Anthony Peter Walters Hodder

THE USE OF PHYSICAL AND CHEMICAL TECHNIQUES IN THE IDENTIFICATION OF TEPHRA (VOLCANIC ASH) IN THE NORTH ISLAND, NEW ZEALAND

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ABSTRACT

Field evidence is no longer adequate to resolve the problems of tephrostratigraphy, particularly in areas far from the likely volcanic source. In such areas the deposits are thin, and consequently more strongly weathered, as they are more or less continually involved in soil development processes. Under such conditions lithologic resemblance of a given ash to the same material closer to source may be lacking. The identification and correlation of tephra in the Waikato Basin of the North Island of New Zealand is one such example. These tephra form the parent materials of the agricultural soils of the region, and are at considerable distances from the likely sources, these being the Egmont volcanic centre in Taranaki, the Okataina volcanic centre in the Bay of Plenty, and the Tongariro and Taupo volcanic centres in the central North Island. In particular, this thesis sought to resolve the problem of the identity of the Tirau and Mairoa Ash beds; whether they are inherently different, or whether they merely represent the products of pedogenesis of the same parent materials under differing weathering conditions.

In the resolution of this problem, many laboratory techniques were exhaustively and systematically investigated, the methods being reviewed and extended in their applicability and their sensitivity being improved where possible. Physical properties of the rhyolitic glass associated with the samples that were found to provide useful data were refractive index, density, and magnetic properties.

(a) Refractive index: This classical method of determination of a parameter indicative of bulk composition was improved an order of magnitude over that typical for petrologic investigation by the development of a thermal variation method. The increased sensitivity so obtained enabled the use of this parameter in the correlation of glass shards.

The use of refractive index for this purpose had previously been abandoned because of its lack of sensitivity.

(b) Specific gravity: The determination of density was investigated by gradient techniques using solutions of acetone in bromoform. The natural variation in density exceeded the precision of the technique, but in spite of this the method was shown to have some application in the solution of tephrostratigraphic problems.

(c) Magnetic properties: Simple methods based on the Guoy magneto-balance were found to provide useful information on the magnetic susceptibility of glass, and were found to be particularly useful in the attempted correlation of the Aokautere and Teviotdale Ashes. More generally, the magnetic susceptibility was found to be a ready method of assessing the ferrous contents of glasses.

In addition to these physical methods the glasses were analysed chemically. As well as these techniques, use was made of mineral assemblages, particularly of felsic minerals; and of the relative proportions of rhyolitic and andesitic glass. The former of these two glasses is easily extracted physically, but the existence and quantitative estimation of andesitic glass, being difficult to determine directly, was determined indirectly by infra-red spectroscopic techniques. The relative proportions of these two glasses was itself found to be a parameter of some importance in correlation work, and has been used in conjunction with a first-order kinetics model for the weathering of glass to allophane to provide approximate dates for the samples.

While the object of this thesis was to review and develop physical, chemical, and mineralogical techniques of use in tephrostratigraphy, the techniques were used to solve some specific tephrostratigraphic problems, in particular, problems involving thin beds in the Waikato region, and some problems in long-range tephra correlation. These specific problems investigated were:

(a) The Tirau-Mairoa Problem: There has been a long-standing debate over whether the ash beds that make up the Tirau Ash and Mairoa Ash sequences are the same or whether the parent materials differ. From the information derived by the use of the techniques described above, the two ash sequences were found to differ: the Mairoa Ash sequence being both older and more andesitic in character than the Tirau Ash sequence. The Mairoa Ash sequence was considered, as a result of this work to underlie and possibly interdigitate with the Tirau Ash. Samples from sites between the type localities of the two sequences showed a composite character. Chemical analysis of the rhyolitic glass and refractive index data suggested, that at least in some localities, the Mairoa Ash was contaminated with material from the underlying Oruanui Formation.

(b) Oruanui-Aokautere Correlation: The Oruanui Formation is a widely distributed bed or sequence of beds in the central North Island and had been previously tentatively correlated with the Aokautere Ash in the southern part of the North Island. Application of the techniques developed in this thesis confirm this correlation specifically between the Oruanui Ash and the Aokautere Ash.

(c) Oruanui-Teviotdale Correlation: The Teviotdale Ash of North Canterbury is believed by some to be correlative with the Oruanui and Aokautere Ashes. The magnetic and chemical properties, however, suggested that the Teviotdale Ash represents a separate eruption.

The soils developed on Kaharoa and Taupo Ashes show elemental deficiencies when exploited for agriculture. Soils developed on similar rhyolitic tephra of greater age show no such deficiency. Accordingly, the relative merits of such deficiencies being caused either by pedogenetic factors or by initially low amounts of the microelements in the parent materials was investigated. In the case of selenium, most of this element potentially available is to be found in the glass. Analysis of the glasses from the various ashes showed little variation in selenium content, and the results obtained bore no relationship to the agricultural selenium status of the derived soils. From this it was inferred that the selenium deficiencies are pedogenetic in origin, being caused principally by the short length of time available for the leaching of selenium from the glass. In that cobalt tends to be enriched in the more mafic minerals rather than in the glass, deficiencies of this element in the soils derived from the Kaharoa and Taupo Ashes may be rather more inherent, since the parent tephra concerned contain but small amounts of these minerals.

GENERAL INTRODUCTION

The status of research in tephrostratigraphy is such that field evidence no longer suffices in the identification and correlation of tephra. This is because work is increasingly concerned with thin or heavily weathered deposits which may bear little lithologic resemblance to their parent materials close to source. Accordingly, the research for this thesis has centred on the study of various physical and chemical techniques available in the solution of such problems, with the aim of assessing their worth in this regard. In the course of such a study it has been found possible to modify some existing techniques and further increase the extent of their applicability, in some cases to the point at which the natural variation of the parameter exceeds the determinative error of the technique.

The laboratory techniques used fall into two broad categories: methods involving the whole tephra unit or derived soil and those which deal with some property of a diagnostic mineral. Of the first type, mineral assemblages are an important and traditional example. Usually, attention is concentrated on the presence and relative proportions of mafic minerals; emphasis is here, however, placed on the relative proportions of the felsic minerals, quartz, feldspar, and glass. Two types of glass are recognised: a glass of low density, occurring abundantly in rhyolitic tephra and being of composition similar to the rock rhyolite; and a glass of greater density, virtually inseparable physically from feldspar and quartz, but whose presence and proportion may be inferred from infra-red spectroscopic techniques. This latter glass is more abundant in tephra of presumed andesitic origin wherein the relative proportion of rhyolitic glass is very low. The relative proportions of these two glasses is a function of the rhyolitic character of the tephra and forms the basis of a crude method of dating the deposits.

The rhyolitic glass itself, being of undoubted volcanic origin, may be considered a diagnostic mineral worthy of detailed study. Properties of the material that lend themselves to investigation are the density, refractive index, and magnetic susceptibilities as well as chemical composition. Determinative methods and the applicability and limitations of such techniques are discussed in detail.

The material of this thesis is described broadly in three sections. The first is an introduction to the volcanic setting in New Zealand, and describes the specific tephrostratigraphic problem that the research has sought to solve. In particular, the historical development of ideas on the identity of the Tirau and Mairoa Ash sequences is described. This particular problem is typical of those for which field criteria are no longer adequate to achieve a solution. In this section, too, details of sample collection and sites are given.

The second section is devoted to the review and development of the various techniques. Separate chapters are concerned with the extraction and estimation of the glasses, the correlation of tephra on the basis of mineral assemblages, density techniques, magnetic susceptibilities and ferrous contents of glass, refractive index and water contents of glass, and chemical analysis. In the discussions within these chapters, the applicability of the various techniques is assessed with reference to possible differences between the two ash sequences.

The final section reviews the use of the techniques collectively as far as the Tirau and Mairoa Ash sequences are concerned. In an attempt to assess further the techniques' applicability, they are used to gain information on the areal extent of the Oruanui Ash, specifically to determine whether the Oruanui Ash, identified as such near Taupo and in the Waikato district is correlative with the Aokautere Ash in the Manawatu and the Teviotdale Ash of North Canterbury.

Since the tephra-derived soils of New Zealand are of agricultural importance, it is fitting that the observed elemental deficiencies in the soils should be considered in relation to the elemental composition of their parent glasses. This, together with comments on the nature of such geochemical imbalances forms the closing chapter of this section.

Finally, the broad results of the investigation, together with suggestions of further problems where the techniques described might be useful, are given. Some speculation on future developments in the subject are included.

To assist the reader in recalling the nature of specific samples and tephra units, a sample concordance is provided at the rear of the volume, following the bibliography.

PART ONE

THE GEOGRAPHIC SETTING

CHAPTER 1: VOLCANIC CENTRES AND TEPHRA DISTRIBUTION

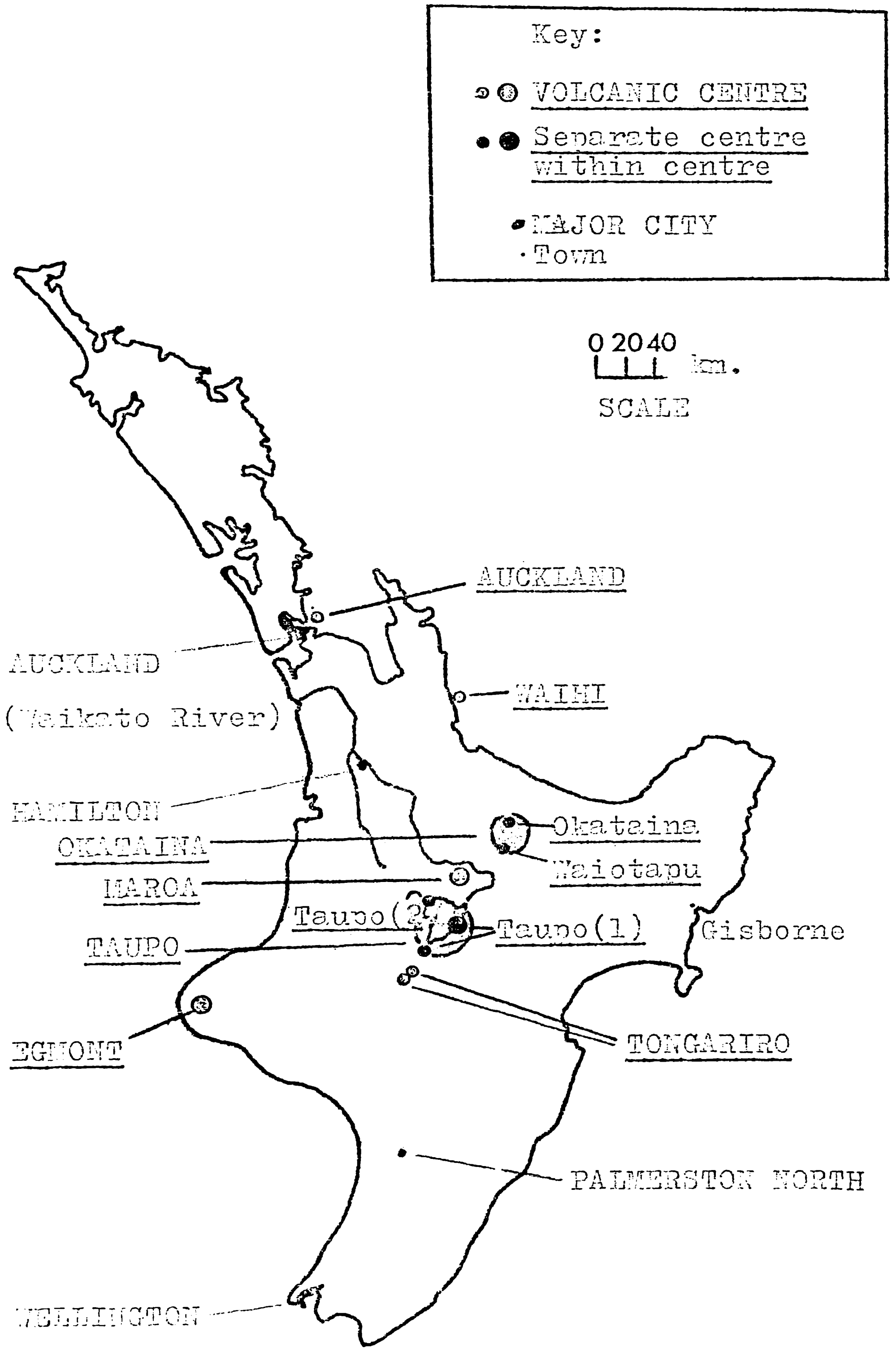
§1-1: Introduction:

Much of the landscape of the North Island of New Zealand is mantled with tephra. In many areas Pleistocene and Holocene tephra is the parent material for present-day soils. The principal sources of this volcanic material are shown on the locality map (Fig. 101). Of these the Okataina, Taupo, and Maroa volcanic centres have erupted material primarily of rhyolitic composition. The air-fall deposits from these eruptions have been the principal parent material for soils in the Bay of Plenty region. To the west and south of the centres referred to above lie the Egmont and Tongariro Centres respectively: the deposits from these sources have been largely andesitic. Typically, andesitic tephra are of smaller extent than their rhyolitic counterparts, although as is indicated later in this chapter, some older andesitic tephra appear to be rather widespread in distribution. As would be expected the land surrounding the andesitic sources is mantled with soils developed from this parent material.

At sites further away from the volcanic sources, the amount of tephra contributing to soil development is rather less. Because of the small volume of material deposited, the soil-forming processes in progress before deposition of the tephra may have continued largely unhindered. This has the effect of making the tephra less distinctive in the stratigraphic profile, and also of making its correlation with occurrences in thicker section closer to source much more difficult. This, then, is the essence of the stratigraphic problems to which the techniques developed in this thesis are applied. Such difficulties are compounded by the possibility of the incorporation of tephra from different sources in a soil distant from proposed sources, and this possibility too is explored.

FIG. 101

Locality map of volcanic centres, North Island New Zealand (after Pullar, Birrell, and Heine (1972))



Notes

Most of the tephra contributing to Tirau Ash is believed to originate from the Okataina centre

Taupo Pumice originates from Taupo 1, Oruanui Ash from Taupo 2

The principal region under study for this thesis is the Waikato-Hauraki region and the northern portions of the King Country. The location of these regions of the North Island of New Zealand are shown in relation to county boundaries in Fig. 102. Also on Fig. 102, these regions are shown in relation to principal settlements within the South Auckland Land District. Comparing Fig. 101 with 102, it may be seen that these regions are at almost equal distance from the Okataina and Egmont volcanic centres, and this should be borne in mind when the discussion of tephrostratigraphic problems in the area is presented.

The application of the physical and chemical techniques described in subsequent sections of this thesis are made in connection with the Tirau and Mairoa Ashes, principal soil-forming tephra in the Waikato-Hauraki and King Country regions. As a prelude to the discussion of these tephras, it is useful to consider the principal tephra erupted from the various centres, and this is given in the next section.

S1-2: The Okataina Volcanic Centre:

The Okataina volcanic centre was the source of a considerable number of Pleistocene and Holocene eruptions, the oldest of which is some 40,000 years old. With the exception of the historic Tarawera eruption, the tephras from this centre are rhyolitic in mineralogical composition. Field characteristics of the more recent eruptives from this centre have been described in detail by Vucetich and Pullar (1964) and with particular reference to the Waikato region by Pullar (1967). The older eruptives (older than 15,000 years) are similarly described by Vucetich and Pullar (1969) In Table 1-1 the names, ages and sources of these tephra are indicated, together with their persistence into the Waikato-Hauraki region on the basis of field criteria.

