Loveland and Bullock, 1975; Perrott *et al.*, 1976a,b), the FR method enables the proportion of short-range-order clays (dominated by “active” Al) to well-ordered clays to be estimated. Conversion of the FR values into percentage units is problematic, however, because of the compositional variations of short-range-order materials. Nevertheless, FR values normally closely parallel gradations from allophane-dominated to halloysite-dominated tephra clay factions [e.g., Kirkman (1975), and Klages (1978)]. This trend is also clearly evident here: bivariate comparison of the whole-sample FR values from the Tapapa, Tao-

^a Based on method of Bracewell *et al.* (1970) and Perrott *et al.* (1976a).

^b Fieldes and Perrott (1966) field test for “allophane” (= Al—OH activity). Abbreviations used are defined as follows: vs, very strong (red, appreciable “allophane”); s, strong (red, appreciable “allophane”); m, moderate (pink, intermediate “allophane”); w, weak (pink, intermediate “allophane”); vw, very weak (almost colorless, little “allophane”); nr, no reaction (colorless, little “allophane”).

^c Kawakawa Tephra.

^d Rotoehu Ash (see note *b* in Table III).

^e Hamilton Ash.

taoroa, and Kakepuku samples with allophane and halloysite abundances (as determined by DTA) gave correlation coefficients of 0.970 and -0.980 , respectively (Lowe, 1981a).

Because low FR values reflect a low $\text{Al}_2\text{O}_3:\text{SiO}_2$ ratio, Perrott *et al.* (1976b) suggested using the fluoroide reaction to indirectly assess the Al:Al + Si mole fraction. Also, Shoji and Ono (1978) demonstrated a close correlation between NaF (1:50) pH values and dithionite-citrate-soluble alumina constituents in Japanese tephra-derived soils. The consistently high FR values at Kakepuku thus reflect high Al-OH activity and are indicative of a high Al:Si ratio, whereas the low Al-OH activity at Rototuna, and in samples from depths at or below Kawakawa Tephra at Tapapa and Taotaoroa, is consistent with a low Al:Si ratio. These conclusions concur with those deduced from the primary mineral compositions (Section 2 and Table II).

4. *Weathering Status*

The degree of weathering at each site may be evaluated from various independent lines of evidence including textural relationships, the proportions of various minerals, and grain surface morphologies.

a. Textural Relationships. At Tapapa, Taotaoroa, and Kakepuku, clay content tends to increase with increasing depth [Table III; Lowe (1981a)]. At Rototuna the clay content is relatively uniform in the cover deposits and similar to or slightly greater than the amounts at and below Kawakawa Tephra at the other three sites. The Hamilton Ash at Rototuna contains much greater amounts of clay-sized material than the late Quaternary tephra deposits.

Ratios of silt ($4-63\ \mu\text{m}$) to clay ($<4\ \mu\text{m}$) (note coarser size of clay) generally decrease with increasing depth at all sites, but average values tend to be higher at Tapapa (5.1) and Taotaoroa (3.9) than at Kakepuku (2.7) and Rototuna (2.9 in cover bed materials; 0.9 in Hamilton Ash). Torrent and Nettleton (1979) demonstrated that under certain conditions an increase in the ratio of fine silt ($2-20\ \mu\text{m}$) to total silt ($2-50\ \mu\text{m}$) may indicate an increase in weathering. Application of this relationship here showed that the average $2-20\ \mu\text{m}:2-50\ \mu\text{m}$ ratios at the Tapapa (0.59), Taotaoroa (0.57), and Kakepuku (0.61) sites differed only slightly, but at Rototuna the ratio was greater in the cover deposits (0.66) and much greater in the Hamilton Ash materials (0.89). Since similar weatherable minerals occur at all of the sites (although proportions differ to a small extent), both sets of these results indicate a slightly greater degree of weathering of the late Quaternary tephra materials at Rototuna than at the other sites.

b. Feldspar, Quartz, and Glass Distributions. Because of the high resistance of quartz to weathering (Jackson, 1968; Wilding *et al.*, 1977), the ratio

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of feldspar (total) to quartz (F:Q) has been used as an index of weathering. Average F:Q values in 2–4 ϕ sand fractions are similar at Tapapa (3.6) and Taotaoroa (3.5), but lower at Kakepuku (2.8) and lowest at Rototuna (2.2 in cover deposits; 1.9 in Hamilton Ash). Similarly, glass, which is relatively easily weathered [e.g., Fieldes (1966) and Kanno *et al.* (1968)], occurs in the lowest amounts at Rototuna. These parallel F:Q and glass distribution trends indicate further a slightly more advanced weathering status for the Rototuna cover bed samples than for samples from the other sites.

c. Heavy Minerals. The Rototuna late Quaternary tephra samples contain an average of 10% (by weight) heavy minerals (in the 2–4 ϕ sand fraction) and 60% (by volume) opaques in the heavy-mineral fraction. These amounts are about two times greater than those at any of the other sites. It is concluded that these higher proportions largely reflect a greater degree of weathering at the Rototuna site. An alternative explanation is that the Rototuna site contains a greater proportion of andesitic tephra accessions than the other sites [because andesitic tephtras usually contain more mafic minerals than do rhyolitic tephtras (Clark, 1960; Fieldes and Weatherhead, 1968; Gow, 1968; D. J. Lowe, unpublished data)], as discussed in Section 2. However, the latter explanation is invalid as the heavy-mineral content at Kakepuku (the site with the greatest andesitic character; Figs. 7 and 8, and shown also by the lake core trends in Fig. 6b), although generally greater than that at Tapapa and Taotaoroa, is much less than that at Rototuna.

d. Titanomagnetite Grain Morphologies. Titanomagnetite is normally relatively resistant to weathering (Aomine and Wada, 1962; Fieldes and Weatherhead, 1968; Ruxton, 1968; Kohn, 1970). The SEM examination indicated that most of the titanomagnetite grains in the Rototuna samples scanned are markedly more weathered and altered than grains of correlative tephtras from the Taotaoroa and Kakepuku sites. These results are illustrated in the micrographs in Fig. 10. Figures 10a and 10b show virtually unweathered grains from Taotaoroa of Rotoehu Ash and Kawakawa Tephra, respectively. These grain surface morphologies contrast markedly with the strongly weathered and severely etched grains in Figs. 10c and 10d, both of Kawakawa Tephra at Rototuna. The etched surface features in Fig. 10d attest that solution and oxidizing processes have operated along {111} parting striations of lamellar twinning [Mason and Berry (1968); also see Berner *et al.* (1980), and Berner and Schott (1982)], and are possibly associated with haematite and/or goethite formation (c.f. Anand and Gilkes, 1984). Some of the trenchlike features in Fig. 10c appear to have coalesced from rows of dissolution pits. Other cracks are possibly phreatomagmatic features (cf. Heiken, 1974) since the Kawakawa Tephra eruption was evidently largely phreato-plinian (Self and Sparks, 1978). However, this severe degree of cracking was

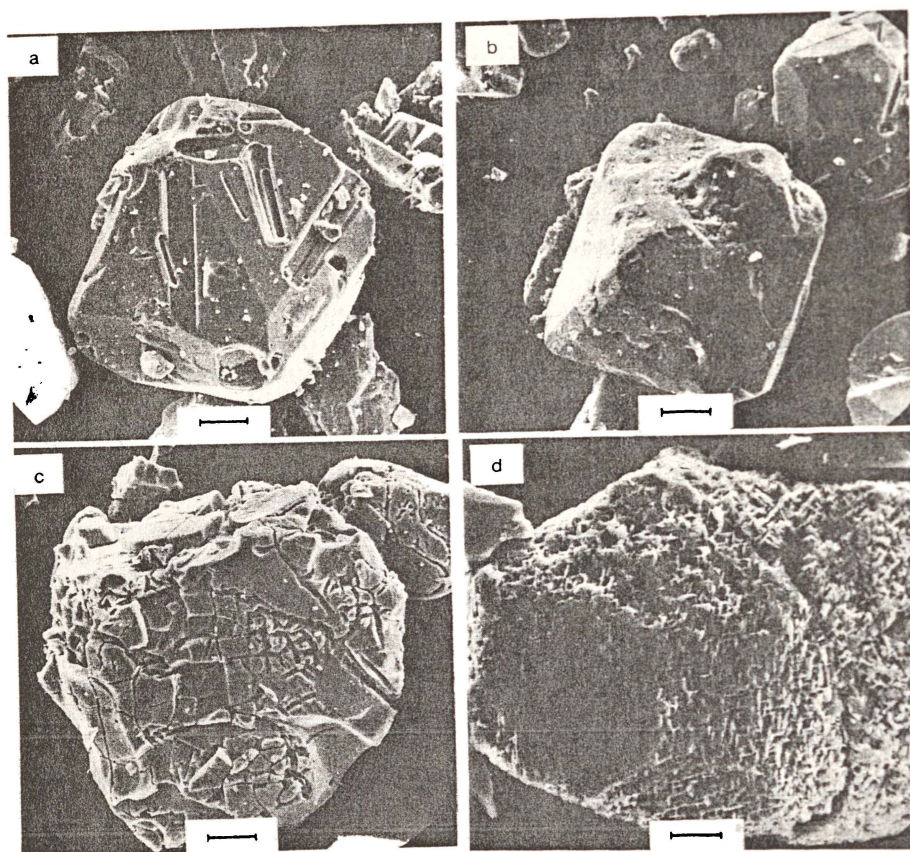


FIG. 10. Scanning electron micrographs of titanomagnetite sand grains of Rotoehu Ash and Kawakawa Tephra showing different degrees of surface modification due mainly to differences in site weathering conditions. (a) Unweathered angular to subangular grain showing well-formed octahedral $\{111\}$ and rhombdodecahedral $\{110\}$ faces, and euhedral, lathlike prismatic intergrowth surface depressions (probably originally occupied by hexagonal apatite crystals). Sample is of Rotoehu Ash from the Taotaoroa site (2.06–2.13 m depth). $\times 220$; bar represents $28 \mu\text{m}$. (b) Weakly weathered subangular grain with a similar appearance to that of (a). Sample is of Kawakawa Tephra from the Taotaoroa site (1.12–1.18 m depth). $\times 220$; bar represents $28 \mu\text{m}$. (c) Strongly weathered grain with deep surface cracking and trenchlike arrays of dissolution etch pits, and spalling of surface blocks (top) (see also text). Sample is of (?)Kawakawa Tephra from the Rototuna site (0.47–0.51 m depth). $\times 270$; bar represents $23 \mu\text{m}$. (d) Strongly weathered and strongly etched grain showing the effect of apparently preferential alteration (to haematite?) along partings. Sample is of Kawakawa Tephra from the Rototuna site (0.32–0.37 m). $\times 810$; bar represents $8 \mu\text{m}$.

not observed in any of the samples of Kawakawa Tephra from the other reference sites. Repetitive spalling of thin surface sheets (manifest as “blocks” in the top of Fig. 10c) was evident on many grains and is usually an indication of intense chemical weathering (Douglas and Platt, 1977).

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Oxidation–reduction cycles, predominantly due to wetting and drying, are evidently especially important in the weathering and breakdown of the titanomagnetite (and other minerals) at Rototuna. Corroboratory evidence is the abundance of Fe–Mn concretions and mottling in the cover bed materials, and climatic data that indicate frequent seasonal drying for short periods near this site. A small number of “fresher looking” grains in the Rototuna samples probably represent accessions of the most recent tephra which have been rapidly admixed with earlier late Quaternary deposits (inset in Fig. 6a).

Thus the Rototuna cover deposits appear more weathered than post-Kawakawa Tephra materials, and similarly or slightly more weathered than the tephra materials of Kawakawa Tephra to Rotoehu Ash age range, at the other three sites. The Rototuna cover deposits are much less weathered than the Hamilton Ash materials, however. Wetting and drying is an important factor in the weathering process at Rototuna.

C. INTERPRETATION AND DISCUSSION OF CLAY MINERAL GENESIS AND WEATHERING

The results show that there are differences in clay mineralogy between the four sample sites. The main differences include the following:

- (1) Differing proportions of allophane and halloysite occur at different depths in each of the profiles.
- (2) Differences in degree of order of the halloysite occur with depth and between sites.
- (3) Much of the halloysite at Rototuna is in the 7-Å phase and is variably hydrated to 10 Å.
- (4) Vermiculite and authigenic cristobalite occur only at Rototuna.
- (5) Relatively high proportions of residual quartz and humus complexes, plus subordinate hydrous iron oxides, occur at Rototuna.
- (6) Different levels of Al–OH activity (as measured by FR) occur at each site and at different depths; these differences probably reflect different Al:Si ratios, related in part to primary mineralogical composition.

In addition, the Rototuna cover deposits (containing about 50% tephra of post-Kawakawa Tephra age) are generally more weathered than their counterpart tephra sequences at Tapapa, Taotaoroa, and Kakepuku. Explanations of these differences in terms of the three broad controls of weathering and clay minerals genesis (Section II) are discussed below.

1. *Age Control*

The general increase in halloysite and decrease in allophane content with increasing depth, hence age, at each of the reference sites is consistent with

the aging effect as discussed in Section II. The increase in degree of order or crystallinity of the halloysite with depth is also in accord with this model. However, that halloysite predominates in Kawakawa Tephra at Tapapa but is sparse in this same tephra bed at Taotaoroa and Kakepuku (Table III) indicates that age cannot be the major operative factor. Similarly, the dominance of allophane and occurrence of only small amounts of halloysite, and its relatively poorly ordered nature, in the pre-Kawakawa Tephra materials at Kakepuku contrasts markedly with the high proportion and well-ordered nature of halloysite in the tephra beds of identical age at Tapapa and Taotaoroa. The coexistence of allophane with the halloysite in the tephra beds older than about 15,000 yr at Tapapa, Taotaoroa, and Kakepuku indicates that allophane persists for relatively long periods of time under the conditions at these sites. Finally, that halloysite occurs throughout the shallow late Quaternary tephtras at Rototuna, and most particularly in the surface deposits mainly of tephtras younger than about 15,000 yr, suggests that the tephtra materials may have weathered directly and rapidly to halloysite (and cristobalite) instead of allophane ($\text{Al}:\text{Si} \approx 2.0$).

2. *Compositional Control*

The high allophane content throughout the Kakepuku profile is consistent with its appreciable andesitic character. Second, gibbsite occurs most frequently at this site, although only in small amounts. At Taotaoroa, the only other site where it was detected, gibbsite occurred in three samples whose titanomagnetites showed high V/Mn ratios, indicative of a significant andesitic influence (cf. Fig. 8 and Table III). Third, the FR values, for both whole samples and clay fractions, are consistently highest at Kakepuku (Table IV)—a high Al–OH activity reflects a high Al:Si ratio, which is to be expected for andesitic tephtra materials. Moreover, the Tapapa site, with the smallest content of andesitic tephtras, has in its lower tephtra beds the highest amounts of halloysite. Taotaoroa seems to fit between the Tapapa and Kakepuku sites in this regard.

A discordance in these apparent compositional effects is evident, however, when the Rototuna data are considered. This site generally contains the second highest (after Kakepuku) andesitic influence, yet has a markedly higher halloysite content, a relatively low allophane content, very low FR values (hence low Al:Si values), and cristobalite present in significant amounts. In addition, biotite-derived vermiculite persists at Rototuna but not at the other sites, which, however, include the same biotite-bearing tephtras. Clearly, these discrepancies, together with the other unusual characteristics of the tephtras at the Rototuna site, cannot be adequately explained by primary composition or age effects.

Nevertheless, a compositional effect is considered to play a measurable role which is especially evident for the Kakepuku site. It also shows up when

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the tephra stratigraphy (hence primary composition) of the Parfitt *et al.* (1983) model [also Parfitt *et al.* (1982b)] (Fig. 2) is critically examined. There are significant differences in stratigraphy, hence composition, across the Parfitt *et al.* (1983) study area [cf. Fig. 6 with p. 44 of Parfitt *et al.* (1983)], which may partly account for some of their results. First, there is a much greater proportion of andesitic tephra at the Mairoa site than at the Kereone site, particularly in the upper, post-Aokautere Ash (i.e., post-Kawakawa Tephra) part of the section. This is significant because the allophane in the Aokautere Ash horizon at Mairoa, having derived from an Al-rich solution [Al:Si = 2.5, Parfitt *et al.* (1983), p. 51], need not have formed within this horizon itself but from dissolution and movement down from the younger and more andesitic (therefore Al-rich, Table II) horizons that overlie it [see also comments in Farmer and Fraser (1979), p. 552]. Second, previous workers (Birrell and Pullar, 1973; Pullar and Birrell, 1973b; Hodder and Wilson, 1976; Hodder, 1978; Lowe, 1981a) have shown that Aokautere Ash (and also Rotoehu Ash) is always contaminated with other tephra in the study area (Figs. 6a and 7). Another possible, but minor, effect of composition is that the greater abundance of halloysite at Rototuna (and mainly in tubular form) may reflect the slightly higher feldspar content.

3. Environmental Control

The environmental factors discussed in Section II demonstrably play the major role in determining the clay mineral types and their distribution in this study. The key differences in site environmental conditions, hence differences in clay mineralogy, are principally a function of (1) the thickness of the late Quaternary tephra column and the shallow occurrence of the Hamilton Ash paleosol at Rototuna, and (2) the tephra/soil microclimate regime. Together, these two broad variables control the degree of leaching and the desilication-resilication balance and the availability of alumina.

a. Tephra Thickness, Depth-of-Burial, and Drainage Effects. At Tapapa, Taotaoroa, and Kakepuku, halloysite is absent in measurable amounts above about 0.8 to 1.4 m depth in the tephra profiles. Below these depths and irrespective of the age of the materials, halloysite generally increases in abundance and in degree of order. Of these three sites, this effect is most marked at Tapapa (the site with the greatest thickness of tephra and with the lowest Al:Si levels) and least marked at Kakepuku (the site with the smallest thickness of tephra and with the greatest Al:Si levels). Taotaoroa occupies an intermediate position. This depth distribution of halloysite can therefore be related, in part, to a depth-of-burial effect whereby the overburden provides a source of silica for resilication at depth. At Tapapa the high ratio of rhyolitic to andesitic materials may have enhanced this effect, whereas the much lower ratio at Kakepuku appears to have minimized the effect.

The depth-of-burial effect, however, does not explain the occurrence of halloysite at the land surface at Rototuna, nor its dominant abundance at depths shallower than 0.50 m. Here, relatively slow drainage due to low permeability in the clay-rich Hamilton Ash paleosol (the compact, silty cover bed materials are also relatively slow draining) has resulted in months-long periods of saturation and a reduced degree of leaching of silica, and consequently aided formation of halloysite and cristobalite (and, presumably, allophane with an Al:Si ratio of ~ 1.0) throughout the cover deposits. In contrast, the materials in the upper parts (post-Kawakawa Tephra) of the thicker profiles at Tapapa, Taotaoroa, and Kakepuku are better drained and undergo relatively greater silica loss through leaching, and therefore are allophane-dominant. Similarly, the sporadic, 1.0- to 1.2-m-thick "fluffy" tephra deposits that occur with the thinner (0.60-m) tephra deposits at Rototuna and elsewhere north of Hamilton (e.g., Fig. 5d) are little affected by the buried impermeable Hamilton Ash paleosol. As a result they have relatively good drainage and maintain an allophanic character—which therefore tends to be self-perpetuating—with high Al–OH activity within the upper 0.75 m or so of the profile. This interpretation is analogous in some ways to that for loess mantle deposits in the United States whereby soil development (or "effective" weathering) increases as the deposits thin away from source, and the depth to less permeable paleosols decreases so that the solum of the modern soil becomes progressively closer to the substratum barrier [e.g., Fehrenbacher (1973), Ruhe (1973), and Harlan and Franzmeier (1977)].

Slow drainage in the Hamilton Ash materials underlying each of the Tapapa, Taotaoroa, and Kakepuku sites may be partly responsible for the enrichment of halloysite in the lowermost late Quaternary tephra. At Tapapa, the large amount of well-ordered halloysite in the Kawakawa Tephra bed is probably due to slow drainage through the well-developed paleosol that underlies it (Fig. 5A). That both 7- and 10-Å halloysites occur in it indicates the possible influence of seasonal dehydration.

Recent studies by Parfitt *et al.* (1984) support these conclusions regarding the effect of drainage on allophane and halloysite formation.

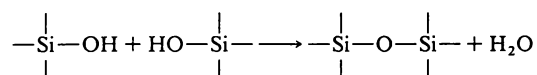
A likely additional tephra thickness effect is due to the component tephra at Rototuna being mostly very thin (Fig. 6a). Weathering and pedological processes there were probably not disrupted by successive tephra increments, but were much more affected at the Tapapa site, for instance, where considerably thicker tephra layers were deposited.

b. Wetting and Drying and Organic Cycle Effects. The cover deposits at Rototuna commonly experience wide moisture fluctuations due to drying out in summer and saturation in winter. The wetting and drying (i.e., reduction and oxidation) is evidenced by the abundant Fe–Mn concretions and mottles, some of the titanomagnetite morphological characteristics, and the

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mixed 7- to 10-Å halloysite (with a decrease in the 7-Å phase with increase in depth). The wet-dry cycles have markedly influenced the clay mineralogy and intensified (accelerated) the weathering processes in the late Quaternary tephros at Rototuna. Because of the relatively intense weathering at Rototuna, feldspar, although normally a reasonably resistant mineral (Jackson, 1968), is more likely to have been broken down here than at the other sites. The occurrence of mainly tubular halloysite at Rototuna is consistent with its having been derived in large part from feldspar. Data in Parfitt *et al.* (1983, p. 48) generally support this conclusion.

Changes in moisture content influence the concentrations of silica in solution (Wilding *et al.*, 1977)—a solution saturated with Si(OH)_4 (120–140 ppm at 20–25°C) is supersaturated with respect to crystalline forms of silica and ensures precipitation of crystallized SiO_2 (Chichester *et al.*, 1969; Millot, 1970; Henderson *et al.*, 1971; Shoji and Masui, 1971). The wet-dry cycles at Rototuna cause fluctuations in silica concentration which result in cristobalite formation: hydrolysis and dissolution of Si from glass (or feldspar) to form a silica hydrogel (Fig. 3) (in saturated conditions) is followed by its recrystallization as cristobalite (in dehydrated conditions in late summer) with the crystals growing by the uniting of tetrahedra and the elimination of water (a mechanism suggested for opal genesis by Jones and Segnit, 1972, p. 419):



The formation of cristobalite (and halloysite) at Rototuna is also favored by an abundant supply of silica (chiefly from glass and feldspar). Regular additions of thin, predominantly rhyolitic tephros (which in turn are rapidly mixed with the previously deposited late Quaternary tephros by bioturbation and other processes) have ensured the constant supply of fresh silica.

The organic cycle has probably intensified the genesis of cristobalite. The formation of acid-organic complexes aids silica dissolution, and water uptake by plants, intensified in summer, increases silica concentration and hence its potential for precipitation. Some of the cristobalite at Rototuna may be indirectly biological in origin, forming from the dissolution products of biogenic opal rather than of glass or feldspar. Weathering always within influence of the organic cycle at Rototuna has resulted in low Al ion activity due to Al-humus complex formation. The Al-humus bonding, particularly in the upper horizons, thus limits the concentration of Al and hence the possibility of its coprecipitation with Si to form allophane.

The occurrence of vermiculite at the Rototuna site alone can also be attributed to the special site conditions as follows: impeded drainage and a high concentration of Si and low concentration of Al, a moderate to high

hydronium concentration with some leaching mainly to remove K (and Mg), and periods of oxidation and wetting and drying [cf. Buol *et al.* (1973), Douglas (1977), Fanning and Keramidas (1977), and see also Calhoun *et al.* (1972), and Wilson (1975)].

c. Rainfall Effect. In considering the effect of mean annual rainfall on the leaching regimes and Si concentrations at the four sample sites, this study supports only in part the model of Parfitt *et al.* (1983) (Fig. 2). The relatively low rainfall at the Rototuna site (1200 mm) may contribute to the reduced level of leaching, hence high Si concentration and abundance of halloysite there, as proposed for the Kereone soil by Parfitt *et al.* (1983). However, the differences between the properties of the cover deposits at Rototuna (Fig. 5c) and those of the slightly thicker nearby fluffy deposits (Fig. 5d) cannot be due to differences in mean annual rainfall as rainfall must be identical at both sites (both now and in the past)—perhaps the “fluffy” deposits occurring in the paleosurface hollows have received more *net* precipitation via runoff or lateral movement [as described by Veneman *et al.* (1984)]. In addition, the Taotaoroa and Kakepuku sites both receive similar annual rainfalls (1250–1300 mm) but show considerable differences in the proportions of allophane and halloysite stratigraphically. The Tapapa site, with the highest rainfall (1500 mm), has a clay fraction at depths below 1.4 m (Kawakawa Tephra) dominated by relatively well-ordered halloysite and indicative of strong resilication, rather than desilication, at these depths. The Tapapa, Taotaoroa, and Kakepuku sites are of intermediate status with respect to the rainfall distribution extremes examined by Parfitt *et al.* (1983), but the evidence presented here demonstrates that other site-specific (microenvironmental) factors together probably play a more important role than the amount of rainfall.

These interpretations do not invalidate the fundamental basis of the Parfitt *et al.* (1983) scheme, which is that rhyolitic tephra clay mineral genesis is determined primarily by the leaching regime and concentration of Si in solution. It is clear, however, that various current microenvironmental conditions in addition to total rainfall influence the levels of Si in solution and its distribution and provide circumstances for its loss, precipitation, or coprecipitation with Al. These conclusions thus support the principles embodied in the Parfitt *et al.* (1983) model and also in Shoji and Fujiwara (1984). The specific site conditions may reinforce the trends associated with the increase or decrease in rainfall (e.g., the greater andesitic character at the Mairoa or Kakepuka sites coincides with a higher degree of leaching of Si due to higher rainfall; at Rototuna, the site micro-relief may influence the net precipitation received, hence degree of leaching).

The factors that significantly contribute to the resilication–desilication balance and the availability of Al for coprecipitation at each of the reference

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sites are composition (proportion of andesitic to rhyolitic material—i.e., initial Al:Si ratios, and glass and feldspar content and composition), degree of drainage, depth of burial, wetting and drying, and the effects of the organic cycle (Fig. 11); pH is also likely to have an influence. One or more of these controls may predominate at any one site, with the effect of one possibly overriding or excluding the effect of another. Any one environmental factor, such as rainfall, cannot be directly related to the clay mineralogy safely without full consideration of other factors [see also Ruhe (1984)].

D. CONCLUSIONS

This study on the weathering of the distal, late Quaternary, multiple tephra sequences of the Waikato region has been unusual in that the original compositions of the subaerial tephra deposits under investigation are known through the preservation of the same tephras, in unweathered condition, in organic-rich, sub-lake sediments adjacent to the reference sites. Moreover, the cores of the tephras in the lakes have provided a far more accurate chronology, stratigraphy, and distribution pattern for tephras in the region than previously known, thereby enabling the controls on weathering and clay mineral formation to be assessed with more certainty.

The Waikato tephra sequences examined show some variations in their clay mineralogy that can be attributed to their age and stratigraphy. However, the contrasts between sites and the peculiar mineralogy at Rototuna in particular are probably related chiefly to differences in site weathering conditions and, to a lesser extent, to primary composition (essentially the proportions of rhyolitic and andesitic components). The fate of the various ionic constituents arising from breakdown of primary minerals, and the consequent types and rates of clay minerals formed and transformed, is dependent on the actual site environmental conditions rather than tephra age or effective weathering time. Time is indirectly responsible in part for the condition of slow drainage at Rototuna in that the strongly weathered clayey paleosol on Hamilton Ash (slow drainage is also associated with some paleosols at other sites) represents a considerable period of previous (relict) soil formation and weathering.

The formation of both cristobalite and halloysite (and probably also Al:Si \approx 1.0), instead of allophane (Al:Si \approx 2.0) or imogolite, is favored at Rototuna because of the specific site microenvironmental conditions that promote silica accumulation (or minimize its loss) and its recrystallation. The conditions also promote Al-humus complexing (Fig. 11), hence restricting Al availability. Allophane, too, is present in the Rototuna clay fractions, the greatest amounts occurring in the upper part of the profile, which has effectively undergone more desilication than the lower part. That allophane predominates in the hollow-infilling “fluffy” deposits nearby is

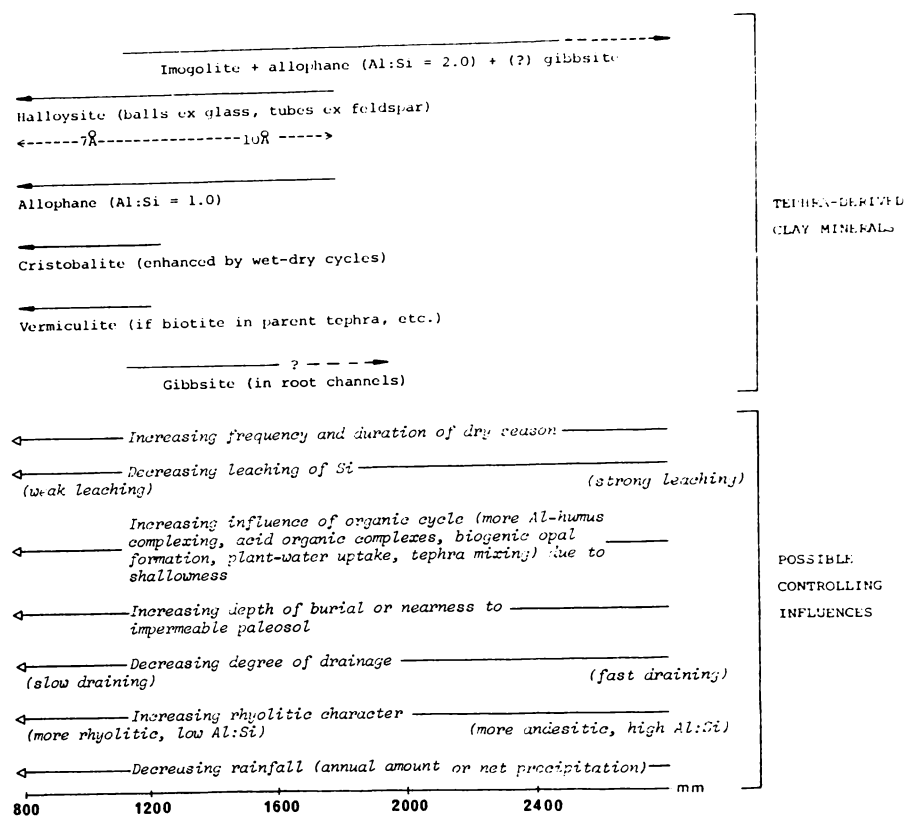


FIG. 11. Provisional weathering sequence for tephra in the Waikato region showing clay mineral formation and persistence with respect to various environmental controls other than tephra age. The clay minerals increase in amount (in direction of solid arrows) as a function of the various environmental influences (open arrows). The sequence could probably be applied to tephra deposits in many other areas as well. Part of the diagram is modified after Fig. 2.

due mainly to their greater thickness and free drainage (as the impermeable Hamilton ash paleosol is buried deeper). Once formed, the properties of the allophane tend to maintain a free-draining, leaching environment that seemingly perpetuates further allophane formation. Vermiculite has formed from biotite and persisted because of the impeded drainage, periodic oxidation, and other conditions noted previously.

Because site environmental conditions have varied over the past 50,000 yr in the Waikato region it is possible that a "memory" effect is inherent in some of the clay fractions. How much of the influence of past conditions is reflected in the clays is impossible to determine with certainty because the current differences between sites are likely to have existed in the past to a similar degree (Parfitt *et al.*, 1983). It is probable, for example, that the formation of halloysite (much in the dehydrated 7-Å form) in the circa

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20,000-yr-old Kawakawa Tephra bed at Tapapa (and, to a lesser degree, at Taotaoroa and Kakepuku) was enhanced by lower total rainfalls and lower temperatures, or by more intense wetting and drying, than at present. However, the current site weathering conditions and climate patterns seem sufficient to account for the differences in clay mineralogy and weathering evident between the sites. Because these conditions will change with time, the rates of weathering and the formation and transformation of clay minerals in the tephra materials are best viewed as dynamic in nature. Thus, although it seems possible to relate in part the clay mineralogy of a well-dated tephra sequence to relict environmental conditions, any attempt to directly assess paleoenvironment just from the clays, and without independent corroboration, must give equivocal results [c.f. Singer (1980) and Retallack (1981)].

IV. Summary and General Conclusions

The factor of time (tephra age or effective weathering time) has frequently been viewed as the main reason why the amounts and types of clay minerals, especially allophane and halloysite, vary in tephra deposits of predominantly acid to intermediate composition and in temperate latitudes. The review section of this chapter showed that the types and rates of formation and transformation of tephra-derived clay minerals are determined chiefly by macro- and microenvironmental factors together with the mineralogical and physicochemical composition of the parent deposits. Period of time of weathering in clay mineral genesis is indirect and subordinate in its effect in that weathering rates and products are chiefly dictated by other controls. Environmental conditions that affect the concentration of silica in solution, the availability of alumina, and the opportunity for coprecipitation of these are paramount and are controlled by the leaching regime, the organic cycle, and pH. In turn, these factors are conditioned by climate (particularly rainfall), drainage, tephra thickness, depth of burial, and the frequency and amount (thickness) of fresh tephra (or "tephric loess") accessions. Allophane and imogolite are possibly reaction end points rather than short-lived transition products. They appear to be able to persist for long periods, if conditions are favorable. Halloysite and gibbsite appear to form directly from the dissolution products of primary or secondary minerals, depending mainly on whether conditions favor resilication or desilication. The occurrence of 2:1 and 2:1:1 type clay minerals in some tephtras has been explained in various ways but their occurrence is still problematic. Support for a pedogenic synthesis model appears to be lessening.

The second part of this chapter illustrated that differences in field properties, clay fraction mineralogy, and weathering in distal, late Quaternary rhyolitic and andesitic tephra deposits in the Waikato region, New Zealand,

could be partially explained by each of the three broad controls reviewed previously. However, the differences were attributed largely to differences in current environmental conditions (and possibly enhanced by past conditions). In reaching such a conclusion, it is clear that in these sorts of studies an accurate tephrostratigraphy and a knowledge of primary composition is vital, as is a full consideration of other factors. The lakes in the Waikato region and the succession of unweathered tephra contained in their sediments provide a unique model to help evaluate the controls and rates of weathering of the subaerial deposits. The environmental conditions having the greatest influence are degree of drainage, tephra thickness, depth of burial and site micro-relief, wetting and drying, and the effects of the organic cycle (Al–humus complexing, formation of organic acid complexes, formation of biogenic opal, plant water uptake, and biological homogenizing). In addition, compositional variations (chiefly the proportion of andesitic to rhyolitic tephra material) were seen to affect the clay mineral genesis, but to a lesser extent, over all than the site weathering conditions. The amount and composition of the dominant primary minerals, notably plagioclase and volcanic glass, determine the initial (“potentially available”) Al:Si ratios. Which of these variables has the predominant effect may vary from site to site, especially as the relative abundances of rhyolitic and andesitic tephra in the profiles change geographically. Together, the environmental and compositional factors control the concentration of Si in solution and its distribution in the profile, and the concentration and availability of Al. These findings generally support the conclusions of the review section.

In the Waikato region the total thickness of late Quaternary tephra decreases northwestward (away from the main tephra sources). At the Rototuna site, where the late Quaternary tephra column thins to a mere 0.60-m-thick composite cover deposit, drainage is mostly restricted because of the close presence of an impermeable paleosol (on Hamilton Ash) in the solum. Weathering has been continuously affected by the organic cycle. These factors, combined with a seasonal moisture deficit and a moderate rainfall (1200 mm per annum), have resulted in intense wet–dry cycles and strong weathering and biological mixing, promoting the accumulation of Si (originating mainly from the dissolution of glass or feldspar) in solution and reducing the availability of Al through Al–humus complexing. Much of the Si in solution (as silica hydrogels) has apparently recrystallized, probably in periods of dehydration, to cristobalite. In addition, halloysite (much in the 7-Å phase) has been formed (some probably originating specifically from the dissolution of feldspar) and occurs throughout the profile, including small amounts in the uppermost surface samples. This distribution is unusual for tephra deposits and attests to the special site weathering conditions at Rototuna. Vermiculite, probably formed solely from tephra-derived biotite, per-

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sists in small amounts at Rototuna also because of the special, dominantly poorly drained conditions there.

The weathering sequence developed in Fig. 11 emphasizes that many site-specific environmental conditions and compositional factors, rather than just rainfall, may control the concentration of Si (and Al) in solution and its distribution through the profile, and provide circumstances for either its loss, its precipitation, or its coprecipitation with available Al. Because these many possible controlling influences have operated both in the past and the present, then studies relating tephra clay mineralogy to paleoenvironment must be interpreted with caution.

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Cross referencing to thesis papers

- Green, J.D.; Lowe, D.J. 1985 = Paper 9
- Lowe, D.J. 1981b = Paper 10
- Lowe, D.J.; Nelson, C.S. 1983 = Appendix A*
- Lowe, D.J. *et al.* 1980 = Paper 1

Errata

- p.265, bottom line of list of contents: "320" should read "319"
- p.279, line 19: "1986" should read "1985"
- P.289, line 2: "1986" should read "1985"
- p.305, second-from-bottom line in footnotes: "note b " should read "note e "
- P.327, reference missing: Rettalack, G.J. (1981). Fossil soils: indicators of ancient terrestrial environments. *In* "Paleobotany, Paleoecology and Evolution, Vol. 1" (K.J. Niklas, ed.), pp.55-102. Praeger Publishers, New York, U.S.A.

* Methods of analysis etc. used in Paper 11 are detailed in Appendix A.

PAPER 12

Late Quaternary volcanism in New Zealand : an integrated record
from distal tephras in lakes and bogs.

Submitted to: *Geology*.

tephras in lakes and bogs

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ABSTRACT

Studies on distal tephras preserved in lake sediments and peats in northern New Zealand have documented the stratigraphic, chronologic, and compositional relationships of 46 eruptives, aged c.700 - 17 000 yr B.P., which originated from six North Island volcanic centers: Taupo (9 tephras), Okataina (8), Maroa (1) (rhyolitic); Mayor Island (2) (peralkaline); Tongariro (11), Egmont (15) (andesitic). Sources were distinguished by mineralogy and composition, field relations, and ^{14}C chronology.

All known rhyolitic tephra-producing eruptions from Taupo, Okataina, and Maroa volcanoes since c.17 000 yr B.P. are represented, but only a small proportion of the known tephras erupted from Tongariro, Egmont, or Mayor Island volcanoes is recorded. The distal tephras from these latter volcanic centres may thus reflect atypically powerful (or oblique) eruptions, or dispersal by unusual wind conditions. An improved record of volcanism for the Tongariro, Egmont, and Mayor Island centres might be obtainable from suitable lakes or bogs more proximal to them.

The study demonstrates the value of investigating lakes and bogs to help erect a detailed and integrated record of explosive volcanic activity through tephrostratigraphy.

INTRODUCTION

New Zealand's North Island contains a number of rhyolitic and andesitic volcanoes that have been active in late Quaternary times (Fig.1; Smith, 1986). Many aspects of the history of these volcanoes have been well documented (e.g., Healy et al., 1964; Pullar et al., 1973; Cole and Nairn, 1975; Suggate et al., 1978; Buck et al., 1981; Wilson et al., 1984; Smith, 1986), but detailed stratigraphic, chronologic, and compositional

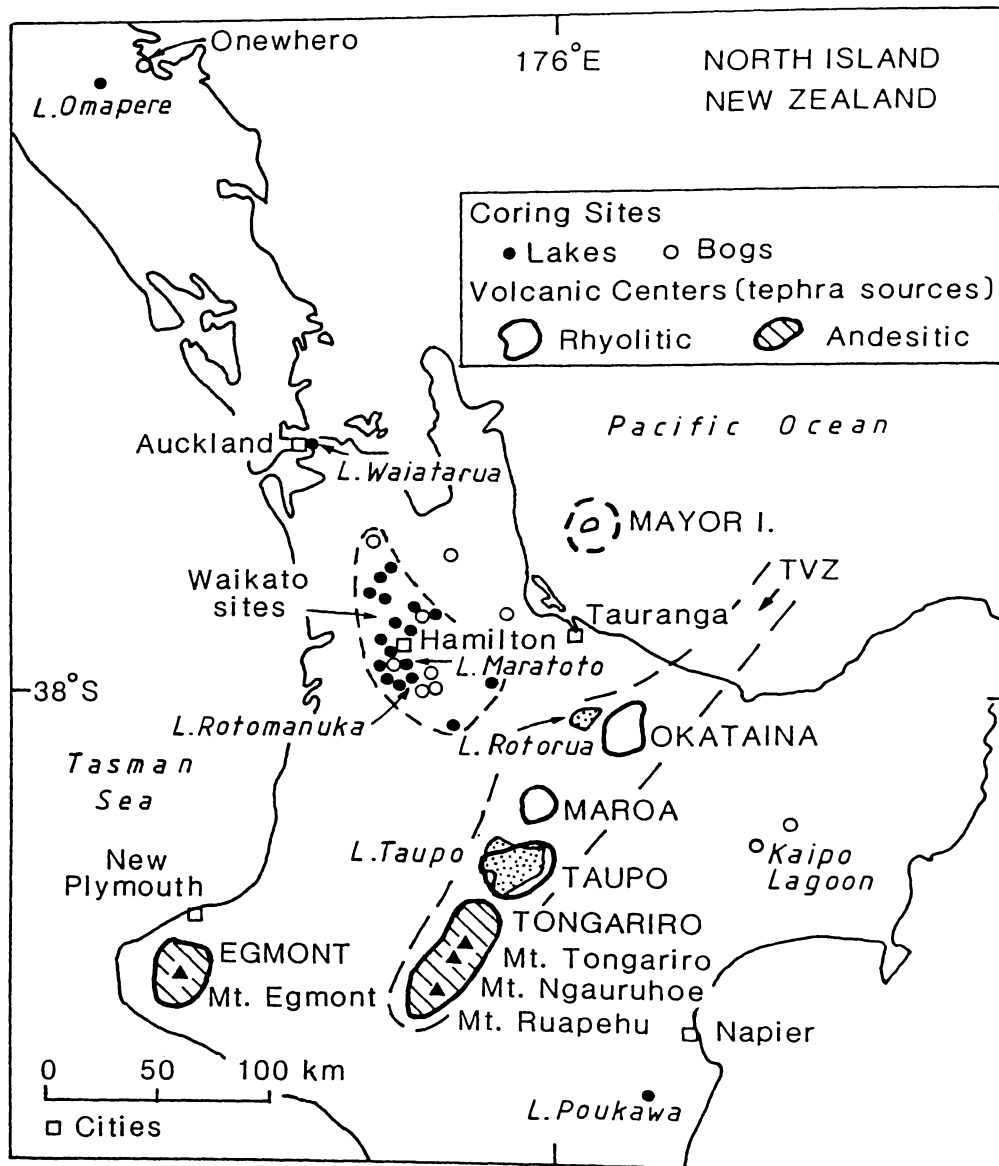


Figure 1. Locations of lakes and bogs studied and containing distal airfall tephras derived from one or more of the six volcanic centers shown (after Cole and Nairn, 1975, and Wilson et al., 1984). TVZ = Taupo Volcanic Zone. Note: Mt. Egmont is also known as Mt. Taranaki.

relationships may commonly be uncertain or are still being established. In this paper I attempt to show how a detailed and potentially comprehensive record of volcanic activity may be obtained by studying tephra deposits preserved in sediments in lakes and bogs. Such environments are favourable places to investigate volcanism through tepthrostratigraphy because they offer exceptional stratigraphic and chronologic control, and because of the essentially pristine condition of the tephra deposits.

I examine here the mineralogical and chemical characteristics of distal tephtras sampled from lakes and bogs in the North island (Fig.1), and thereby characterize and identify the volcanoes from which the tephtras originated. Hence, by taking into account the stratigraphy and chronology (based on ^{14}C dating) of the tephtras, an integrated record of explosive rhyolitic and andesitic volcanism in the North Island during the past c.17 000 years is determined. This is one of the most comprehensive records obtained for this period, and shows for the first time the stratigraphic interrelationships of tephtras derived from six major volcanic centres in New Zealand.

TEPHRA SAMPLES AND ANALYSIS

Locations of the sites sampled are shown in Fig.1. Cores c.2-4 m in length were taken from the lakes with a modified Livingstone piston corer; bogs were sampled mainly using a Russian-type peat corer. At Kaipo (Fig.1), coring was not needed because an accessible section had been exposed by erosion (Lowe and Hogg, 1986). Generalised tepthrostratigraphic columns are summarized in Fig.2.

The longest and most complete tephtra sequences are found in the cores from the Waikato lakes (Fig.2), most of which were formed c.17 000 yr ago (Green and Lowe, 1985; Lowe and Green, 1987). Thus the majority of my analyses were done on samples from these cores, particularly from Lakes

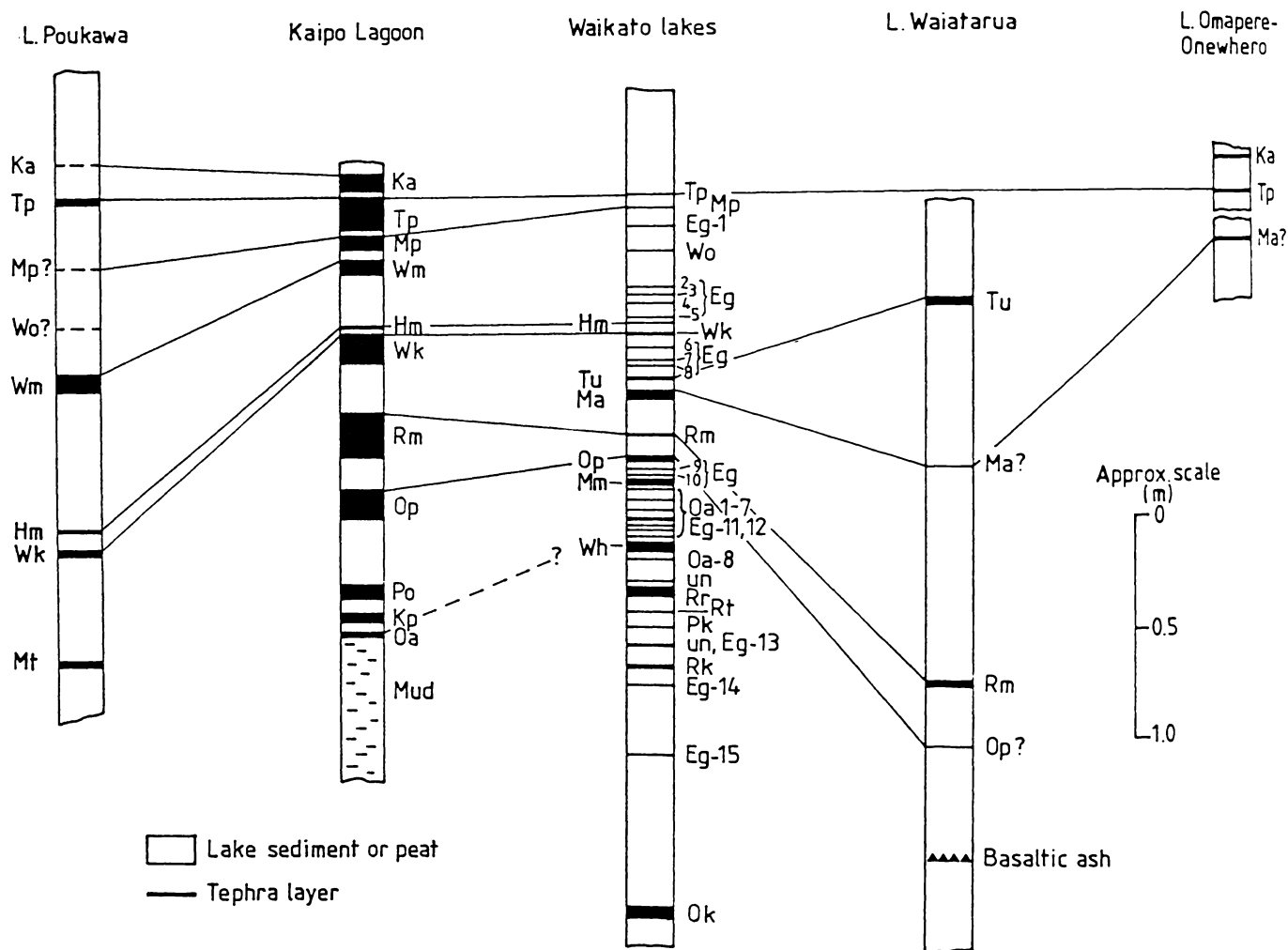


Figure 2. Summary of composite tephrostratigraphic columns of cores or sections from lakes and peats at five locations (Fig.1) in the North Island. Lake Poukawa column is after Howorth et al. (1980), Froggatt (1981b), and B.P.Kohn, V.E.Neall, and R.B. Stewart *in* Lowe (1986b); Lake Omapere-Onewhero column is partly based on Pullar et al. (1977).

Maratoto and Rotomanuka (Fig.1; Lowe, in prep.).

The tephras, considered essentially primary fallout deposits, typically comprise unweathered, pale-colored, compact, occasionally bedded, macroscopic, fine ash to medium lapilli layers of c.2-200 mm thickness that stand out against the darker lake sediment and peat (e.g., see plate 1 in Lowe, in prep.). In the Waikato lakes, many tephra layers can be readily correlated from core to core and from lake to lake in the field using their color, lithology, bedding characteristics, and stratigraphic position (Lowe et al., 1980; Green and Lowe, 1985; Lowe, in prep.). Others, particularly from the andesitic sources, are less distinct and occur either as diffuse, gritty zones in the sediment or as very thin (c.1-2 mm), occasionally microscopic, layers best revealed by x-radiography (Lowe et al., 1981). Where the layers are closely spaced in the cores, some mixing between them may occur. The stratigraphic sequence of the tephra layers is always the same, though not all are necessarily represented in any one core.

A total of 46 tephras have been identified, and each is likely to represent a separate eruptive event (cf. Anderson et al., 1984; see also Lowe, in prep.).

The 63-250 μm (2-4 ϕ) size fractions of samples of each of the tephras were split into heavy mineral (ferromagnesian silicates, Fe-Ti oxides) and light mineral (glass, feldspars, quartz) components and analysed by petrologic microscope (pointcount), x-ray diffraction, and electron microprobe (e.m.) methods (Froggatt and Gosson, 1982; Froggatt, 1983). Slices of sediment (usually 1-2 cm thick in the lake cores, 5 cm in the peat cores) from above and below most of the tephra layers were ^{14}C dated at the Waikato University Radiocarbon Dating Laboratory (Hogg et al., 1987). Around 100 samples were dated.

COMPOSITION OF TEPHRAS AND CHARACTERIZATION OF SOURCE VOLCANOES

The results, when considered together and with reference to previous work, permit all of the 46 tephras, aged \leq c.17 000 yr B.P., to be matched to a

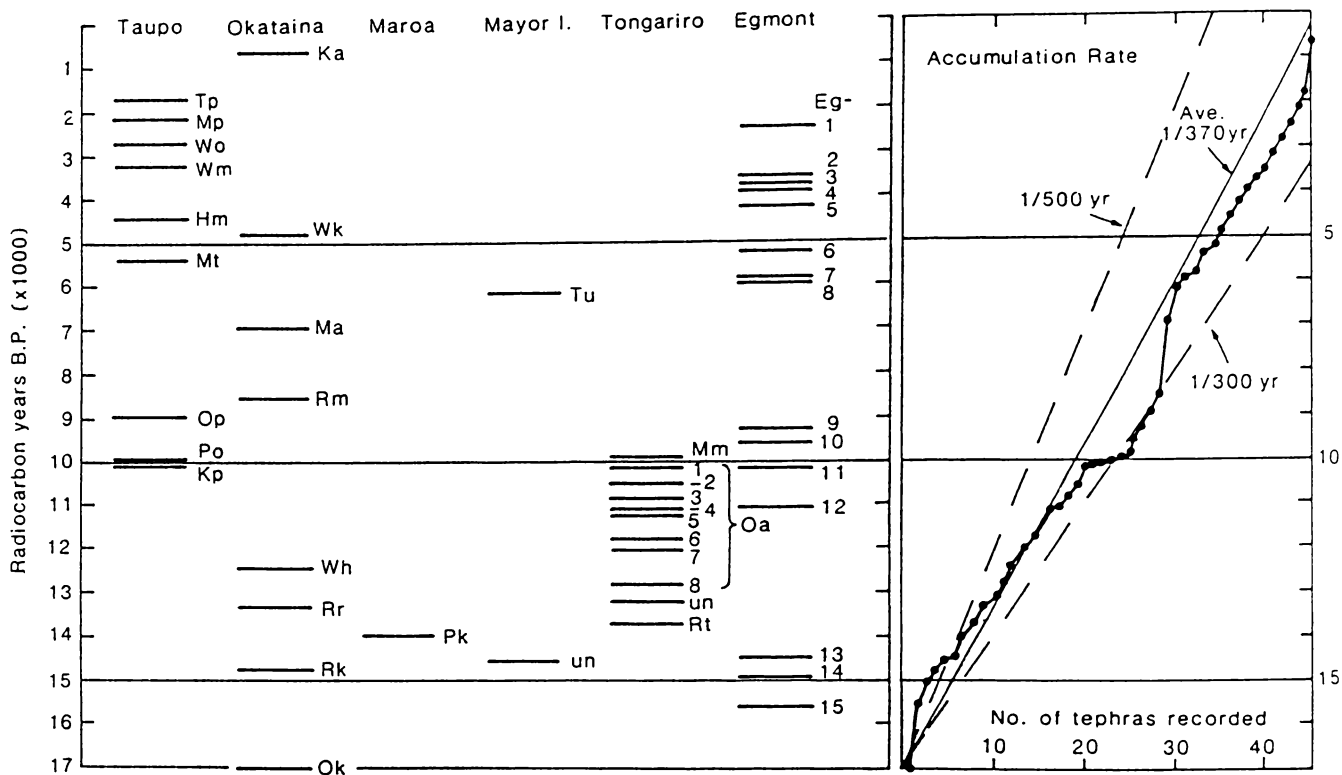


Figure 3. Integrated tephrostratigraphy based on cores from the lakes and peats shown in Fig.2. Tephra names are: Tp, Taupo; Mp, Mapara; Wo, Whakaipo; Wm, Waimihia; Hm, Hinemaiaia; Mt, Motutere*; Op, Opepe; Po, Poronui; Kp, Karapiti; Ka, Kaharoa; Wk, Whakatane; Ma, Mamaku; Rm, Rotoma; Wh, Waiohau; Rr, Rotorua; Rk, Rerewhakaaitu; Ok, Okareka; Pk, Puketarata; Tu, Tuhua; Mm, Mangamate; Oa, Okupata (units 1 to 8); Rt, Rotoaira; Eg-1 to Eg-15, uncorrelated Egmont-derived tephras; un, uncorrelated or unnamed tephra. Ages on old half-life basis.

*The inclusion of this tephra is based on studies by Howorth et al. (1980) and Froggatt (1981b) at Lake Poukawa (Fig.2).

particular source volcano, as depicted in Fig.3. In this figure, each eruptive event recorded is denoted by a horizontal bar with the chronology on the vertical axis. The data providing the basis for these tephra-volcano affinities are summarised and discussed below. Named tephra formations are referred to using the abbreviations defined in Fig.3. The detailed examination of compositional trends associated with eruptive sequences from particular volcanoes is beyond the scope of this paper.

Heavy Minerals

Fig.4 shows the proportions of heavy minerals and Fe-Ti oxides (mostly titanomagnetite, rarely magnetite and ilmenite) in the tephtras. The tephtras from the andesitic Tongariro and Egmont volcanic centers have a relatively high content of heavy minerals (c.15-25%) but a low content of Fe-Ti oxides (c.10%). The opposite applies to the rhyolitic Taupo and Okataina-derived tephtras, which are low in heavies (c.<5%) but relatively high in oxides (c.20-30%), especially Okataina. Samples of the pantelleritic Mayor Island-derived tephtras are very low in both heavies (c.1%) and oxides (c.5%).

The dominant ferromagnesian silicate assemblages (determined by modal analysis) are summarized in Fig.5. (Zircon and apatite may also be present.) These assemblages characterize each source volcano with reasonable consistency (cf. Ewart, 1971; Cole and Nairn, 1975; Kohn and Glasby, 1978; Howorth et al., 1980; Lowe et al., 1980; Froggatt, 1981a; Hogg and McCraw, 1983): (1) The Taupo-derived tephtras are dominated by hypersthene, commonly with small amounts of augite. (2) Most of the Okataina-derived tephtras contain calcic hornblende, hypersthene, and augite in varying amounts, and hence plot as a relatively wide scatter in Fig.5. Two of the Okataina tephtras (Wk, Rm) are dominated by cummingtonite. three others (Ka, Rk, Ok) by biotite, which are distinctive marker minerals for these particular tephtras. (3) One of the Mayor Island-derived tephtras (Tu) contains a particularly diagnostic set of marker minerals (not plotted). The dominant one is aegirine but also included are subordinate amounts of ferrohedenbergite, aenigmatite, riebeckite, olivine, and very rare tuhualite. The other tephtra (un) is microscopic and occurs wholly as glass. (4) The solitary Maroa-derived tephtra (Pk) consists

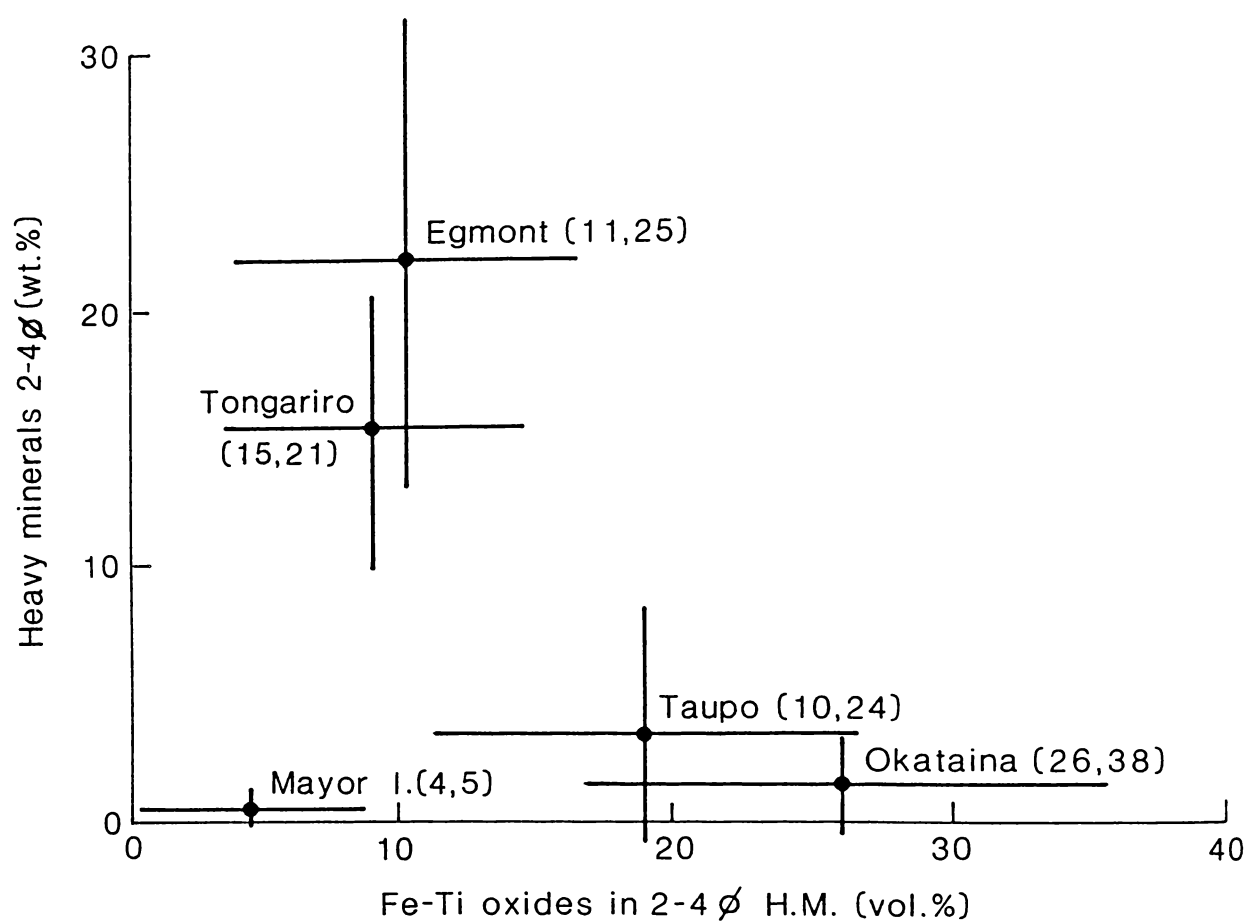


Figure 4. Proportions of heavy minerals and Fe-Ti oxides. Dots, bars = mean values ± 1 S.D.; numbers in brackets = no. of samples analysed for heavy mineral wt.%, for Fe-Ti oxide vol.%.

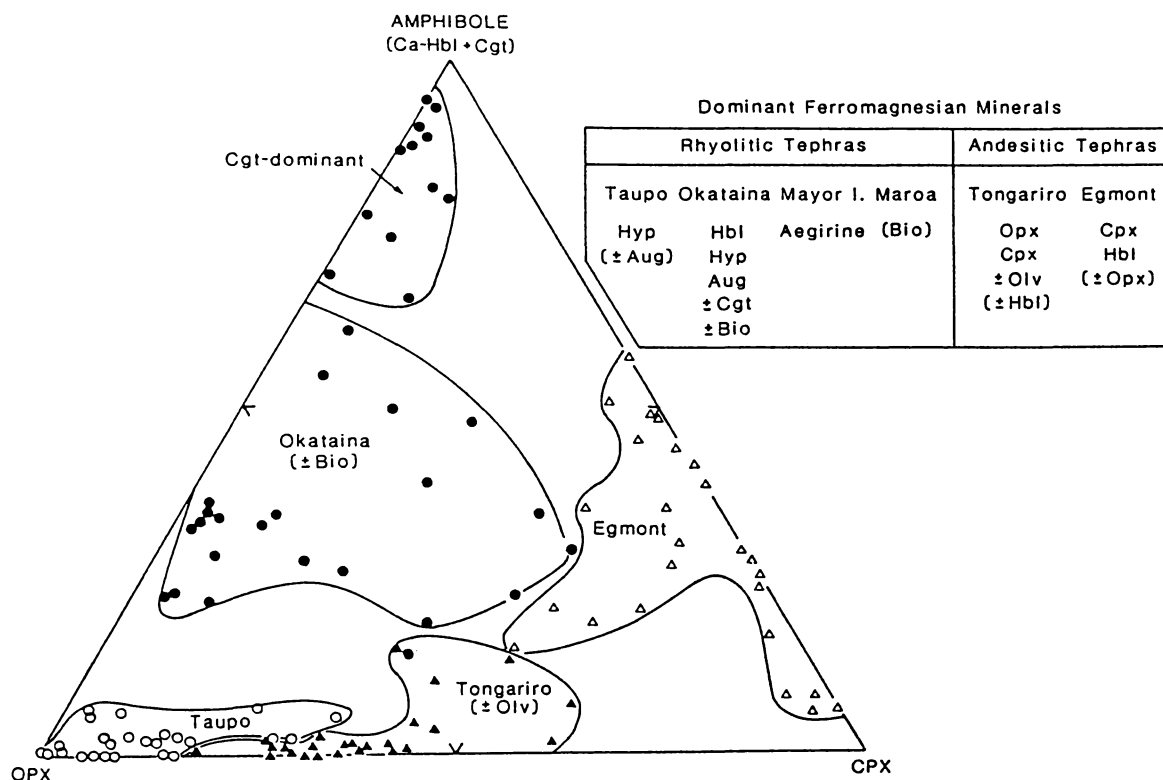


Figure 5. Dominant ferromagnesian minerals associated with tephras from each source volcano. Opx = Orthopyroxene; Cpx = Clinopyroxene; Ca-Hbl = Calcic Hornblende; Cgt = Cummingtonite; Hyp = Hypersthene; Aug = Augite; Bio = Biotite; Oliv = Olivine.

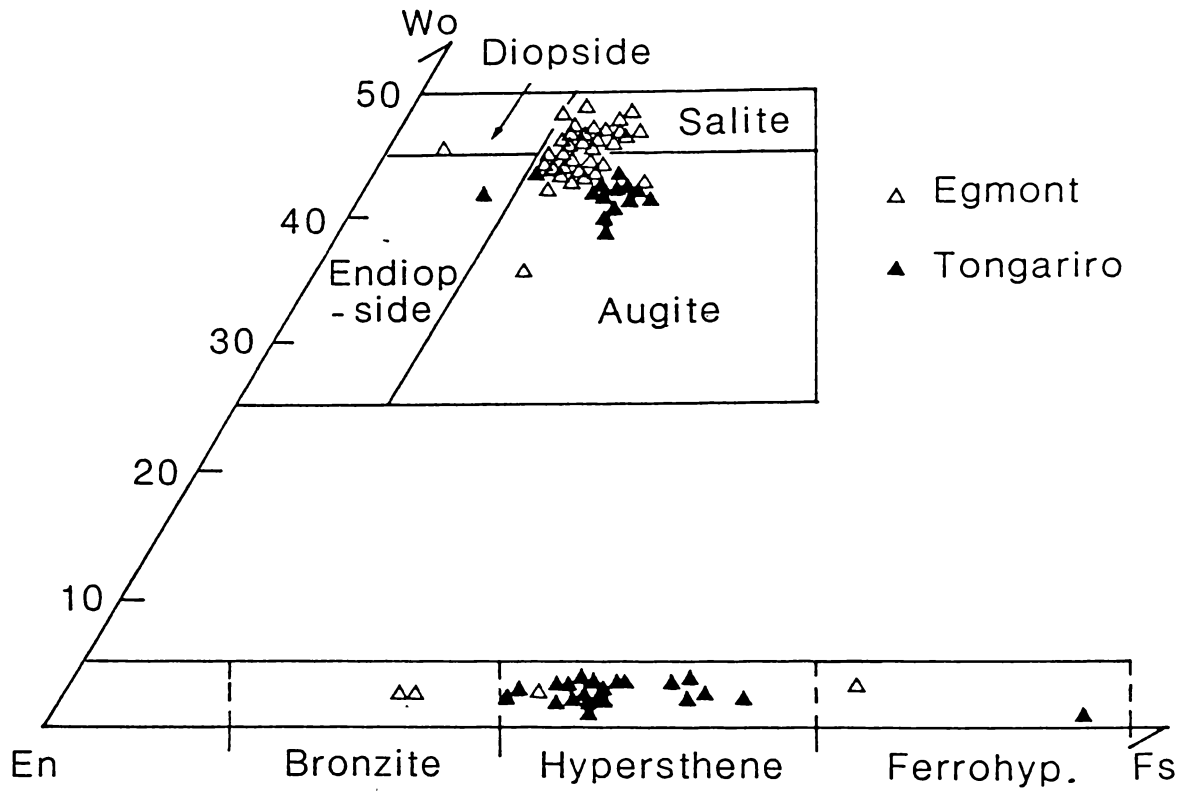


Figure 6. Pyroxene compositions (mol. %) based on microprobe analyses of grain cores.

solely of glass, but near source it characteristically contains mainly biotite with hornblende (Topping and Kohn, 1973). (5) The Tongariro-derived tephras are dominated by orthopyroxene and clinopyroxene. Many also contain forsteritic olivine (Fo_{84-87} by e.m.), usually in only small quantities, and a few contain sparse hornblende. (6) The Egmont-derived tephras contain mainly clinopyroxene and calcic hornblende. Some orthopyroxene may also occur, but it is typically the presence of hornblende that initially distinguishes the Egmont tephras from the Tongariro tephras.

I examined the chemistry of some of the pyroxenes (77 analyses) and amphiboles (32 anal.) in the Tongariro and Egmont-derived tephras using the e.m. Analyses of the pyroxenes (commonly zoned) are given in Fig.6. The Tongariro clinopyroxenes plot chiefly as augite, whereas many of the Egmont clinopyroxenes plot as salite in addition to high-Ca augite. The Tongariro orthopyroxenes are usually hypersthene (total range En_{33-69}), but the few Egmont analyses show variable composition (En_{46-75}).

Most of the Egmont hornblendes are optically of the green-brown type. Using Leake's (1978) nomenclature, and assuming all FeO (total iron) is in the Fe^{2+} form (hence $Fe^{3+} \leq Al^{VI}$), the varieties represented are ferroan pargasite (14 anal.), pargasite (3 anal.), or ferroan pargasitic hornblende (8 anal.) (Lowe, in prep.). A second population of dark reddish-brown amphiboles are probably oxyhornblendes, and are classified as magnesio-hastingsite (5 anal.) or magnesio-hastingsitic hornblende (2 anal.), assuming an $Fe^{3+} : Fe^{2+}$ ratio of approx. 4:1 (hence $Fe^{3+} > Al^{VI}$) based on analyses in Deer et al. (1963).

These chemical analyses on the Tongariro and Egmont ferromagnesian minerals broadly agree with previous work, which has been done mostly on phenocrysts in near-source rock samples (e.g., Cole, 1978; Cole et al., 1986; Neall et al., 1986; Wallace et al., 1986).