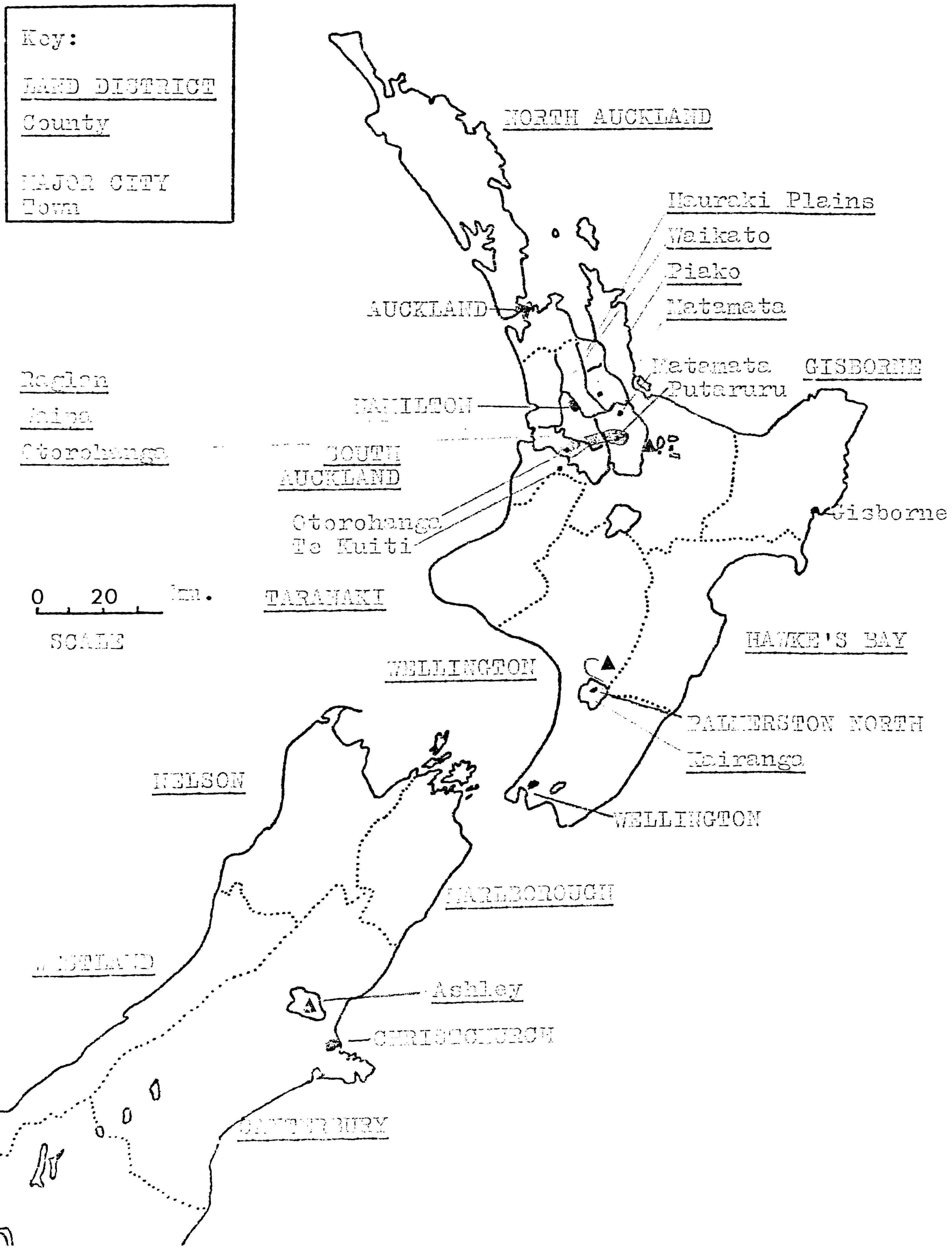
From the table it is clear that in the last twenty thousand years, Rotoma and Rotorua Ashes are likely to be the parent ashes for soils in at least the eastern Waikato-Hauraki region and are underlain by the

FIG. 102

Location of principal region under study in relation to county boundaries and New Zealand land districts

Principal area under study indicated thus: ▨

Other areas from which samples were taken for more limited investigation indicated: ▲



telescoped column of Okareka Ash and Te Rene Ash on Oruanui Formation. The Oruanui Formation has its cource near Taupo (the Maroa Volcanic

TABLE 1-1: Tephra from the Okataina Volcanic Centre

Tephra	Age(1) (t x 10^3/yr)	Source	Composition (a)	Occurrence relative to Waikato region	Extent of soil development (b)
Tarawera) Rotomahana) Mud (c))	0.09	Mt Tarawera	A	Historic eruption: no sighting recorded	
Kaharoa (d)	1.07	Mt Tarawera	R	Insignificant	
Rotoma (e)	8.0	East Lake Rotoma	R	Possibly as far as Morrinsville	
Rotorua (e)	13.5	Lake Tikitapu	R	Identified to Tirau	
Rerewhakaiitu	14.7		R	No evidence	
Okareka	19 (f)	Mt Tarawera	R)	Persists as a single bed into Waikato	(Weak
Te Rere	-	Mt Tarawera	R)		(Weak
(Oruanui	20)(g)				
Mangaone	27(2)	L. Rotoma and Mangaone	D(3)	Probably only local patches	Extensive (h)
Rotoehu (i)	ca 42	Mt Tarawera	R	At least to Parawera (j)	Significant

References: Unless otherwise indicated data for tephra younger than Rerewhakaiitu after Pullar (1967) that for older tephra after Vucetich and Pullar (1969)

(1) Pullar and Heine (1971)

(2) Healy et al., (1964)) in Vucetich and Pullar (1969)

(3) Ewart and Healy (1965))

Notes: (a) A is an andesitic assemblage, R rhyolitic and D dacitic.

(b) The extent of soil development is an indication of the time interval between the named tephra and that which overlies it and undoubtedly a function of the weathering regime at the time of deposition. Data for tephra younger than Rerewhakaiitu after Vucetich.

(c) Sampled at Waimungu Road and used as a sample of known age.

(d) Sampled at Ash-Pit Road (site 10) and used as a sample of known age.

(e) Sampled at Tapapa Road (site 9) and used as a sample of known age.

(f) Radiocarbon ages are greater than this, but the tephra is younger than Oruanui Formation itself radiocarbon dated to reasonable precision as 20.7 thousand years.

(g) Oruanui Formation is not an eruptive deposit from the Okataina centre, but is similar to Okareka Ash in field appearance and allegedly these two beds together with Te Rere coalesce in the Waikato district.

(h) There appears to be an appreciable interval of time between the eruptive episodes that make up the tephra, sufficient to give 'red' weathering in some localities.

(i) This tephra is considered the end of an eruptive sequence involving the Haroharo massif. There is a significant time interval before deposition of Mangaoni Lapilli, as evidenced by the degree of soil formation and the difference in physico-chemical parameters (see Chapter 6).

(j) Rotoehu tephra is sufficiently distinct in the eastern Waikato to be used as a lower marker bed to establish stratigraphic relationships, but see text.

centre), but since it is invariably associated with eruptives from the Okataina centre, at least in the area under study, it is convenient to include it in the discussion of these eruptives. The Oruanui Formation is characteristically pumiceous and is usually a lighter colour than overlying ashes; Vucetich and Pullar (1969) noted that it lacks the structure of a buried soil, which is of assistance in its identification, and described its occurrence in the eastern Waikato district as:

> ".... on the Mamaku Plateau the bed is pale brown and is sandy loam in texture with a fine white ash base with occasional chalazoidites and numerous small manganese concretions; at Parawera and Okoroire in the Waikato district it assumes a pale yellow colour and has a distinct basal layer of white ash ...."

It is this basal layer of white ash that makes the Oruanui Formation a very useful stratigraphic marker bed and as will be indicated in the next section, gives a maximum age to the base of the Mairoa Ash sequence.

Rotoehu Ash is another useful marker bed in the Waikato-Hauraki region, and appreciable thicknesses persist into the region, as much as 90 cm at Arapuni for example. The character of this ash-member in the locality under study is described by Vucetich and Pullar (1969) as:

> "The Rotoehu Ash always has distinctive shower bedding at the base and in many places has a thin layer of loose sand at the contact with older deposits ..... west of Arapuni and in the Tirau and Horohoro localities, the basal layer is pale yellow compact sand and projects as a jutting ledge."

S1-3: The Egmont Volcanic Centre:

The stratigraphy and chronology of the eruptives from Mount Egmont have been recently reviewed by Neall (1972). The tephra deposits from this source are in marked contrast to those from the Okataina Centre both in thickness and areal extent; Neall states that:

> "rhyolitic volcanicity is generally violent in contrast to the gradual build-up of composite andesitic cones and the associated eruption of comparatively small volumes of tephras."

A generalised stratigraphic sequence of material erupted from Mount Egmont is given in Table 1-2. The tephra of largest areal extent and thickness are the Oakura and Okato Tephras which, together, are identified with the "Egmont shower" earlier described by Grange and Taylor (1933). The combined isopach map for the two tephras after Neall and the distribution of the "Egmont ashes" of Gibbs (1968) is given in Fig. 103. Both of these tephra are highly allophanic and friable, the texture being a coarse sandy clay loam near the source and a fine sandy clay loam at greater distances. Although the time-span for deposit of the tephras is not known, radiocarbon dating indicates a maximum age for the Oakura Tephra as seven thousand years. Of its distribution and source Neall (1972) wrote:

> "The formation extends as far north as Waitara, although at this distance the unit is obscure. It is the youngest widespread ash and mantles most land surfaces in Taranaki, outside Egmont National Park...... The distribution shows a broad lobe towards New Plymouth suggesting a southerly vector influenced deposition."

The distribution and source of the underlying Okato Tephra is similar on the basis of the isopach maps of Neall (1972). Radiocarbon dating of charcoal from material above and below this latter tephra suggests a minimum age of twelve thousand years and maximum age of sixteen thousand. There appears to be appreciable time interval between the deposition of these and older tephra and this may represent the limit in age for contribution of Egmont-derived material to the Mairoa Ash sequence, since as is indicated in the field descriptions of Sec. 2-2, the Mairoa sequence appears to be bounded below by Oruanui Ash dated at twenty thousand years.

FIG. 103

Isopach map for combined Oakura and Okato Tephras (Neall, 1972) with the distribution of the Egmont and Mairoa Ashes (Gibbs, 1968)

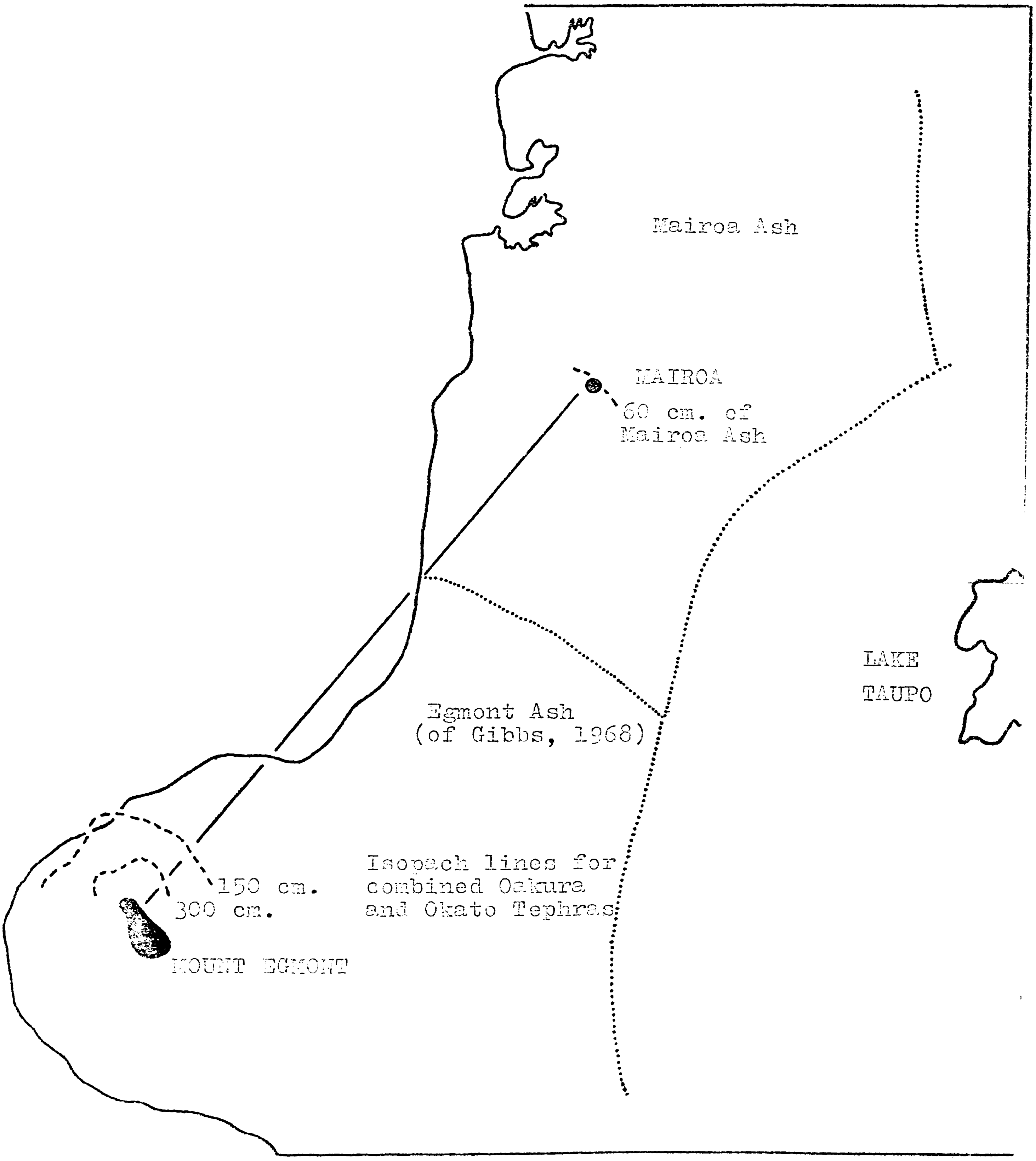


TABLE 1-2: Tephras from the Egmont Volcanic Centre (after Neall (1972))

Formation	Members	Age ($t/10^3$ yr)	Thickness (T/cm) (a)	Eruption Type
Tahurangi	Tahurangi Ash	0.22	10 (b)	small air-fall
Burrell	Puniho Lapilli 2	0.32		flow
	Puniho Lapilli 1		- (b)	small flow
	Burrell Lapilli			small air-fall
	Burrell Ash		- (b)	small flow
Newall	Waiweranui Ash	0.47		small fall
	Waiweranui Lapilli		60 (b)	small flow
	Newall Lapilli		80 (b)	moderate flow
	Newall Ash		20 (b)	probably flow
	Un-named ash beds			
Inglewood Tephra		5.0 (c)	- (b)	airfall
Korito Tephra			- (b)	airfall
Oakura Tephra (d) (un-named ash basal lapilli)		6.97 ± 0.08	125	airfall
Stent Ash (d)		6.97 ± 0.08	10	
Okato Tephra (d) (un-named ash Ahuahu lapilli)		12 - 16	100	airfall
Saunders Ash		16.1 ± 0.2		probably flow
(e)				
Carrington Tephras		3.6 (f)	75	fall
Koru Tephra	Koru Ash			
	Koru Lapilli		20	fall
Pukeiti Tephra			10	
Weld Tephra	Weld ash	(Not present at site)		
	Weld tuff			
	Un-named ash			
	Un-named lapilli			
New Plymouth Ashes and buried soils		70 - 100 (g)	225	

Notes: (a) relative to Oakura Tephra thickness, from type section for Oakura and Okato Tephras N108/593842.