Kohn and Neall (1973) suggested that the chemistry of Fe-Ti oxides

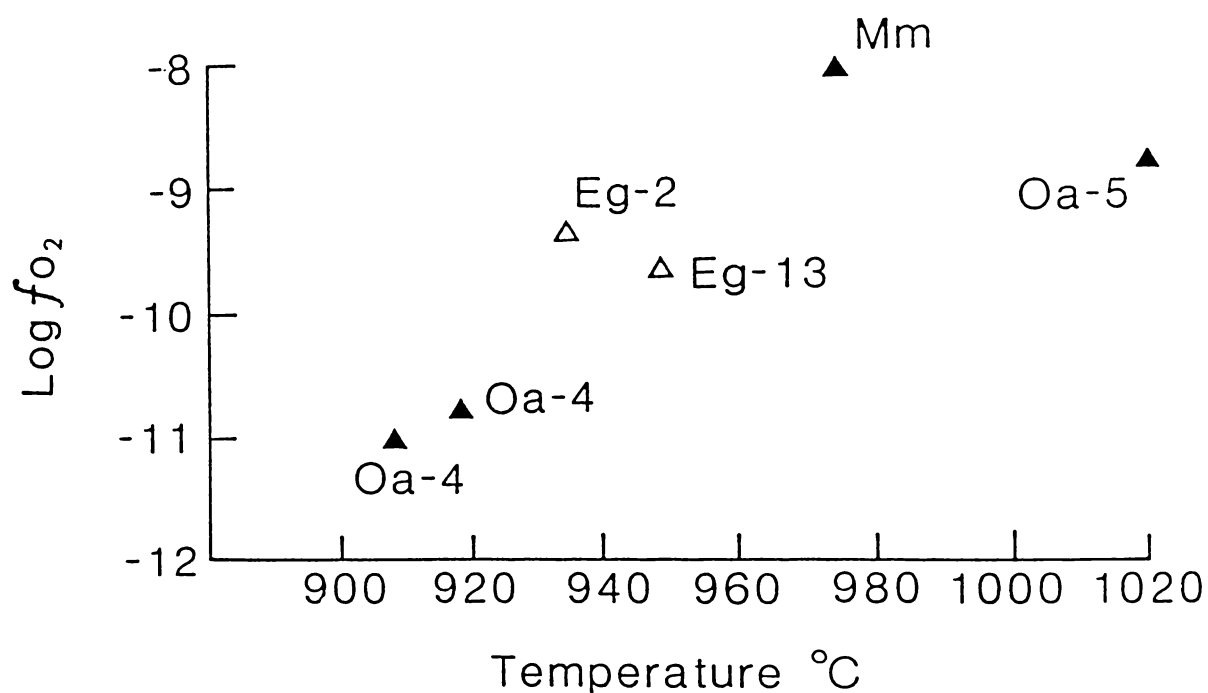


Figure 7. Oxygen fugacity-temperature diagram for Fe-Ti oxides in 6 Tongariro (closed triangles) and Egmont (open triangles) samples (see Fig.2), based on calculation procedures of Carmichael (1967) and Anderson and Lindsley (1985) using J.C.Stormer's OXCALC2 and OXTEMP3 programs.

(titanomagnetite) enabled Tongariro tephras to be distinguished from those of Egmont, with the most useful diagnostic elements being Cr, V, Mn, and Ni (especially Cr). These findings are generally supported here, based on e.m. analyses of titanomagnetite grains from a limited number of Tongariro and Egmont samples (Lowe, in prep.). Cr (as Cr_2O_3) always occurs in measurable quantities (c.0.2 - 0.3%) in the Tongariro-derived samples, but only as traces in the Egmont-derived samples; MnO concentrations in the Egmont samples (c.0.5 - 1.0%) usually exceed those of the Tongariro samples (c.0.3-0.5%). Analyses of Fe-Ti oxide pairs enable pre-eruptive temperature estimates and oxygen fugacities to be deduced by geothermometry for several Tongariro and Egmont tephras (Fig.7). Estimated oxide equilibrium temperatures range from 917-1020°C for 3 Tongariro eruptives, 934-948°C for 2 Egmont eruptives.

Light Minerals

Light fractions of the tephras from the rhyolitic volcanoes comprise mainly glass (\geq c.80 wt.%) plus plagioclase feldspar, quartz, and rare alkali feldspar. The tephras from the andesitic volcanoes are dominated by plagioclase feldspar with much less glassy material (c.15-45 wt.%), which may contain microlites. The composition of the feldspars, normally strongly zoned, differs between these two broad groups (Lowe, 1986a), although there may be relatively wide compositional ranges within individual tephra beds, as would be expected (e.g., see Cole and Nairn, 1975).

In the Tongariro and Egmont-derived tephras, labradorite predominates (Fig.8). The Tongariro samples are generally more calcic than those from Egmont, but both groups range from bytownite to andesine.

The tephras from the rhyolitic sources contain feldspars that are much less calcic. The Taupo and Okataina-derived tephras usually contain oligoclase and andesine (An_{23-38} ; Lowe, 1986a), whereas Mayor Island tephras contain sanidine (Or_{53-73}) or anorthoclase (Or_{35}) (cf. Buck et al., 1981; Hogg and McCraw, 1983).

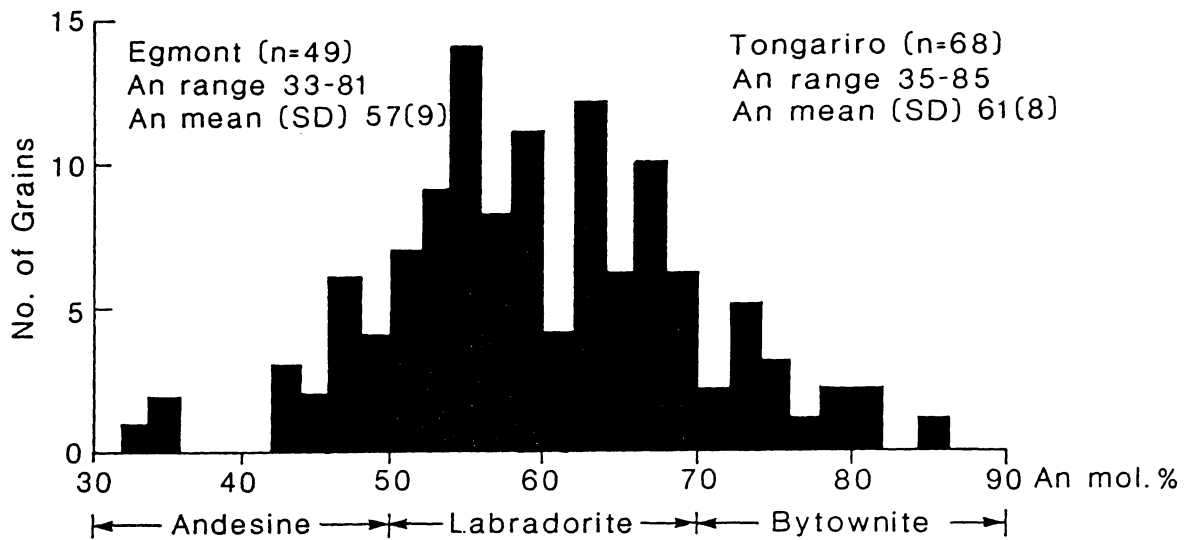


Figure 8. Histogram of anorthite contents of 117 plagioclase grains (cores) in Egmont and Tongariro samples. Analyses by microprobe.

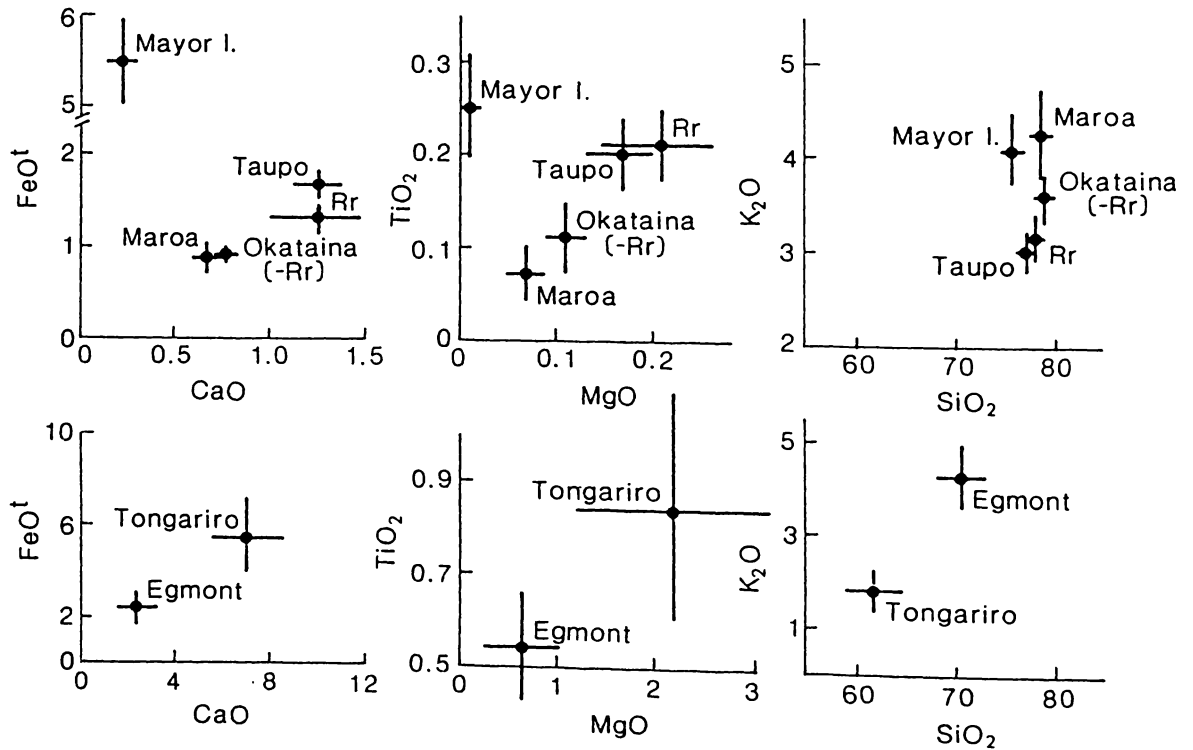


Figure 9. Differences between tephra sources exemplified by bivariate plots of major-element glass chemistry (wt.%). Dots, bars = mean values \pm 1 S.D.; Okataina (-Rr) = Okataina-derived tephras other than Rotorua Ash; Rr = analyses on Rotorua Ash. See Table 1 and text.

The e.m. is well suited in many ways to analyse glass for correlating tephras (e.g., Smith and Westgate, 1969; Federman and Carey, 1980; Westgate and Gorton, 1981; Froggatt, 1983; Sarna-Wojcicki et al., 1984; Davis, 1985; Ledbetter, 1985; Riehle, 1985; Lowe, 1986b), particularly in distal settings where fewer but more distinct units than nearer source may be found. Furthermore, because the e.m. method is grain-discrete, any weathering products, inclusions, or microlites in the grains may be avoided, and mixed populations readily identified (Westgate and Gorton, 1981). Grains of suitable andesitic glass were very sparse in some samples and occasionally glass selvages were probed.

The glass chemistry is perhaps the single most useful means of fingerprinting the sources of the distal tephras in this study. Based on available analyses (Table 1), each volcanic center appears to have a distinctive major element chemistry. Oxides particularly useful for discriminating between sources are plotted (on an anhydrous basis) in Fig.9. Several comments can be made. (1) The Mayor Island glass is distinctive because of its peralkaline composition, being particularly high in alkalis and FeO^t (total iron) and low in Al_2O_3 and MgO (the peralkaline index, $[\text{Na}_2\text{O} + \text{K}_2\text{O}]/\text{Al}_2\text{O}_3$, is 1.33 ± 0.1). (2) The Taupo, Maroa, and Okataina glasses are all rhyolitic and very similar chemically, but can usually be distinguished from one another by some combination of elements, e.g., very low TiO_2 and MgO , and high K_2O concentrations characterize the Maroa-derived tephra; differing abundances of FeO^t and CaO generally allow the Taupo and Okataina tephras to be separated from each other. (3) One tephra (Rr) from the Okataina center differs significantly from the others (its chemistry is closer to that of Taupo eruptives), so it has been recorded separately (Table 1, column B; Fig.9). (4) The Egmont glasses and especially the Tongariro glasses contain relatively large abundances of FeO^t , CaO , TiO_2 , and MgO , typical of a more basic affinity (e.g., they contain 8-10 times as much CaO and MgO as the tephras from the rhyolitic sources). (5) The Tongariro glass (mean $\text{SiO}_2 = 61$

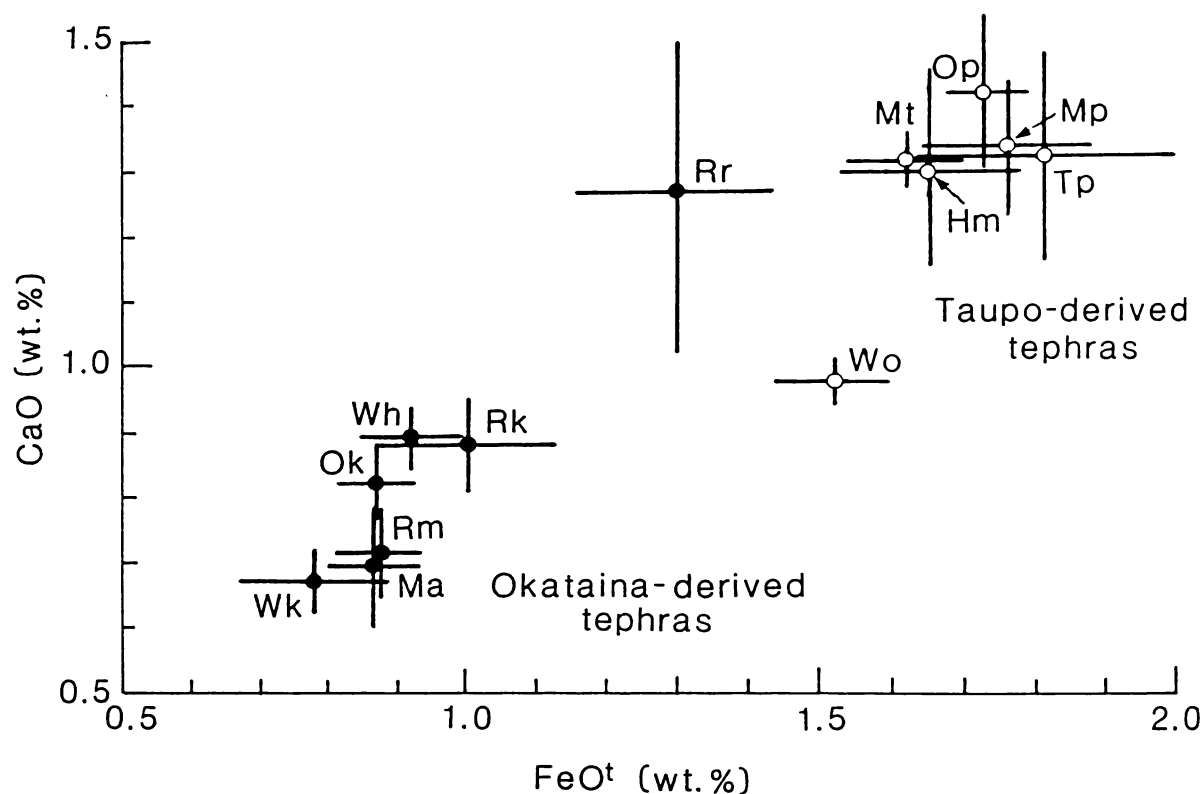


Figure 10. CaO vs FeO (total iron) in glass in tephra derived from the Taupo (open circles) or Okataina (closed circles) volcanic centers (tephra names are given in Fig.2). Bars are ± 1 S.D. of mean values. Some data are from Green and Lowe (1985) and Lowe (1986b); see also Lowe (in prep.). Shards analysed per tephra: Tp 10, Mp 9, Wo 11, Hm 33, Mt 9, Op 7, Wk 20, Ma 14, Rm 10, Wh 10, Rr 17, Rk 10, Ok 10.

$\pm 2\%$) can be classed (Gill, 1981) as andesitic (high silica, medium-K) whereas the Egmont glass (mean $\text{SiO}_2 = 70 \pm 2\%$) may be regarded as rhyolitic to dacitic in composition (cf. Wallace et al., 1986). The Egmont glass is also enriched in K_2O (usually $>4\%$).

In considering individual eruptives from each volcanic center, the glass major element chemistry is usually insufficient on its own or without stratigraphic control, to identify a particular (named) tephra unit. In Fig.10, for example, each group of tephras (representing Okataina and Taupo sources) can easily be separated on the basis of CaO and FeO^t , but most tephras within each group are effectively indistinguishable when standard deviations are taken into account. Two exceptions, however, are the Rotorua (Rr) and Whakaipo (Wo) tephras.

These glass analyses are consistent with the previous work on eruptives from the source volcanoes, although remarkably few analyses on glass (as distinct from whole rock) have been published, least of all for Tongariro or Egmont eruptives (Ewart, 1963; Cole and Nairn, 1975; Neall, 1977; Cole, 1979, Kohn, 1979; Froggatt, 1983; Froggatt and Solloway, 1986; Houghton and Wilson, 1986).

Chronology

Although the ages of most of the tephras from the Taupo and Okataina volcanoes are reasonably well known (e.g., Vucetich and Pullar, 1973; McCraw, 1975; Froggatt, 1981a, 1982), some have only a few or no dates available. Similarly, relatively few dates have been published on eruptives from the Tongariro and Egmont volcanoes (Topping, 1973; Neall, 1979; Neall and Alloway, 1986) or from Mayor Island (Houghton and Wilson, 1986). Thus the c.100 new ^{14}C dates obtained in this study, necessarily given in only summary form in Fig.3 but published fully in Hogg et al. (1987), greatly improve this current chronologic record. The reliability of the dates is enhanced by the unequivocal stratigraphic control afforded by the continuous lake sediment cores, and by cross-checking through dating the same tephra more than once and

TABLE 1. AVERAGE MICROPROBE CHEMISTRY OF GLASSES IN SOME POST-20 KYR TEPHRAS DERIVED FROM NORTH ISLAND VOLCANOES.*

	Taupo	Okataina(A)	Okataina(B)	Maroa	Mayor Is.	Tongariro	Egmont
SiO ₂	76.90 (0.52)	78.52 (0.32)	77.42 (0.34)	78.46 (0.49)	75.35 (0.53)	61.38 (2.41)	70.46 (2.19)
Al ₂ O ₃	12.90 (0.25)	12.32 (0.12)	12.68 (0.27)	12.29 (0.11)	9.43 (0.25)	17.62 (2.52)	15.18 (1.16)
TiO ₂	0.20 (0.04)	0.11 (0.04)	0.21 (0.04)	0.07 (0.03)	0.25 (0.06)	0.84 (0.24)	0.54 (0.12)
FeO [†]	1.66 (0.15)	0.90 (0.08)	1.30 (0.14)	0.87 (0.18)	5.48 (0.46)	5.45 (1.76)	2.35 (0.68)
MgO	0.17 (0.04)	0.11 (0.02)	0.21 (0.05)	0.07 (0.02)	0.01 (0.01)	2.19 (0.98)	0.63 (0.40)
CaO	1.26 (0.13)	0.78 (0.07)	1.26 (0.23)	0.68 (0.09)	0.22 (0.06)	7.07 (1.60)	2.33 (0.84)
Na ₂ O	3.75 (0.25)	3.55 (0.22)	3.65 (0.20)	3.17 (0.45)	5.00 (0.40)	3.53 (0.29)	4.04 (0.55)
K ₂ O	3.04 (0.20)	3.59 (0.26)	3.13 (0.30)	4.24 (0.48)	4.08 (0.36)	1.82 (0.43)	4.32 (0.76)
Cl	0.12 (0.02)	0.12 (0.02)	0.14 (0.04)	0.15 (0.03)	0.18 (0.06)	0.10 (0.05)	0.15 (0.06)
<i>N</i>	76	111	17	17	28	17	36

* Normalised to 100%-loss-free. Analysed by Jeol JXA-733 Superprobe at the Analytical Facility, Victoria University of Wellington. Beam diameter 10 μ m; current 8 nA (see Froggatt, 1983).

† All Fe calculated as FeO

A = tephras other than Rotorua Ash

B = Rotorua Ash

N = number of glass shards (usually ≥ 10 per tephra) analysed in mean; numbers in parentheses are 1 S.D. Note that not all of the tephras shown in Fig.3 are represented. Coverage of tephras from the andesitic centers (Tongariro, Egmont) is the lowest, these having generally low contents of glass suitable for analysis (see text).

at different sites.

COMPREHENSIVENESS OF THE RECORD

The composite record of late Quaternary North Island volcanism based on the distal tephras in the lakes and peats (Fig. 2) is shown in Fig. 3. The 46 tephras identified represent, on the average, an eruptive event every c. 370 yr. Their accumulation rate (Fig. 3, right-hand side) has fluctuated but shows no sign of diminishing. All of the volcanic centers may be considered to be active. On many occasions at least two of the North Island volcanoes were erupting virtually contemporaneously.

All of the explosive rhyolitic tephra-producing eruptions known to have taken place in the Taupo, Okataina, and Maroa volcanic centers since c. 17 000 yr B.P. are represented (cf. Vucetich and Pullar, 1973; McCraw, 1975; Froggatt, 1981a; Wilson et al., 1984). (Two basaltic eruptions from Okataina, Tarawera A.D. 1886 and Rotokawau c. 4000 yr B.P. (Cole and Nairn, 1975), have relatively localised distributions and are not considered here.) The Taupo and Okataina eruptions occur at c. 1000-2000 yr intervals throughout the record. The latest activity at Maroa is marked by the Puketarata eruption (Pk) at c. 14 000 yr B.P. (Lowe, in prep.).

Regarding the Mayor Island volcano, previously only the Tuhua Tephra (Tu), aged c. 6200 yr B.P., was known to have reached mainland North Island (Lowe et al., 1980; Hogg and McCraw, 1983), but an unnamed tephra aged c. 14 500 yr B.P. has been newly identified in this study. It appears that most of the Mayor Island tephras were blown eastwards, away from the North Island (Buck, 1985).

Eruptives from the andesitic volcanic centers of Tongariro and Egmont, although mostly very thin (<c. 5 mm), outnumber those from the rhyolitic centers (Fig. 3). However, these andesitic centers are known to have erupted much more frequently in late Quaternary time than is reflected in the composite record here (Cole and Nairn, 1975; Cole et al., 1986; Neall et al., 1986; Neall and Alloway, 1986). Assuming that the sediments in the lakes and

bogs studied (particularly the Waikato lakes) have been deposited continuously since their inception, it seems that these environments have recorded only those tephras that were widely dispersed and thick enough to be detected in the organic sediments. For example, the eruption of Mt. Ngauruhoe in the Tongariro volcanic center in February 1975 resulted in fine ash being "dusted" on Hamilton and Tauranga cities (Fig.1; Nairn and Self, 1978), but the deposit was not substantial enough to be detected in the lake sediments. Thus the record of andesitic volcanic activity in Fig. 3 presumably reflects substantial eruptions (bigger than the 1975 Ngauruhoe event) that were relatively powerful or were dispersed by unusual, strong southerly or southwesterly winds. The Tongariro activity recorded is concentrated between c.10 000-14 000 yr B.P., and contrasts with the more extensive record for Egmont that shows eruptive events between c.2500-6000 yr B.P., c.9000-11 000 yr B.P., and c.14 500-15 500 yr B.P.

DISCUSSION AND IMPLICATIONS

In this paper my primary aim has been to show how the study of tephras preserved in suitable lakes and bogs may usefully supplement the more usual (proximal) ways of studying volcanoes. The chief advantages arising from studying tephras in such a setting are the unequivocal stratigraphic and chronological control, the excellent preservation of the tephras, and the high degree of resolution attainable.

In the North Island of New Zealand, investigations on the distal tephras in lakes and bogs in various regions have elucidated the stratigraphic, chronologic, and compositional relationships of 46 separate eruptives aged from c.700-17 000 yr B.P. and derived from six volcanic centers. The sources were characterized using the tephras' mineralogic assemblages and glass and mineral compositions. These data are the first to be obtained on some of the tephras, particularly those from the andesitic volcanic centers of Tongariro and Egmont and from the offshore peralkaline volcano of Mayor Island.

The record of explosive volcanic activity in the Taupo, Okataina, and

Maroa volcanic centers (all rhyolitic) is fully represented, but that of the Mayor Island, Tongariro, and Egmont volcanoes is less complete.* Nevertheless, the distal occurrences of the tephras, particularly those erupted from these last three volcanoes, clearly demonstrate that many have much wider dispersals than previously mapped (cf. Neall, 1972; Pullar and Birrell, 1973; Topping, 1973; Vucetich and Pullar, 1973; see also isopach maps in Lowe, in prep.). This may imply emplacement by powerful (or oblique) eruptions or by strong winds, or both (e.g., Walker, 1980). Consequently, because widely dispersed rhyolitic and andesitic tephras have been deposited at an average rate of one event per 370 yr since c.17 000 yr B.P., and because the latest such eruption (Ka) took place c.700 yr ago, then a powerful eruption producing a widely dispersed tephra might be expected from any one of the six volcanic centers at any time.

* A more comprehensive record could be obtained at bogs or lakes nearer these volcanoes, and thus suitable proximal sites should be sought for possible coring.

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Cross referencing to thesis papers

- Green, J.D.; Lowe, D.J. 1985 = Paper 9
- Hogg, A.G.; Lowe, D.J.; Hendy, C.H. 1987 = Paper 8
- Lowe, D.J. 1986a = Paper 11
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- Lowe, D.J.; Green, J.D. 1987 = Appendix B
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- Lowe, D.J.; Hogg, A.G.; Hendy, C.H. 1981 = Paper 3

CONCLUSIONS

CONCLUSIONS

VALUE OF LAKES AND BOGS FOR TEPHRA STUDIES

The broad aim of this thesis has been to elucidate the stratigraphy, distribution, chronology, and composition of late Quaternary tephra in parts of northern North Island, especially the Waikato region, and thus to help advance the understanding and application of tephrostratigraphy and tephrochronology in New Zealand. The approach to this general objective has been unusual in that the main focus of study has been on tephra deposits preserved in sediments in lakes and bogs. At distal localities, where previously tephra identifications have proved difficult, lakes and bogs have provided one of the most comprehensive and detailed records of tephra deposition for the late Quaternary in New Zealand.

The utilisation of suitable lake sediments and peats in this study of distal tephra deposits has emphasised the advantages of such environments. Some of these are listed:

(1) The tephrae are preserved more or less as discrete layers, relatively little affected by postdepositional mixing or reworking processes. (Lake sediments are usually finer-grained and have slower sedimentation rates than peats, hence normally show more stratigraphic detail.) Continuous cores provide unequivocal stratigraphic control, and enable the stratigraphic relationships of tephrae erupted from different sources to be determined.

(2) The tephras can be:

- (a) identified with confidence much further from source, and
- (b) mapped much further from source and with a degree of thickness resolution perhaps 10-100 times better than previously possible.

(3) The organic-bearing sediments enclosing the tephras allow multiple radiocarbon dates to be obtained on them; additional ages may be inferred from rates of sedimentation. The reliability of the dates can be tested by:

- (a) dating stratigraphic successions of samples, and
- (b) comparing the dates with those obtained for the same tephras in other environments.

(4) The preservation of the tephras in essentially unweathered condition enables their innate petrographical and chemical characteristics to be determined. This is useful for:

- (a) identifying and correlating the tephras (i.e., tephra fingerprinting);
- (b) petrological studies;
- (c) studies on the weathering of counterpart tephras in adjacent subaerial deposits and soils.

(5) The dated tephras provide a geochronological framework for associated palaeoenvironmental studies including palaeolimnology, palynology, and studies of palaeomagnetism.

SUMMARY OF CONCLUSIONS

Detailed conclusions are embodied in each of the preceding 12 papers. The main findings from these studies are summarised below with reference to the objectives given in the introduction to the thesis (p.25-26).

Objective 1

"to determine the occurrence, stratigraphy, chronology, and origin of distal late Quaternary tephras in the Waikato and other regions in northern North Island, and, where possible, to map and account for their distribution"

Waikato region

Cores from 14 lakes in the central Waikato area show that 41 distal tephras of rhyolitic or andesitic composition were deposited in the region over the past c.17 000 years (Paper 4). They originated from six North Island volcanic centres, and have been correlated with named proximal eruptives using the tephras' mineralogy and composition together with stratigraphic position and ^{14}C chronology. The correlated tephras associated with each source, and the ages adopted (radiocarbon years B.P.. old $T\frac{1}{2}$ basis). are : **Taupo** - Taupo (c.1800), **Mapara** (c.2200), **Whakaipo** (c.2800), **Hinemaiaia** (c.4500), **Opepe** (c.8900); **Okataina** - Whakatane (c.4800), **Mamaku** (c.7000), **Rotoma** (c.8500), **Waiohau** (c.12 200), **Rotorua** (c.13 300), **Rerewhakaaitu** (c.14 700), **Okareka** (c.17 000); **Maroa** - Puketarata (c.14 000); **Mayor Island** - Tuhua (c.6200), uncorrelated (c.14 500); **Tongariro** - **Mangamate** (Te Rato Lapilli?) (c.9950), **Okupata** (8 informal units Oa-1 to Oa-8: c.10 100, c.10 500, c.10 800, c.11 050, c.11 200, c.11 700, c.12 100, c.12 700), uncorrelated (c.13 100), **Rotoaira** (c.13 700); **Egmont** - 15 informal (uncorrelated) units Eg-1 to Eg-15 (c.2500, c.3700, c.3750, c.4100, c.4400, c.5250, c.5850, c.5900, c.9300, c.9600, c.10 100, c.11 050, c.14 500, c.15 000, c.15 500).

In the Ohaupo-Hamilton area, the total thickness of the lacustrine tephras younger than c.15 000 years is c.25 cm (approximately equivalent to c.47 cm on dry land); in the Whitiakahu-Morrinsville area, the thickness is c.20 cm (c.37 cm); and near Tirau the thickness is c.42 cm (c.78 cm). Of these total thicknesses, rhyolitic tephras make up c.65-95%; andesitic tephras are more common in the south (c.30-35%), decreasing to the north (c.10-15%) and east (c.5%). Thickness distribution patterns for eleven of the more distinctive tephras (Whakaipo, Eg-2, Tuhua, Mamaku, Rotoma, Opepe, Mangamate, Waiohau, Oa-8, Rotorua, Rerewhakaaitu) are given in provisional isopach maps for the central Waikato area (p.151-154, Paper 4). The thickness resolution of these maps is one to two orders of magnitude better than in most previous tephra distribution maps for the North Island. Isopach thickness-distance plots show some tephras to have an exponential rate of thickness decrease away from source; others have an overthickened fine "tail" that may reflect the addition of co-ignimbrite ash fallout, or a change in dispersal mechanism. Many of the tephras were probably emplaced by powerful eruptions, or were dispersed by strong winds, or both.

Three diffuse ash layers of late Pleistocene age were found within colluvium underlying lake sediments in cores from Lake Maratoto (Paper 9). The upper two beds were tentatively identified from their ferromagnesian mineralogy as Hauparu and Tahuna tephras (both c.10-20 cm thick, and possibly aged c.37 000 and c.38 000 years old, respectively),¹ and the lower as Rotoehu Ash (c.30 cm thick, and aged

¹ New data recently obtained for these two tephras indicate that the provisional identifications may be incorrect. It is possible that the tephras correlate instead with two of the upper tephra formations of the Mangaone Subgroup (Omataroa and Mangaone tephras?).

c. 50 000 years). (Kawakawa Tephra, c.20 000 years old, is also known to have been deposited in the region (c.10 cm): Pullar & Birrell 1973; Lowe 1981.)

Kaipo Lagoon area

Peat bogs at Kaipo Lagoon and Te Rangaakapua in Urewera National Park (Paper 5) contain eleven Holocene tephras (total thickness c.1.2 m) that originated from the Taupo (7 tephras), Okataina (3), and Tongariro (1) volcanic centres. The tephras were identified from their field properties, stratigraphy, and ferromagnesian mineralogy, and ages obtained for them by ^{14}C dating and rates of sediment accumulation. The tephras and adopted ages (years B.P., old $T\frac{1}{2}$ basis) are: Kaharoa (c.700), Taupo (c.1800), Waimihia (c.3100), Hinemaiaia (c.4500), Whakatane (c.4800), Rotoma (c.8400), Opepe (c.8700), Poronui (c.9900), Karapiti (c.10 100), and Okupata (c.10 300). The identification of the Opepe, Poronui, Karapiti (all from Taupo volcano), and Okupata (from Tongariro volcanic centre) tephras has extended their known distribution in eastern North Island.

The stratigraphic and chronologic relationships of Hinemaiaia Tephra (definition of Froggatt 1981) and Whakatane Ash, uncertain from prior studies in the Taupo area, have been resolved through the identification of Hinemaiaia Tephra at Kaipo Lagoon, and at other distal localities in the North Island (see Paper 6). Hinemaiaia Tephra stratigraphically overlies Whakatane Ash. It is much more widespread than previously demonstrated and, with a possible dispersal index (D) value of the order of 10^4 km^2 , may have been emplaced by a very powerful "above average" plinian eruption.

Auckland and Northland

Cores from Lake Waiatarua (Auckland City) and Lake Omapere (near Kaikohe, Northland), contain relatively thin (<c.100 mm) rhyolitic tephras derived from the Okataina, Taupo, and Mayor Island volcanoes (Paper 7). Based on mineralogy, glass chemistry, ^{14}C dates, and stratigraphy, the tephras identified (some provisionally) in Lake Waiatarua are (ages in years B.P., old $T\frac{1}{2}$ basis): Tuhua (c.6200), Mamaku(?) (c.7000), Rotoma (c.8500), and Opepe(?) (c.8900) (a locally-derived basaltic ash from Mt. Wellington volcano. "Mt. Wellington ash", also occurs; its age is probably c.9000-9300 years B.P.). In Lake Omapere, tephras of late Quaternary age identified include Mamaku Ash (c.7000 years B.P.) and Rotoehu Ash (c.50 000 years B.P.). The latter deposit, c.100 mm thick, may partly comprise littoral co-ignimbrite ash-fall (cf. Walker 1979).

These are evidently the first rhyolitic tephras other than Kaharoa Ash and Taupo Pumice to be positively identified in Auckland and Northland.

Objective 2

"to help establish compositional criteria, particularly using the electron microprobe, for identifying and correlating late Quaternary rhyolitic and andesitic tephras in New Zealand"

Taken together, various persistent mineralogical and chemical compositional features of the distal late Quaternary rhyolitic and andesitic tephras examined in this thesis enable their source volcanoes to be established. The dominant ferromagnesian mineralogical assemblage (determined by petrographic microscope), and glass chemistry (determined by electron microprobe), are generally the most useful and readily determinable parameters. Egmont and Tongariro sources may additionally be distinguished using electron microprobe-

determined Fe-Ti oxide compositions (e.g., by differences in Cr_2O_3 and MnO concentrations), thus supporting the earlier findings of Kohn & Neall (1973). Pre-eruptive temperatures and oxygen fugacities calculated by geothermometry from analyses of suitable Fe-Ti oxide pairs may provide an adjunct way to aid tephra correlation.

Another potential means for discriminating eruption sources, and worthy of further testing, is through variations in the chemistry of ferromagnesian silicate minerals (e.g., wollastonite levels differ by small amounts in clinopyroxenes in Egmont and Tongariro tephra). The electron microprobe is ideally suited for such analyses (see also Smith & Leeman 1982).