(b) These were essentially 'local' eruptive deposits, frequently of the flow or "nuée ardente" type. The thickness quoted are the maximum observed in the region studied by Neall, and are suggestive of restricted lateral distribution.

(c) "The unit mantles the present-day topography and is probably not older than about 5,000 years" - Neall.

(d) These tephras are believed to constitute the "Egmont shower" of Grange and Taylor (1933).

(e) Probably the lower chronological limit to the contributing ashes to the Mairoa sequence.

(f) Radiocarbon dating not possible because of the absence of charcoal. Evidence from buried soils suggests a time interval of 20,000 years, so that the base of the deposit is not younger than 36,000 years, and this assumes no significant time interval between the depositions of the uppermost member of the Carrington Tephras and the Saunders Ash.

(g) Dates estimated on the basis of the formation's upper contact with the Rapanui Formation and its lower contact with the Ngarino Formation.

S1-4: The Tongariro Volcanic Centre:

Like the material erupted from the Egmont volcanic centre, the material from the Tongariro centre is andesitic and as expected are of more local extent. Deposits from this source have been recently discussed by Topping (1973). There have been a considerable number of small eruptions but few are probably of significance to the Waikato-Hauraki region and in fact Pullar (1973) gives no Tongariro-derived tephras (other than the recent Ngauruahoe Ash) on his map of "at-surface tephra formations occurring within 45 cm of surface, (which tephra) are soil forming parent materials," nor on his map of "near-surface tephra formations occurring within 45 to 100 cm of surface," for 30 and 15 cm isopach. Topping (1973) indicates that the volume of ejectamenta is about 19 cm^3 typically for the Tongariro-derived tephras by the method of Cole and Stephenson (1972). Analogous calculations on some of the Okataina-derived tephra give a volume some ten times this figure. Considering the distance the former material would need to have travelled to have reached the region under study and the small "power output," material from this source seems unlikely to have contributed to the soil-forming tephras. However, as will be seen subsequently, the alleged contamination of rhyolitic tephra in the Waikato-Bay of Plenty region has recently been attributed to the accretion of material from this source, rather than from Egmont as was earlier proposed. Such consideration can however only be made after an outline of the principal tephra relationship problem of the region under study is given, as is described in the next section.

S1-5: A Problem of Thinly-Bedded Tephras: Tirau and Mairoa Ashes:

The problem of identification and differentiation of the Tirau and Mairoa Ashes has its roots in the difficulties associated with the characterising of tephra that contribute to thin beds. The Mairoa Ash, principally mapped in the King Country, and the Tirau Ash, principally described in the eastern Waikato region, occur at sites distant from the projected sources whose tephrachronology and stratigraphy have been cited. Not only this but the climatic regimes are undoubtedly different and this has certainly affected the interpretation of field evidence.

The problem has its basis in that early geological mapping in the Mairoa locality was carried out by workers familiar with Taranaki stratigraphy, in particular the so-called "Egmont shower," whereas mapping in the eastern Waikato district, and in particular, in the Tirau locality, was carried out by workers more familiar with the ashes from the Okataina volcanic centre. It was therefore, perhaps inevitable that the Mairoa Ash came to be associated with the Egmont Centre and Tirau Ash with the Okataina Centre. But difficulties arose in the identification of the strata in the Waikato district. As recently as

1967, there was clear disagreement:

> "A common (tephra) column has been examined by both Ward (a) and Vucetich and Pullar (b); the former would regard the top 52" as Mairoa, whereas the latter have mapped the upper portion of 41" as including Taupo Pumice, Rotoma Ash, Rotorua Ash, pinkish brown beds (c) and a fine ash-cap to the yellow block and white block beds (d)." (- Pullar, 1967)

If nothing else this conflict indicates the inadequacy of field evidence alone to resolve the problems of thin tephra beds.

In the eastern Waikato district the correlation of Tirau Ash with the Okataina volcanics has never really been in doubt. A paper by Taylor (1953) refers to this as a "rhyolitic ash attributed to a source near Taupo" which "feathers out westward beneath the more andesitic Mairoa Ash."

More recently Pullar (1967) writes that near Tirau itself "correlation of soil horizons with ash beds suggests that the top 27 inches most likely comprises the Taupo, Rotoma and Rotorua ashes and the lower six feet the pinkish brown beds (Okareka Ash, Te Rere Ash and Oruanui Formation) yellow block and white block beds (Mangaone Lapilli) and grey banded bed (Rotoehu Ash)." As a result of this Pullar considers that the Tirau Ash is unlikely to be older than the Rotorua Ash (13,000 years). Birrell and Pullar (1973) have more recently proposed that the Rerewhakaiitu Ash may be involved also in the Tirau Ash sequence.

(a) Ward was involved in the mapping of Mairoa Ash.

(b) Vucetich and Pullar have written extensively on the stratigraphy and chronology of Okataina devised tephra.

(c) A descriptive term for Okareka Ash, Te Rere Ash and Oruanui Formation.

(d) A descriptive term for Mangaone Lapilli.

Mairoa Ash was first named by Grange (1931) who applied it to "a brown andesitic ash with an average thickness at Mairoa of two feet (60 cm) and was said by Grange and Taylor to "agree closely with undoubted Egmont Ash occurring at Stratford and Te Were." Because they observed both that the "Egmont ash is not always brown in colour" and that the profile of Egmont Ash under high rainfall and leaching conditions resembled that developed on Taupo Pumice and Kaharoa Ash where rainfall was also heavy, they proposed that Egmont Ash might be significant as far away from Egmont as Tirau and Putaruru. A composite character of the tephra (a) was implied, with the uppermost layer from Egmont and the earlier layers including rhyolitic material. The material immediately beneath Mairo Ash has been subsequently considered to be Oruanui Formation (Vucetich and Pullar, 1969) and this places a maximum age of twenty thousand years on the Mairoa Ash. This information together with the maximum age for the Tirau Ash given earlier would suggest that the Mairoa Ash should underlie Tirau Ash. However, Taylor (1953) indicated that the Tirau Ash "feathers" out under the Mairoa Ash. Consequently, either two sources were involved with contemporaneous deposition of tephra, or else the two tephra sequences are merely differently weathered forms of the same material.

The possibility of two sources has been refuted by Ward (1967) who considered that the Mairoa Ash and the underlying Hamilton Ashes were but differently weathered forms of the same parent material. Ward stated that the presence of the allophanic Mairoa Ash over halloysitic Hamilton Ash, together with the "laboratory evidence that weathering of allophane leads to the production of halloysite (b) suggests that the "Hamilton bed is derived from the Mairoa shower (Mairoa Ash) by weathering and elatriation of clay. To determine the source of the

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(a) The work described in Chapter 5 confirms this observation.

(b) This refen. to M. Fieldes' work on dating soils by predominant clay type. This is discussed in Sec. 6-1.

Hamilton Ashes, Ward describes a method based on isopach mapping:

"The probable source of the Hamilton ash beds is presumed to be either Mount Egmont to the S.W. or a centre in the Rotorua-Taupo volcanic field to the S.E., but the thickness of the individual Hamilton ash-beds when plotted on the map give no clear indication of its direction. Presumably the original thicknesses of the beds have been affected by weathering. To eliminate random effects the measurements were grouped and averages taken as follows. Taking the ash beds one at a time, a circle centred on Mount Egmont was drawn so that half the observations lay inside and half outside the circumference....." The same was done with the circle centred on the Rotorua-Taupo volcanic field (previously referred to in this chapter as the Okataina volcanic centre) and the conclusion reached that "the average thickness of most beds in the group far from Mount Egmont is not very different from the average thickness in the group near to Mount Egmont" but "there is a marked increase in thickness towards the Rotorua-Taupo volcanic field indicating that the eruptive source lay in this direction."

Pullar (1967) stated that Hamilton Ash is older than 36,000 years because it underlies the Rotoehu Ash. He noted that "Ward is inclined towards an age greater than the last glaciation of more than 70,000 years." Either of these ages make the correlation of Mairoa Ash with Hamilton Ash untenable, since the Mairoa Ash post-dates the Oruanui Formation. Consequently Ward's proposal of an eastern rather than western source for the Hamilton Ash does not deny the possibility of a western source for Mairoa Ash.

At the risk of repeating Ward's failure in correlation work based on studies of bed thickness a mathematical model for thickness-distance relationships is described in Sec. 2-3 and compared with the stratigraphy observed, the latter being presented in Sec. 2-2.

It would thus appear that, in spite of much field work over the past forty years, the problem of the identity of the Mairoa Ash and Tirau Ash is no closer to resolution, there being still debate as to whether the tephra represent differently weathered forms of a parent material from the Okataina centre or whether eruptives from Egmont are also involved. A further complication has been exposed in recent work by Birrell and Pullar (1973) who recognised andesitic contamination in many of the tephra of the Bay of Plenty and Waikato-Hauraki regions. While this in itself is consistent with the data described subsequently in this thesis, they attribute such contamination to eruptives from Tongariro and are thus at variance with Topping (1973). In the course of this thesis, it will be shown that there is evidence for a basic difference between the Tirau Ash and the Mairoa Ash, consistent with their being of differing source and tephra type.

CHAPTER 2: COLLECTION OF SAMPLES:

S2-1: Introduction:

Samples representative of the Tirau and Mairoa Ashes were collected at various localities, generally at 15 cm intervals down the stratigraphic sequence. Where possible, the sampling procedure, included either or both the marker beds Oruanui Ash or Rotoehu Ash. As the plates show, in many instances, there is little lithologic difference in the material overlying the markers - hence the reason for sampling simply on a depth basis. In addition to samples of Tirau Ash and Mairoa Ash, samples of other tephras from localities nearer the projected source were taken. These tephra, of known age, were sampled, with the intention of using them as dated standards with which to compare the Tirau Ash and Mairoa Ash samples.

The localities chosen were road cuttings, since the stratigraphy here is typically exposed for several metres, and enables photographs of the site to be taken.

In the next sections the sites and stratigraphy of the samples are described in detail. For reference in subsequent chapters, the sample numbers and tentative identifications are summarised in the Sample Concordance at the close of the work.

As has been indicated, the lithologic changes in the stratigraphic columns are difficult to determine in the field, and thus the identifications are uncertain. As a prelude to laboratory techniques, an extrapolation of the technique of isopach mapping is described later in this chapter. Although the method does not yield diagnostic information on the tephra, it suggests whether or not the field identifications made are reasonable on the basis of the thickness of tephra calculated to have been deposited.

S2-2: Description of field sites for samples of Tirau and Mairoa Ashes:

The geographical localities are indicated on Fig. 201, the sequence for the Tirau Ash lying to the east of the Waikato-Hauraki region and those for Mairoa Ash to the west and in the King Country. In addition to these, samples were taken at other localities to provide 'standards' whose identification was reasonably certain. The nature of these samples is indicated briefly in Table 2-1 and those that are used in comparison and correlation work in this thesis are given in the Sample Concordance.

TABLE 2-1: Nature of samples at collection sites

Site (Locality No.)	Samples	Used	Nature
Leslie Road (1)*	101-116	A, C	Late Pleistocene tephra : Okareka Ash to Rotoehu Ash (Oruanui Format and Rotoehu Ash used in correlation)
Tirau (2)	201-206	B	Tirau sequence of ashes
Findlay Park (3)	301-307	B	Tirau Ash and Mairoa Ash underlain by Oruanui Format
	308-309	C	Rotoehu Ash
Parawera (4)	401-406	B	Mairoa underlain by Oruanui Ash
	407-409	C	loess? and Rotoehu Ash
Kakepuku (5)	501-503	B	Mairoa underlain by Oruanui Ash
	504-505	C	loess? and Rotoehu Ash
Mairoa (6)	601-606	B	Mairoa underlain by Oruanui Ash
Pio Pio (7)	701		Rotoehu Ash
Hauturu (8)	801	C	Oruanui Ash
Tapapa Road (9)	901-905	B	Tirau sequence underlain by Oruanui Format
Ash-pit Road (10)	1001-1003	A, C	Kaharoa Ash
Whaka Forest (11)	1101-1115	A, C	Tephra and paleosols, upper Tirau Ashes including Rotoma Ash
Aokautere	1701	C	(Possible correlatives of
Amberley	1801	C	(Oruanui Ash

FIG. 201

Geographical localities of sites from which samples were taken

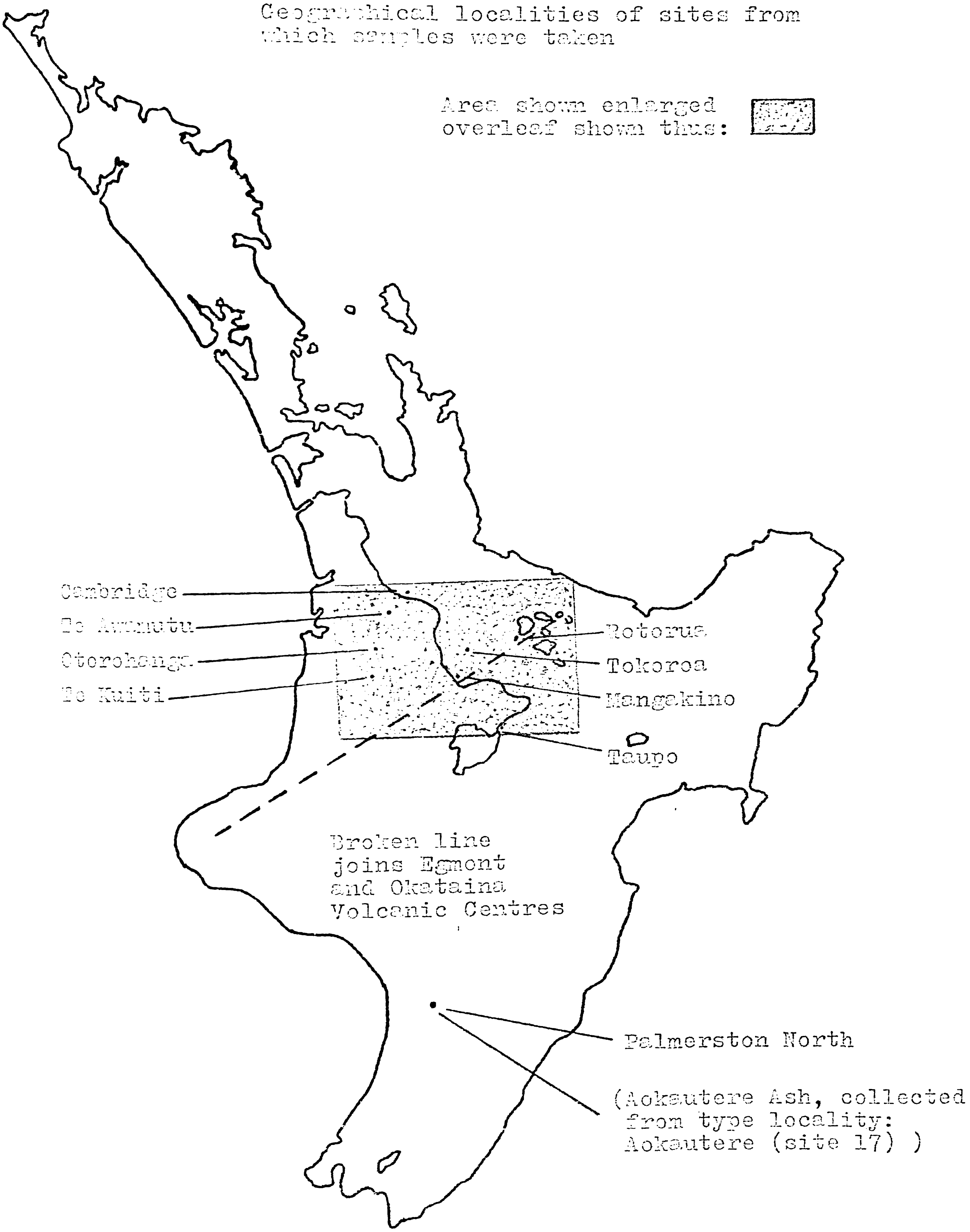
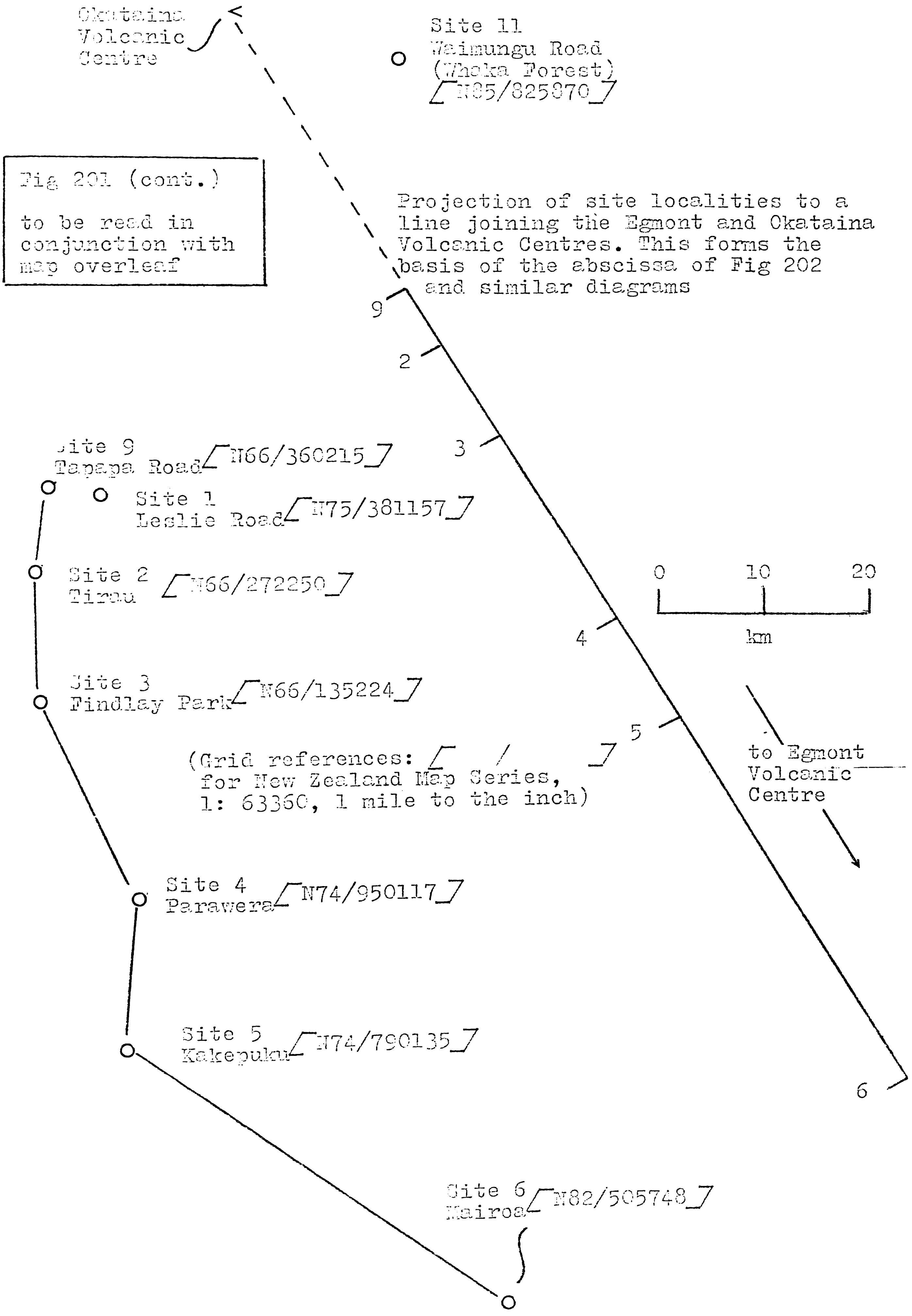


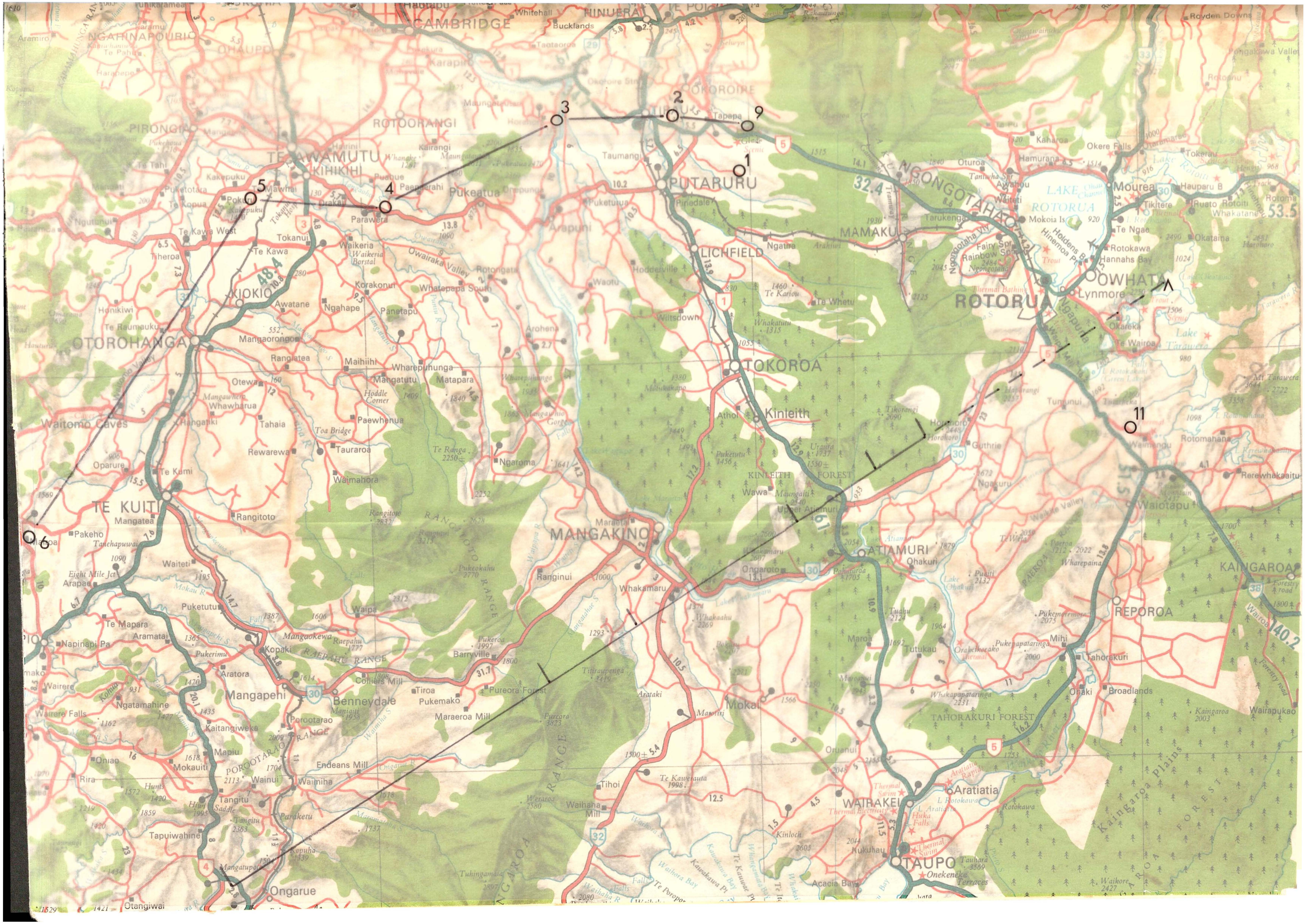
Fig 201 (cont.)

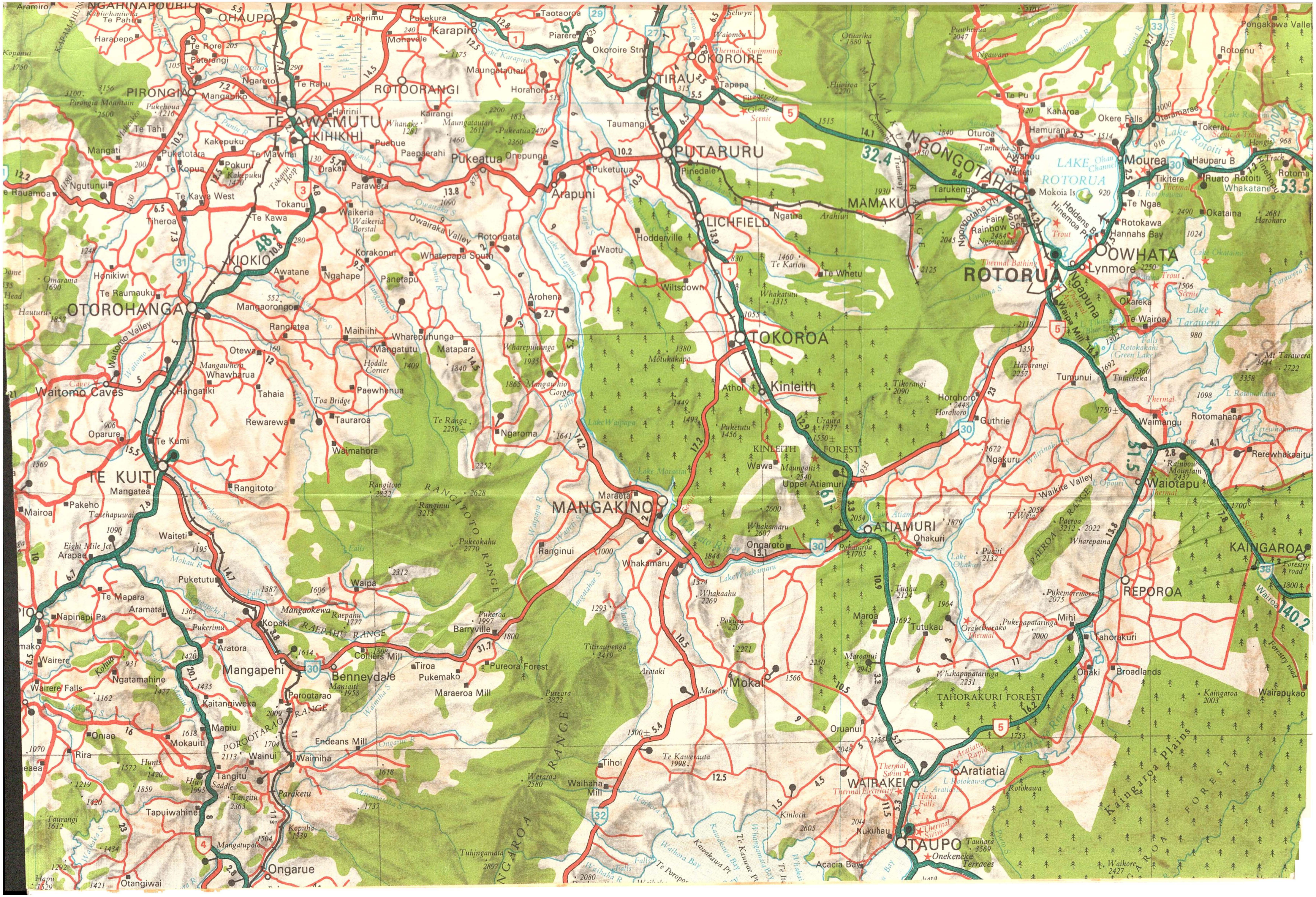
to be read in conjunction with map overleaf



Projection of site localities to a line joining the Egmont and Okataina Volcanic Centres. This forms the basis of the abscissa of Fig 202 and similar diagrams

(Grid references: [/] for New Zealand Map Series, 1: 63360, 1 mile to the inch)