The relative abundances of heavy minerals, opaque minerals, and the proportion of glass to feldspar, may assist in identifying tephra sources. However, these properties are liable to vary, hence they should be used in conjunction with other data.

The main diagnostic compositional criteria found to characterise the six tephra-source volcanoes considered here are summarised as follows (see also Table 11, p.147, in Paper 4):

Taupo: hypersthene \pm augite, sodic plagioclase, glass with rhyolitic composition (part analysis mean weight % \pm 1 standard deviation: TiO_2 0.20 ± 0.04 , FeO^* (total Fe) 1.66 ± 0.15 , MgO 0.17 ± 0.04 , CaO 1.26 ± 0.13); **Okataina:** hornblende + hypersthene + augite \pm cummingtonite \pm biotite, sodic plagioclase, glass with rhyolitic composition (tephras other than Rotorua Ash: TiO_2 0.11 ± 0.04 , FeO^* 0.90 ± 0.08 , MgO 0.11 ± 0.02 , CaO 0.78 ± 0.07 ; Rotorua Ash: TiO_2 0.21

± 0.04, FeO* 1.30 ± 0.14, MgO 0.21 ± 0.05, CaO 1.26 ± 0.23); **Maroa:** glass with rhyolitic composition (TiO₂ 0.07 ± 0.03, FeO* 0.87 ± 0.18, MgO 0.07 ± 0.02, CaO 0.68 ± 0.09); **Mayor Island:** aegirine ± aenigmatite ± riebeckite ± olivine, alkali feldspar, glass with peralkaline composition (peralkaline index 1.33 ± 0.1); **Tongariro:** clinopyroxene (Wo_{42±2}) + orthopyroxene ± olivine, calcic plagioclase, Fe-Ti oxides with high Cr₂O₃ (c.0.2-3%) and low MnO (c.0.3-0.5%), glass with andesitic composition (SiO₂ 61.38 ± 2.41%); **Egmont:** clinopyroxene (Wo_{45±2}) + hornblende ± orthopyroxene, calcic plagioclase, Fe-Ti oxides with low Cr₂O₃ (<c.0.05%) and high MnO (c.0.5-1.0%), glass with rhyolitic-dacitic composition low in SiO₂ (70.46 ± 2.19%) and high in K₂O (4.32 ± 0.76%).

It is emphasised that the individual tephras derived from each volcanic centre were identified, where possible, by additionally considering their stratigraphic position and radiometric age. For most tephras, the glass major element chemistry, for example, is insufficient on its own or without stratigraphic control to identify a named tephra from a particular eruptive centre. However, some tephras have certain peculiar compositional properties that may facilitate their correlation (e.g., the presence of aegirine and peralkaline glass in Tuhua Tephra; abundant cummingtonite in Whakatane and Rotoma tephras; abundant biotite in Kaharoa, Rerewhakaaitu, and Okareka tephras; a Taupo-like glass chemistry for the Okataina-derived Rotorua Ash; glass very low in TiO₂ and MgO, and high in K₂O, in Puketarata Ash). Nevertheless, in almost all cases a degree of stratigraphic control (as was available in this study) is essential for positive identification. Numerical analysis (e.g., cluster analysis or discriminant function analysis) of the compositional variations of

glass. Fe-Ti oxides, or other minerals may aid in identifying tephras where stratigraphic control is less certain (e.g., see Sarna-Wojcicki 1976; King et al. 1982; Beaudoin & King 1986).

Detailed compositional characteristics of most of the tephras studied are contained mainly in Paper 4 (Tables 3-11) and Paper 12.

Objective 3

"to investigate new methods for detecting thin tephra layers in lake sediments and peats"

Three new methods were investigated: the application of x-radiography to unopened, small diameter sediment cores containing thin (c.0.5-10 mm) tephra deposits; a rapid x-ray fluorescence (XRF) method for detecting tephras in peats or organic deposits; and the application of subsurface interface radar (SIR) to lake sediments and peats containing thin tephras.

X-radiography provides a simple and rapid means of determining the accurate stratigraphic position, structure, and thickness of tephra layers, particularly of very thin or visually indistinct deposits. The x-radiographs, which provide a permanent record of core stratigraphy, help in assessing the degree of dissemination and bioturbation of the tephras (Papers 3 and 4).

The XRF method is a useful and easy way of detecting indistinct tephric deposits (or any inorganic material) disseminated in peaty or organic sediments. Differences in tephra composition may also be determinable, as demonstrated for the calcalkaline and peralkaline tephras in a core from the Hauraki bog (Paper 3).

The SIR study at Lake Maratoto, the first of its kind in New Zealand (Paper 2), showed that the system offers considerable potential as a tool for shallow subsurface profiling. SIR is fast, precise, and reasonably accurate compared with conventional coring and probing methods, but still requires good stratigraphic control for reliable interpretation. Maximum radar penetration depths of 10 m were attained on Lake Maratoto, 8 m on Rukuhia peat. About a dozen or so interfaces, assumed to correspond to some of the thicker, more compact tephra layers that occur within the lake sediments were readily detected by SIR. Scale expansion showed that the tephra layers may vary in thickness, but generally follow the shape of the lake basin topography. Tephra layers in the peats were more difficult to make out using SIR.

SIR could thus be very effective in various studies involving tephrochronology and palaeoenvironmental reconstructions from limnic and possibly peat deposits. It could also be useful in mapping shallow tephra layers in other geological environments.

Objective 4

"to improve the chronology of late Quaternary rhyolitic and andesitic tephras in New Zealand"

About 100 new ^{14}C dates were obtained on distal late Quaternary tephras. Almost all of the tephras dated are younger than c.17 000 years B.P. Tephras older than this generally remain poorly dated. Of the new dates, c.42% apply to Okataina-derived tephras, c.25% to Taupo-derived tephras, c.20% to Egmont-derived tephras, c.10% to Tongariro-derived tephras, and c.3% to the Mayor Island-derived Tuhua Tephra.

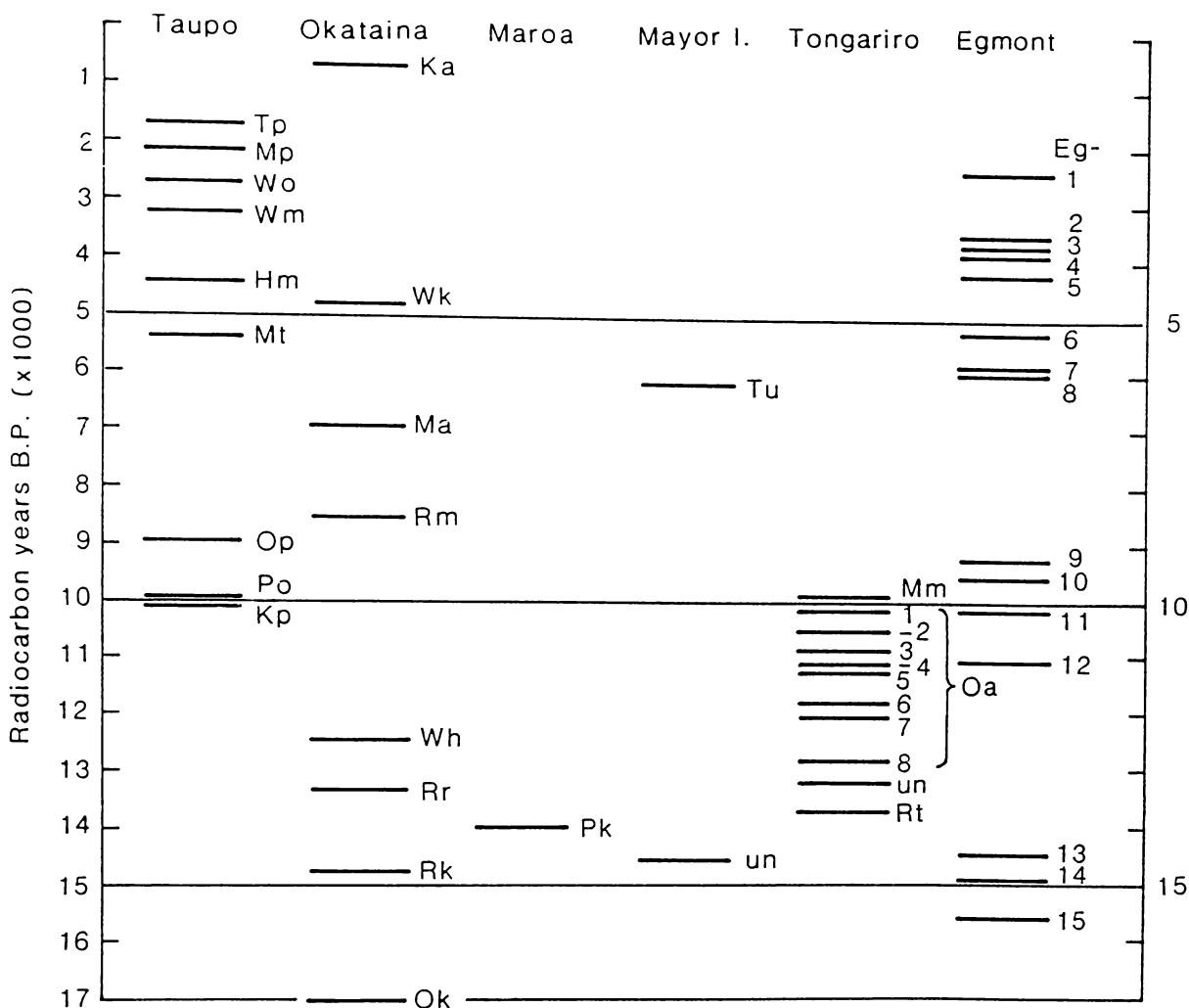


Fig. 1. Integrated stratigraphy and chronology of late Quaternary distal tephras from six volcanic centres, based on occurrences in lake sediments and peats in the Waikato and other regions in northern and eastern North Island.

Tephra names are : Tp, Taupo; Mp, Mapara; Wo, Whakaipo; Wm, Waimihia; Hm, Hinemaiaia; Mt, Motutere; Op, Opepe; Po, Poronui; Kp, Karapiti; Ka, Kaharoa; Wk, Whakatane; Ma, Mamaku; Rm, Rotoma; Wh, Waiohau; Rr, Rotorua; Rk, Rerewhakaaitu; Ok, Okareka; Pk, Puketarata; Tu, Tuhua; Mm, Mangamate; Oa, Okupata (units 1 to 8); Rt, Rotoaira; Eg-1 to Eg-15, uncorrelated Egmont-derived tephras; un, uncorrelated or unnamed tephra. Ages on old half-life basis.

Most of the dates were obtained on slices of lake sediment or peat enclosing the tephra layers. Because these sediments represent an accumulation interval, the resultant dates may be limited in their accuracy, with respect to the age of deposition of the tephras, by perhaps up to several hundred years. Errors associated with the dating laboratory counting procedures also limit the degree of resolution that may be obtained using the ^{14}C method. However, sediment cores provide exceptional stratigraphic control and the opportunity to cross-check dates by correlating the tephras to equivalent deposits in other environments. The development of new dating technology whereby smaller samples are needed than at present might help to reduce the current levels of imprecision.

The dates are reported in full, and their reliability discussed, in Paper 8 (see also Papers 4, 5, 6, 9, and 12). The ages adopted for the post-c.20 000 years B.P. tephras examined in the study are summarised in Fig. 1 (see also Objective 1 above).

To a large extent the dates agree closely with those obtained for the same tephras elsewhere, although relatively few dates are available for the stratigraphically complex andesitic eruptives from Tongariro and Egmont. Discrepancies are associated with the eruption ages of the Okataina-derived Rotoma Ash and Waiohau Ash. Rotoma Ash is thought to be aged c.8500 years B.P. (previous dates range from c.7000 to c.8900 years B.P.), and Waiohau Ash c.12 200 years B.P. (previous range is c.11 100 to c.11 800 years B.P.).

The results obtained show that with appropriate care in sampling and interpretation, tephra-bearing lake sediments and peats offer one

of the best means for obtaining an accurate and comprehensive chronology of late Quaternary tephra eruptions in New Zealand.

Objective 5

"to investigate the developmental history of Lake Maratoto using tephrochronology to help our understanding of palaeoenvironmental changes in the Waikato region"

Changes in Lake Maratoto and its catchment over the past c.17 000 years were inferred from studies of the sediments in cores from the lake and from the peat around it, the correlation and timing being based on tephrochronology and ^{14}C dating. The dated marker tephras used (with dates in years B.P., old $T\frac{1}{2}$ basis) were: Taupo Pumice (c.1730), Tuhua Tephra (c.6210), Mamaku Ash (c.6830), Opepe Tephra (c.9370), Mangamate Tephra (c.9950), Waiohau Ash (c.12 400), Rotorua Ash (c.13 450), and Rerewhakaaitu Ash (c. 14 700).

Lake Maratoto, like most of the other peaty lakes in the Hamilton Basin (Lowe & Green 1987), originated c.17 000 years ago when a small valley was dammed by volcanogenic alluvium (Hinuera Formation). From c.17 000 to c.14 000 years ago the lake was about 2 m deep with clear water. Marginal peat first developed at c.15 000 years ago, reducing the area of the lake by about one-half by c.13 000 years ago. Lake area then expanded, possibly because of marginal erosion or oxidation of the peat, or both, to its maximum size at the present day. The adjacent Rukuhia peat bog grew rapidly from c.11 000 years ago and is now 8 m thick immediately to the west of the lake. As a result of this growth, the lake became dystrophic and deepened (3.5 m at c.7000 years ago, 6.4 m at c.2000 years ago, and 7.1 m today).

The developmental history suggests that net precipitation increased at c.15 000 years ago, increased further at c.11 000 years ago, remaining high to c.7000 years ago at least, but with a decline at or before c.2000 years ago. There may have been a distinctly wetter or windier period from c.10 000 to c.9000 years ago. This interpretation is generally consistent with other reconstructions of postglacial climate in the Southern Hemisphere.

Further multidisciplinary palaeoenvironmental studies on Lake Maratoto and other Waikato lakes are in progress.

Objective 6

"to critically review the various controls of clay mineral genesis in tephras, and to develop a new model of tephra weathering and clay mineral formation and transformation based partly on tephra compositional and distributional data from objectives 1 and 2"

The factor of time (tephra age or effective weathering time) has frequently been viewed as the main reason why the amounts and types of clay minerals, especially allophane and halloysite, vary in tephra deposits of predominantly acid to intermediate composition and in temperate latitudes. The review section of Paper 11 (p.350) showed that the types and rates of formation and transformation of tephra-derived clay minerals are probably determined chiefly by macro- and microenvironmental factors together with the mineralogical and physicochemical composition and the parent deposits. Period of time of weathering in clay mineral genesis is indirect and subordinate in its effect in that weathering rates and products are chiefly dictated by other controls. Environmental conditions that affect the concentration of silica in solution, the availability of alumina, and the opportunity for coprecipitation of these are paramount and are

controlled by the leaching regime, the organic cycle, and pH. In turn, these factors are conditioned by climate (particularly rainfall), drainage, tephra thickness, depth of burial, and the frequency and amount (thickness) of fresh tephra (or "tephric loess") accessions. Allophane and imogolite are possibly reaction end points rather than short-lived transition products. They appear to be able to persist for long periods, if conditions are favourable. Halloysite and gibbsite appear to form directly from the dissolution products of primary or secondary minerals, depending mainly on whether conditions favour resilication or desilication. The occurrence of 2:1 and 2:1:1 type clay minerals in some tephras has been explained in various ways. Support for a pedogenic synthesis model appears to be lessening.

The second part of Paper 11 (p.368) illustrated that differences in field properties, clay fraction mineralogy, and weathering in distal, late Quaternary rhyolitic and andesitic tephra deposits in the Waikato region, New Zealand, could be partially explained by each of the three broad controls reviewed previously (i.e., effect of length of time of weathering, compositional controls, and environmental controls). However, the differences were attributed largely to differences in current environmental conditions (and possibly enhanced by past conditions). In reaching such a conclusion, it is clear that in these sorts of studies an accurate tepthrostratigraphy and a knowledge of primary composition is vital, as is a full consideration of other factors. The lakes in the Waikato region and the succession of unweathered tephras contained in their sediments provide a unique model to help evaluate the controls and rates of weathering of the subaerial tephra deposits and soils (see also Paper 10).

The environmental conditions having the greatest influence are degree of drainage, tephra thickness, depth of burial and site micro-relief, wetting and drying, and the effects of the organic cycle (Al-humus complexing, formation of organic acid complexes, formation of biogenic "opal", plant water uptake, and biological homogenising). In addition, compositional variations (chiefly the proportion of andesitic to rhyolitic tephra material) were seen to affect the clay mineral genesis, but to a lesser extent over all, than the site weathering conditions. The amount and composition of the dominant primary minerals, notably plagioclase and volcanic glass, determine the initial ("potentially available") Al:Si ratios. Which of these variables has the predominant effect may vary from site to site, especially as the relative abundances of rhyolitic and andesitic tephtras in the profiles change geographically. Together, the environmental and compositional factors control the concentration of Si in solution and its distribution in the profile, and the concentration and availability of Al.

The weathering model developed in Fig. 2 emphasises that many site-specific environmental conditions and compositional factors, rather than just rainfall, may control the concentration of Si (and Al) in solution and its distribution through the profile, and provide circumstances for either its loss, its precipitation, or its coprecipitation with available Al. Because these many possible controlling influences have operated both in the past and the present, then studies relating tephra clay mineralogy to palaeoenvironment must be interpreted with caution.

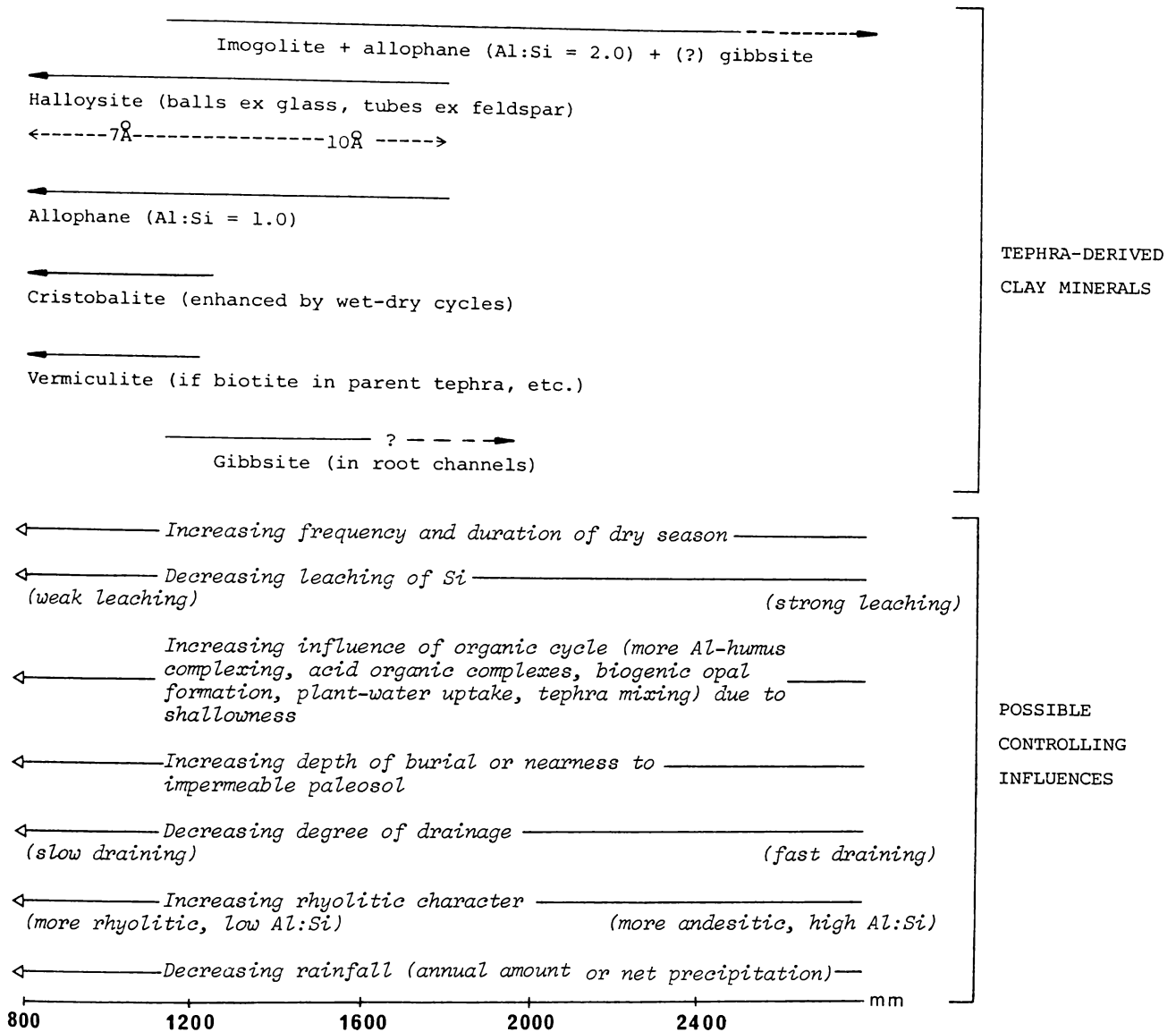


Fig. 2. Provisional weathering sequences for tephras in the Waikato region. I have attempted to show clay mineral formation and persistence with respect to various environmental controls other than tephra age. The clay minerals increase in amount (in direction of arrows with solid heads) as a function of the various environmental influences (arrows with open heads). The sequence might be applicable to tephra deposits in other areas. Part of the diagram is based on Parfitt et al. (1983).

Objective 7

"to demonstrate the value of lake sediments and peats as recorders of volcanism, and to assess the comprehensiveness of the record obtained for late Quaternary eruptions in New Zealand"

An integrated and potentially comprehensive record of volcanic activity may be obtained by studying tephra deposits preserved in sediments in lakes and bogs. The studies on tephras in these environments in distal localities in northern North Island (Paper 12) have elucidated the stratigraphy, chronology, and compositional relationships of 46 rhyolitic or andesitic eruptives, aged from c.700 to c.17 000 years B.P., which originated from six volcanic centres (see Fig. 1). These tephras document an eruptive event every c.370 years on average since c.17 000 years ago.

The record of explosive volcanic activity in the Taupo, Okataina, and Maroa volcanic centres (all rhyolitic) is fully represented, but that of the Mayor Island, Tongariro, and Egmont volcanoes is less complete. The tephras erupted from these last three volcanoes may thus reflect atypically powerful eruptions, or dispersal by unusual wind conditions. A more comprehensive record of volcanism for the Mayor Island, Tongariro, and Egmont volcanic centres might be obtained from cores from suitable lakes or bogs nearer to these centres.

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APPENDICES

- A. Guide to the nature and methods of analysis of the clay fraction of tephras from the South Auckland region, New Zealand.

- B. Comment on paper by Lowe & Green (1987).

APPENDIX A.

Guide to the nature and methods of analysis of the clay fraction of tephras from the South Auckland region, New Zealand.

This manual was published as Occasional report No.11 (1983), University of Waikato, Department of Earth Sciences, as a companion to Occasional report No.10 by Hume & Nelson (1982).

The manual is in two parts. Part 1 reviews the nature and genesis of tephra-derived clay materials. Part 2 summarises methods and interpretation of the analysis of clay fractions. Some results from my M.Sc. thesis (Lowe 1981) chapter on clay mineralogy (Chapter 6) are included in Part 2 as examples of data presentation and interpretation.

The manual gives details of some of the methodology used in Paper 11, and, as in the latter, emphasises how an accurate knowledge of site tephrostratigraphy is fundamentally important to the development of models of tephra weathering and argillisation.

(See manual for references.)

I thank my co-author, Dr C.S.Nelson, for his assistance in the preparation of the manual.

GUIDE TO THE NATURE AND
METHODS OF ANALYSIS OF THE
CLAY FRACTION OF TEPHRAS FROM
THE SOUTH AUCKLAND REGION,
NEW ZEALAND

by

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ABSTRACT

South Auckland tephras often contain a significant amount of clay-sized (<2 μ m) material derived principally from the in situ weathering of glassy and other components in the deposits. The clay fraction generally increases with age and is mainly dominated by allophane and/or halloysite, but can include also small quantities of other secondary constituents, such as imogolite, poorly ordered iron and aluminium oxides and hydroxides, silica polymorphs of cristobalite, tridymite or opaline silica, humus and humus complexes, and 14Å clay-vermiculite. This manual firstly reviews briefly the nomenclature and nature of these clay components and their general occurrence in South Auckland tephras. Concerning weathering sequences, it is emphasised that separate 'mineral' transformation pathways appear to exist for the various components according to their chemistry and to site weathering conditions, particularly as they affect the concentration of Si in solution and the availability of Al, and the opportunity for co-precipitation of these.

The main intention of the manual is to outline some of the more common laboratory procedures available for qualitatively and quantitatively analysing the composition of the tephric clays, many of which are difficult to determine because of their short range order or "amorphous" nature. Techniques described and assessed in terms of their rapidity and quantitiveness include X-ray diffractometry (XRD), infrared spectroscopy (IR), differential thermal analysis (DTA), transmission and scanning electron microscopy (TEM and SEM), sodium fluoride reactivity, chemical dissolution analyses, and surface area measurements. No one technique alone produces a definitive clay fraction analysis of tephric deposits.

The reference list includes more than 200 entries relevant to tephric clay studies in general, allowing for more specialist investigations where appropriate.

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ADDENDUM

In the discussion of the XRD patterns of tephric clays on p. 28-31 mention is inadvertently made of interstratification between 10Å halloysite and 7Å halloysite, formed as a result of dehydration of the 10Å halloysite and represented by XRD peaks between 7 and 10Å. In fact these peaks correspond to variably dehydrated 10Å halloysite, of which 7Å halloysite is the collapsed end-member, and not to genuine interstratification of the 7 and 10Å halloysite phases.

INTRODUCTION

Tephra is a collective term for predominantly unconsolidated pyroclastic materials of both air-fall and flow origin (Schmid 1981; Self and Sparks 1981), although the term has previously been restricted to pyroclastic fall deposits only (Wright et al. 1980). This latter sense is generally retained for this article.

Tephra, predominantly of Quaternary age and of mostly rhyolitic or andesitic composition, form widespread near-surface and surficial blanket deposits in the South Auckland region* of North Island, and consequently they are of paramount importance as soil-forming parent materials. They have originated mainly from peripheral volcanic centres on Coromandel Peninsula, from the Taranaki and Tongariro-Taupo-Rotorua districts, and from Mayor Island in the Bay of Plenty (Pullar and Birrell 1973a; Pullar et al. 1973; Howorth 1975; McCraw 1975; Vucetich and Howorth 1976; Hogg and McCraw 1983). Because of erosion, non-deposition, and other factors, the stratigraphic sequence of surficial tephra deposits varies widely from place to place. To date about 75 separate air-fall tephra formations have been named, ranging in age from a few hundred years to possibly a million years or more, and having a combined total thickness of as much as 10-12m (e.g., see references above and in Howorth et al. 1981, p. 131). Table 1 lists the tephra that have been identified to date in the Hamilton-Raglan area, and includes their generalised thicknesses and ages. Individual tephra may be separated by well defined paleosols (Gibbs 1980), although detailed laboratory analyses have indicated the composite nature of several of the otherwise apparently homogenous tephra deposits (e.g. Pullar and Birrell 1973b; Hodder and Wilson 1976; Hogg 1979; Lowe 1981; Hogg and McCraw 1983). In addition, subsurface drilling in the South Auckland lowlands shows that several pyroclastic flows (distal ignimbrites) reach into the region (e.g., Todd 1982), and future work will undoubtedly indicate also the presence of associated air-fall deposits at depth.

This manual outlines some laboratory procedures applicable to the mineralogical analysis of tephra deposits in the South Auckland region, with major emphasis on their clay fraction. A companion report exists describing X-ray diffraction (XRD) techniques of mineralogical analysis appropriate for many sedimentary deposits in South Auckland (Hume and Nelson 1982). The tephra deposits are treated

* This is generally taken to include the Pukekohe-Waikato-Bay of Plenty-Coromandel-King Country-Taupo areas.

Table 1. Names, sources, ages, and thicknesses of known tephras which have been deposited in the Hamilton-Raglan area. Unnamed tephras in addition to those listed also occur (Lowe, in prep.). Data mainly after Lowe (1981, 1981a, p. 70) and references therein.

Tephra Formation	Source (volcanic centre)	Approx. age years B.P.*	Max. thickness (cm)
Ngauruhoe Tephra	Tongariro	Historical	<1
Taupo Pumice	Taupo	1,800	5
Whakaipo Tephra	Taupo	2,800	1
Tuhua Tephra	Mayor Island	6,200	5
Mamaku Ash	Okataina	7,000	4
Rotoma Ash	Okataina	8,300	1
Opepe Tephra	Taupo	8,800	2
Andesitic Ash (Tsg19)	Egmont or Tongariro	9,000	2
Mangamate Tephra	Tongariro	10,000	4
Waiohau Ash	Okataina	11,500	3
Okupata Tephra	Tongariro	12,500	1
Rotorua Ash	Okataina	13,500	4
Rotoaira Lapilli	Tongariro	13,800	1
Rerewhakaaitu Ash	Okataina	14,700	3
Okareka Ash	Okataina	19,000	5
Kawakawa Tephra ¹	Taupo	20,000	15(?)
?Okaiia Tephra	Taupo	25,000	?
Tahuna Tephra ²	Okataina	39,000	15(?)
?Tihoi Tephra	Taupo	39,000	?
Rotoiti Breccia - Rotoehu Ash Mb. ⁺	Okataina	42,000	30(?)
Hamilton Ash (beds H1-H7)	Unknown (?central North Island)	~100,000- 400,000 ³	500
Kauroa Ash (many beds)	Unknown (?Coromandel & central North Island)	~200,000- 1,000,000 ⁴	900

* Old half-life basis

⁺Mb. Member

? Uncertain

¹ Previously reported as Oruanui Ash

² Previously reported as (undifferentiated) Mangaoni Lapilli

³ Various estimates by McCraw (1975), Vucetich et al. (1978), and Hendy et al. (1980), among others

⁴ Various estimates by Pullar and Birrell (1973a), McCraw (1975), Pain (1975), Davoren (1976), and Salter (1979), among others

Table 2. Relationship between tephra age and clay content of some predominantly rhyolitic tephras from the Waikato-Bay of Plenty regions. Data after Birrell and Pullar (1973), Hogg (1974), Davoren (1976), Salter (1979), Lowe (1981, and unpublished information).

Tephra	Approx. age years B.P.	Av. % clay (<2 μ m) in tephra	No. of samples analysed
Kaharoa Ash	700	6	1
Taupo Pumice	1,800	5	7
Waimihia Formation	3,400	5	2
Whakatane Ash	4,600	7	4
Mamaku Ash	7,000	8	8
Waiohau Ash	11,500	18	3
Rerewhakaaitu Ash	14,700	9	7
Okareka Ash)	19,000	15	7
and Te Rere Ash)			
Kawakawa Tephra	20,000	18	11
Tahuna Tephra)	c.30,000	16	10
and others)			
Rotoehu Ash	42,000	25	9
Hamilton Ash	~100,000	65	10
Kauroa Ash	~500,000	85	43

separately because of several special properties, including their glassy nature, their often considerable clay content, and their unique clay mineral compositions. For completeness, and to aid data interpretation, the manual is divided into two parts, the first describing the nature and nomenclature of the potentially complex array of tephra-derived clay mineral types, as well as commenting briefly on their genesis, and the second the various methods of sample preparation and analysis. A large number of references are included purposely for additional specialist reading and to provide follow-up details on either genesis or methodology. The reader interested solely in analytical procedures is referred directly to the introductory remarks of Part 2 (p. 22), as well as to Table 5 (p. 24), which aims to help guide the non-specialist clay mineralogist in the choice of analytical techniques which might best suit his or her intentions.

PART 1 : NATURE AND GENESIS OF TEPHRA-DERIVED CLAY MATERIALS

With increasing age the amount of clay-sized ($<2\mu\text{m}$) material in tephras generally increases dramatically as glassy and other components are broken down and transformed to clay minerals. For example, tephras less than about 2,000 to 3,000 years old have $<5\%$ clay, those from 3,000 to 10,000 years age have between 5 and 10% clay, those from 10,000 to 50,000 years age typically contain 15 to 30% clay, while those older than about 50,000 years contain $>60\%$ clay (Table 2). Environmental parameters such as depth of burial, climate, vegetation, and degree of leaching also influence the proportion of clay-sized material in a deposit, and, together with the primary composition of the deposit, determine the types of clay minerals within the clay fraction.

The clay fractions comprise mainly authigenic minerals with subordinate amounts of residual (primary) or accessory minerals. A notable feature of almost all tephra-derived clay fractions is the occurrence of short range order (often referred to as "non-crystalline", "poorly ordered", or "amorphous"; see Brindley 1977; Bailey 1980) clay minerals, in addition to well ordered or crystalline species. A key characteristic of the short range order materials is the dominant presence of active aluminium which occurs in various mineralogical forms (Wada 1980). Short range order minerals can also occur, usually in small amounts, in some soils (notably podzols) derived from non-tephric and non-vitric materials (e.g., Wada and Harward 1974; Milestone and

Wilson 1977; Tait et al. 1978; Ross 1978; Farmer et al. 1980; Wada 1980; Young et al. 1980; Farmer 1982). Studies on these minerals have helped elucidate the actual conditions and mechanisms of formation of their counterparts derived from tephric materials.

Types of clay components in South Auckland tephra materials

The most abundant secondary minerals occurring in the clay fractions of tephra are allophane and halloysite. Subordinate amounts of imogolite, poorly ordered iron and aluminium oxides and hydroxides (including gibbsite), secondary silica polymorphs of cristobalite, tridymite, and opaline silica, humus and humus complexes, 14Å clay-vermiculite, and very rare kaolinite have been additionally reported in central North Island and overseas tephra deposits. Other 2:1 and 2:1:1 layer lattice silicates and their intergrades occur in substantial amounts in some Japanese tephra-derived soils. Allophane-like constituents (defined by method of extraction) are also reported in the Japanese literature. Residual (primary) quartz, feldspar, cristobalite, and glass may also occur in tephra clay fractions. For most studies only a few of these minerals, excepting allophane and/or halloysite, are likely to be encountered in any one sample, and then in small amounts only. However, in specific and detailed "clays-oriented" studies some of the components other than allophane and halloysite may form a more critical part of the investigation. Consequently, explanatory background notes on each of the minerals listed above, and their general occurrence in South Auckland tephra, are summarised below.

For more detailed information some recent articles discussing the chemical compositions, chemical and physical structures, surface properties, and reactivities of these tephra-derived secondary minerals include Quantin (1974), Wada and Harward (1974), Giesecking (1975), Dixon and Weed (1977), Maeda et al. (1977), Brown et al. (1978), Sudo and Shimoda (1978), Schwertmann (1979), Theng (1980), Tuohy (1980), and Theng et al. (1982).