CAMBRIDGE
HINUERA
TE POI
Whitehall
Bucklands
Taotaoroa
Karapiro
OKOROIRE
Okoroire Str
NGAHINAPOURI
OHAUPO
Aramiro
Harapepe
PIRONGIA
ROTOORANGI
TE AWAMUTU
KIHIKIHI
Kairangi
Maungatautari
Horahora
Pukeatua
Arapuni
TIRAU
Tapapa
Taumangi
PUTARURU
Pinedale
Puketurua
LICHFIELD
Hodderville
Ngatira
MAMAKU
NGONGOTAHA
Tarukenga
Oturoa
Hamurana
Kaharoa
Okere Falls
Mourea
Hauparu B
Ruato Rotoiti
Tikitere
Whakatane
Royden Downs
Pongakawa Valley
Rotorua
Lake Rotorua
Lake Rotoiti
Mokoia Is
Te Ngae
Rotokawa
Hannahs Bay
Okataina
Holdens Bay
Hinemoa Pt
Fairy Spr
Rainbow Spr
Ngongotaha Vly
Trout
Thermal Bathing
OWHATA
Lynmore
ROTORUA
Okareka
Te Wairoa
Lake Tarawera
Mt Tarawera
Waimangu
Rotomahana
Rerewhakaaitu
Waiotapu
KAINGAROA
REPOROA
Broadlands
Tahorakuri
Mihi
Orakeikorako
Pukepapataringa
Tutukau
Waikite Valley
Ngakuru
Guthrie
Horohoro
Tikorangi
Tumunui
Te Whetu
Te Kariou
Whakatutu
Wiltsdown
TOKOROA
Kinleith
Athol
KINLEITH FOREST
Wawa
Upper Atiamuri
ATIAMURI
Ohakuri
Ongaroto
Maroa
Mokai
Oruanui
WAIRAKEI
Aratiatia
Huka Falls
TAUPO
Nukuhau
Acacia Bay
Onekeneke Terraces
Kinloch
Tauhara
Kaingaroa Plains
KAINGAROA FOREST
TAHORAKURI FOREST
Wairapukao
Rotokawa
Pukete
Tihoi
Waihaha Mill
Te Kawerauta
Titiraupenga
MANGAKINO
Maraeta
Whakamaru
Ranginui
Ngaroma
Wharepuhunga
Mangatutu
Matapara
Hoddle Corner
Paewhenua
Toa Bridge
Tauraroa
Waimahora
Rangitoto
RANGITOTO RANGE
Te Ranga
Pukeokahu
Waipa
Mangaokewa
Raepahu
Barryville
Pureora Forest
Pureora
Pukemako
Tiroa
Maraeroa Mill
Benneydale
Colliers Mill
Endeans Mill
Waimiha
RANGITOTO RANGE
HAUROA RANGE
Tuhingamata
Ongarue
Mangatupoto
Parekete
Poro-o-tarao
POROOTARAO RANGE
Mangapehi
Aratora
Kopaki
Puketutu
Pukerimu
Mapiu
Mokauiti
Tangitu
Hurri Saddle
Tapuiwahine
Otangiwai
Wainui
Kaitangiwewe
Oniao
Rira
Ngatamahine
Wairere Falls
Wairere
Napinapi Pa
Te Mapara
Aramatai
Arapae
Eight Mile Jct
Waiteti
Mangatea
TE KUITI
Pakeho
Tanehapuwai
Te Kumi
Hangatiki
Oparure
Waitomo Caves
OTOROHANGA
Mangaorongo
Rangiatea
Otewa
Mangawhero
Whawharua
Tahaia
Rewarewa
Maihiihi
Awatane
Ngahape
Panetapu
KIOKIO
Te Kawa
Te Kawa West
Tiheroa
Honikiwi
Te Raumauku
Korakonui
Whatapapa South
Rotongata
Waotu
Arohena
Owairaka Valley
Waikeria
Tokanui
Pokuru
Kakepuku
Puketotara
Te Kopua
Te Tahi
Ngutunui
Parawera
Puahue
Paengaroa
Orakau
Wharepaina
Pukemoremore
Whakapapataringa
1
2
3
4
5
6
9
11
1
3
4
5
30
32
33
38
48 A
32.4
53.5
140.2
31.7
13.9
12.9
10.9
10.5



Aramiro
NGAHINAPOURI
Te Pahu
OHAUPO
Pukerimu
Pukekura
Karapiro
Taotaoroa
Piarere
Okoroire Stn
Selwyn
OKOROIRE
Thermal Swimming
Otuarika 1880
Puwhenua 2047
Ngawaro
Pongakawa Valley
Rotoenu
Harapepe
Koponui
Te Rore
Paterangi
Ngaroto
Te Rahu
Monavale
Maungatautari
Horahora
TIRAU
Tapapa
Hiwiroa 2270
Te Pu
Kaharoa
Okere Falls
Otaramarae
Tokerau
Lake Rotoiti
Hongis
PIRONGIA
Pirongia Mountain
Mangapiko
Pukehoua 1216
ROTOORANGI
TE AWAMUTU
KIHIKIHI
Hairini
Kairangi
Whanake 1281
Maungatautari 2611
Pukeatua 2470
Taumangi
Glade Scenic
Oturoa
Hamurana
Moureа
Hauparu B
Rotoma
Te Tahi
Kakepuku
Te Mawhai
Puahue
Paeparerahi
Pukeatua
Orepunga
PUTARURU
Pinedale
NGONGOTAHA
Tarukenga
MAMAKU
Awahou
Waiteti
LAKE ROTORUA
Mokoia Is
Tikitere
Ruato
Rotoiti
Whakatane
Mangati
Puketotara
Te Kopua
Pokuru
Orakau
Parawera
Arapuni
Puketurua
Ngatira
Arahiwi
MAMAKU RANGE
Te Ngae
Okataina
Harohoro
Ngutunui
Te Rauamoa
Te Kawa West
Tokanui
Te Kawa
Waikeria
Waikeria Borstal
Owairaka Valley
Rotongata
LICHFIELD
Hodderville
Ngongotaha Vlg
Fairy Spr
Rainbow Spr
Ngongotaha
Holdens B.
Hinemoa Pt
Rotokawa
Hannahs Bay
Tiheroa
KIOKIO
Korakonui
Wharepapa South
Waotu
Te Kariou
Te Whetu
Thermal Bathing
OWHATA
ROTORUA
Lynmore
Lake Okataina
Lake Tarawera
Honikiwi
Omarama
Awatane
Ngahape
Panetapu
Lake Arapuni
Wiltsdown
Whakatutu
Ngapuna
Okareka
Te Wairoa
OTOROHANGA
Te Raumauku
Mangaorongo
Arohena
Ranginui
Ranglatea
Maihiihi
Wharepuhunga
Mangatutu
Matapara
TOKOROA
Waipa Mill
L. Rotokakahi (Green Lake)
Mt Tarawera
Waitomo Valley
Otewa
Mangawhero
Whawharua
Hoddle Corner
Wharepuhunga
Mangapuhio Gorge
Motukakapo
Athol
Kinleith
Haparangi
Tumunui
Tuhaheka
Waitomo Caves
Hangatiki
Tahaia
Paewhenua
Toa Bridge
Tauraroa
Rewarewa
Te Ranga
Ngaroma
Lake Waipapa
Puketutu
Tikorangi
Horohoro
Guthrie
Thermal
Waimangu
Rotomahana
L. Rotomahana
Oparure
Te Kumi
Waimahora
KINLEITH FOREST
Uraura
Ngakuru
Rerewhakaaitu
TE KUITI
Mangatea
Rangitoto
Pakeho
Tanehapuwai
Rangitoto
RANGITOTO RANGE
Rangiuni
Pukeokahu
MANGAKINO
Maraeta
Lake Maraetai
Wawa
Maungaiti
Upper Atiamuri
Waikite Valley
Rainbow Mountain
Waiotapu
Mairoa
Waiteti
Eight Mile Jct
Arapae
Mokau R.
Ranginui
Whakamaru
Whakamaru
ATIAMURI
Lake Atiamuri
Ohakuri
Ongaroto
Pohaturoa
T. Weta
Paeroa
PAEROA RANGE
Wharepaina
KAINGAROA
Forestry road
Puketutu
Te Mapara
Aramatai
Napinapi Pa
Waipa
Mangaokewa
Raepahu
RAEPAHU RANGE
Kopaki
Pukeroa
Barryville
Whakaahu
Lake Whakamaru
Tuahu
Lake Ohakuri
Puaiti
REPOROA
Wairoa
Wairere
Kohua
Aratora
Pukerimu
Mangapehi
Colliers Mill
Benneydale
Maniaiti
Tiroa
Pukemako
Maraeroa Mill
Pureora Forest
Titiraupenga
Arataki
Pokuru
Maroa
Tutukau
Orakeikorako
Thermal
Pukemoremore
Pukepapataringa
Mihi
Tahorakuri
Wairere Falls
Ngatamahine
Kaitangiweka
Porootarao
POROOTARAO RANGE
Pureora
Mokai
Marotiri
Maroanui
Whakapapataringa
TAHORAKURI FOREST
Ohaki
Broadlands
Kaingaroa
Wairapukao
Oniao
Mapiu
Mokauiti
Wainui
Endeans Mill
Ongarue R.
Waimiha
Oruanui
Kaingaroa Plains
Rira
Tangitu
Hurakia Saddle
Tangitu
Werаroa
Tihoi
Te Kawerauta
WAIRAKEI
Thermal Swim
Thermal Electricity
Aratiatia
Aratiatia Rapids
L. Rotokawa
Huka Falls
Rotokawa
KAINGAROA FOREST
Taurangi
Tapuiwahine
Parakeke
Mangatupoto
Kopuha
Tuhingamata
RANGITOTO RANGE
Waihaha Mill
Kinloch
Nukuhau
TAUPO
Thermal Swim
Tauhara
Onekeneke
Terraces
Acacia Bay
Hapu
Otangiwai
Ongarue
Waihaha R.
Te Poporo
Kawakawa Bay
Kawakawa Pt
Te Kauwae Pt
Whangamata Bay
Waikore

* Grid references for the sites given in the Sample Concordance and on Fig. 201.

A : used as "standard" tephra in assigning dates, chemical compositions etc.

B : used in resolution of problem of Tirau and Mairoa Ashes.

C : used in long-range stratigraphic work.

For the sites of the Tirau and Mairoa Ash sequences, all sites are in road cuttings under farm land. The field data and profile are given in Table 2-2.

TABLE 2-2: Site data for Tirau and Mairoa Ash deposits

Tirau: Site 2:	Sample 201	76 cm above base of Tirau Ash sequence
	202	61
	203	45
	204	30
	205	base of Tirau Ash sequence
	206	material under Tirau Ash sequence, presumably older than 13,000 years (a), but no evidence of its being one of the marker beds.
Findlay Park: Site 3:	Sample 301	30 cm below surface, very friable sandy loam
	302	45 cm below surface, Tirau Ash
	303	61 cm below surface, top of Mairoa Ash (soil processes operating)
	304	76 cm below surface, near base of Mairoa Ash
	305	91 cm below surface
	306	106 cm below surface, a yellow pumice possibly Te Rere Ash (b)

	307	121 cm below surface, identified as Oruanui Formation (c) (d)	
	308	35 cm above base of Rotoehu Ash (e)	
	309	basal Rotoehu Ash (marker bed) (e)	
Parawera: Site 4:	401	45 cm below surface - Mairoa Ash	
	402	61 cm below surface - Mairoa Ash	
	403	81 cm below surface	No apparent field difference
	404	96 cm below surface	
	405	112 cm below surface	
	406	121 Oruanui Formation (c)	
	407	136 'loess' (f)	
	408	20-25 cm above base of Rotoehu Ash (e)	
	409	base of Rotoehu Ash (e)	
Kakepuku: Site 5:	501	30 cm below surface - Mairoa Ash	
	502	45 cm below surface - Mairoa Ash	
	503	61 cm below surface, Oruanui Formation, marker bed (c)	
	504	76 cm below surface, 'loess' (f)	
	505	126 cm below surface, Rotoehu Ash, marker bed (e)	
Mairoa: Site 6:	601	33 cm below surface - Mairoa Ash	
	602	68 cm below surface	
	603	89 cm below surface	
	604	101 cm below surface - Oruanui Ash (g)	
	605	104 cm below surface, Oruanui Ash	
	606	112 cm below surface, material immediately below Oruanui Ash	
Tapapa Road: Site 9:	901	15 cm above base of Rotoehu Ash	
	902	immediately below Rotorua Ash	
	903	30 cm below Rotorua Ash	
	904	61 cm	

	307	121 cm below surface, identified as Oruanui Formation (c) (d)	
	308	35 cm above base of Rotoehu Ash (e)	
	309	basal Rotoehu Ash (marker bed) (e)	
Parawera: Site 4:	401	45 cm below surface - Mairoa Ash	
	402	61 cm below surface - Mairoa Ash	
	403	81 cm below surface	No apparent field difference
	404	96 cm below surface	
	405	112 cm below surface	
	406	121 Oruanui Formation (c)	
	407	136 'loess' (f)	
	408	20-25 cm above base of Rotoehu Ash (e)	
	409	base of Rotoehu Ash (e)	
Kakepuku: Site 5:	501	30 cm below surface - Mairoa Ash	
	502	45 cm below surface - Mairoa Ash	
	503	61 cm below surface, Oruanui Formation, marker bed (c)	
	504	76 cm below surface, 'loess' (f)	
	505	126 cm below surface, Rotoehu Ash, marker bed (e)	
Mairoa: Site 6:	601	33 cm below surface - Mairoa Ash	
	602	68 cm below surface	
	603	89 cm below surface	
	604	101 cm below surface - Oruanui Ash (g)	
	605	104 cm below surface, Oruanui Ash	
	606	112 cm below surface, material immediately below Oruanui Ash	
Tapapa Road: Site 9:	901	15 cm above base of Rotoehu Ash	
	902	immediately below Rotorua Ash	
	903	30 cm below Rotorua Ash	
	904	61 cm	

905 101 cm below Rotorua Ash, Oruanui Ash (banded) (h)

906 fine sand 20 cm above base of Oruanui Ash member

Notes: (a) on the basis of Pullar (1967) op.cit.

(b) Te Rere Ash is an undated tephra of age around 20,000 years, being stratigraphically between Okareka and Oruanui Ashes both of which have ^{14}C dates of near 20 thousand years.

(c) Oruanui Formation is the name given to a widespread ash deposit of some 20 thousand years of age believed to originate near Lake Taupo (see Sec. 1-3 and Chapter 12).

(d) Oruanui Formation and Rotoehu Ash appear in the stratigraphic sequence as a white or yellow sandy deposit. Clearly the material has been much less weathered than the material that both overlies and underlies it, and it therefore persists as a convenient marker even in localities where the bed is thin.

(e) Rotoehu Ash is the name given to a series of ash beds erupted from two sources, near Lake Rotoehu and Matahina some 42,000 years ago (see Sec. S1-2).

(f) These deposits are so-named because of their textural difference from volcanic ashes in general and anomalous thickening.

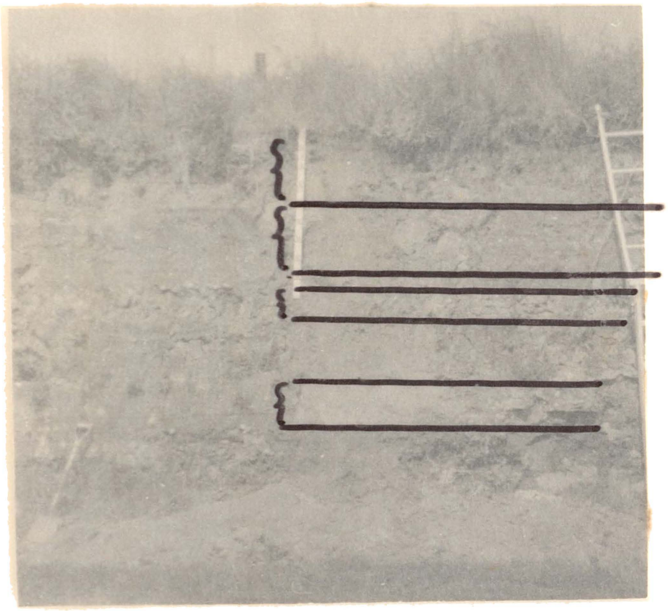
(g) In this locality, the marker bed (Oruanui Formation) was sufficiently thick to sample its upper and lower portions as samples 604 and 605 respectively.

(h) At this locality there is a considerable thickness of Oruanui Formation, comprising a banded deposit of alternately coarse and fine pumiceous sand on a fine-grained base of white pumice sand, and is sampled from both layers as 905 and 906 respectively.

PLATE 21

Sampled localities in Waikato district where Tirau Ash overlies Mairoa Ash

Site 3: Findlay Park



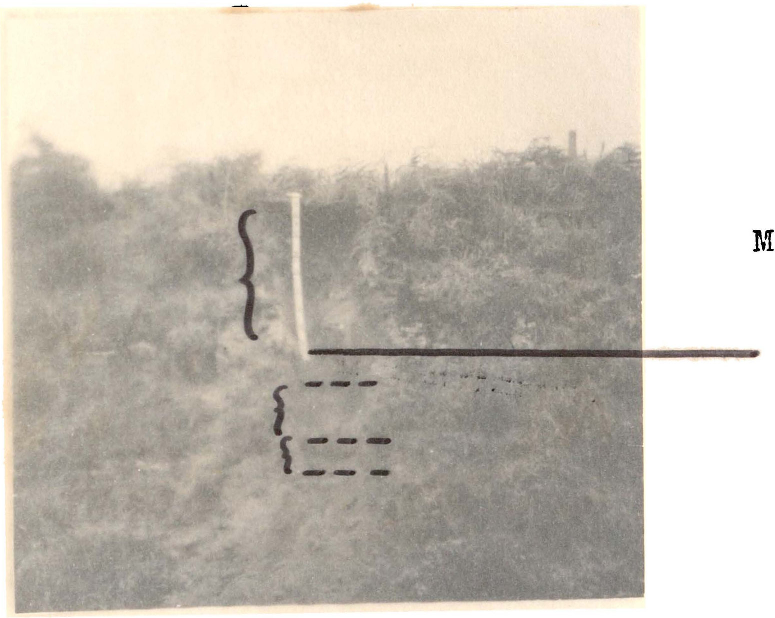
Tirau Ash

Mairoa Ash

Oruanui Formation

Rotoehu Ash

Site 4: Parawera



Mairoa Ash

Oruanui Ash

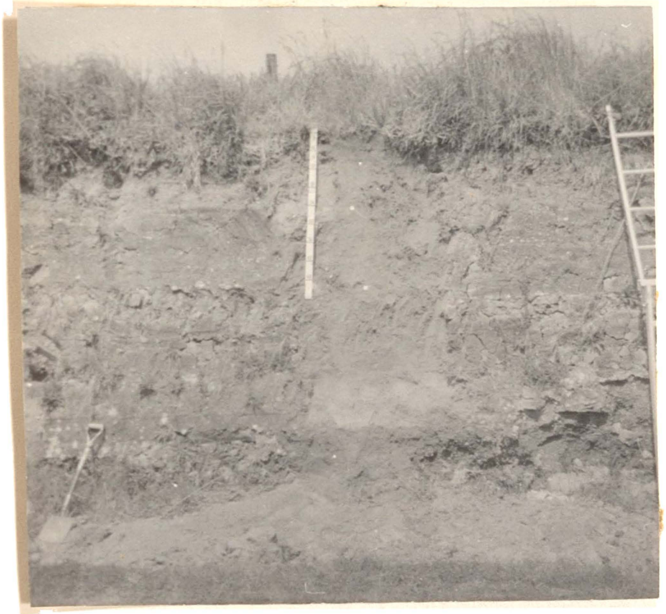
"loess"

Rotoehu Ash

PLATE 21

Sampled localities in Waikato district where Tirau Ash overlies Mairoa Ash

Site 3: Findlay Park

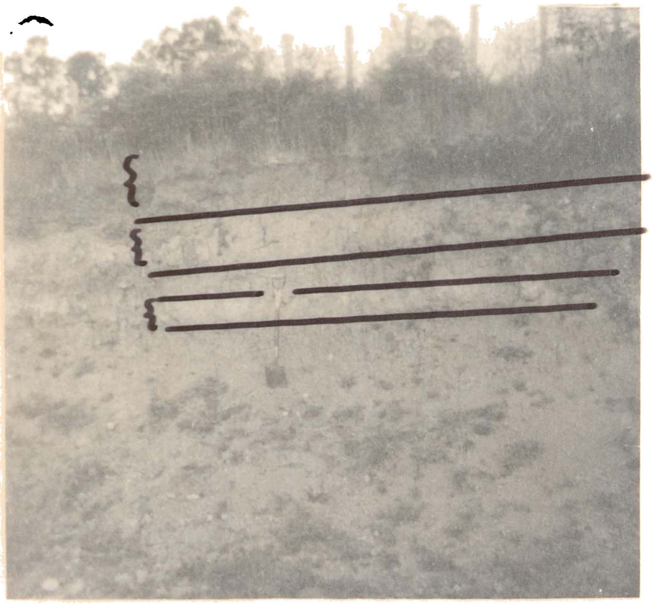


Site 4: Parawera

PLATE 22

Sampled localities for Mairoa Ash in western Waikato district and northern King Country

Site 5: Kakepuku

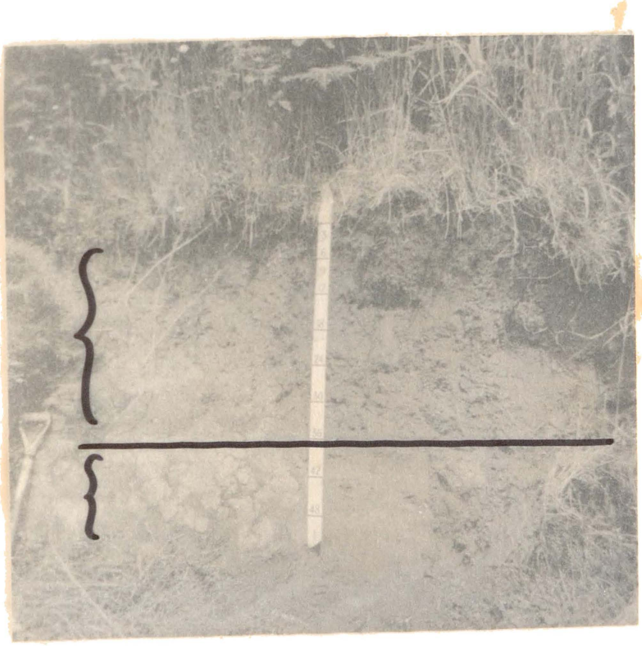


Tirau and Mairoa Ash

Oruanui Ash

Rotoehu Ash

Site 6: Mairoa (type locality for Mairoa Ash)



Mairoa Ash

Oruanui Formation

PLATE 22

Sampled localities for Mairoa Ash in western Waikato district and northern King Country

Site 5: Kakepuku

Tirau and Mairoa Ash

Oruanui Ash

Rotoehu Ash

Site 6: Mairoa (type locality for Mairoa Ash)

Mairoa Ash

Oruanui Formation

It is important to recognise that the identification given the various samples in Table 1-2 , . made on the basis of field evidence, is but tentative. The Oruanui Formation which is very easily recognised in the field is taken to be a stratigraphic marker, and is assumed to be correctly identified at all localities. The stratigraphic relationships of the samples relative to this marker are shown diagrammatically in Fig. 202. This diagram also indicates the relationship of respective thicknesses of the Tirau and Mairoa Ashes at the various localities and will be compared subsequently with that obtained from considerations of isopach data given in the literature.

In addition Taupo Pumice and Rotoma Ash and its basal lapilli were sampled at a site near Waimungu, and Kaharoa Ash sampled near Lake Rerewhakaiitu. These are detailed in Table 2-3 and are used only in the tephrachronologic interpretations in this thesis.

TABLE 2-3: Site data for Kaharoa and Rotoma Ashes and Taupo Pumice

Site	Tephra	Sample
Whaka Forest (near Waimungu)	1101	Rotomahana Mud - Tarawera eruption 1886
	1103	Taupo Pumice - from paleosol
	1110	Rotoma Ash
	1115	Lapilli bed at base of Rotoma Ash
Ash-Pit Road (Lake Rerewhakaiitu)	1001	upper 10 cm of Kaharoa Ash
	1002	sampled some 30 cm above base of Kaharoa Ash
	1003	basal 10 cm of Kaharoa Ash

FIG. 202

Stratigraphic relationships of samples of Tirau Ash and Mairoa Ash from various localities in the Waikato-Hauraki and King Country regions, using the Oruanui Formation as a marker bed

THE FORMAT OF THIS FIGURE IS USED SUBSEQUENTLY TO ILLUSTRATE THE VARIATION OF VARIOUS PHYSICAL AND CHEMICAL PARAMETERS. IN THESE SUBSEQUENT FIGURES THE SAMPLE IDENTIFICATIONS ARE GENERALLY OMITTED FOR REASONS OF CLARITY

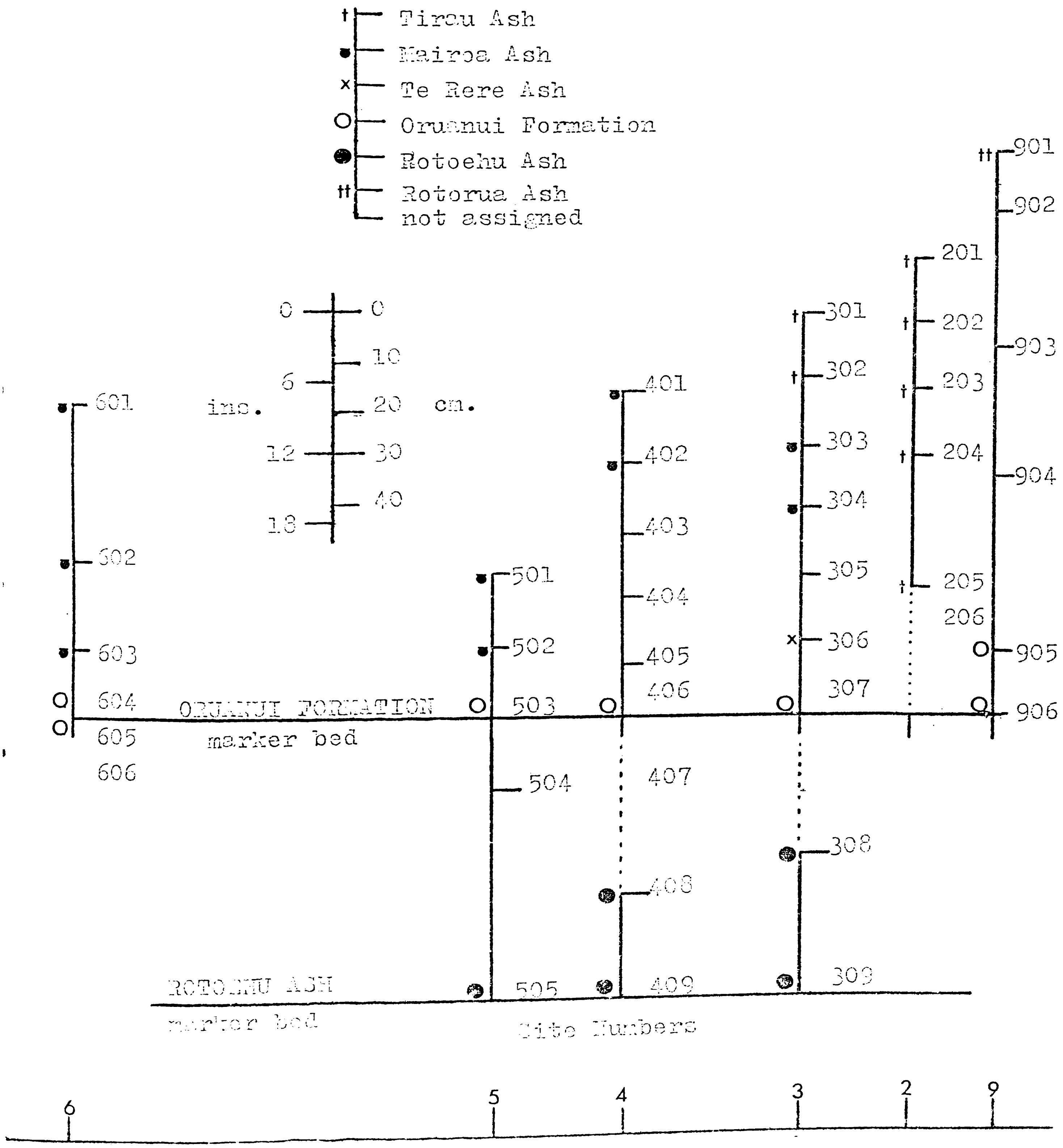


PLATE 23

Parent materials for Tirau Ash, tephra sequence at Waimungu Road from Rotomahana Mud to the basal lapilli of Rotoma Ash

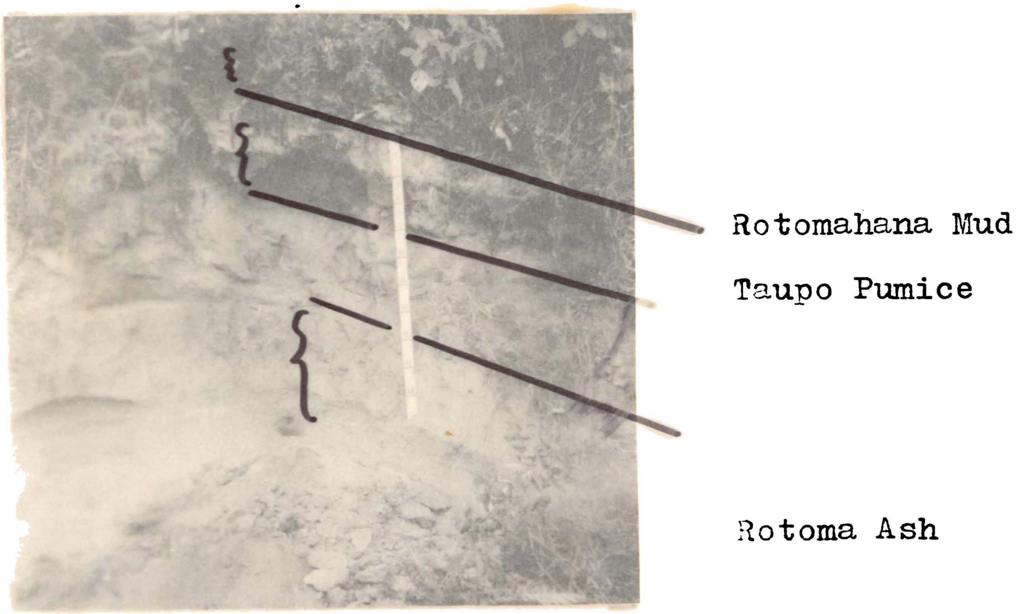


PLATE 23

Parent materials for Tirau Ash, tephra sequence at Waimungu Road from Rotomahana Mud to the basal lapilli of Rotoma Ash

S2-3: The Variation of Tephra Thickness with Lateral Distance:

The thickness of a tephra deposit observed at a given locality is a function of the initial mode of deposition , contributing factors being the nature of the erupted material, the distance from the source, weather conditions at the time of eruption, and the subsequent effects of weathering and possible reworking. Reference to isopach maps for many New Zealand tephra shows that a given thickness generally occurs at greater distances east than west of the projected vent, this presumably results from the effects of the prevailing westerly winds. It is interesting that the Rotorua Ash, one of the units that may make up the Tirau Ash shows the reverse lateral distribution. This may be interpreted as the effect of an atypical easterly, in which case it is suggestive that the deposited material is the product of a single outburst, rather than a gradual accretion of several eruptions in a protracted volcanic episode.

Another isopach distribution that is atypical is the Oruanui Formation. In this case there is rather less directional influence which is suggestive either that there was little wind at the time of eruption or that the eruption was paroxysmal enough to negate such an effect.