Allophane

Allophane is the name given to a series of naturally occurring hydrated aluminosilicate clays characterised by short range order and the predominance of Si-O-Al bonds. Their chemical composition varies but typically they show Al:Si molar ratios between 1.0 and 2.0 and H₂O(+):Al₂O₃ molar ratios between 2.0 and 4.5 (Wada 1977, 1980; Parfitt et al. 1980). This definition of allophane, despite its wideness, has been generally adopted by workers in Japan and U.S.A. (van Olphen 1971),

as well as in New Zealand (Rankin and Churchman 1981). Recent work has identified two main forms of allophane, one having an Al:Si molar ratio close to 1.0 and another with a ratio of ~ 2.0 . The latter form, which appears to predominate, has been termed 'proto-imogolite' allophane (Parfitt et al. 1980) and is discussed further below.

Allophane was originally described as being "amorphous" (to X-rays) and therefore having little or no structural organisation. However, high resolution electron microscopy has shown that all forms of allophane consist of irregular aggregates constructed of hollow, spherically shaped particles with diameters of 35 to 55 Å (Fig. 1; Henmi and Wada 1976), and with surface areas of about 800m²/g (Parfitt and Henmi 1980) or more (Wada 1980). The wall thickness of individual spherules is between about 7 and 10 Å and each contains about 8-10 pores (broken bond defects)

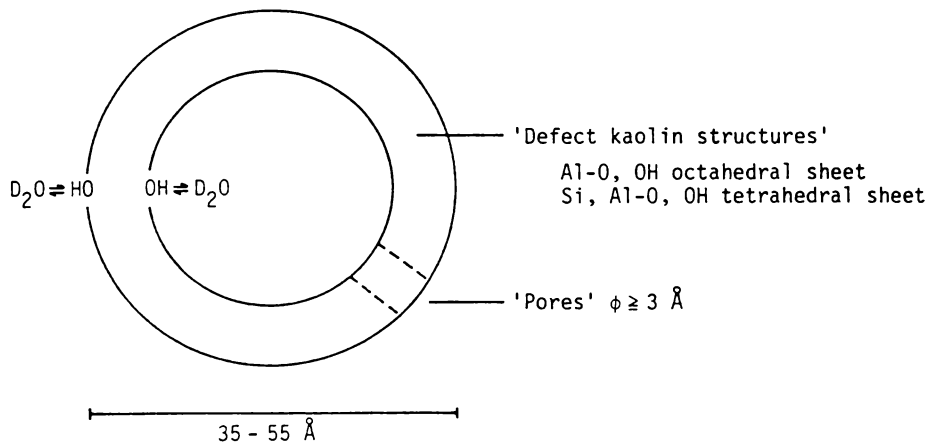


Fig. 1. A schematic representation of the spherical 'structural unit' of allophane (from Wada 1979, p. 538).

which allow the passage of water. Parfitt et al. (1980) suggested that the framework for the allophane structure is a gibbsitic Al octahedral sheet. The short range order or non-crystalline character of allophane derives from the local, non-repetitive nature of the spherical "structural unit" (Fig. 1; Okada et al. 1975; Wada and Wada 1977; Wada 1979).

Allophane is ubiquitous in tephras in the South Auckland region and in many cases is the dominant constituent of the clay fraction.

Imogolite

Imogolite is an hydrous aluminosilicate that was first described in a Japanese soil known as imogo, derived from glassy volcanic ash.

It is similar in many ways to allophane, but occurs as smooth and curved "filiform" threads, several microns long and 100 to 300Å in diameter (Wada 1980). The threads comprise finer tubular units with inner and external diameters of about 10 and 20Å respectively (Fig. 2), and an external surface area of about 1450m²/g (Theng et al. 1982).

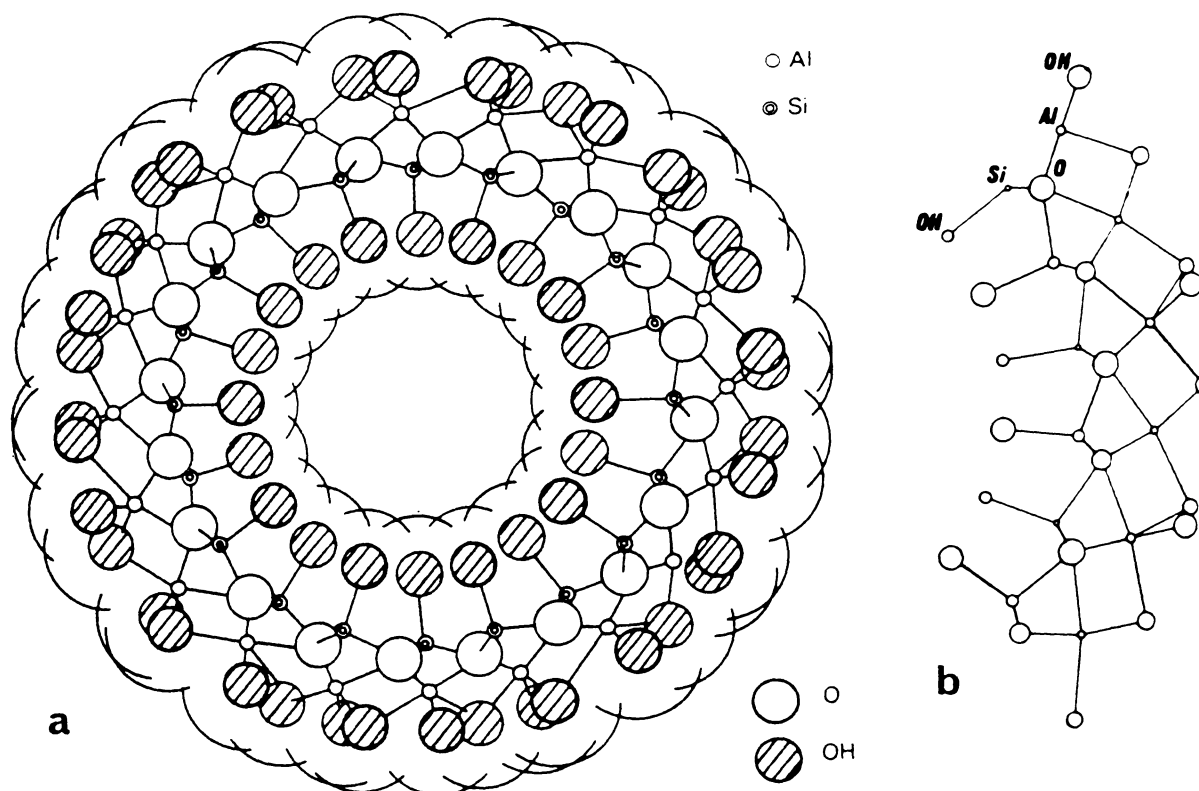


Fig. 2. (a) Cross-section of an imogolite tube viewed down the tube axis. The outside diameter is 21.4Å, the inside diameter 6.4Å. The external surface of the tube comprises a gibbsite-like structure but the internal surface has exposed Si-OH groups (SiO₃OH) with the Si in isolated tetrahedral sites (after Parfitt, 1980b, p. 169). (b) Curling of the gibbsite hydroxide sheet by contraction of one surface to accommodate the SiO₃OH tetrahedra (after Wada 1977, p. 618).

Cradwick et al. (1972) explained the tubular units as paracrystalline (i.e., 1-dimensional structural units somewhere between short and long range order; Wada 1977) cylindrical structures in which the OH groups of one side of a gibbsite sheet lose protons and bond to Si atoms, with the Si atoms out of the plane of the sheet. Because Si-O bonds are shorter than Al-O bonds, the unit is forced to contract to form a cylinder with a circumference of 10, 11 or 12 modified gibbsite unit cells (Fig. 2; Brown et al. 1978; Parfitt 1980b; Wada 1980). Compositionally, the SiO₂:Al₂O₃ range for imogolite appears to be slightly narrower than

for allophane, being 1.05 to 1.15 (Wada 1977).

Imogolite is usually present in only small amounts in New Zealand tephras (Yoshinaga et al. 1973; Parfitt et al. 1982) and has been reported in tephra material in the Waikato region (Jessen 1977).

'Proto-imogolite' allophane

This informal term refers to allophanes which have imogolite structures on the atomic scale but do not exhibit the tubular morphology of imogolite (Parfitt and Henmi 1980). Infrared spectroscopy yields an imogolite spectra, similar to that exhibited by synthetic 'proto-imogolite' gels, but electron micrographs indicate that the imogolite structural arrangement is distorted to give hollow spherules rather than tubes. 'Proto-imogolite' allophanes apparently have Al:Si ratios close to 2.0 and are the dominant type of naturally occurring allophane.

Samples of allophane with molar Al:Si ratios between 1.0 and 2.0 have been shown by Parfitt et al. (1980) to be mixtures of their allophane structure (Al:Si \sim 1.0), and a proto-imogolite allophane structure (Al:Si \sim 2.0), indicative of an allophane structural series (see also Wada 1979 ; Wada 1980, p. 90). Continued use of the term 'proto-imogolite' allophane is not generally favoured (Rankin and Churchman 1981) but appears to be well established in the literature. There is a trend, however, to qualify the allophane "type" simply by reporting its Al:Si ratio as a prefix or suffix.

'Proto-imogolite' allophane, initially characterised in New Zealand in samples from the Taranaki region, has been shown to be the dominant form of allophane (reported as allophane with Al:Si = 2.0) in the Waikato region (Parfitt et al. 1983).

Allophane-like constituents

These are defined as non-crystalline aluminosilicates, dissolved by citrate-dithionite and 2% Na₂CO₃ reagent (Wada 1977, 1980). As such, they are never directly observed and their infrared spectra are recorded only by a difference method, using samples before and after treatment. Parfitt et al. (1980) suggested that they may represent the Fe- or Al-rich part of the allophane wall or other defects, rather than representing a separate structure. Wada (1980) suggested that they are possibly polymeric hydroxy-aluminosilicate cations.

They are not generally reported in New Zealand tephras.

Halloysite

Halloysite is a kaolinite subgroup 1:1 layer silicate mineral. It occurs mainly as spherical, roughly concentrically-banded particles, or as tubes, scrolls, or curled flakes (Dixon 1977). Kirkman (1981) describes these morphologies as squat and elongate ellipsoids. Platy, tabular and disc-shaped halloysite has also been reported.

Halloysite can occur in two phases (Brown et al. 1978), one with two interlayer water molecules per formula unit (10Å spacing), and the other without (7Å spacing). The presence or absence of this interlayer water is one way of distinguishing hydrated halloysite from kaolinite (7Å).

The existence of these hydrated and dehydrated phases of halloysite has led to much confusion in the literature with respect to nomenclature. Brindley and Pedro (1975) have recommended that halloysite be referred to as either 10Å halloysite (equivalent to "hydrated halloysite" or "endellite") or 7Å halloysite (equivalent to "dehydrated halloysite" or "metahalloysite").

Halloysites have much larger unit particles than allophane (about 3000-6000Å cf. 50Å) and their properties and reactivities relate to this particle size as well as particle morphology, a relatively high degree of crystallinity, and a Si-O-Si outer surface in contrast with the Al-OH-Al surface of (Al:Si~2.0) allophanes (Theng et al. 1982).

In the South Auckland region halloysite is often the dominant clay mineral constituent in old or deeply buried tephras, such as the Hamilton Ash and Kauroa Ash beds (Table 1), and also occurs in varying amounts in other tephras older than about 10,000 years age and usually at depths of a metre or more below the modern land surface. It has been reported in Taupo Pumice and Mapara Tephra formations, aged 1,800 and 2,200 years respectively, buried beneath 2-2.5m of Taupo Pumice overburden (McIntosh 1979, 1980; see also genesis section below).

Secondary silica polymorphs

These include cristobalite, tridymite, and opaline silica (Table 3). Cristobalite and tridymite are crystalline and can be identified by their X-ray diffraction pattern, with characteristic d-spacings at 4.05Å and 4.08Å respectively (provided that the content of feldspar is low as it gives secondary peaks near these values; Wilding et al. 1977). Opaline silica occurs as laminar particles and is thought to be of pedogenic origin (Wada 1977, 1980; Shoji and Saigusa 1978; Henmi and Parfitt 1980). It appears to occur in the early stages of weathering

of tephtras in temperate climates, perhaps due to suppression of Al ion activity because of formation of Al-humus complexes (Henmi and Parfitt 1980).

Both cristobalite and tridymite can occur as primary or secondary minerals in tephtras (see references in Lowe 1981). Oxygen isotope ($^{18}\text{O}:^{16}\text{O}$) measurements may help determine the provenance and primary or secondary origin of these silica polymorphs, including quartz (e.g., Henderson et al. 1971, 1972; Jackson et al. 1977; Stewart et al. 1977). Significant amounts of secondary cristobalite occur in late Quaternary tephtras in the Waikato region (Hogg 1974; Lowe 1981). Here, the conditions of poor drainage, intense wetting and drying, and weathering always within the influence of the organic cycle have apparently promoted Si accumulation and Al-humus bonding, thereby limiting co-precipitation of Al and Si (Lowe 1981). Tridymite occurs in two beds in the Kauroa Ash Formation (Salter 1979) and possibly in the Rotongaio and Mapara tephtras (McIntosh 1979), but it is rarely reported in tephtra beds elsewhere (Yamada and Shoji 1977).

Humus and humus complexes

Potential reactions between humus and inorganic constituents are reviewed by Wada and Harward (1974) and Wada and Higashi (1976). Extraction and infrared spectroscopy analysis indicate that humus evolves from forms with a very low complexing ability for Al and Fe to forms that complex Al and Fe in the organic horizon (A_1) of soils; humus also interacts with allophane and imogolite in buried A_1 horizons (Wada 1980). The humus complexes are very stable, even when subjected to ultrasonic probe treatment and peroxidation (Fieldes 1957; Fieldes and Taylor 1961; Birrell and Fieldes 1968; Wada 1980). The complexes are best identified by selective chemical dissolution and difference infrared spectroscopy (Wada and Higashi 1976) or by differential thermal analysis (DTA) (Fieldes 1957; Jackson 1969; Satoh 1976; Schnitzer and Kodama 1977).

A deep (1m or so) accumulation of very dark to black humus is a striking feature of many Japanese, South American, and Mexican tephtra-derived soils which may have a C content of 5-10%, even up to 20% (Wada and Harward 1974; Shoji and Ono 1978). In Japan (where these soils were originally called "Ando" soils, giving the various soil classification terms such as Andosols, Andepts, and Andisols), these dark horizons are typically associated with a grass (especially pampas) vegetation (Wada and Harward 1974). Much smaller amounts of humus and humus complexes occur in New Zealand tephtras, and they have been studied less intensively

than have their Japanese counterparts. In fact, most studies have concentrated on removing the organic component by oxidation prior to clay analysis (see Part 2).

Poorly ordered iron and aluminium oxides and hydroxides

Iron and aluminium oxides and hydrous oxides, mostly with short range order, are common constituents of tephra clays and occur in several mineralogical forms as discrete particles or associated with surfaces of other minerals (Brown et al. 1978). Iron oxides are largely responsible for the red, orange, yellow, and brown colours in weathered tephra and soils and they also affect soil structure and fabric. With the exception of magnetite (or titanomagnetite) all are secondary weathering products and they tend to have variable properties due to differences in their environments of formation.

Terminology is frequently a problem. For example, ferrihydrite is now used to describe hydrous iron oxide phases previously called "amorphous ferric hydroxide" or "iron oxide gel". Other names are listed in Table 3.

Table 3. Names of naturally occurring hydroxides, oxyhydroxides and oxides of Fe, Al, Mn, Ti, and Si. After Brown et al. (1978, p. 135).

Iron		Aluminium		Manganese		Titanium		Silicon	
Goethite	α -FeOOH*	Diaspore	α -AlOOH	Pyrolusite	MnO ₂	Rutile	TiO ₂	Quartz	SiO ₂
Lepidocrocite	γ -FeOOH	Boehmite	γ -AlOOH	Birnessite		Brookite	TiO ₂	Cristobalite	SiO ₂
Akaganeite	β -FeOOH	Corundum	α -Al ₂ O ₃	Lithiophorite		Anatase	TiO ₂	Tridymite	SiO ₂
Hematite	α -Fe ₂ O ₃	Gibbsite	Al(OH) ₃	Hollandite				Opaline silica	SiO ₂
Ilmenite	FeTiO ₃	Nordstrandite	Al(OH) ₃	Todorokite					
Maghemite	γ -Fe ₂ O ₃	Bayerite	Al(OH) ₃						
Magnetite	Fe ₃ O ₄								
Ferrihydrite	Fe ₅ H ₉ .4H ₂ O								

* Greek letters are used to denote different polymorphs of the same chemical constitution. The γ -forms have structures based on cubic close packing of anions whereas the α -forms are based on hexagonally close-packed anions.

The most commonly used methods for detection of the oxides and hydroxides are XRD and DTA, although infrared and Mössbauer spectroscopy are increasingly being employed (e.g., Childs et al. 1979). Because of their short range order and often low abundances it is frequently necessary to concentrate the materials, for example by particle size separation of the very fine clay fractions or by dissolution of other minerals. X-ray patterns are usually weak or very weak; diagnostic characteristics of some iron oxide minerals are given in Table 4. A quick field test for free ferrous iron and ferric-organic complexes in soils has recently been developed by Childs (1981).

Table 4. Diagnostic characteristics of some iron oxide minerals. After Schwertmann and Taylor (1977, p. 147).

	Hematite	Maghemite	Magnetite	Goethite	Lepidocrocite	Ferrihydrite
X-ray spacings (Å)	2.70,3.68 2.52	2.52,2.95	2.53,2.97	4.18,2.69 2.45	6.26,3.29,2.47	2.50,2.20, 1.97,1.71, 1.50
DTA peaks (°C)	Nil	Exotherm 600-800	Nil ¹	Endotherm 280-400	Endotherm 300-350, exotherm 370-500	Endotherm 150, loss of adsorbed H ₂ O
IR spectroscopic peaks (cm ⁻¹)	345,470, 540	400,450, 570,590, 630	400,590	890,797	1026,1161,753	Nil ²
Usual crystal morphology	Hexagonal plates	Cubes	Cubes	Fibrous ³ or acicular	Laths, serrated elongated plates	Spherical
Colour (Munsell)	Bright red 5R-2.5YR	Reddish- brown	Black	Yellowish- brown 7.5YR-10YR	Orange 5YR-7.5YR	Reddish-brown 5YR-7.5YR

¹ Magnetite converts via maghemite or directly to hematite, depending on particle size

² Russell (1979) gives IR evidence of structural hydroxyl groups

³ Reported by Nakai and Yoshinaga (1980)

Other useful references for these minerals include Wada and Higashi (1976), Hsu (1977), Schwertmann and Taylor (1977), Brown et al. (1978), Schwertmann (1979), Nakai and Yoshinaga (1980), and Schwertmann et al. (1982).

In studies on tephra materials in the Waikato region, goethite and lepidocrocite have been identified in Horotiu and Te Kowhai soils derived from tephra and volcanogenic alluvium (McQueen 1975). Subordinate gibbsite occurs in both the Hamilton Ash (Taylor 1933; Tonkin 1970; Hogg 1974) and the Kauroa Ash (Salter 1979; Kirkman 1980a), and lepidocrocite occurs in two beds in Kauroa Ash (Kirkman 1980a). Gibbsite is reported to occur in the Egmont loam profile derived from late Quaternary andesitic tephtras and "tephric loess" (Russell et al. 1981) but appears to be absent in andesitic tephtras and paleosols in western Taranaki (Kirkman 1980b). Traces (<1%) have recently been reported for clays derived from mixed rhyolitic and andesitic late Quaternary tephtras in the Waikato region by Lowe (1981) and Parfitt et al. (1983). Iron-manganese concretions occur frequently in tephra materials weathering under gleying or wetting and drying conditions in the Waikato region (McQueen 1975; Lowe 1981).

2:1 and 2:1:1 minerals

These include minerals such as vermiculite, smectite, illite, and chlorite (Hume and Nelson 1982). Their occurrence in tephtras, sometimes in substantial amounts, has been almost exclusively reported from Japanese studies (e.g., Shoji and Saigusa 1977; Mizota 1978; Yamada et al. 1978; Shoji et al. 1981) but they have also been reported from studies in Colombia by Calhoun et al. (1972) and Cortes and Franzmeier (1972a, b), and elsewhere. Some Japanese workers suggest that the 2:1 clays, which are most common in dacitic and andesitic tephtras, form from "amorphous" minerals, especially K-enriched volcanic glass, and possibly coevally with the formation of opaline silica or quartz under conditions characterised by excess silica and a low allophane content (Wada and Aomine 1973; Tokashiki and Wada 1975; Wada 1977; Kurashima et al. 1981; Shoji et al. 1981). Shoji et al. (1981) determined that in particular the mobilities of SiO_2 , MgO , and K_2O were strongly related to the weathering of volcanic glass and the abundant formation of 2:1 minerals. Other explanations, all controversial, include: the transformation of mafic minerals (e.g., pyroxenes, amphiboles, and micas) by weathering; the incorporation of 'exotic' layer silicates into volcanic ash during eruption; the incorporation of layer silicates from underlying paleosols by mixing when the tephra

deposit is thin; and the addition of layer silicates as loess (Dudas and Harward 1975b; Mizota 1976; Wada 1980; Mizota and Takahashi 1982; plus Japanese studies referred to above).

In New Zealand, 2:1 minerals are rarely reported in tephra (Birrell and Pullar 1973; Kirkman 1975; McIntosh 1979) but are common in soils formed on loess derived predominantly from mica-bearing quartzo-feldspathic sedimentary rocks and alluvium, which also contain admixed accessions of tephra. Thus most New Zealand workers are suspicious of the pedogenic pathways suggested by the Japanese to account for the occurrence of 2:1 clays in tephras in Japan, and prefer a "loessic contamination" explanation (e.g., Stewart et al. 1977; Russell et al. 1981).

Lowe (1981) detected (by XRD) a 14\AA trioctahedral clay-vermiculite in clay fractions from a late Quaternary tephra composite in the Waikato region. He ascribed this to the weathering of biotite (derived from biotite-containing air-fall tephras) under special site conditions which favoured complete release of K (and Mg) from interlayers. A high concentration of Si and low concentration of Al is required (Buol et al. 1973) and the associated occurrence of authigenic cristobalite with the clay-vermiculite demonstrated that this condition was met (cf. Colhoun et al. 1972). That clay-vermiculite does not seem to occur in tephras of similar composition (i.e., biotite-rich) and origin is attributed to unsuitable site weathering conditions. Hogg (1979) identified sand-sized (macro-) vermiculite as a replacement product of biotite flakes in a paleosol developed on Rotoehu Ash in the Coromandel region, and a "vermiculite-intergrade" mineral in the H1 bed of Hamilton Ash (Hogg 1974). A smectite-vermiculite intergrade occurs in several beds in the Kauroa Ash Formation (Salter 1979), and traces of smectite have recently been identified in highly weathered, iron-rich, short range order clays derived from a strongly weathered distal ignimbrite in the Waikato region (D.J. Lowe, unpublished data).

Residual primary minerals

Quartz and feldspar may occur in small amounts in clay fractions and, if present in sufficient quantities, are readily identified by XRD (Hume and Nelson 1982). Their occurrence in South Auckland tephra clay fractions is common.

aged less than 2,500 y.

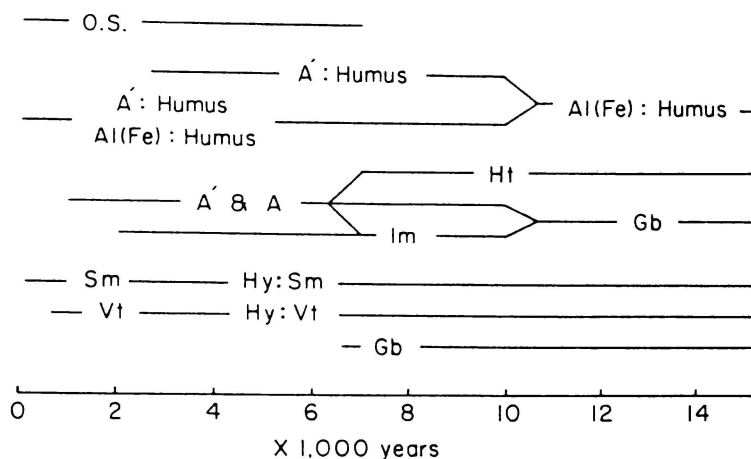
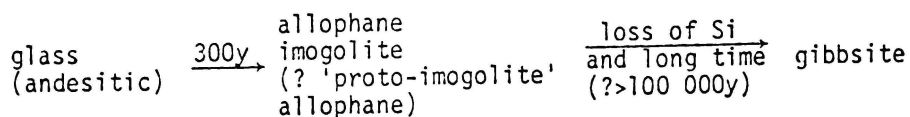


Fig. 3. Formation and transformation of clay minerals and their organic complexes in soils developed from tephras in humid, temperate climatic zones in Japan. A = allophane; A' = allophane-like constituents; Al(Fe) = sesquioxides; Ch = chlorite; Gb = gibbsite; Ht = halloysite; Im = imogolite; Sm = smectite; Hy-Sm = hydroxy interlayered smectite; O.S. = opaline silica; Vt = vermiculite; Hy-Vt = hydroxy interlayered vermiculite. Horizontal bars indicate approximate duration of the various constituents. From Wada (1977, p. 620).

Andesitic glass, with an intrinsically greater Al:Si ratio than rhyolitic glass, weathers much more rapidly and with marked loss of SiO₂ and mobile cations (Neall 1977; Kirkman and McHardy 1980). Kirkman and McHardy (1980) and Kirkman (1981a) concluded that the structure and chemical composition of allophane, and hence its behaviour and persistence, are governed chiefly by the chemical composition and bonding characteristics of the parent glass. This conclusion supports a previous study by Trichet (1969) involving laboratory leaching of glasses of differing compositions.

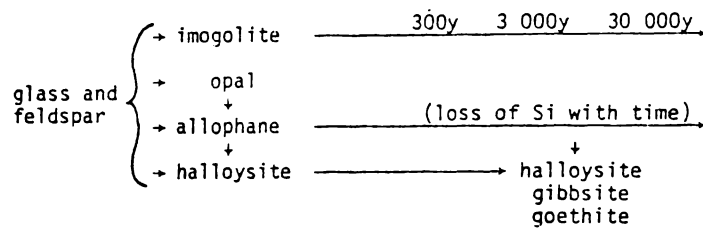
A weathering sequence for andesitic glass suggests that under humid temperate conditions allophane and possibly imogolite are stable for long time periods, and also predicts the ultimate formation of gibbsite (Kirkman 1978, 1980b, 1981, 1981a; Kirkman and McHardy 1980; Parfitt et al. 1982):



Gibbsite, however, generally occurs in minor amounts in weathered tephras in New Zealand (Fieldes and Taylor 1961; Hogg 1974; Salter 1979; Kirkman 1980a; Lowe 1981; Parfitt et al. 1983), presumably because of either unfavourable site conditions which essentially minimise desilication (Schwertmann 1979; Farmer et al. 1979; Kirkman 1980b) or possibly the presence of additional inhibitors such as iron oxide gels

(Kirkman and McHardy 1980). In contrast, significant amounts of gibbsite occur in clay fractions from tephras older than about 3,000-6,000y and weathering under humid, temperate conditions in Japan (Fig. 3; Mizota 1976). This, together with other evidence (e.g., Eswaran and de Coninck 1971; Macias Vazquez 1981), indicates that gibbsite formation is not restricted to a long period, nor is it necessarily dependent upon hot-humid (tropical) climatic conditions.

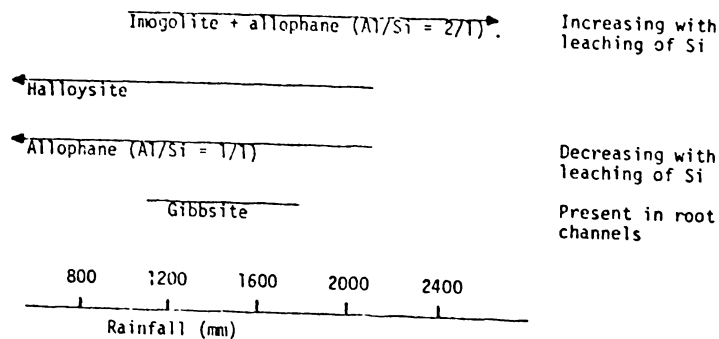
In a study of clay minerals formed in dacitic and andesitic tephra-derived soils under tropical conditions in Papua New Guinea, Parfitt (1975) suggested the following tentative weathering scheme:



He noted that the glass phase weathers rapidly and can form stable imogolite or allophane, as in Kirkman's scheme above. Halloysite may form directly from feldspars or from allophane, depending on the leaching and biotic conditions in the deposit. Gibbsite was found mainly in the older beds (30,000y) together with allophane, which tends to support the sequence postulated by Kirkman, but also occurred in much younger beds as shown above (see also Fig. 3).

The formation of gibbsite thus appears to rely on specific Si-deficient microenvironmental conditions, possibly together with an Al-rich primary mineral composition.

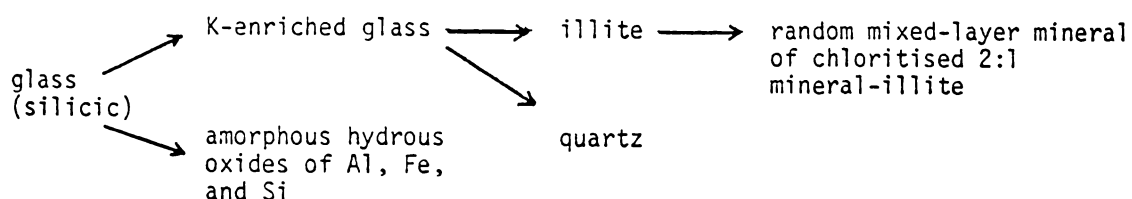
A weathering scheme which emphasises leaching (rainfall) and Si concentration more than time in clay mineral transformations for rhyolitic tephras aged between 2,000 and 100,000 years in New Zealand has been proposed by Parfitt et al. (1983) from studies in the Waikato region:



This work refines previous ideas on rainfall-clay mineral relationships postulated first by Taylor (1933) and later Ward (1967). It is

innovative in that it shows clearly the effects of environmental conditions, rather than time, on clay mineral genesis. Parallel studies by Lowe (1981) and Lowe and Gibbs (1981) in the region have emphasised the effect of seasonal distribution of rainfall (i.e., wetting and drying) in addition to the total amount of rainfall.

A markedly different weathering sequence has been determined by Shoji et al. (1981) from work in Japan on rhyolitic and dacitic tephra-derived topsoils weathering under humid temperate conditions. Their postulated sequence is:



They thus suggest that the dominant source of 2:1 type clay minerals frequently observed in Japanese tephra-derived soils is illite formed by alteration of volcanic glass in a solid-state reaction. That preferential retention of potassium occurs in the volcanic glass has been demonstrated by Yamada and Shoji (1982).

These workers also determined the facility of release of elements from the parent tephra materials as: $\text{CaO}, \text{Na}_2\text{O} > \text{Al}_2\text{O}_3, \text{Fe}_2\text{O}_3, \text{MgO} > \text{SiO}_2, \text{K}_2\text{O}$, and a mobility sequence of the major elements during pedochemical weathering (Kurashima et al. 1981; Shoji et al. 1981) as: $\text{CaO}, \text{Na}_2\text{O} > \text{SiO}_2 > \text{MgO} > \text{Al}_2\text{O}_3, \text{Fe}_2\text{O}_3, \text{K}_2\text{O}$. These results differ from previous studies in the order of mobilities of $\text{SiO}_2, \text{MgO},$ and K_2O ; in particular, SiO_2 has the highest mobility of the three elements whereas normally it is shown to have the lowest (Kurashima et al. 1981). Overall, the mobility sequence indicates that loss by leaching is relatively large for CaO and Na_2O and small for SiO_2 , where $\text{Al}_2\text{O}_3, \text{Fe}_2\text{O}_3,$ and K_2O accumulate relative to the chemical composition of fresh tephra.

An alternative viewpoint for the origin of the 2:1 type minerals in the Japanese soils is that they derive from continental aerosolic dusts carried by westerly winds. Evidence for this possibility comes from distinctive $^{18}\text{O}:^{16}\text{O}$ ratios of fine, silt-sized quartz particles isolated from various soils in Japan (Mizota 1982).

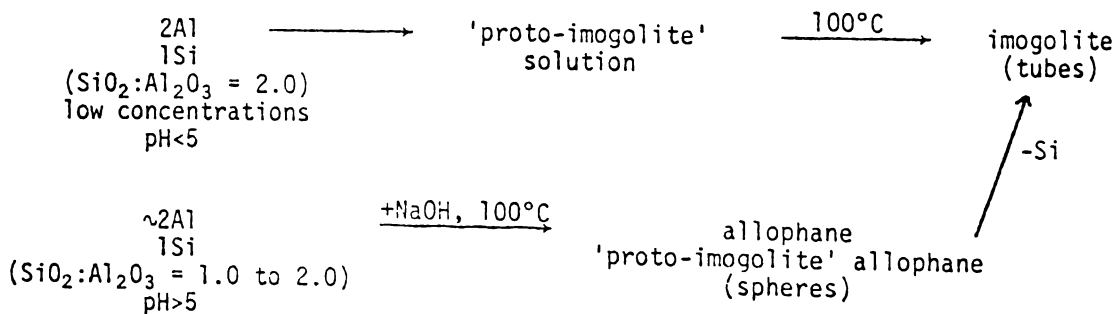
In conclusion, the framework of thinking in examining weathering sequences now tends to favour separate formation pathways for the various minerals according to their chemical composition and to site weathering conditions, particularly as they affect the concentration of Si in

solution and the availability of Al, and the opportunity for co-precipitation of these. Second, short range order minerals such as allophane, imogolite, and 'proto-imogolite' allophane are, in some cases, possibly transformation reaction end-points rather than short-lived transition products and are able to persist for long periods of time if conditions are favourable. Other clay minerals such as halloysite and gibbsite, often envisaged as time-dependent transformation products of precursory allophane and imogolite, are apparently able to form directly from the dissolution products of primary (or secondary) minerals depending mainly on whether the conditions favour resilication or desilication.

Genesis

The proposed mechanisms and conditions for formation of allophanic short range order minerals and halloysite from tephric deposits are detailed by Wada and Harward (1974), Wada (1977, 1978, 1980), Nagasawa (1978a), and Brown et al. (1978), among others. Recent work characterising New Zealand allophanes and halloysites is reported in Parfitt et al. (1980, 1982), Parfitt and Henmi (1980), Kirkman (1977, 1981), and Theng et al. (1982).

Studies involving synthesis of allophane and imogolite by Scottish and Japanese workers are reported in Wada (1980), and summarised as:



Allophane requires a neutral or alkaline pH to give maximum Al in 4-fold coordination, whereas imogolite requires an acid pH to maintain Al in 6-fold coordination in contact with monomeric silica (Brown et al. 1978). These differences in conditions for synthesis and the concomitant co-existence of allophane and imogolite are satisfied by observations on naturally-occurring counterparts. It appears that in tephra deposits allophane forms inside weathered glass or pumice fragments in which hydrolysis of the glass proceeds at a high Si concentration and pH. Imogolite forms outside, possibly by alteration of allophane exposed to external solutions of lower Si concentration and lower pH (<5), or by precipitation from such solutions (i.e., Al and Si form a soluble

complex (proto-imogolite) whose solutions are stable at pH less than 5; Farmer and Fraser 1979; Farmer et al. 1979).