If a diagram of tephra thickness versus distance is considered, as for example Fig. 203 for the combined Holocene tephra, it is readily seen that an inverse relationship holds between these two variables. If this relationships has the form

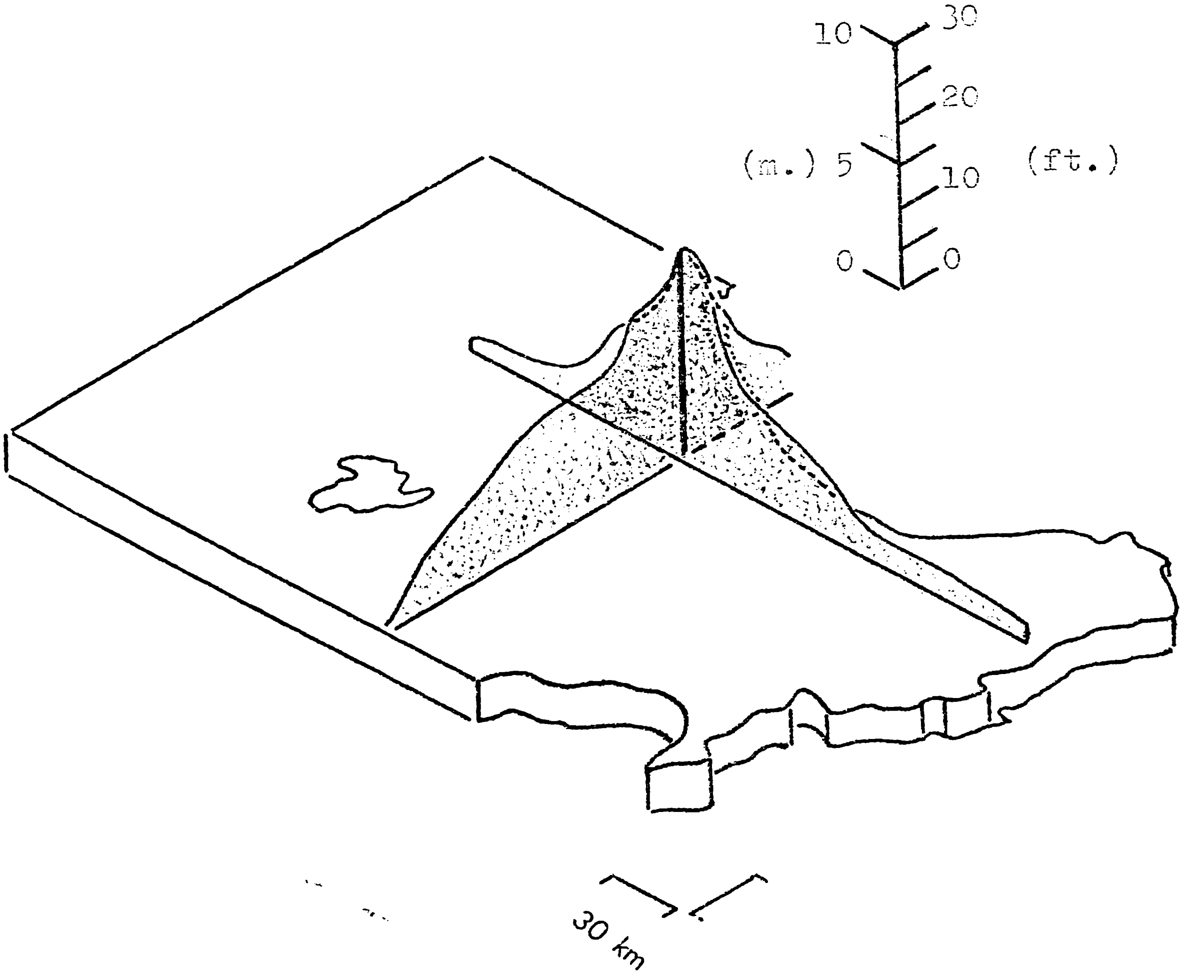
$$h = k(s^{-n})$$

where h is the thickness of tephra, s is the distance of locality to source, and k and n are constants. This can be expressed as a logarithmic function: $\log h = \log k - n \log s$.

FIG. 203

Tephra thickness as a function of distance from source

The diagram below constructed from isopach data for the combined Holocene tephras of Pullar (1967), being "products of eruptions during the last 15000 years", shows the inverse nature of the relationship



Difficulties arise when plotting a function of this kind if the value of n is not constant, but worse, since the function is undefined at the source (i.e. when s = o), the procedure must be confined in its application to tephra at reasonably large distances from the source.

A preferable way of defining the parameter n for a wide range of values of s is by the solutions of the differential equation:

$$-dh/ds = kh^n$$

(where k and n are constants, but not necessarily the same as those above). Now the solution of such a differential equation has been shown by Powell (in Frost and Pearson (1961)) to be capable of graphical interpretation in terms of dimensionless parameters. These relationships are usually used in the determination of reaction order in reaction kinetic studies, but apply generally to any physical situation defined by such a differential equation. The dimensionless parameters in this case are the relative thickness (z) defined by:

$$z = h/h_o$$

where h_o is the thickness of the tephra at the source, and a distance parameter (σ) defined by:

$$\sigma = k(h_o^{n-1}).s.$$

For any given value of n there is a unique relationship between z and σ and typical plots are shown in Fig. 204. If, then, values of z are plotted as a function of log σ, this experimental curve will match one of the theoretical curves, except that it will be displaced along the σ-axis by an amount - log $k_o h_o^{n-1}$. If the value of n is itself a function of σ, then matching portions of the curves should still be able to be found.

Plots of z as a function of log σ are given in Fig. 205 for various directions of the distribution of Holocene tephra for which the isopach map is given by Pullar (1967). Superposition of the theoretical curves of z versus σ, indicates that at large distances from the source n = 2

FIG. 204

Dimensionless parameter plot: z vs σ for various values of n

being relative thickness, that is the thickness at the sampled site over that at the source

$$z = h/h_o$$

being a distance parameter, related to the thickness at source (itself written h_o) and the distance from source to the sampled locality (s) by:

$$\sigma = k(h_o^{n-1}).s$$

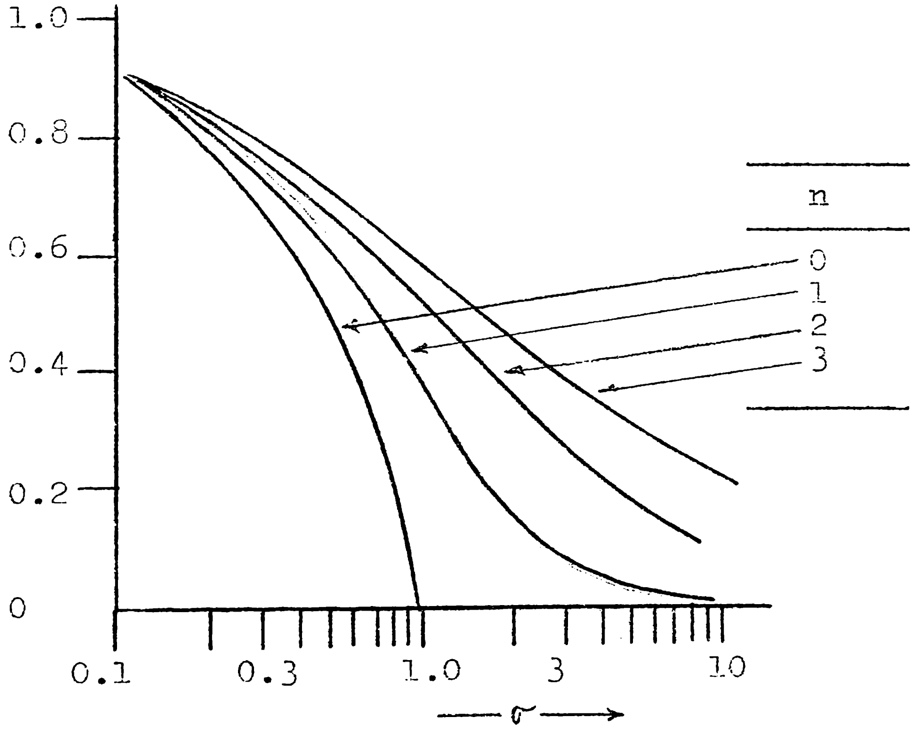
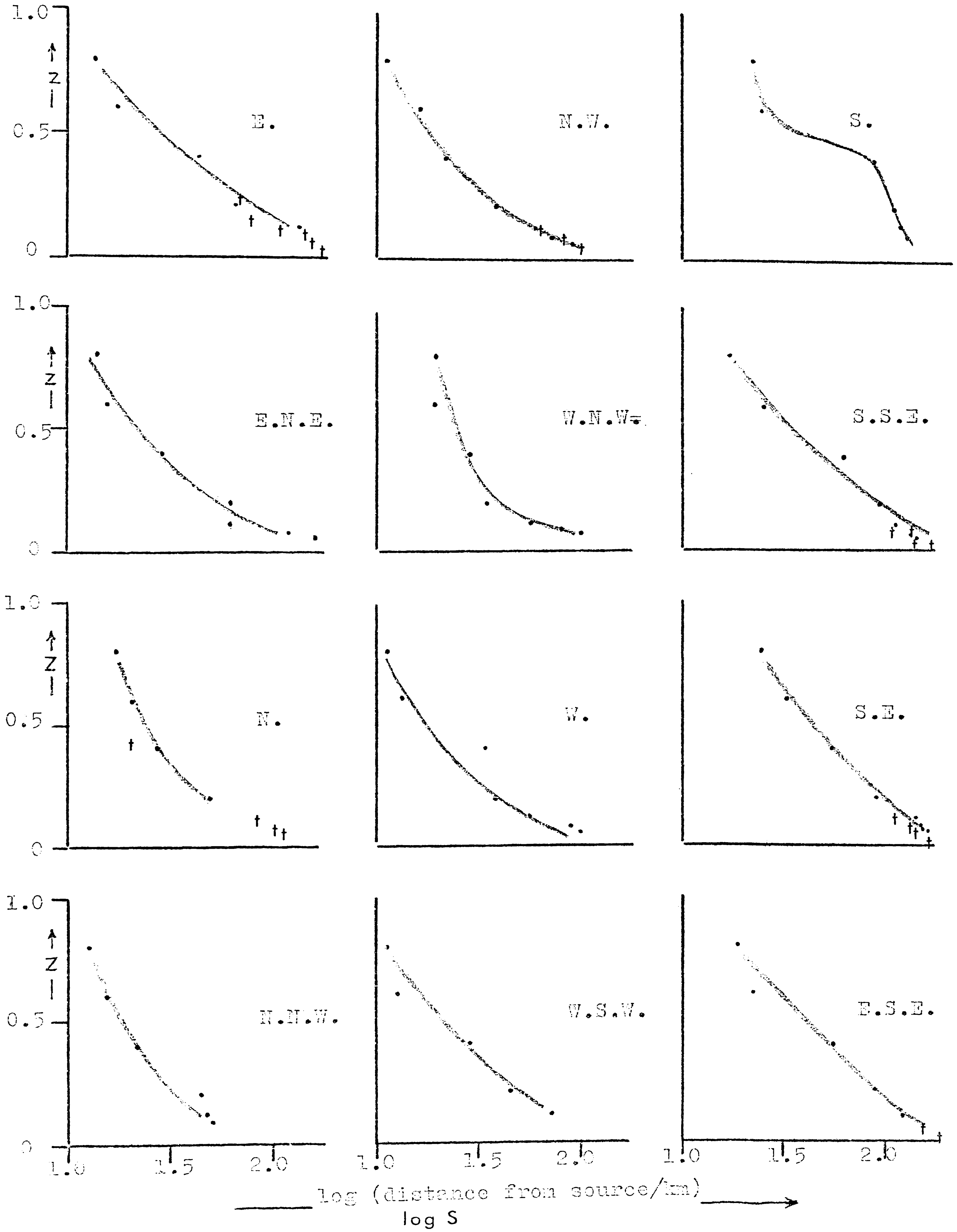


FIG. 205

Z *vs* S for various directions of the combined Holocene tephras



and the thickness is thus a direct inverse of distance, for rather lesser distances n = 1.0 and the thickness is logarithmically related to distance, and for smaller distances still there is fractional power relationship. The approximate cut-off values for the range of z for given n for the plots in Fig. 20S are given in Table 2-4.

TABLE 2-4: Range of relative thickness for given n at various directions from the generalised source of combined Holocene tephras.

Orientation.	n-value : fractional	n = 1.0	n = 2.0*
	Relationship : $(1/_{n-1})(1/_{h}{}^{n-1} - 1/_{h_o}{}^{n-1}) = k_s$	$1/_s = \ln(h/h_o).k$	$1/_h - 1/_{h_o} = ks$
		Range of z	
E	0.3	0.3 - 0	-
ENE	0.5	0.5 - 0.1	0.1
NE	0.4	0.4 -	-
N	0.3	0.3 -	-
NNW	0.1	0.1 - 0	-
NW	0.5	0.5 - 0	
WNW	0.26	0.16 - 0.26	0.16 - 0
W	0.50	0.60 - 0.10	0.10 - 0
WSW	0.6	0.62 - 0	-
S		indeterminate	-
SSE	0.8	0.8 - 0	-
SE	0.6	0.6 - 0.1	0.1 - 0
ESE	0.6	0.6 - 0.02	0.02 - 0

* Data not available at sufficiently large distance from source to determine whether n exceeds 2.0

From Table 2-4 and Fig. 205 it is readily seen that there is a change from a logarithmic to reciprocal distance relationship at low values of z, (that is greater distances). The value of z at which this occurs is a function of direction, being larger for more northerly oriented deposits. This variation almost certainly is caused by the prevailing wind. That it is due to this and not just to accretion of Taupo material from the south[a] can be shown by plotting z versus log s curves based on Vucetich and Pullar's (1969) isopach map of Oruanui Formation. Such points are indicated by crosses in Fig. 205 and are seen to follow the same trends as that already established.

In that the distances from the projected sources to the sampled localities is large, and the values of z for the tephra postulated as contributing to these deposits is small (for the Holocene tephra of Pullar, z is less than 0.1) it is reasonable to use the relationship for n = 2, that is

$$1/h - 1/h_o = ks$$

whence it can be shown that $1/s \propto h.h_o/(h_o - h)$

For small values of z, h_o is very large compared with h and thus the thickness of the deposit is proportional to the reciprocal of the distance from source.