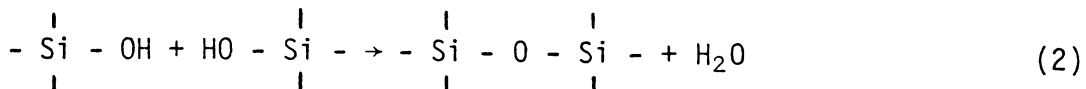
Gibbsite may also coexist closely with allophane and imogolite, it being associated with certain minerals in a rock fragment whilst the latter two minerals, as discussed above, occur actually within or adjacent to the glass or pumice fragment (Wada and Matsubara 1968; Brown et al. 1978). Gibbsite can apparently form at any stage of weathering given that an environment with <1 ppm SiO_2 in solution exists to prevent Al-silicate formation (Schwertmann 1979), as in highly leached tephra sequences.

The original proposal of Fieldes (1966) that halloysite essentially "crystallised" through increased cross-linkage of random aluminosilicate gels through (seasonal) dehydration is in large part misleading. It is now known that allophane and related minerals are not "random gels" and have short range order, and that halloysite may crystallise directly from dissolution products of glass or feldspar (i.e., without an intermediate or transition allophane phase). However, the apparent relationship between rainfall distribution and degree of leaching with the occurrence of a particular mineral type has been recently re-considered in transformation pathways by Parfitt et al. (1982). Allophane, allophane-like constituents, imogolite, and 'proto-imogolite' allophane generally occur where rainfall (i.e., leaching) is moderate or high (Wada and Harward 1974; Birrell et al. 1977; Wada 1980) and halloysite and allophane ($\text{Al}:\text{Si} \sim 1.0$) where rainfall is lower (Miehlich 1981; Benny et al. 1982; Parfitt et al. 1983). The principal effect of the rainfall distribution, hence degree of leaching, is in governing the relative proportions of the main chemical constituents, SiO_2 and Al_2O_3 , from which either allophane and imogolite or halloysite form. Parfitt et al. (1982) report that current evidence suggests that Al-rich allophane (with a 'proto-imogolite' structure) does not normally alter to halloysite as Si tetrahedra are considered to occur on the interior surface of the hollow allophane spherules as isolated SiO_3OH groups with apices directed away from outer gibbsitic units (Fig. 2; Farmer and Fraser 1979), the reverse of the kaolin structure. Thus alteration to halloysite would necessitate the allophane effectively turning "inside out" by passing through a solution phase with concomitant enrichment with polymerised silica.

Allophane and other short range order aluminosilicates may transform, via solution, to halloysite or gibbsite depending on whether the environment favours resilication (for halloysite) or desilication (for

gibbsite) (Parfitt 1975; Wada 1977; Saigusa et al. 1978; Mielich 1981). Under a high leaching regime, and low pH, SiO₂ and mobile cations are rapidly lost. Hence the formation of allophane (and possibly gibbsite), with an Al:Si ratio around 2 or more (i.e., SiO₂:Al₂O₃ = 1.0), is preferential to the formation of halloysite with an Al:Si ratio nearer 1 (SiO₂:Al₂O₃ = 2.0).

Clearly, as mentioned earlier, the Al:Si composition of the primary minerals will partly affect this resilication-desilication balance. The thickness of depositional overburden may also have an effect in that a thick sequence (>~2m) potentially provides a silica-rich environment for a buried tephra and hence favours the formation of halloysite (Wada 1977; Shoji and Saigusa 1977; Saigusa et al. 1978; Sudo and Shimoda 1978; McIntosh 1980). Similarly, poor drainage and hence minimal loss of soluble silica favours halloysite formation (Dudas and Harward 1975a). Lowe (1981) postulated that under poor drainage conditions and in an intense wetting and drying regime which promotes silica accumulation, secondary cristobalite, together with halloysite, forms in preference to allophane. There is some evidence that Al-humus complexing also favours the formation of secondary silica as cristobalite (Lowe 1981) or opaline silica (Wada and Higashi 1976; Shoji and Saigusa 1978) in that it inhibits co-precipitation of active Al and Si. The silica dissolves from glass (or from biogenic opal) and precipitates through seasonal concentration (by dehydration) coupled with Al-humus complexing. A possible method of crystal growth is by the uniting of tetrahedra and elimination of water (Jones and Segnit 1972, p. 419):



The role of living plants in determining monosilicic acid concentration, and biogenic opal formation, is discussed by Wilding and Drees (1971), Parfitt (1975), Wilding et al. (1977), Claridge and Weatherhead (1978), and Parfitt et al. (1983). Depending on conditions, uptake by plant cells of Si in solution to form biogenic opal and the drying and oxidising effect of plant roots may help formation of allophane (Al:Si~2.0) and gibbsite (as root pseudomorphs, for example; Hogg 1974). Alternatively, biogenic opal may be dissolved (under humid conditions) and either leached or precipitated with available Al to form allophane (Parfitt 1975), or the redissolved silica may form another polymorph such as cristobalite, as discussed above (equations 1 and 2; Lowe 1981).

The morphological forms of halloysite (i.e., as spheres or tubes, etc.) are possibly directly related to primary mineralogy; spherical halloysite may originate from glass, tubular halloysite from feldspar (e.g., studies by Parham 1969; Ngasawa and Miyazaki 1976; Violante and Violante 1977; Tazaki 1979; Kirkman and Pullar 1978; Kirkman 1981). Various mechanisms have been proposed to account for the different forms (e.g., see Dixon and McKee 1974; Kirkman 1977, 1981, 1981a; Sudo and Yotsumoto 1977; Kohyama et al. 1978; Wada et al. 1977; Salter 1979).

The occurrences and transformations of iron oxide minerals are summarised in Schwertmann and Taylor (1977) and Schwertmann (1979).

PART 2 : METHODS OF ANALYSIS OF CLAY FRACTIONS

Normally, no one technique is adequate alone to determine the clay mineralogy of tephric deposits, especially in quantitative studies of samples containing both crystalline and short range order materials. Hence several methods must be applied. The most useful method, at least initially, is X-ray diffraction (XRD). This has quantitative limitations in tephra studies because of their often high proportion of short range order (hence X-ray amorphous) clays, with widely varying chemical compositions.

Methods used in addition to XRD in tephra clay mineral studies include thermal analyses (differential (DTA) or thermogravimetric), electron microscopy (scanning (SEM) and transmission (TEM)), electron diffraction, infrared (IR) and Mössbauer spectroscopy, chemical analyses, dissolution analyses, sodium fluoride (NaF) reactivities, phosphate and chloride adsorption, X-ray fluorescence (XRF) spectroscopy, electric charge characterisation, gas chromatography, electron paramagnetic analysis, and surface area and porosity measurements. Several of these methods are highly specialised and are not discussed further in this report (see instead, e.g., Fripiat 1982). The methods described below are those most commonly used at the University of Waikato.

General sample preparation and selection of analytical methods

It is particularly important that whole tephra samples are not air dried prior to analysis. They should be maintained in field-moist condition until analysis is under way. This is especially important if particle-size determinations are being carried out in conjunction with the clay separation. Storage at 4°C in sealed plastic bags minimises irreversible alteration of the clay components.

Dry grinding procedures should be minimised because of various effects on the structure and properties of clay minerals. Henmi and Yoshinaga (1981) report that imogolite, for example, is very susceptible to alteration by prolonged grinding (more than a few minutes) which causes disruption of Si-O-Al bonds, polymerisation of the SiO₂ component released and loss of structural OH groups, and finally complete structural breakdown.

Sample preparation for most analytical methods usually involves suspension in distilled water, dispersion, and fractionation into <2µm and/or <1µm size fractions. Which of these (or other) size fractions is investigated depends partly on the nature of the project. In a general study in which the analysis of the clay fraction is but one part,

examination of the $<2\mu\text{m}$ fraction is normally sufficient. A more detailed study biased towards clay fraction composition in itself would usually necessitate examination of at least some selected $<1\mu\text{m}$ fractions for comparative purposes. Alternatively, analysis of the $<1\mu\text{m}$ clay fraction alone may be advisable as it tends to reflect mainly authigenic (secondary) minerals, whereas the $<2\mu\text{m}$ fraction often contains glass (residual) which is difficult to distinguish from allophane or other short range order minerals (e.g., see Kirkman 1975; McIntosh 1979). Hume and Nelson (1982) have emphasised the importance of size segregation of crystalline clay mineral species generally in sedimentary deposits from the South Auckland region.

Complete dispersion of tephric samples is often difficult to achieve, but the best method appears to be ultrasonication for 5-10 min. (see Lowe 1981, p. 372). Chemical treatment to alter the pH of the suspension is usually required, but should not be used if chemical dissolution studies on specific clay components are envisaged. Unless samples contain a very high proportion of organic matter, peroxidation with H_2O_2 , or deferration by dithionite (CBD) extraction, should not be routinely carried out because of degradation and dissolution of constituent clay materials (Lowe 1981). However, peroxidation or deferration may be necessary as an aid in dispersion, and for adequate analytical resolution (e.g., Hogg 1974; Salter 1979; Brewster 1980).

Fractionation can be achieved^e by sedimentation, filtration, or centrifuging. The easiest method is probably to decant, or extract by pipette, then filter the $<2\mu\text{m}$ or $<1\mu\text{m}$ fraction from the appropriate top part of a mud suspension in a 1l cylinder after routine particle size analysis (e.g., as in Folk 1968, and various Earth Sciences Department handouts on laboratory methods for sedimentology and soils courses; a centrifuging method appropriate for University of Waikato equipment is given in Lowe 1981, p. 134). Resultant clay-sized suspensions are then flocculated and saturated with either a Mg or K salt (such as MgCl_2). This is because most of the literature reports clay mineralogical analyses as either Mg- or K-saturated clay for diagnostic purposes (Rich and Barnhisel 1977). The saturated clay must be washed several times with distilled water, and either refiltrated or re-centrifuged, to remove excess salt.

The fate of the clay separate then depends on the analytical method being undertaken, which in turn relates chiefly to the nature of the materials under study and to the actual purpose of the study. For example, it depends on whether the study is general or specialised,

Table 5. General guide to selection of methods for analysing particular tephric clay materials based on the rate at which numbers of samples are able to be processed and whether results are qualitative or quantitative. The table is a subjective, preliminary guide for the non-specialist worker and applies to the general case only. Each of the methods outlined in Part 2 of this manual should be consulted, if even briefly, prior to beginning analysis. For the specialist, references containing further details of method and application are given under each method section. Examples of the use of the table are: A, 4 = the method is fast but usually gives only qualitative results; B, 1 = the method is moderately fast and accurate absolute amounts of the clay constituent under investigation can be determined; and C, 4 = the method is relatively time consuming and gives qualitative results only.

COMPONENTS	XRD	IR	DTA	SEM	TEM	NaF	CHEM. DISS. Δ	S. AREA
Allophane	-	A,2	B,2	C,4	D,4	A,3	C,1	C,3
Imogolite	-	A,2	B,2	C,2	D,2	A,3	C,1	C,3
'Proto-imogolite' allophane	-	A,2	B,2	C,4	D,4	A,3	C,1	C,3
Allophane-like constituents	-	A,4	-	-	-	-	C,4	-
Halloysite	A,3 [†]	A,2	B,2	C,4	D,4	-	C,3	C,3
Secondary silica polymorphs	A,4 [†]	A,4	-	-	-	-	C,4	-
Humus, humus complexes	-	-	B,3	-	-	-	C,2	-
Fe and Al oxides, hydroxides	B,4 ^{††}	A,4	B,3	-	D,4	-	C,3	-
2:1, 2:1:1 minerals	A,4 [†]	-	B,4	-	-	-	C,3	-
Residual primary minerals	A,3 [†]	A,4	-	-	-	-	-	-

Abbreviations for analytical techniques: XRD, X-ray diffraction; IR, Infrared; DTA, Differential thermal analysis; SEM and TEM, Scanning and Transmission electronmicroscope respectively; NaF, Sodium fluoride reactivity; CHEM. DISS., Chemical dissolution; S. AREA, Surface area measurements.

Capital letters refer to numbers of samples able to be processed: Many ————— Few

A B C D

Numbers refer to degree of 'quantification' of results: Quantitative ————— Qualitative only

1 2 3 4

- = not generally applicable or only in a 'negative' sense (e.g., low NaF reactivity implies a high proportion of layer silicate clays due to low Al-OH activity; similarly, XRD of allophane and imogolite gives a negative result, which in itself is often useful, but does not allow distinction between glass and allophane).

+ Degree of quantification depends partly on the proportion of short range order minerals present as these, through absorption of X-rays, tend to suppress the peaks of the crystalline minerals (Hume and Nelson 1982).

†† Method depends on degree of crystallinity of samples, and samples usually require extraordinary pretreatment.

Δ These methods, although reasonable routine, usually require comparison of materials before and after treatments using differential IR and XRD methods, hence are ranked C rather than B.

whether qualitative or quantitative results are required, the number of samples to be analysed, and the amount of time available for the investigation. A simple, subjective attempt to help guide the non-specialist novice clay mineralogist determining which methods to use is given in Table 5.

Some of the analytical methods available, such as XRD and IR, are relatively rapid and enable a large number of samples (50-100 or so), once prepared, to be run in a routine manner. XRD in particular, however, is largely qualitative or at best semi-quantitative for crystalline minerals (e.g., see Hume and Nelson 1982) and gives a negative result for short range order materials which are X-ray amorphous. Other methods, such as DTA and TEM, require more preparation and analytical time per sample and hence, in general, considerably fewer and carefully selected samples should be analysed. If a study is a specialised one on, say, clay mineral morphology, the EM methods are likely to be paramount but, because of the interpretative difficulties associated with these techniques, additional methods such as XRD or DTA are essential. Similarly, an investigation of the chemical structure of clays would certainly employ the IR method, while one involving soil genesis and mapping might be advised to measure NaF reactivity since this is one of the criteria used in some soil classification systems. However, it is re-emphasised that any one technique alone is unlikely to provide a definitive clay mineralogical analysis of tephric materials.

Where short range order clays are being examined and semi-quantitative results are required, DTA is appropriate for a limited number (say 20 or so) of selected samples; results necessitating greater "accuracy" should utilise chemical dissolution methods, possibly together with IR analysis.

Finally, it should be remembered that the interpretation and subsequent presentation of results normally takes at least 2-3 times longer than the time to simply prepare and analyse the samples. Clay mineralogical analysis and interpretation requires considerable judgment at every step of the way.

X-ray diffraction (XRD)

Preparation

A good review account of sample preparation is given in Rich and Barnhisel (1977). Oriented paste mounts of the Mg- or K-saturated clays are made using the smear-on-glass-slide (SOGS) method (Thiesen and Harward 1962; Gibbs 1971; Hume and Nelson 1982) which avoids size-

segregation (Schoen et al. 1972; Hume 1978). Dropper-on-glass-slide (DOGS) mounts containing allophanic materials often crack and peel from the slide upon drying. Some cracking of the SOGS paste may occur due to the short range order constituents (Cortes and Franzmeier 1972a) and/or high Fe content (Hume 1978), but it is usually negligible compared with that of DOGS mounts. The mounted specimens may be air dried (under cover to avoid dust contamination), usually for about 24h. Alternatively, slides may be dried slowly over distilled water (i.e., 100% r.h.) for 24 to 72h. The latter procedure has been adopted to prevent low temperature dehydration of 10Å halloysite (Nagasawa 1969, 1978b). This is important in some studies (Lowe 1981) as (a) it enables determination of the halloysite component in its actual 'field' hydration state; and (b) unequivocal distinction between halloysite and kaolinite species by XRD is difficult if all the halloysite is in the dehydrated (7Å) form. The dehydration process is irreversible in most circumstances (Grim 1968; Kirkman and Pullar 1978), hence rehydration of the 7Å halloysite to 10Å halloysite during this treatment is unlikely.

Sample mounts should be X-rayed immediately upon drying, since prolonged dehydration at ambient temperature reduces the size of the first order reflections (Lowe 1981). This effect was noted also by Nagasawa and Miyazaki (1976) and Kirkman and Pullar (1978) who overcame it by X-raying moist clay mounts.

Procedure and mineral identification

Specimens are scanned from 3° to 28°2θ at 2°2θ min⁻¹, using the instrument settings shown in Table 6. Clay minerals are identified

Table 6. Instrument settings for XRD analysis at University of Waikato using a Philips X-ray diffraction spectrometer system (CuKα radiation, λ = 1.5418Å). (See also Hume and Nelson 1982).

kV	30	High voltage	56%
mA	13	Window level	L-α
Time constant	4	Lower level	17%
Attenuation	2	Oscillator	High
Chart speed	20 mm. min ⁻¹	Divergence slit	1°
Scanning speed	2° 2θ min ⁻¹	Scatter slit	1 mm
Rate meter setting (RMS)	400 or 1000 cps		

by the position and movement of mainly their (001) reflections following heat and glycolation treatments (Table 7; see also Hume and Nelson 1982, fig. 8, and Brindley and Brown (1980) for more details).

Allophane, imogolite, and glass lack diffraction patterns, apart from occasional poorly defined background maxima commonly associated with X-ray amorphous materials (e.g., Campbell et al. 1977; Okada et al.

Table 7. Diagnostic XRD peak positions for identification of oriented tephra-derived Mg-clays and associated minerals. Compiled from various sources (after Lowe 1981, p. 178).

Mg-clay	Air-dried in humid atmosphere 24-72h. (100% r.h.)		Glycolated in ethylene glycol vapour 12h.	Heated 110°C 1h.	Heated 550°C 1h.
	d(001) in Å	c.2θ°			
Allophane (± imogolite)	X-ray amorphous ¹				
Halloysite (10Å)	9.8-10.2	8.8	Slight expansion to 10.6Å	Dehydrates to 7.0-7.3Å	Becomes X-ray amorphous
Halloysite (7Å) (or Kaolinite)	7.0-7.3	12.3	No change	No change; increases if 10Å halloysite present before heating	Becomes X-ray amorphous
Vermiculite ²	14.0-14.2	6.2	No change	Partial or complete dehydration from 14Å to 10Å (usually 11-12Å)	All to 10Å
Gibbsite ³	4.85 (002)	18.3	No change		
All of the above crystalline clays	(i) 3.5-3.6 (002, 003 or 004) [Larger peak if halloysite present]	25.0	No change	No change [Peak increases if halloysite present]	Becomes X-ray amorphous
	(ii) 4.4 (021)	19.9	No change	No change	Becomes X-ray amorphous
<u>Other Minerals⁴</u>					
Quartz	3.3 (101)	26.7			
Feldspars	3.18-3.2 (002, 202, 040)	27.5-28.4			
Cristobalite ⁵	4.05 (101)	21.9			
Tridymite	4.08 (101)	21.7			
Micas ⁶	10.0 (001)	8.8	No change	Persists at 10Å	Persists at 10Å

¹ Apart from broad background maxima (see text).

² Heat treatments may be inconclusive if micas-illites present (see 6 below).

³ Will not be detected unless >5% (or special pretreatments made).

⁴ Iron oxide minerals given in Table 4; for other minerals refer to Hume and Nelson (1982)

⁵ Positively identified only if primary feldspar peaks are low.

⁶ Identification can be uncertain as may have other 10Å minerals present in sample, both untreated (e.g., 10Å halloysite) and heat treated (e.g., clay-vermiculite). See also Brindley and Brown (1980) and Hume and Nelson (1982).

1975) (Fig. 4a). Crystalline mineral species in tephra clay fractions identified relatively easily by XRD reflections are 10Å and 7Å halloysite, clay-vermiculite, cristobalite, tridymite, and quartz. Less easily identified components are gibbsite and iron oxides, especially when present in low concentrations (see below). Mica may be difficult to positively identify if both 10Å halloysite and clay-vermiculite are present since the characteristic 10Å peak for mica may be over-shadowed by peaks from halloysite or vermiculite at various stages of treatment. The identification of cristobalite is usually straightforward because feldspars, which have a secondary peak at the same d-spacing as cristobalite (4.05Å), occur infrequently and in very low quantities in clay fractions.

A potential identification problem may arise where both 7Å halloysite and kaolinite are suspected to be present together (such as in reworked materials). The presence of kaolinite can usually be discounted where 7Å peaks invariably occur in combination with 10Å halloysite peaks with interstratification. The 7Å peak will increase in magnitude following heat treatment (110°C) due to loss of interlayer water from the 10Å halloysite. Furthermore, if the 7Å and 4.4Å peaks are broad and poorly defined, then an halloysitic nature is generally indicated (Churchman and Carr 1975; Brindley 1977; Lowe 1981). Churchman et al. (1982) have recently developed a rapid test for distinguishing 7Å halloysite from kaolinite based on the relative abilities of these minerals to intercalate polar organic compounds such as formamide and N-methylformamide. Formamide rapidly (<1 h.) and completely intercalates into dehydrated halloysite which consequently then gives a peak at 10Å, whereas the intercalation of formamide into kaolinite is very much slower (days) and incomplete.

Kaolinite has not been reported in South Auckland tephra materials except for the occurrence of b-axis disordered kaolinite (as relatively large "books") in several strongly weathered Kauroa Ash beds (Salter 1979).

The identification of iron (or aluminium) oxide minerals by XRD (Table 4) is often difficult because of their low concentrations, the diffuseness of patterns caused by small particle sizes and/or poor crystallinity, and the nature of the other minerals present. Schwertmann and Taylor (1977) recommend the use of CoK_α or FeK_α radiation in preference to CuK_α radiation to reduce background. A comparison of sample traces before and after extraction of the "free" iron oxides (e.g., by CBD method) is often helpful. A new method for identifying iron oxides by differential XRD is described by Schulze (1981) and this

should be consulted if a study is concentrating on the iron oxide minerals.

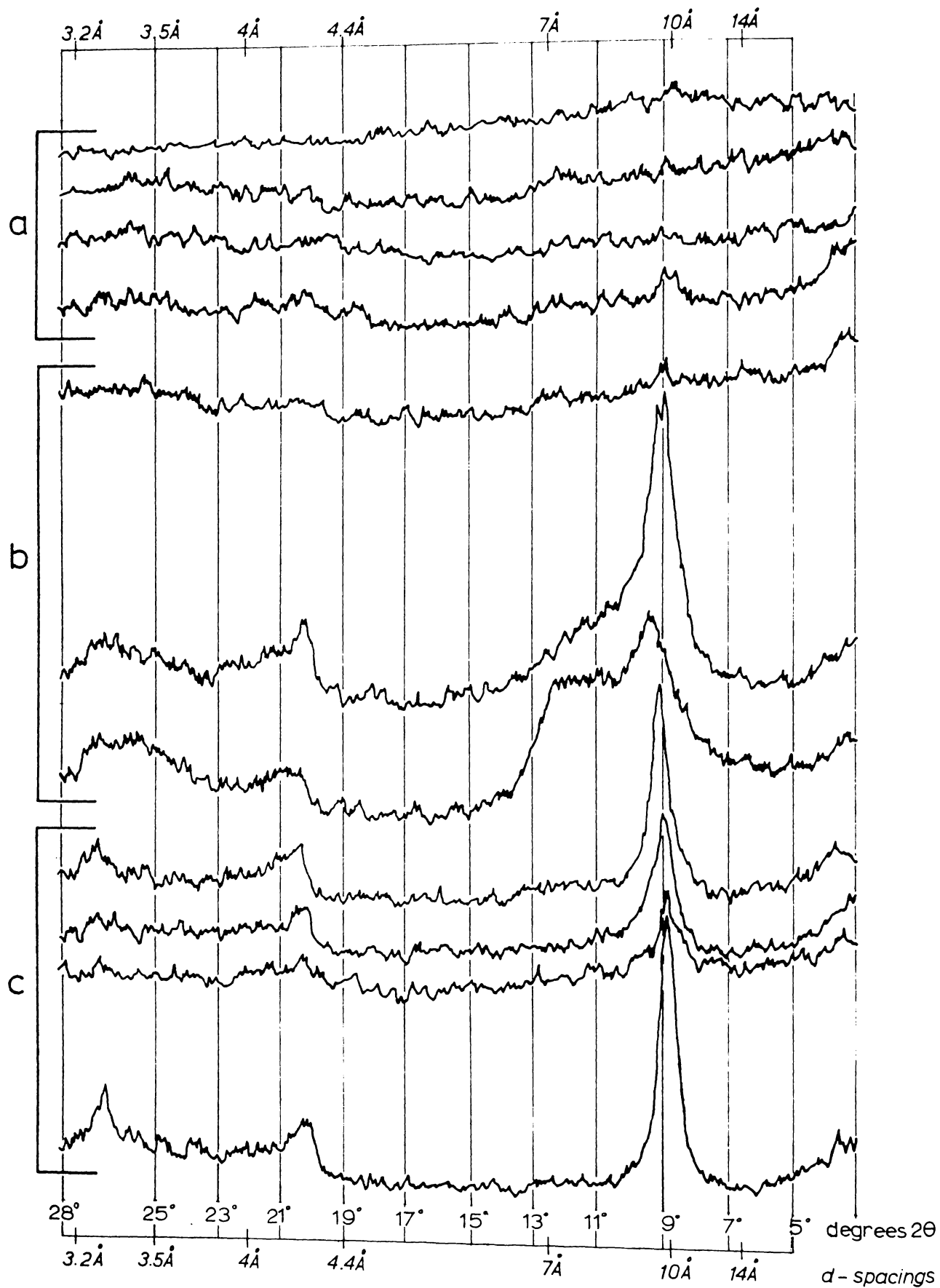
Application

Examples of XRD patterns of some Waikato tephra-derived clay fractions are given in Fig. 4. A series of examples is given to show the range of patterns which are liable to be encountered. More often than not, poorly defined peaks and high backgrounds rather than sharp and distinct or large peaks are typical. The dominant constituents in Fig. 4 are allophane (X-ray amorphous) and halloysite (peaks at 7Å and 10Å) with small quantities of clay vermiculite, cristobalite, and gibbsite in some samples.

Quantification of constituent mineral species is difficult because peak intensities and areas vary according to composition and other factors. However, an approximate estimate (at best $\pm 10\%$) of halloysite content from peak height (10Å plus 7Å) may be determined from Fig. 5. This graph was derived from comparison of semi-quantitative thermal analysis (DTA) data with XRD peak heights using late Quaternary tephra samples from the Waikato region and an halloysite standard. The amount of short range order material (which may include glass, imogolite, and poorly ordered iron oxides and humus complexes, as well as allophane) can be roughly estimated by difference. That is, the occurrence of only very small peaks of well ordered minerals such as halloysite implies that the sample is dominated by short range order material.

The degree of crystallinity of halloysite may be gauged partly from the sharpness of the 7Å and 10Å peaks. A broad or only moderately defined peak (e.g., Fig. 4d-i) indicates relatively poor crystallinity, but also may reflect the effect of partial dehydration of the halloysite. Peaks tend to become sharper and better defined, however, with increasing age or depth of burial of tephra materials (e.g., Fig. 4a-c,d-1) (Kirkman 1975; Lowe 1981).

The relative stability of interlayer water can be estimated from peak height-area relationships (e.g., Nagasawa and Miyazaki 1976; Wilke et al. 1978; Lowe 1981). The degree of interstratification has been related to climatic conditions by Lowe (1981) in that interstratification implies unstable interlayer water and seasonal dehydration.



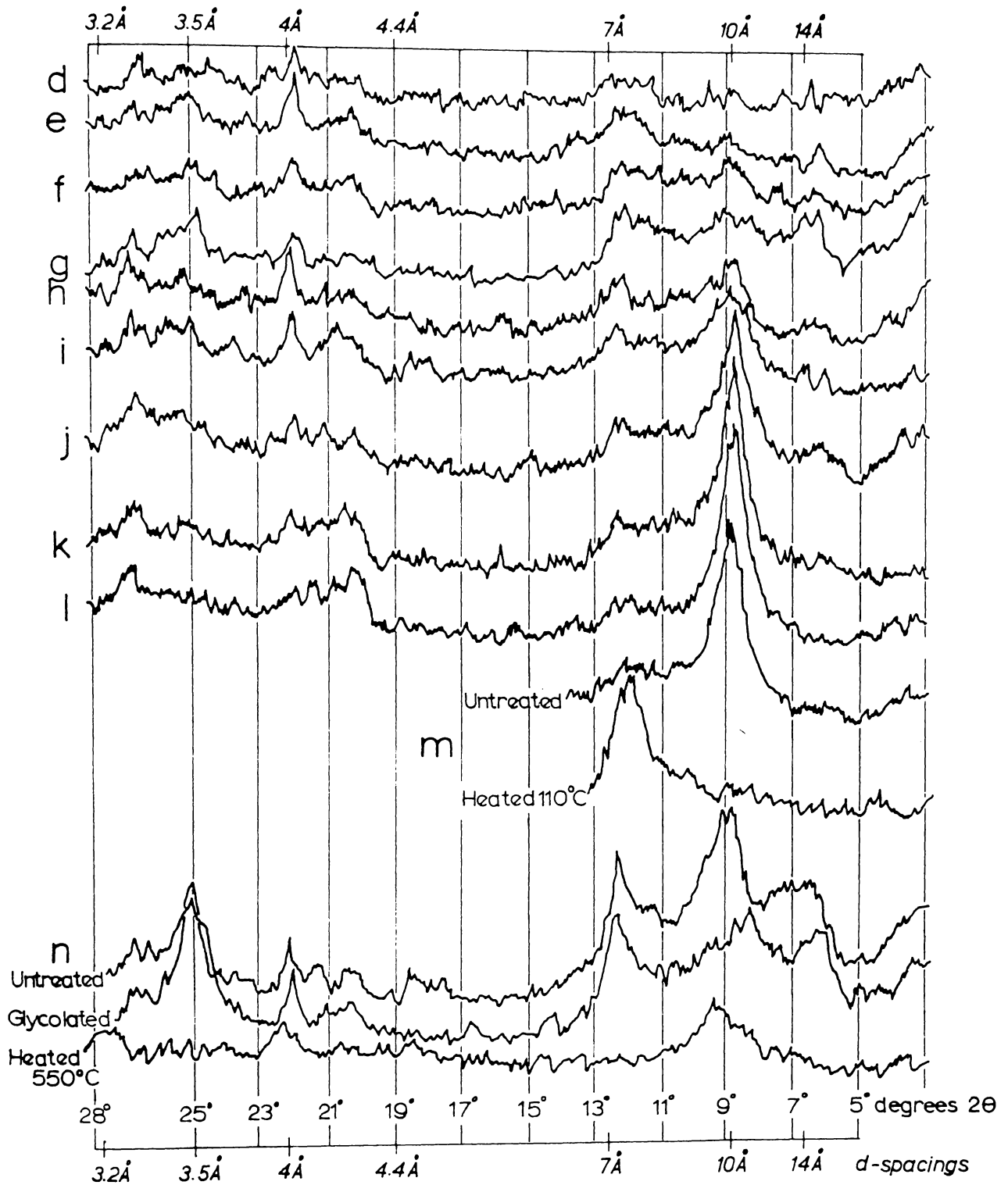


Fig. 4. XRD traces of some $<2\mu\text{m}$ Mg-clay fractions from tephras in the Hamilton Basin (see Table 1). a, tephras aged $<10,000$ years; b, Kawakawa Tephra (c. 20,000 years age) from different sites; c, tephras aged c.30,000-42,000 years age - bottom curve is Rotoehu Ash, others from Mangaone Lapilli; d-j, composite tephras of $\leq 42,000$ years age - samples arranged in order of increasing depth below surface; k-l, Hamilton Ash; m, composite tephra sample showing effect of low heat treatment - 10Å halloysite peak dehydrates to 7Å after 110°C heating for 1h.; n, composite tephra sample showing effects of glycolation and high heat treatment - glycolated trace shows slight expansion of 10Å halloysite peak, some interstratification between 7-10Å halloysite peaks, and no expansion of 14Å vermiculite peak; trace of sample heated to 550°C for 1h. shows disappearance of 7Å and 10Å halloysite peaks (become amorphous) and the dehydration of vermiculite at 14Å to heat-stable 9.8Å peak (refer also to Table 7). The diffractograms show that allophane (X-ray amorphous e.g., a traces) and halloysite (both 10Å and 7Å e.g., c, g-l) are the dominant constituents. Small amounts of clay-vermiculite (14Å e.g., d-g, n), α -cristobalite (4.05Å e.g., d-k, n), and possibly gibbsite (4.85Å e.g., lowest traces of a,b; and l,n) also occur. Interstratification between 7-10Å halloysite occurs in some samples (e.g., lowest trace of b, traces f-k). For further details see Lowe 1981, Ch. 6. From Lowe (1981, p. 180-181).

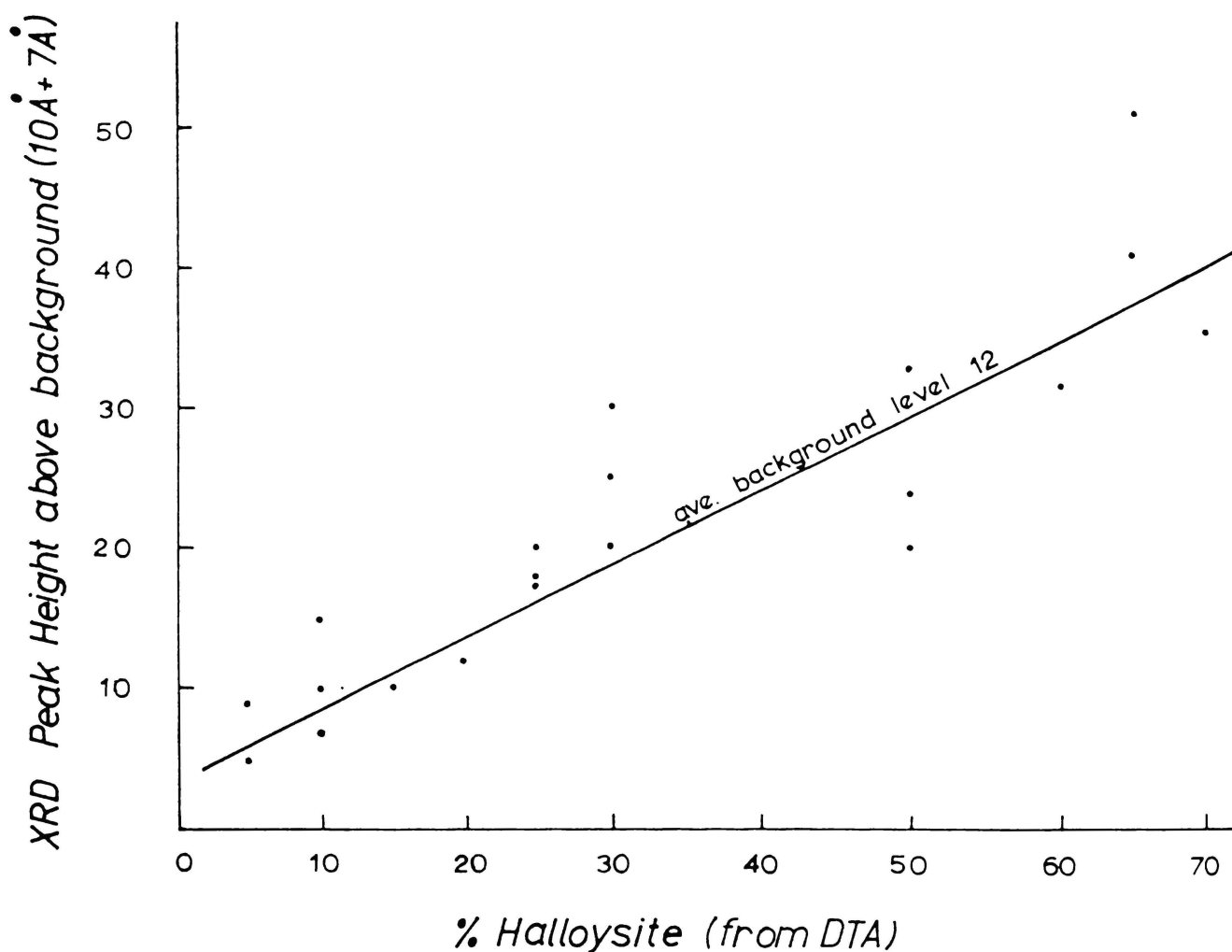


Fig. 5. Relationship between % halloysite as determined from DTA with XRD peak heights of 7Å + 10Å halloysite. XRD samples were untreated, oriented <2µm Mg-clay fractions run with instrument settings as in Table 6 (ratemeter setting 400cps). DTA analysis procedures were as given in DTA section below and Fig. 8. From Lowe (1981, p. 198).

Infrared spectroscopy (IR)

Infrared absorption involves passing a beam of infrared radiation (4000-200cm⁻¹) through a specimen and measuring the amount of absorption. Energy absorption will occur when the frequency of the incident radiation strikes a sample containing a bond between two atoms with a corresponding vibration frequency; radiation at other frequencies is not absorbed (Brown et al. 1978).

IR is equally applicable to gases, liquids, and glasses, as well as crystalline solids, and hence, together with chemical dissolution analyses, is becoming increasingly utilised as a major diagnostic

tool in studies of short range order clays from tephras. Quantitative determinations can be made, usually by comparing absorption or transmittance intensity with that of a suitable reference (e.g., Fieldes et al. 1972; Russell et al. 1981; Parfitt and Henmi 1982). An inherent limitation, however, is that the particulate nature of minerals and light scattering phenomena (known as the Christiansen effect) affect the relationship between the concentration of a given mineral component and the infrared radiation (see below; White 1977). A lack of "standard" reference minerals having the same structure, particle size distribution, composition, and spectral features as the component in the sample further limits the instances in which quantitative determinations can be accurately made. Nevertheless, reasonable agreement between chemical dissolution and IR methods has been achieved for estimates of allophane content in tephras (see Table 8, from Parfitt and Henmi 1982).

Some useful references on infrared studies include Fieldes et al. (1972), Farmer (1974), Giesecking (1975), Farmer and Palmieri (1975), van der Marel and Beutelspacher (1976), Dixon and Weed (1977), Brown et al. (1978), Farmer et al. (1979a), Theng (1980), and Parfitt and Henmi (1980).

Preparation

One of the major problems encountered in the application of IR in earth sciences is the distortion of absorption due to the Christiansen effect. The mineral samples must have a particle size less than the wavelength of the IR radiation used. The usual wavelength range is from 2.5 to 50 μm (i.e., frequency range of 4000 to 200 cm^{-1}), hence the <2 μm clay fraction is suitable. Coarser fractions need to be reduced in size by careful grinding (see White 1977; Henmi and Yoshinaga 1981).

Several methods of sample preparation exist. At University of Waikato alkali halide discs (KBr) or oil mulls have been used. Disc preparation is as follows:

- (1) Grind the sample to a particle size that is less than the shortest wavelength likely to be examined. For the majority of spectrometers this is 2 microns.
- (2) Weigh approximately 200mg of spectrographically pure KBr (or KCl) and 1mg of sample. Mix the two intimately and transfer to a vacuum die for pressing. Mount inside a paper ring (which should not be destroyed later).
- (3) Raise the pressure on the die slightly and maintain while evacuating the die. When the die is totally evacuated, increase the pressure

on the die to approximately 8 to 9 tons. This pressure is not critical, but it is very important never to exceed the maximum pressure quoted by the die manufacturers as this may cause cracking of the polished surface or, worse, an explosion of the die wall. The KBr becomes liquid at these pressures and flows around the mineral fragments.

- (4) After maintaining the pressure for 3 to 5 min., release the vacuum and then the pressure. Using suitable spacers press out the completed disc. Ideally, this disc should be quite clear. If it is cloudy, either the KBr or the sample contained moisture, or the die was not sufficiently evacuated. The disc can be ground and pressed again if necessary.
- (5) The transparent disc thus obtained is brought into the path of the beam of the infrared spectral photometer. A tablet of pure KBr made by the same method is brought into the other path of the beam.

Procedure, mineral identification, and application

The University of Waikato has four infrared spectrometers, the least complex being a Perkin-Elmer Infracord which covers the 2.5 to 15 μm (4000-650 cm^{-1}) range. The absorption of the specimen for the infrared spectrum is measured by linking the reference filter to a chart recorder pen and the prism to the chart drive. The prism is driven round slowly so that each wavelength in turn falls on to the detector. As the chart paper is linked to the prism the chart moves in synchronisation with the changing angle of the prism. The pen records the amount of attenuation required to bring the two beams into balance at each wavelength. The net result is a chart showing a measure of the absorption against wavelength.

Major absorption bands of allophane and imogolite occur in three regions: 2800 to 3800 cm^{-1} , 1400 to 1800 cm^{-1} , and 650 to 1200 cm^{-1} (Fig. 6; Wada 1977). The absorption bands in the first region are due to OH stretching vibrations (either structural OH groups or absorbed water). In the second region, an absorption band due to the HOH deformation vibration of absorbed water appears at 1630 to 1640 cm^{-1} . There may also appear absorption bands due to the vibrations related with COO (1700-1740 cm^{-1}) or COO⁻ (1580 and 1425 cm^{-1}) groups (due to humic materials or pretreatment decomposition products or anions, all of which are strongly retained by allophane and imogolite). The absorption bands in the third region are attributed mainly to Si(Al)O stretching vibrations and partly to SiOH and AlOH deformation vibrations (Wada 1977). The frequency of the Si(Al)O absorption maximum of allophane

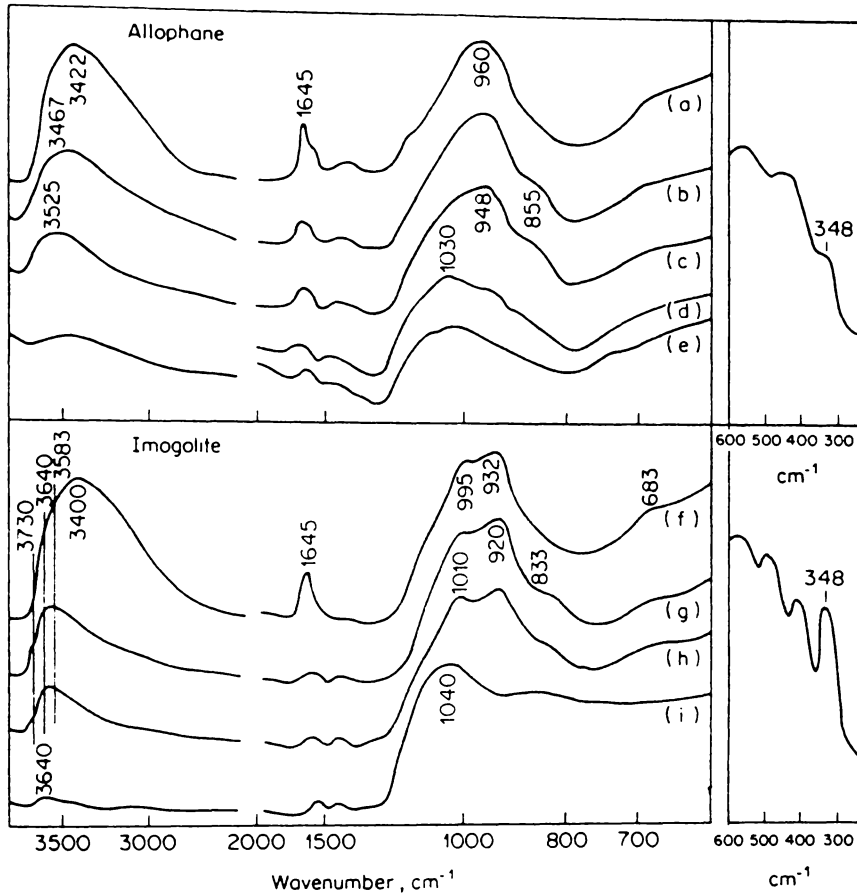


Fig. 6. Infrared spectra of allophane and imogolite showing their major absorption bands. The band at 348cm^{-1} is useful for recognising imogolite structures and has been used for quantitative analysis (see text and Table 8). The traces labelled (a)-(i) reflect differing analytical conditions in which temperature and evacuation pressures were varied. These conditions were: 20°C : a,f; 20°C , 10^{-2}mmHg : b,g; 150°C , 10^{-2}mmHg : c; 250°C , 10^{-2}mmHg : d; 350°C , 10^{-2}mmHg : e; 300°C , 10^{-2}mmHg : h; 475°C , 10^{-2}mmHg : i. The weak OH vibration at 3640cm^{-1} is due to a trace of micaceous impurity. Samples were prepared as films. From Brown et al. (1978, p. 157).

is between 940 and 1040cm^{-1} , the frequency increasing as the $\text{SiO}_2:\text{Al}_2\text{O}_3$ ratio increases (Wada 1980). The IR spectrum of imogolite shows two absorption maxima at 990 to 1010cm^{-1} and 925 to 935cm^{-1} , and a band at 348cm^{-1} is useful for recognising imogolite structures (Fig. 6; Brown et al. 1978; Wada 1980; Parfitt and Henmi 1980; Parfitt et al. 1980). This last absorbance at 348cm^{-1} has been used for estimating the amount of allophane ($\text{Al}:\text{Si}\sim 2.0$) or imogolite in a sample by comparing absorption intensity with that of a suitable reference material (Farmer et al. 1979; Russell et al. 1981; Parfitt and Henmi 1982) (Table 8). Pure air-dried allophane ($\text{Al}:\text{Si}\sim 2.0$) has a 348cm^{-1} absorbance of about 0.17 and air-dried imogolite has an absorbance of 0.27 (Parfitt and Henmi 1982).

Table 8. Comparison of analyses of clay fractions and % allophane estimated using chemical extraction methods and IR spectroscopy (from Parfitt and Henmi, 1982, p. 186). The % allophane (Al:Si=2.0) is estimated using the chemical composition of imogolite as a reference where 100% imogolite contains 27.2% Al and 14.1% Si. For example, the Egmont sample contains 19.1% oxalate-extracted Al (Al_o) which equals, from the proportion 19.1/27.2, about 70% allophane. Similarly, it contains 10.0% oxalate-extracted Si (Si_o) which also equates with 70% allophane from the proportion 10.0/14.1.

Sample	Oxalate extraction ^b				Pyrophosphate extraction ^b		Mole ratio	% Allophane (Al/Si=2/1)			
	C (%)	Al _o (%)	Si _o (%)	Fe _o (%)	Al _p (%)	Fe _p (%)	$\frac{Al_o - Al_p}{Si_o}$	Al _o ^c	Al _{o-p} ^d	Si _o ^e	IR ^f
Ohaewai	8.4	18.8	7.0	5.9	2.1	0.6	2.5	70	60	50	50
Papakauri	4.3	9.0	2.6	6.9	3.3	2.4	2.3	30	20	20	10
One Tree Point	5.3	24.2	11.2	0.2	2.5	0.2	2.0	90	80	80	85
Mairoa	7.5	23.0	11.2	5.3	4.5	0.7	1.7	85	70	80	85
Patua	9.7	20.9	8.6	2.7	4.6	1.1	2.0	75	60	60	70
Pumice	4.0	25.6	13.3	4.0	1.7	0.2	1.9	95	90	95	90
Egmont	4.5	19.1	10.0	4.1	0.8	0.2	1.9	70	65	70	70
Addison	— ^a	24.2	12.1	2.8	2.7	0.9	1.8	90	80	85	80
Flagstaff	— ^a	18.2	6.7	4.9	5.9	2.5	1.9	65	45	50	45
Te Anau	16.0	13.2	2.5	5.8	8.5	5.0	2.0	50	20	20	30

^a Insufficient sample. ^b Based on 150°C oven-dry clay. ^c Calculated from % Al_o. ^d Calculated from % Al_o-% Al_p. ^e Calculated from % Si_o. ^f Calculated from IR absorbance at 348 cm⁻¹.

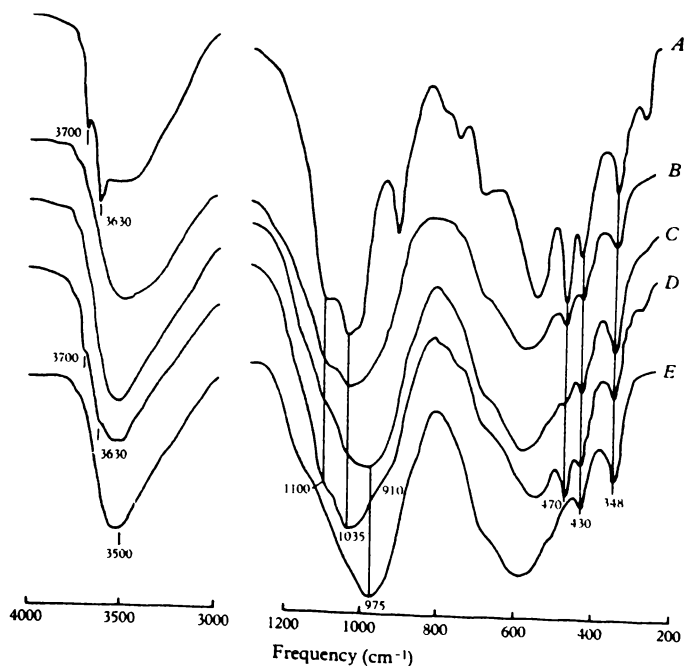


Fig. 7. Infrared spectra of halloysite and 'proto-imogolite' allophane from tephra-derived <2µm clay fractions. Sample A is largely halloysite only, sample E 'proto-imogolite' allophane only. The other samples (B-D) contain mixtures of both. The diagnostic bands for halloysite occur at 470, (530), 910, 1035, 3630, 3700cm⁻¹ whereas those of 'proto-imogolite' allophane occur at 348, 430, 570, 690, 990, and 3500cm⁻¹ (cf. Fig. 6 - note that the transmittance axis is inverted). These samples were prepared as KBr discs heated to 150°C, and derive from Waikato and Taranaki tephras. After Russell et al. (1981, p. 188).

Examples of $<2\mu\text{m}$ clay samples containing mixtures of mainly halloysite and 'proto-imogolite' allophane (which has an imogolite IR spectrum) are given in Fig. 7. IR spectra of halloysite and other minerals which occur in tephra clays in New Zealand are shown in Hogg (1974), Kirkman (1975, 1980a,b), McQueen (1975), Kirkman and Pullar (1978), McIntosh (1980), Russell et al. (1981), Theng et al. (1982), and Parfitt et al. (1983).

Diagnostic IR peaks for some iron oxide minerals are listed in Table 4, and a table summarising the main absorption bands for some other minerals is given in White (1977, p. 857).

Differential thermal analysis (DTA)

DTA is a semiquantitative technique which is especially important in the study of short range order materials since it is applicable irrespective of the degree of crystallinity. The method determines the differences in temperature (T) between a sample and reference material as the two are heated at a controlled rate. When the sample undergoes a transformation, the heat effect causes a difference in temperature between the sample and reference materials. The difference in temperature (ΔT) is normally plotted against the temperature at which this difference occurs (Fig. 8).

Reviews of DTA and other related methods such as thermogravimetric analysis are contained in Mackenzie (1970), Mackenzie and Caillère (1975), and Tan and Hajek (1977).

Preparation

Aliquots of Mg-clay (or K-clay) $<2\mu\text{m}$ fractions separated for XRD analysis are air dried (this takes several days), lightly ground in a mortar (preferably agate if very accurate work is being undertaken) and equilibrated to constant humidity (56% r.h.) over saturated $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ for 7 to 14 days. Standards must also be equilibrated.

In many cases, samples need not be heated above about 700°C because: (a) exothermic peaks between 800 and 1000°C are markedly affected by pH (which varies according to dispersion and peroxidation treatments), particle size, and organic matter content (Campbell et al. 1968); and (b) high temperature peaks are qualitatively ambiguous i.e., they can be attributed to several crystalline clays in addition to short range order components (Hamblin and Greenland 1972; Fieldes and Claridge 1975). In addition, analytical time per sample is increased by an hour or more with the higher upper temperature limit, mainly because of the increased time required for the apparatus to cool.

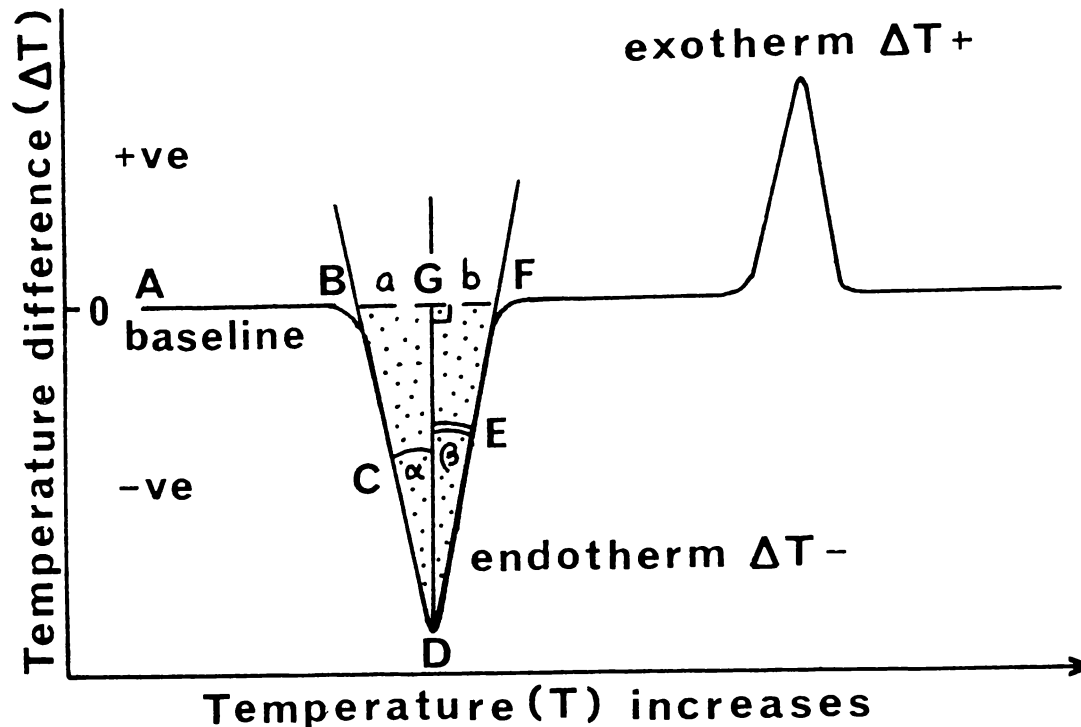


Fig. 8. Idealised DTA curve showing endothermic and exothermic peaks and the basis for determining peak area for quantification and slope ratio of the endo- or exotherm. The theory and nomenclature of the DTA method is as follows. Along the baseline AB, ΔT is 0 as no reaction occurs in the sample. At point B, roughly where an endothermic reaction begins, heat is absorbed by the sample which thus cools with respect to the reference (ΔT become -ve). ΔT increases until the rate of heat inflow into the sample equals the amount of heat absorbed by the reaction. This occurs, near the end of the reaction, at point D, after which the curve returns to the baseline at F. An exothermic reaction gives a peak in the opposite direction (i.e., ΔT is +ve).

Point D, peak temperature (although point B is actually more critical in terms of physical change to the specimen but is often difficult to position accurately); BF, peak width; DG, peak height (amplitude). The maximum rate of reaction occurs at about C, the end of the reaction at about E.

The degree of symmetry of the peak is given by the slope ratio, $\tan\alpha/\tan\beta$ ($=a/b$) (Bramao et al. 1952). The peak area (stippled) can be calculated from the relationship $(BF \times DG)/2$ (or by "counting squares" on the chart paper) and is usually denoted in $\text{cm}^2 \cdot \text{g}^{-1}$ of $<2\mu\text{m}$ clay or whole sample. For example, a 50mg sample of $<2\mu\text{m}$ clay giving a peak area of $10\text{cm}^2 = 0.5\text{cm}^2 \cdot \text{g}^{-1}$ $<2\mu\text{m}$ clay. Diagram after Tan and Hajek (1977, p. 867).

Because of the long time required to analyse a sample (2 to 3h.), samples should be selected with care. It is impractical in most cases to analyse more than about 10 to 20 samples for a project, taking into account the need to run duplicates as well.

Procedure and mineral identification

Analyses at University of Waikato are made with STONE DTA apparatus using the following instrumental settings:

Heating rate	10°C min ⁻¹
Thermocouple amplifier	300 μ V (150 x 2)
Chart speed	0.1 in min ⁻¹

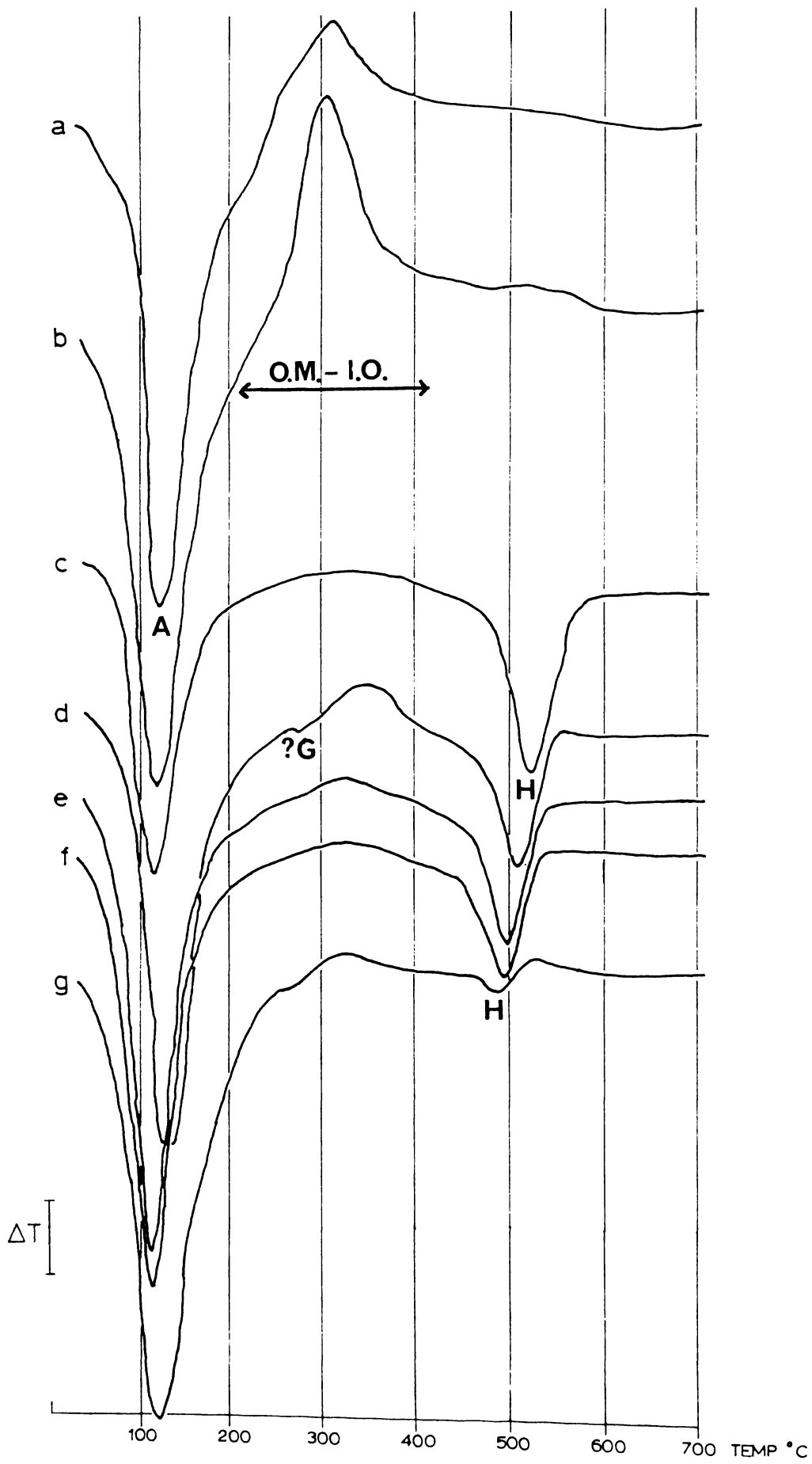
The thermocouple amplifier setting may be increased or decreased on an ad hoc basis.

Samples must be carefully and accurately weighed for quantitative analysis, and packed as uniformly as possible into the sample holder for each successive analysis to ensure valid intersample comparisons. 50 \pm 1mg samples are heated to about 1000°C using calcined (preheated) Al₂O₃ as the diluent (160mg) and reference (i.e., a 210 \pm 1mg sample of clay plus Al₂O₃ is packed into the sample holder; the reference cell contains pure Al₂O₃ and does not need to be replaced for each run). They may be heated in air, or in an oxygen or nitrogen atmosphere, which is advantageous for pyrolysis of organic matter.

Relative abundances of the chief constituents are determined from the endotherm peak areas, measured according to the criteria shown in Fig. 8 and as discussed in Mackenzie and Caillère (1975). Precise determination of the base line ($\Delta T = 0$) position may be difficult because of base line drift or displacement, or because of almost concurrent exothermic and endothermic peaks (e.g., Fig. 9h-k). In some cases, it is easiest to arbitrarily join the reaction peak shoulders (i.e., points B and F in Fig. 8) (see Tan and Hajek 1977, p. 876). Because of this potential problem, and for other reasons, experimental procedures must be maintained as constant as possible and replicate analyses carried out for quantitative work.

The most common constituents of New Zealand tephra clay materials, allophane and halloysite, are readily identified and quantified by DTA by comparing peak areas from prepared standards (available in Department of Earth Sciences) with those of unknown samples. Other minerals may be difficult to detect unless present in relatively large quantities or suitable pretreatments have been undertaken (Table 9).

Allophane (also imogolite) is identified by a low-temperature (110-120°C) dehydration endotherm (Fig. 9; Mitchell et al. 1964; Bracewell et al. 1970; van Olphen 1971; Fieldes and Claridge 1975), the area of which provides a measure of relative abundance. Water adsorbed on most clay-size materials, including organic matter, will contribute to this peak, as is evident from the sample comprising around 100% halloysite in thermogram n in Fig. 9. Consequently, the amount of allophane determined from the peak area is corrected by deducting a factor proportional to the amount of halloysite in the sample. The



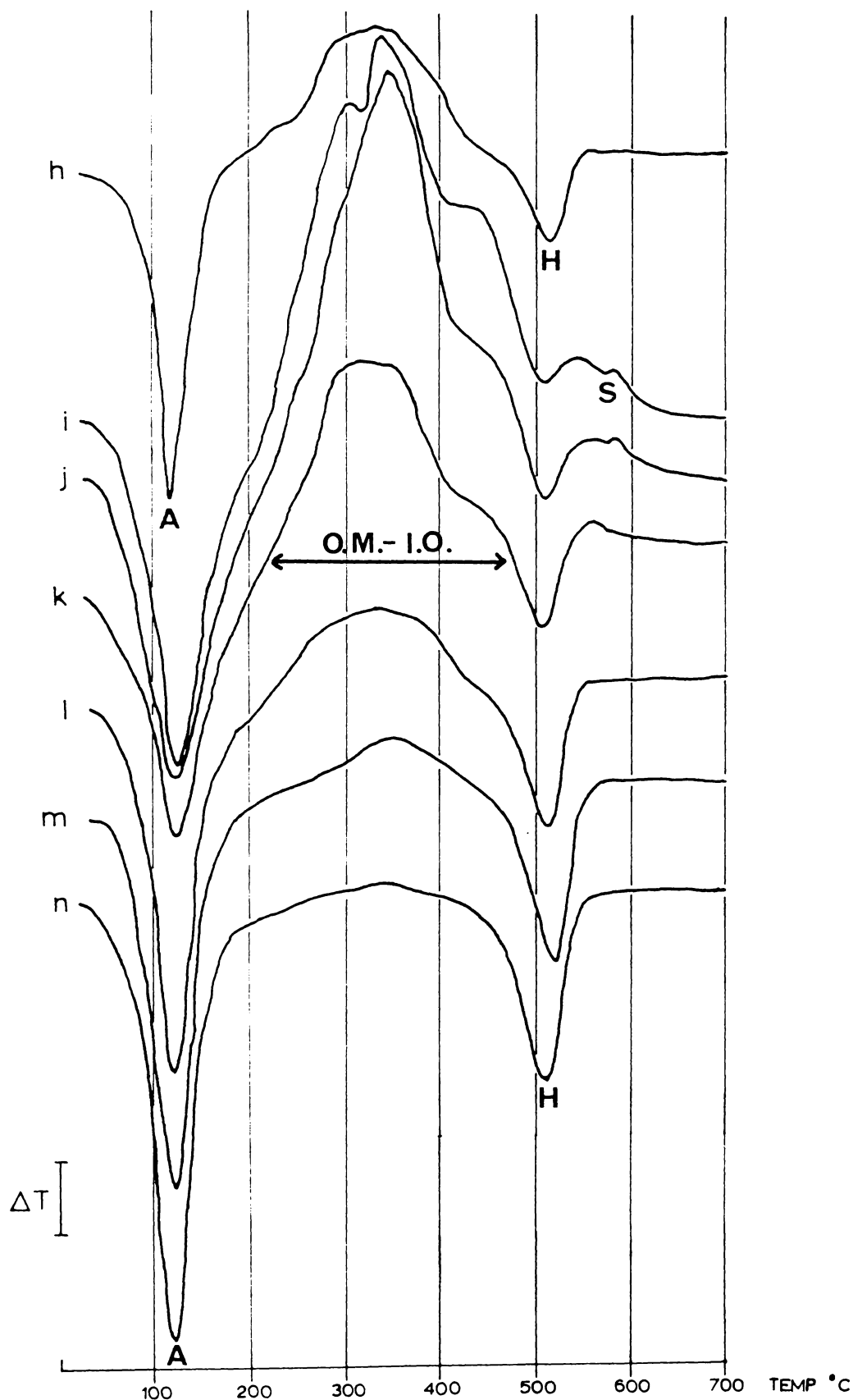


Fig. 9. DTA thermograms of some $<2\mu\text{m}</math>Mg-clay fractions from tephras in the Hamilton Basin. a-b, tephras aged $<10,000$ years; c, Kawakawa Tephra (c. 20,000 years); d-e, tephras aged c. 30,000 years; f-g, Rotoehu Ash (c. 42,000 years); h-l, composite tephras of c. 42,000 years age arranged in order of increasing depth; m-n, Hamilton Ash. The thermograms illustrate that allophane (endothems A at 120°C) and halloysite (endothems H at 500°C) predominate in most samples. Organo-mineral complexes (O.M.), possibly together with some iron oxides (I.O.), are evident as strong exotherms in traces a, b, d, h-l. A trace of ?gibbsite (endotherm ?G at 280°C) may be present in trace e but the small peak may have been largely suppressed by the O.M.-I.O. exotherm. The small endotherms at 570°C in curves i and j probably represent silica (S) phase changes. Samples were prepared and analysed as outlined in the text. After Lowe (1981, p. 193-194).$

humidity equilibrium ensures that this remains relatively constant. Alternatively, the samples and standards may be glycolated, thereby replacing the adsorbed water, and allowing the allophane content to be estimated more directly (e.g., Sand and Bates 1953; Lowe 1981).

Imogolite (and gibbsite - see below) may display an endotherm at 390-420°C (Kanno et al. 1968; Yoshinaga et al. 1973; Dudas and Harward 1975a) due to dehydroxylation. The sample usually has to be selectively purified to show this, however, but the peak can be used for quantitative estimation.

Halloysite is indicated by weak to strong dehydroxylation endothermic peaks at about 500°C (Mackenzie 1970). Most late Quaternary tephra samples from the Waikato region show peak temperatures of 470-490°C (Fig. 9). These temperatures are consistent with those for halloysite formed from volcanic ash material elsewhere (e.g., Yoshinaga et al. 1973; Dudas and Harward 1975a; Kirkman 1975; Kirkman and Pullar 1978) and suggest a low degree of crystallinity, partially related to small particle size and possibly to the presence of amorphous material (Lowe 1981). Particle shape may also influence the peak temperature.

Bramao et al. (1952) suggested that halloysite and kaolinite are distinguishable on the basis of endotherm peak symmetry, measured as slope ratio (Fig. 8) : halloysite is usually more asymmetric than kaolinite because of a low temperature shoulder arising from weakly bound hydroxyls in the structure (Churchman and Carr 1975). While the technique seemed to apply to Kauroa Ash deposits (Salter 1979), the use of slope ratio to distinguish between halloysite and kaolinite is not universally applicable because of "overlap" of values in many instances (Nagasawa 1969; Mackenzie 1970; Lowe 1981). Thermograms of halloysite from Kauroa Ash show a mean slope ratio of 2.24 (Salter 1979), whereas those of halloysite from late Quaternary tephra examined by Lowe (1981) are <2, and often <1. These variations may be attributed to differing degrees of crystallinity, particle shape or size, or the effect of organo-mineral complexes in the clay fractions (Kirkman and Pullar 1978; Lowe 1981).

Gibbsite, if it occurs in sufficient quantity, is characterised by an endothermic peak around 300°C (280-330°C) (e.g., Fig. 9d; Hsu 1977). This peak overlaps with those of iron oxides which show endotherms (Table 4) in the range of 280 to 400°C (γ -FeOOH also shows exotherms from 370-500°C) (Schwertmann and Taylor 1977). In many cases, however, overlapping peaks may be resolved by chemical dissolution pre-treatments (Table 9; Mackenzie and Caillère 1975).

"Organo-mineral" or humus-complexes (probably involving Fe or Al oxides) are indicated by exotherms between 200 and 500°C, or higher (Jackson 1969; Satoh 1976); exotherms at about 330°C and 450°C arise from complex decarboxylation and oxidation respectively (Schnitzer and Kodama 1977). The humus complexes which occur in tephra materials are influenced by the organic cycle in the soil (Lowe 1981), and may have an important role in Al-humus formation and the limitation of Al and Si coprecipitation (Wada and Higashi 1976; Wada 1977; Lowe 1981). The humus complexes appear to be resistant to breakdown (Birrell and Fieldes 1968; Wada and Higashi 1976). This is illustrated in Fig. 9 in which sample h, which was peroxidised with H₂O₂, shows only moderate reduction in exotherms compared with equivalent sample i which was not peroxidised.

Quartz/crystalline silica $\alpha \rightleftharpoons \beta$ phase changes (Mackenzie 1970) may be identifiable in DTA curves (e.g., Fig. 9i,j).

Application

Some DTA curves of tephra materials are shown in Fig. 9. These thermograms illustrate a predominance of allophane (e.g., especially curves a,b) and halloysite (curves c-n) together with humus complexes and/or iron oxides (e.g., especially curves a,b,h-k) and possible traces of gibbsite (curves d,g). A variety of traces are shown to demonstrate the diversity, particularly of peak size and position, which can be expected from tephra samples.

Electron microscopy

There are two basic types of electron microscopes and microscopy : transmission (TEM) and scanning (SEM). Generally, larger particles or aggregates are studied by SEM, and dispersions of individual clay-size particles by TEM, which has better resolution (5Å cf. 200Å) (Gard 1971). Electron microscopy must be used in combination with other techniques such as XRD and thermal (DTA) or infrared (IR) analysis because many clay mineral species show several external shapes which are difficult to distinguish. For example, the apparent transition between allophane and halloysite frequently precludes micrographic identification of a given particle belonging to one or the other mineral species (Bates 1971). Another constraint is that sample sizes are, of necessity, very small and hence possibly "unrepresentative". Further, because the specimen is exposed to a high intensity electron beam it must be analysed in a high vacuum and will be in a dehydrated form, although special environmental cells to observe "natural" forms have been used (e.g., Parsons 1974; Kohyama et al. 1978). Special procedures

were operated by Jones and Uehara (1973) to detect "amorphous" coatings on mineral surfaces too thin to be resolved by most electron microscopes. A special problem in many analytical techniques which can be accentuated in TEM and SEM studies is the formation of artifacts by sample preparation methods. Accordingly, considerable care is necessary when interpreting EM images.

Projects involving clay mineralogical analysis should normally restrict electron microscope examination to a few carefully selected samples only. Both SEM (in the School of Science) and TEM (Meat Research Institute, Ruakura), the latter to a lesser extent, are available to workers at University of Waikato.

Transmission electron microscopy (TEM)

The TEM geometry is similar to that of the optical microscope. Electrons are emitted from a hot tungsten filament at the top of an evacuated column and are propelled down the column at a constant speed by a high electric potential between the filament and the anode. The electron beam is focused by an electromagnetic condenser lens on to the sample where diffraction and scattering occur. The resultant electron beams are focused from an initial image by the objective lens (McKee and Brown 1977).

The penetrating power of the electron beam is low and TEM samples must consist of either very thin films of material or very small particles supported on thin film substrates. The examination of opaque surfaces requires a SEM or the preparation of a TEM thin-film replica which duplicates the topography of the original surface. The replica is usually made by evaporating a thin film of metal and carbon directly onto the sample surface and then dissolving the sample while retaining the metal-carbon replica to be viewed by TEM (McKee and Brown 1977). Thus in TEM work the surfaces of clay particles are not directly observed.

Advantages of the TEM are the very high resolution and great depth of field. The TEM is now capable of showing that allophane consists of extremely small hollow spherules with an external diameter of 35 to 50Å and wall thicknesses similar to those of imogolite tubes (~10-20Å), the latter usually occurring as threads or bundles of parallel fibre pairs (Fig. 10; Henmi and Wada 1976; Jessen 1977; Wada and Wada 1977; Parfitt and Henmi 1980).

An important analytical capability of the TEM is the formation of an electron diffraction pattern from a crystalline sample (similar to

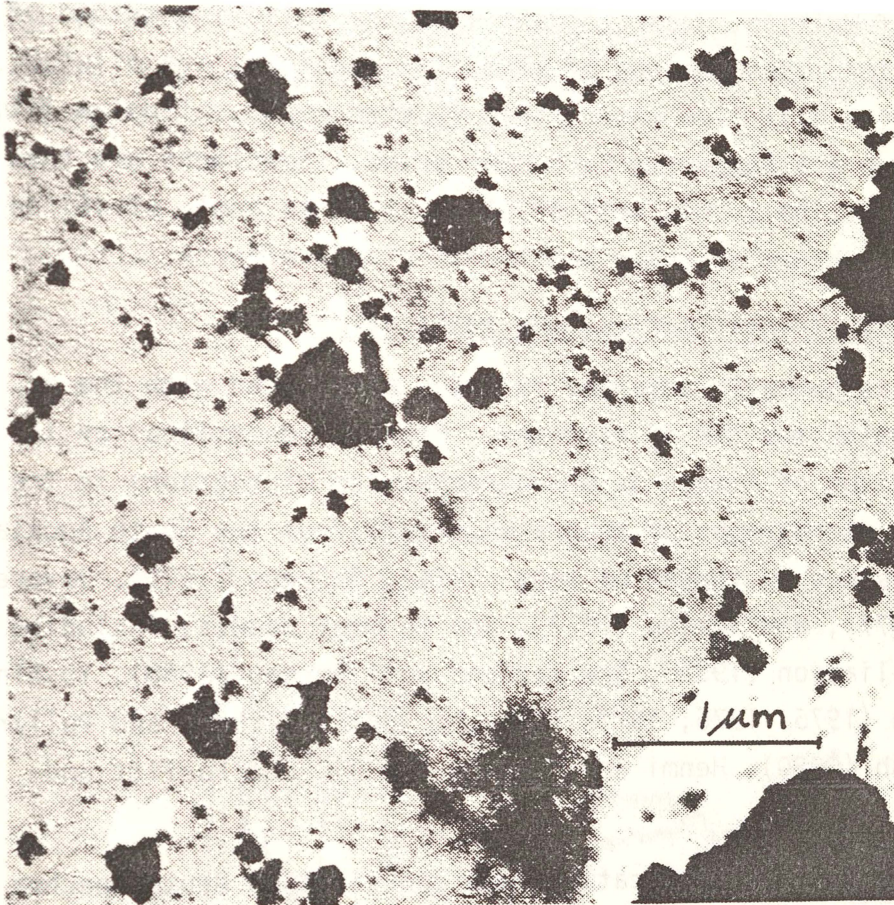


Fig. 10. High resolution electron micrograph of clay fraction containing imogolite threads and bundles and very fine allophane particles. The larger dark masses probably represent aggregates of allophane and in some cases felsic minerals. Sample is from Waihou silt loam, a freely drained soil derived from admixed tephra and tephric alluvium. Bar represents 1 μ m. From Jessen (1977, p. 116).

those obtained by XRD) which is useful for identifying particles or thin films below the detection limit of XRD (Gard 1971; Andrews et al. 1971; McKee and Brown 1977; Fripiat 1982).

Preparation

A good general review has been written by McKee and Brown (1977). At University of Waikato, Jessen (1977) used the following method of sample preparation: suspensions of $<1\mu\text{m}$ clay particles are diluted to 1% or less with distilled water, then spotted on to collodian films ("Formvar") which are supported by copper grids. Specimens are then shadowed by depositing a thin film of platinum at an angle of 45° to the specimen to enhance contrast and 3-dimensional effects.

Procedure, mineral identification, and application

Procedure is normally detailed in notes associated with the laboratory in which the TEM is operated. Mineral identification is based on comparison of images or micrographs with micrographs in the literature. TE micrographs of tephra materials from the South Auckland region are contained in theses of Hogg (1974), McQueen (1975), Davoren (1976), Fry (1977), and Jessen (1977), and in many papers, including Fieldes and Williamson (1955), New Zealand Soil Bureau (1968), Yoshinaga et al. (1973), Kirkman (1975; 1976; 1977; 1980a,b; 1981), Kirkman and Pullar (1978), McIntosh (1980), Henmi and Parfitt (1980), and Parfitt and Henmi (1980).

General reviews and applications are contained in Beutelspacher and van der Marel (1968), Bates (1971), Gard (1971), Giesecking (1975), Wenk (1976), Dixon and Weed (1977), Greenland and Hayes (1978), Whalley (1978), Sudo and Shimoda (1978), Theng (1980), Smart and Tovey (1981), and Sudo et al. (1981).

Scanning electron microscopy (SEM)

The SEM provides an enlarged, 3-dimensional view of the unmodified clay surface with high depth of focus. The SEM forms an image by scanning the surface of a sample with a finely focused electron beam (about $10^{-2}\mu\text{m}$ diameter) (McKee and Brown 1977). The high energy beam stimulates the emission of secondary electrons, back-scattered electrons, X-rays, and sometimes light photons from the sample surface. In the normal mode of scanning microscopy, the electrical signal derived from the collected secondary or back-scattered electrons is used to form a television-type image of the surface under examination. The X-rays emitted are characteristic of the elements present in the sample and can be collected and analysed (usually with a Li-drifted Si detector)

and counted with an energy dispersive multichannel analyser. Hence, in addition to particle size and morphological examination, the SEM is capable of determining the chemical identity and spacial distribution of the elements in the area under the electron beam. These data can be presented as spot mode spectral plots (Fig. 11) or as X-ray elemental maps (e.g., McKee and Brown 1977; Salter 1979). Another function is fabric study, whereby fracture planes in soil materials, for example, may be examined in 3-dimensions (e.g., Rogers 1978; Parker 1978; Ross and Walker 1982).

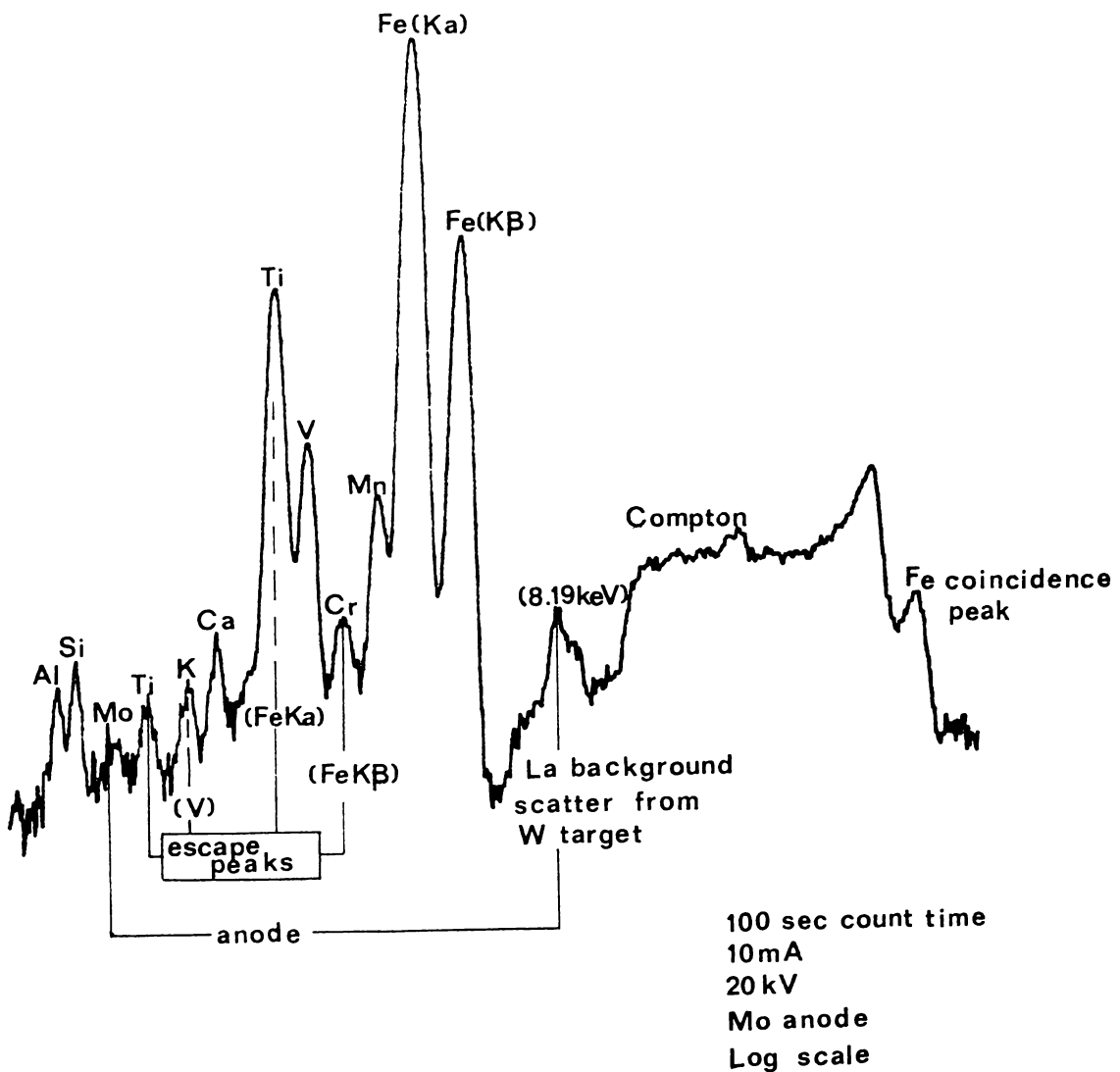


Fig. 11. Spectral plot of α titanomagnetite grains analysed by XRF (energy dispersive). From Lowe (1981, p. 253).

Additional advantages of the SEM are its great depth of field and wide range of magnifications which allows correlation of optically visible features with features well beyond the resolution of optical systems (for example, sand and silt sized grains are very easy to study). Another advantage is the ease of sample preparation, and generally the lack of problems related with artifacts (McKee and Brown 1977).

Preparation

Prolonged storage of samples may result in the morphological alteration of some minerals (especially halloysite), hence preparation for analysis should be done as soon as possible after sample collection (Lowe 1981). The nature of the study will determine in part the preparation technique, but in most cases the sample must be separated, suspended and diluted, mounted and coated. (If soil fabric is being studied, the samples must be dehydrated to preserve the particle arrangement by critical point-drying or rapid freeze-drying (McKee and Brown 1977)). Prospective users should consult the SEM operator for advice on special preparation methods which may be required to suit their particular needs. A method used by Lowe (1981) for clays at University of Waikato is as follows:

- (1) 1 to 2cm³ of the <2 μ m Mg-clay suspension fractionated for XRD analysis is diluted with 50cm³ of distilled water and subjected to ultrasonic vibrations, in either a BRANSONIC 52 tank (20-30 min.) or with a DAWES SONOPROBE with microtip (3-6 min.), to ensure disaggregation. After a settling period of several hours most of the very fine colloidal material in suspension is decanted, and the coarser residual particles resuspended in \sim 10cm³ of specially double distilled water; the suspension is briefly (2-3 min.) re-ultrasonicated. Aliquots of 1 to 2cm³ are then successively diluted in \sim 10cm³ of water (3-4 times) until the ultimate suspension appears virtually clear.
- (2) Several drops of *tert.*-Butylamine [(CH₃)₃C.NH₂] are added to a similar amount of the dilute clay suspension as a peptiser (Beutelspacher and van der Marel 1968), mixed well, and a drop of the resultant suspension mounted on a polished brass SEM stub. Disposable Pasteur pipettes are used throughout to prevent carry-over contamination of samples.
- (3) The suspension is subsequently dried, initially under a heat lamp, then in an oven for 1 to 2 h. at 90°C. This alleviates low image quality observed during trial scans and attributed to evaporation

of hygroscopic water (Bohor and Hughes 1971) by the electron beam. The mounted specimen is almost invisible, appearing at most as a slight dullness on the stub surface.

- (4) Samples are coated for 2 min. with 200 to 500Å of gold-palladium in a diode sputtering system (POLARON E5000). The coating serves to prevent a build-up of electrons on the specimen surfaces by conducting away static electricity (Bohor and Hughes 1971).

If flocculation problems occur with the sample mounted on the stub, the specimen can alternatively be mounted on a fine-mesh metal grid (as for TEM) to aid dispersion of the constituent particles (McKee and Brown 1977; C.K. Beltz, pers. comm.).

Sample stubs must be stored in a dessicator.

Procedure and mineral identification

Samples are usually tilted to 45° and subjected to accelerating voltages between 10 and 25kV. The University of Waikato SEM is a JEOL JSM-35 model.

Problems potentially likely to be encountered include:

- (1) Charging effects (regions of the image appear excessively bright, often as lines or streaks on the micrograph in the direction of scan) - this occurs when all portions of the sample do not remain at the same electrical potential, and is usually alleviated by using lower scanning beam potentials and rapid scan rates (McKee and Brown 1977).
- (2) Sample contamination - contaminants have been known to originate from distilled water used in sample suspension and dilution (Lowe 1981), hence the need for an ultra-pure water source.
- (3) Poor image focus and astigmatism difficulties when magnification exceeds 15,000 times (Lowe 1981).
- (4) Inadequate resolution of some constituent clay species because of particle aggregation (mainly with allophanic materials) and with very fine particle sizes.

Application

The SEM has been applied in various studies at University of Waikato on tephra materials (e.g., Salter 1979; Phillips 1980; Lowe 1981). Most of the papers listed for TEM, plus Borst and Keller (1969), Askenasy et al. (1973), Dixon and McKee (1974), Espinoza et al. (1975), Keller (1978), Tazaki (1979), Smart and Tovey (1981), and Sudo et al. (1981), illustrate morphological features of tephra-derived clay minerals using the SEM. Allophane normally occurs as sponge-like, globular

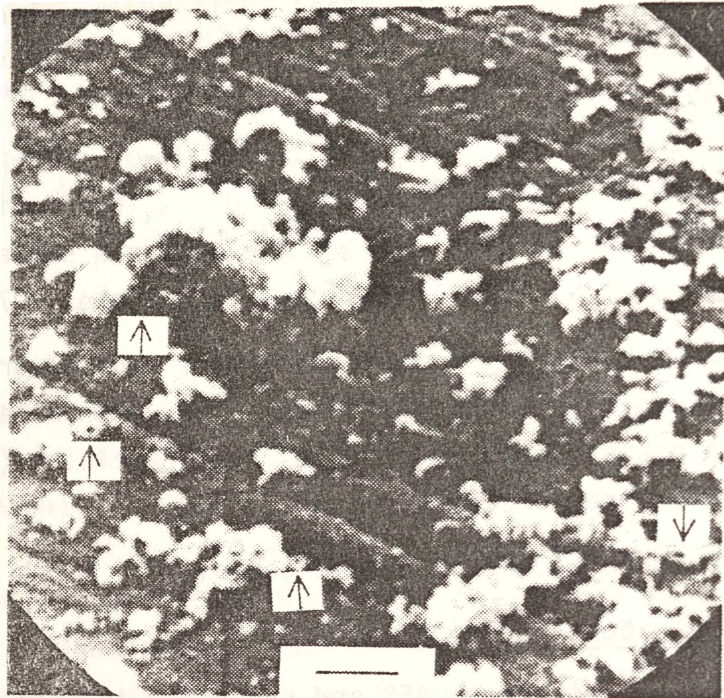


Fig. 12. Scanning electron micrograph showing sponge-like short range order material (arrowed) and fluffy aggregates and globules characteristic of allophane. Note that SEM resolution is unable to distinguish individual 'structural unit' allophane spheres which are only 35-50Å in diameter (see Figs 1 and 10). Sample is from Holocene tephra. Magnification 11,000X. Bar represents 0.9µm. Accelerating voltage 12kV. From Lowe (1981, p. 225).

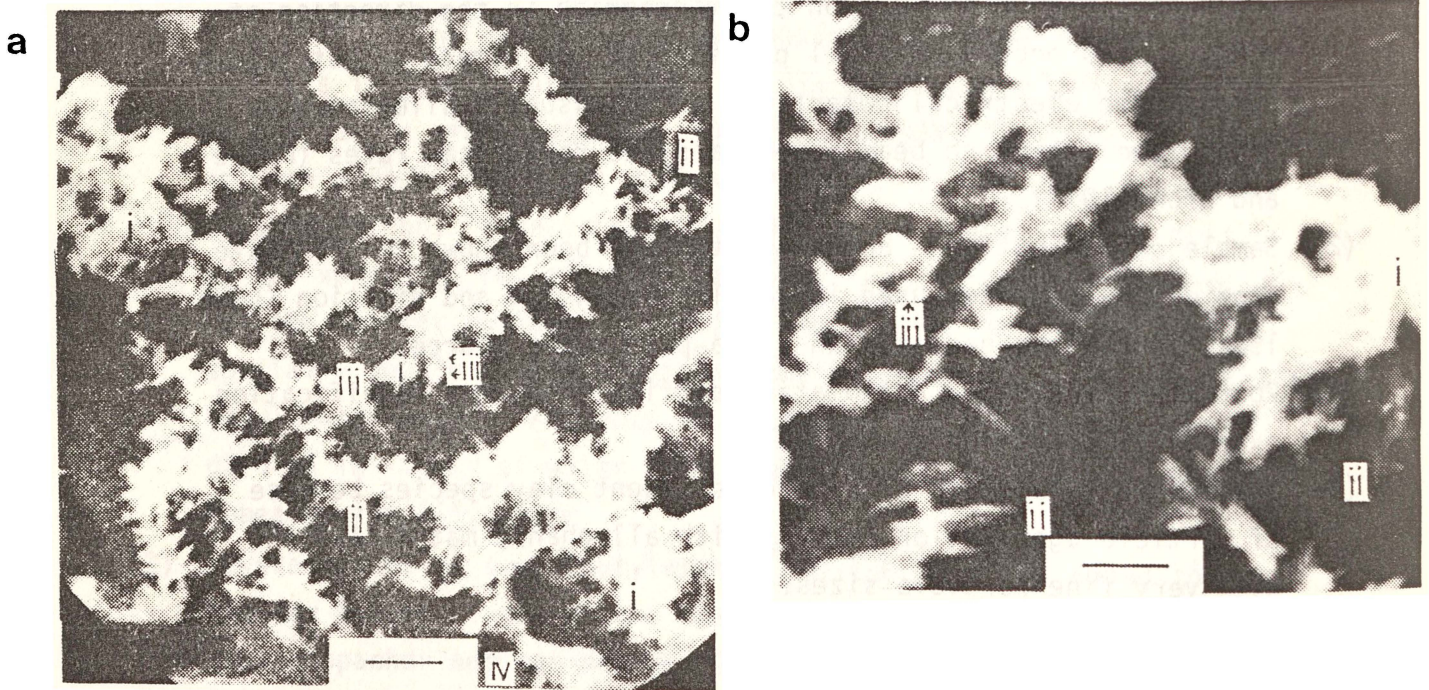


Fig. 13. Scanning electron micrographs showing interlaced halloysite tubes or laths which are frequently embedded in an "amorphous-gel" matrix (i). The tubes average 0.07µm x 0.3µm in size and occasionally appear split (ii), probably due to partial unrolling (to give "scrolls") or perhaps to interlayer separations between packets of layers along halloysite tube c-axes. The fine (0.1-0.15µm) semi-spheroidal particles (arrow iii) may represent allophane clusters, spheroidal halloysite or cross-sectional views of halloysite tubes. The gel-like platy material (iv) looks similar to the amorphous coatings in aluminosilicate systems described by Jones and Uehara (1973). Sample is from Hamilton Ash. (a) Magnification 12,000X. Bar represents 0.8µm. 23kV accelerating voltage. (b) 22,000X magnification. Bar represents 0.5µm. 23kV accelerating voltage. From Lowe (1981, p. 229).

aggregates (Fig. 12). Halloysite occurs in spherical, tubular (Fig. 13), and platy forms. Iron oxide minerals show a variety of forms (Table 4).

It must be stressed that the morphology of particles as shown by SEM (or TEM) is an aid to their identification, but not necessarily definitive. Similarly, relative abundances of species can seldom be accurately determined from SEM or TEM alone.

Sodium fluoride reactivity

Rapid (field) tests using NaF

Large OH^- release takes place when NaF is added to allophanic materials, and Fieldes and Perrott (1966) proposed this reaction as a rapid field test for allophane. The U.S. Soil Taxonomy system (Soil Survey Staff 1975) also utilises the test for classifying materials with an "exchange complex dominated by amorphous materials". Here the pH of a suspension containing 1g of soil in 50ml of 1N NaF is measured after 2 min.; a value of 9.4 or greater is taken as indicating an appreciable allophane content. Although these tests are not necessarily specific for allophane, as the reagent will react with any available Al associated with hydroxyls (Brydon and Day 1970; Wada 1977), their continuing use, in conjunction with other methods for determining allophane content, is generally supported (Rankin and Churchman 1981). The tests are used for distinguishing the B₂ horizons of podzols (which contain 'proto-imogolite' allophane) and other soils as well as in tephra-derived soils (Brydon and Day 1970; Loveland and Bullock 1975; Tait et al. 1978; Farmer 1982).

Laboratory tests using NaF

The kinetics of OH^- release are not yet clearly understood, but the reaction, summarised as $\text{M}(\text{OH})_{\gamma} + 6\text{F}^- \rightarrow \text{MF}_6^3 + \gamma \text{OH}^-$, occurs more slowly for crystalline material because of more stable structural hydroxyl groups (Kitagawa 1974), and hence has been used to differentiate well and poorly ordered inorganic materials by measurement of OH^- release at constant pH by titration under standardised conditions (Bracewell et al. 1970; Perrott et al. 1976a). Data in Brydon and Day (1970), Loveland and Bullock (1975) and Perrott et al. (1976a) demonstrate that Al-bonded OH^- (hydroxyaluminium) is more readily replaced by F^- than silica- or (free) ferric oxide-bonded OH^- . This trend is confirmed for synthetic aluminosilicate gels (Perrott et al. 1976b; Salter 1979), hence indicating that in general low $\text{Al}_2\text{O}_3:\text{SiO}_2$ ratios result in low reactivity values. As a corollary, Perrott et al. (1976b) suggested

using the reaction of fluoride to assess the Al:(Al + Si) mole fraction indirectly. Also, Shoji and Ono (1978) demonstrated close correlation between NaF(1:50) pH values and dithionate-citrate-soluble alumina constituents in Japanese tephra-derived soils.

Preparation

Samples of either whole soil or clay-size fractions ($<2\mu\text{m}$ or $<1\mu\text{m}$) can be used. The method of preparation and analysis used at the University of Waikato is essentially that of Bracewell et al. (1970) and Perrott et al. (1976a) as modified by Salter (1979) and Lowe (1981).

The $<2\mu\text{m}$ or $<1\mu\text{m}$ clay fractions separated previously for XRD or DTA are air dried, lightly ground in a mortar, and equilibrated to constant humidity over saturated $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ prior to titration. If whole soil samples are used, they must be air dried and ground to $<150\mu\text{m}$, then equilibrated (the clay content should be known to enable the reactivity of the clay fraction to be calculated later).

Procedure and mineral identification

- (1) A $100 \pm 1\text{mg}$ soil or clay sample is introduced at zero time into 20ml 0.85M NaF solution maintained at $25 \pm 0.5^\circ\text{C}$, and stirred vigorously.
- (2) The OH^- released is titrated continuously with 0.1M HCl using a Radiometer Autoburette ABull and Titrator TTT60 for a 25 min. period, so that the pH is maintained constant at 6.8, as monitored by a PHM 64 Research pH meter. The titration is best set up in a constant temperature room.

The amount of OH^- released in 25 min., reported as mmol (meq) $\text{OH}^-/100\text{g}$, is taken as the fluoride reactivity (FR) value. All samples should be analysed in duplicate or triplicate and the results averaged. Under these conditions the technique is very precise; relative deviations rarely exceed 3%, and are merely proportional to the magnitude of the fluoride reactivity values (Lowe 1981).

Conversion of the fluoride reactivity values into accurate percentages of short range order material is liable to inaccuracy because the constituents vary compositionally (e.g., Fieldes and Furkert 1966; van Olphen 1971; Henmi 1977), and the reaction with fluoride is compositionally dependant (Bracewell et al. 1970; Perrott et al. 1976a).

Application

Kirkman (1975) applied the technique to Holocene and late Pleistocene tephras in central North Island and showed that the fluoride reactivity

values reflect the gradation from allophane- to halloysite-dominated clay (<1 μ m) fractions. The Holocene tephras generally contained allophane, and hence highly reactive clay fractions (1000-2000 mmol OH⁻/100g clay), whereas the late Pleistocene tephras, with mainly (7Å) halloysite clay fractions, exhibited much lower reactivity values (100-600 mmol OH⁻/100g clay). Similar results are described by Klages (1978) for tephras in U.S.A..

Reactivities of <2 μ m clay fractions from late Quaternary tephras in the Waikato region (Lowe 1981) range from 185 to 1152 mmol OH⁻/100g and generally match those of Kirkman (1975) except that the very high values reported for his Holocene tephras do not occur. Comparison of the reactivity values with DTA estimates of allophane and halloysite content showed good correlation for sites under free-draining weathering conditions (Lowe 1981).

For the older halloysite-rich Kauroa Ash beds, Salter (1979) reports relatively low reactivity values (95-185 mmol OH⁻/100g), consistent with a low content of short range order aluminosilicate material. Some of the reactivity in this case was attributed to the fine particle size (see also Campbell et al. 1977) and hydrated status of the halloysite material.

Parfitt and Henmi (1980) used NaF reactivity, together with other tests, to show that imogolite is more ordered than allophane and has fewer defect sites and broken bonds where F can react with Al to break up the structure.

Comparison of the Fieldes and Perrott (1966) field test with the laboratory-determined reactivities shows excellent correlation (Lowe 1981). The field test is as reliable as, though less precise than, the laboratory procedure for determining the relative abundance of allophane (or rather the presence of active Al-OH groups) in whole soil samples under most site conditions.

Modified versions of the NaF reactivity field test are currently under trial in the Department of Soil Science, Lincoln College.

Chemical dissolution analyses

Short range order clay minerals have a large specific surface area and high chemical reactivity. These materials are thus more sensitive to chemical dissolution than crystalline clay minerals and dissolve differentially according to their elemental composition (Wada 1977). Thus, selective chemical dissolution can be used for determination of short range order clay constituents. The dissolution

of Al, Fe, and Si in various clay and humus constituents by treatment with different reagents is given in Table 9. This shows, for example, that allophane is dissolved by treatment with hot 0.5N NaOH or oxalate-oxalic acid (Tamm's solution) but not with dithionite-citrate or 2% Na₂CO₃ solution. However, because dissolution with one reagent only has some limitation in the specificity of the reaction, simultaneous characterisation of the dissolved material is recommended. This is

Table 9. Dissolution of Al, Fe, and Si in various clay constituents and organic complexes by treatment with different reagents. References detailing the extraction methods can be found in Wada (1977, p. 615; 1978, p. 152). After Wada (1978, p. 152).

Element in: Specified component and complex	Treatment with:				
	0.1 M Na ₄ P ₂ O ₇	Dithionite -citrate	2% Na ₂ CO ₃	0.15-0.2 M oxalate- oxalic acid (pH 3.0-3.5)	0.5 N NaOH
Al in:					
Organic complexes	good	good	good	good	good
Hydrous oxides					
Noncrystalline	poor	good	good	good	good
Crystalline	none	poor	poor	none	good
Fe in:					
Organic complexes	good	good	none	good	none
Hydrous oxides					
Noncrystalline	poor	good	none	good	none
Crystalline	none	good	none	none	none
Si in:					
Opaline silica	none	none	poor	none	good
Crystalline silica	none	none	none	none	poor
Al and Si in:					
Allophane-like	poor	good	good	good	good
Allophane	poor	poor	poor	good	good
Imogolite	poor	poor	poor	good-fair	good
Layer silicates	none	none	none	none	poor-fair

carried out typically by difference infrared spectroscopy (i.e., comparison of the IR spectra of the material before and after treatment), or from dissolution kinetics, whereby the steady-state portion of the dissolution-time curve is taken to indicate a limited attack on crystalline material (Wada 1977). Hodges and Zelazny (1980) report a procedure based on the loss in weight of a sample after it had been selectively dissolved by ammonium oxalate or sodium hydroxide as a measure of the non-crystalline material content of the sample. A differential XRD method involving selective dissolution treatment for identifying some iron oxide minerals is discussed by Schulze (1981) and Schwertmann et al. (1982).

Recent studies by Russell et al. (1981) and Parfitt and Henmi (1982) have demonstrated that for clays from predominantly andesitic tephras the acid-oxalate dissolution and infrared spectroscopy methods showed good agreement in determining allophane content where the Al:Si ratio of the extract is near 2.0 (Table 8, p.36). The methods compared

IR absorbance at 348cm^{-1} (characteristic of allophane and imogolite) with %Al and %Si extracted by acid-oxalate.

If the non-crystalline material content of samples is to be related to soil systems, Hodges and Zelazny (1980) recommend that whole samples be used for analyses, rather than only the $<2\mu\text{m}$ fractions. (See also method-related studies by Hetier et al. (1977) and Higashi and Shinagawa (1981)).

Useful references for dissolution methods and applications include Jackson (1969), Wada (1977), Dixon and Weed (1977), Brown et al. (1978), Theng (1980), Hodges and Zelazny (1980), and Parfitt et al. (1983), and papers cited therein.

Surface area measurements

Specific surface areas can be measured for allophanic clays using various adsorbates such as glycerol, ethylene glycol monoethylether, ethylene glycol, and water (Wada 1977), and low temperature nitrogen adsorption (Paterson 1977).

Specific surface area calculations for allophane range from 800 to $2210\text{m}^2/\text{g}$ using 43 and 50\AA as the inner and external diameters of the "spherule unit" respectively, and a density of 2.6 to $2.65\text{g}\cdot\text{cm}^{-3}$ (Espinoza et al. 1975; Wada 1980; Parfitt and Henmi 1980). Thus measurement of surface area can provide an estimate of allophane content.

Ethylene glycol and water adsorption methods used by Allbrook and Codlin (1981) to estimate allophane contents showed good correlation with determinations based on Tamm's acid-oxalate dissolution of Al, Si, and Fe, and OH^- release by titration to pH 6.8 after addition of NaF. Another study, by Claridge and Fieldes (1975), applied ethylene glycol retention measurements to particle morphology studies of allophane and halloysite.

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APPENDIX B

Comment:

Lowe, D.J.; Green, J.D. 1987: Origins and development of the lakes. Chapter 1 in : Viner, A.B. ed. Inland waters of New Zealand. Wellington, New Zealand Department of Scientific and Industrial Research: p.1-64.

This chapter was prepared in part for the International Society for Theoretical and Applied Limnology (S.I.L.) Congress held in Hamilton, New Zealand, in February 1987. The chapter is not reproduced here because it is largely peripheral to the thesis. However, part of the chapter highlights the role, actual and potential, of tephrochronology in studies on New Zealand lakes. It also identifies those lakes likely to contain long records of volcanic activity in the form of lacustrine tephras. These lakes are therefore potentially valuable sites for future coring programmes investigating both tephrostratigraphy and palaeolimnology.

Palaeolimnological studies in New Zealand are briefly reviewed. These have begun only in recent years, and most have been done on North Island lakes. The studies are implemented by well-dated tephra layers that provide a time-stratigraphic framework in the lake sediments.

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