On this basis the thickness of the Holocene tephra (up to 15,000 years of age) from the Okataina volcanic centre at the sampled localities can be estimated, using an h versus 1/s plot in a westerly direction. Similarly the corresponding thickness of the combined Oakura and Okato Tephras can be obtained from a plot in a north-easterly direction from Mount Egmont (Fig. 206a). These derived thicknesses are given in Table 2-5. Also shown in this table are the thicknesses of the Te Rere Ash and Okareka Ash at the localities. These are based on the isopach

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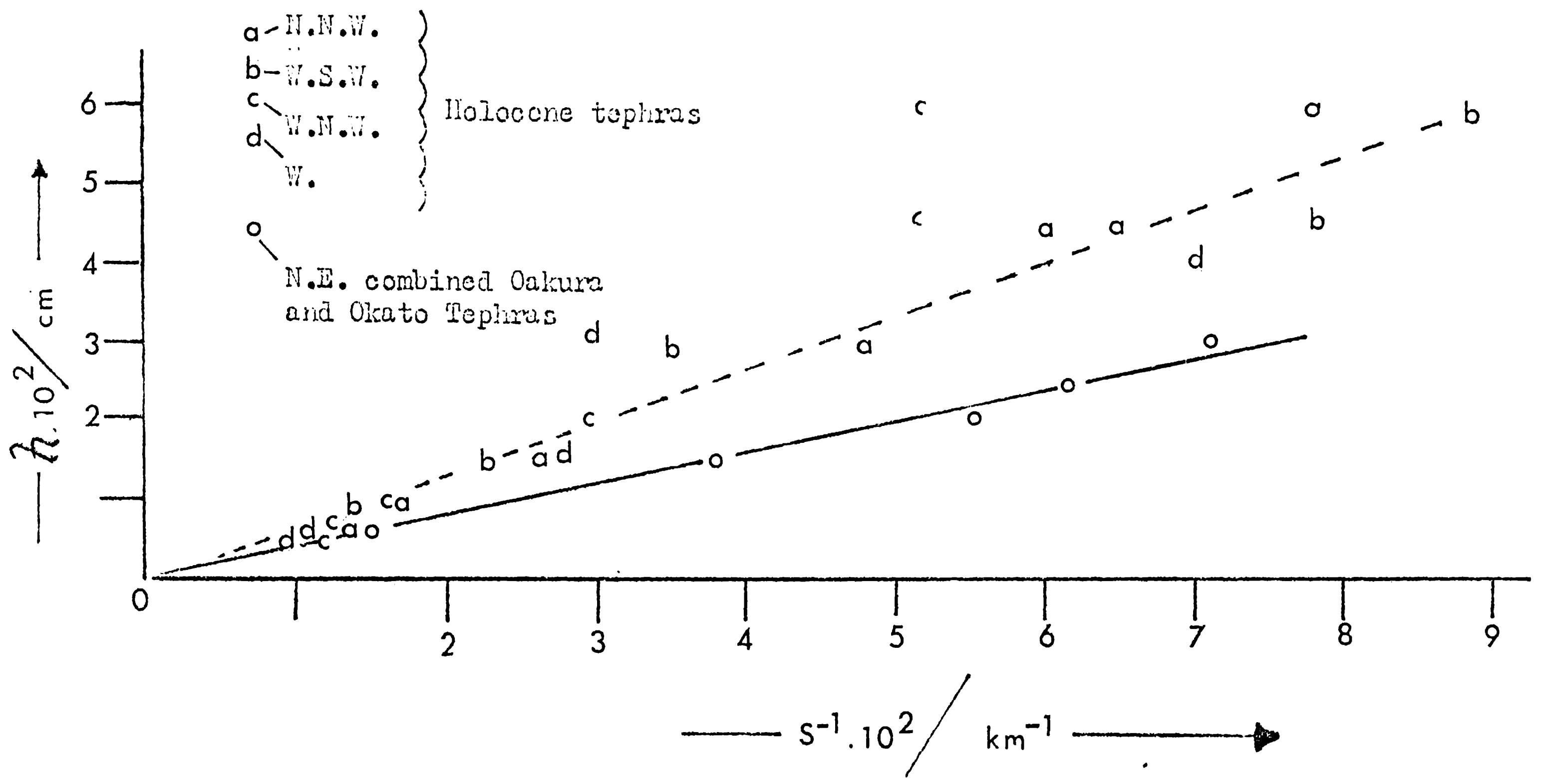
(a) The isopach map given in Pullar (1967) suggests that all the erupted material originates from the Okataina volcanic centre. Since Taupo Pumice is included in this distribution, this is an approximation.

FIG 206a

Thickness (h) vs reciprocal distance (s^{-1}) for various directions of combined Holocene tephras, and of the combined Oakura and Okato Tephras



maps of Vucetich and Pullar (1969) and underly the Holocene tephra of Pullar (1967) but overlie the Oruanui Formation. Thickness-distance plots for these last tephras are given in Fig. 206b.

TABLE 2-5: Predicted thicknesses of tephra at selected localities:

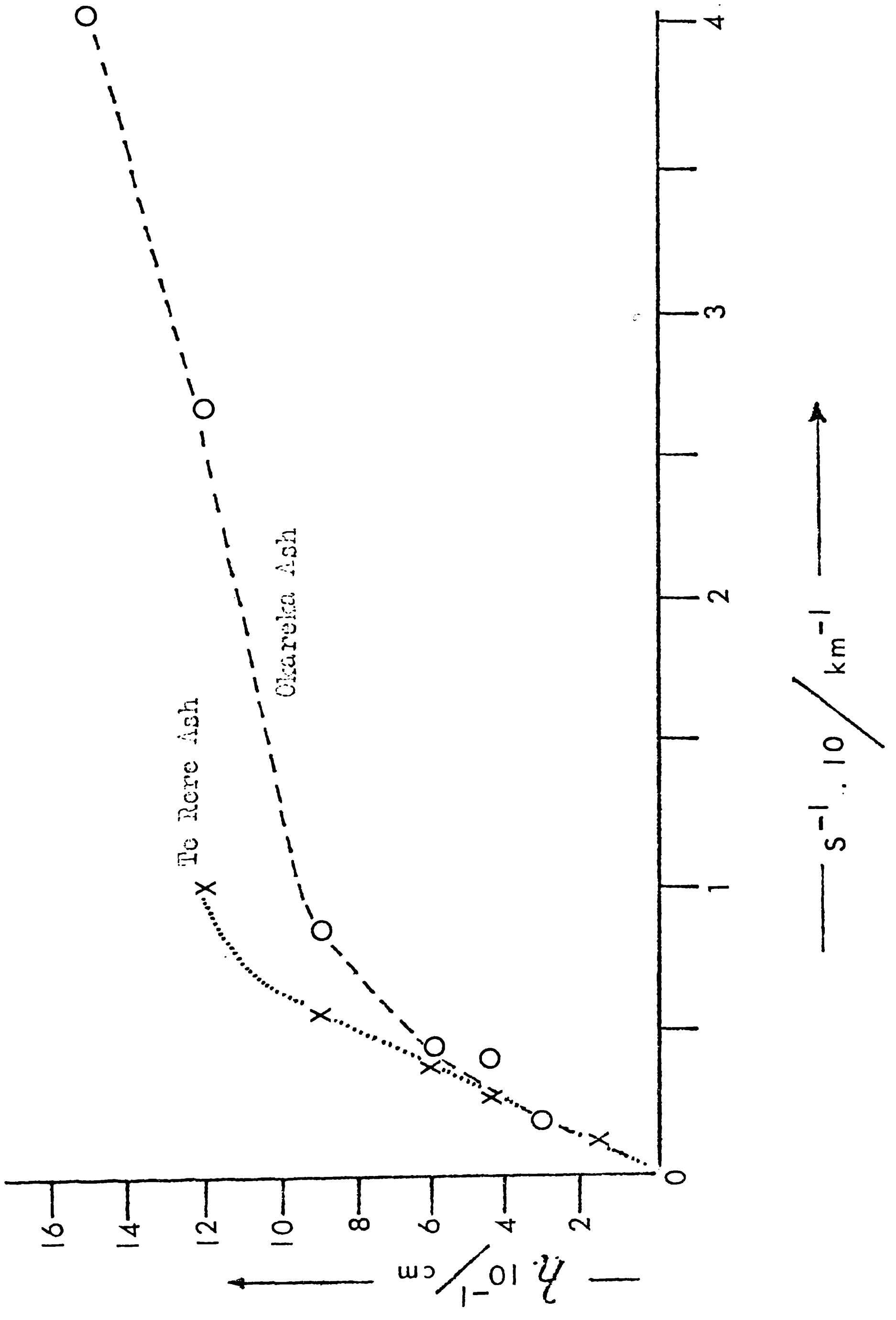
Tephra: Thickness-distance plot: Direction+		Holocene tephras Fig.206a N.W. ○	Okareka Ash* Fig.206b N.W. ●	Te Rere Ash* Fig.206b N.W. ◯		Oakura and Okato Tephras Fig.206a N.E. ⊛
Locality±	Distance from Okataina source (s/km)	Thickness (h/cm) ○	●	◯	Distance from Egmont source (s/km)	Thickness (h/cm) ⊛
Findlay Park, Waikato district	69	60	22	22	190	27
Tirau, Hauraki district	60	70	24	24	206	25
Parawera, Waikato district	86	50	19	19	179	30
Kakepuku, Waikato district	103	25	15	15	172	30
Mairoa, King Country district	127	0	13	13	129	40
Tapapa, Hauraki district	53	80	30	30	211	20

Notes: * Deviation from linearity higher for these tephra because the isopach lines correspond to a higher value of z (relative thickness) than is the case for the other tephra considered.

\+ being the direction on the isopach map for which data is used to plot figure.

FIG 206b

Thickness (h) *vs* reciprocal distance (s^{-1}) for Te Rere Ash and Okareka Ash erupted in a westerly direction from the projected source



* These localities are chosen as the sites from which samples are collected, see Chapter 2.

This data is plotted in Fig. 207, where it would appear that the "Egmont showers" are sufficient to contribute even to the deposits on the Mamaku Range and further that the ejectaments from the Okataina centre contributes to the total thickness at Mairoa.

It is important to note, however, that this is but an idealised consideration and takes no account of local variation caused by rainscavenging and the effects of weathering and wind. The concept is of use however in assessing whether field identifications are likely to be correct, as is shown in the stratigraphic sequence field data superposed on this data. One further point of note is that the material from Egmont is shown on Fig. 207 as underlying the Holocene tephra deposits. There may, in fact, be interdigitation of the deposits from the two courses; but the total thickness will still be comparable.

In the interpretation of the observed stratigraphy in relation to the estimated thicknesses of the deposits it is probable that the member of the "Egmont shower" lowest in the stratigraphic sequence predates the oldest Holocene tephra-bed, and certainly the upper Holocene beds are younger than the youngest "Egmont shower." This is not to say that the deposition of some Mairoa Ash does not post-date some Tirau Ash at some stage within these limits. Thus, sample 304 near the base of the Mairoa Ash (as identified at Findlay Park) is likely to be predominantly "Egmont," but sample 401 also identified in the field as Mairoa Ash is not, on the basis of Fig. 207 to be necessarily considered as incorrectly identified and, in fact, an Okataina-derived Holocene tephra.

FOR SAMPLE NUMBERS REFER TO FIG. 202

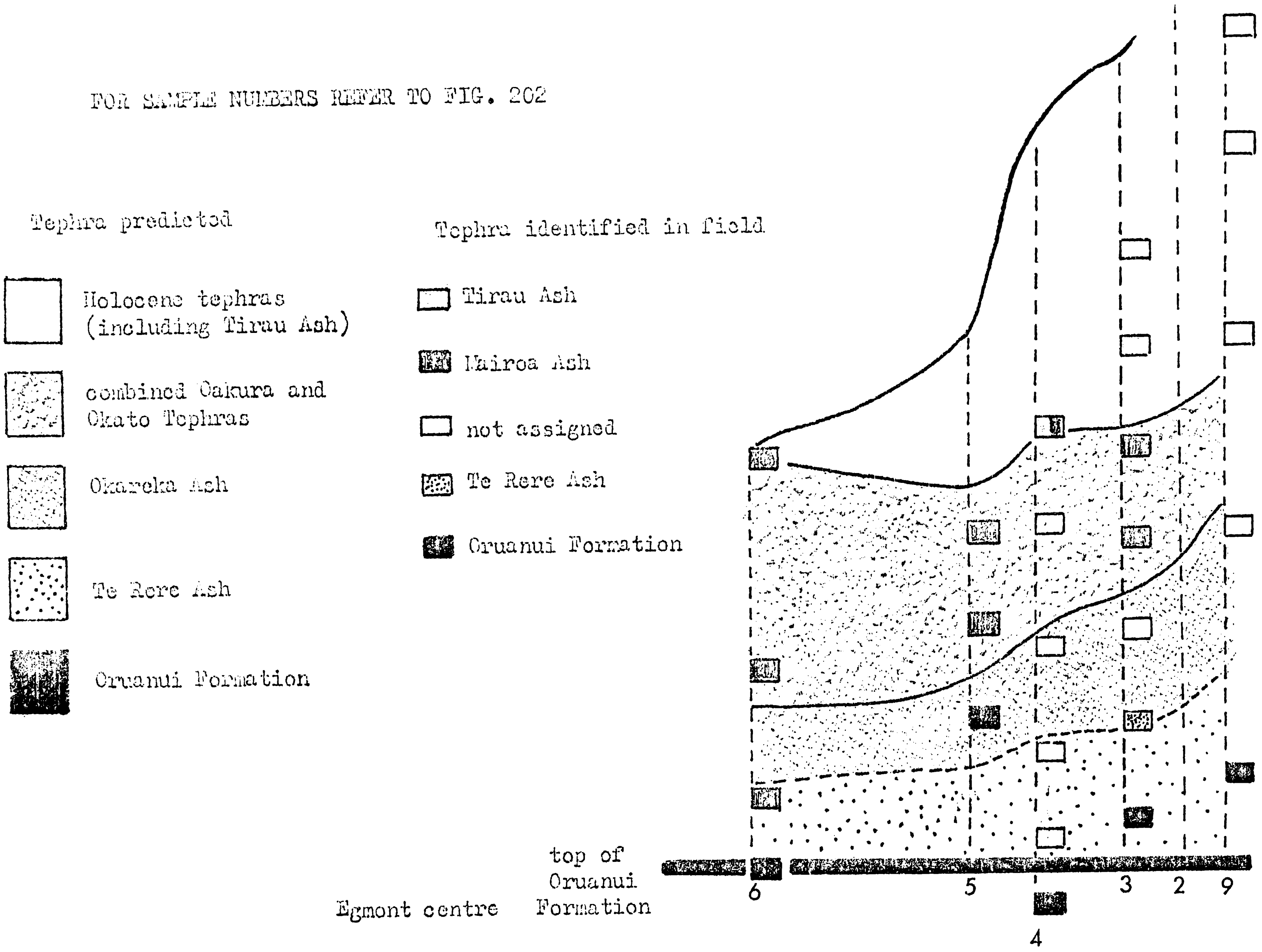


FIG. 207 Stratigraphic relationships predicted on the basis of thickness estimates, and a comparison with field identifications of samples.

It is noteworthy that the predicted and observed thicknesses concur well for the more eastern of the sites of the Waikato district (viz. 2, 3, 4). For site 5, (Kakepuku), the predicted thickness exceeds that observed: this may be explained by erosion. At Mairoa itself, the observed thickness is greater than predicted, for which the most likely cause is incorporation of other material by local reworking or perhaps by accretion of material from the Tongariro Volcanic Centre.

S2-4: Conclusion:

In this section the geographic locality of the region under study in relation to the recognised sources of late Pleistocene and Holocene tephra has been discussed, and possible correlations of the Tirau and Mairoa Ashes considered. On the basis of idealised thickness relationships it appears that at least two sources for the Tirau and Mairoa Ashes are involved; one being Egmont, where the most likely contributions (having regard to the likely chronology of the deposits) are the Okato and Oakura Tephra; and the other being the Okataina Volcanic Centre. Minor discrepancies between observed and predicted thicknesses of deposits do not entirely rule out the possibility of the accretion of material from the central volcanic region. Subsequent chapters will develop further the distinction between the two sequences and the relationships to the proposed parent materials.

PART TWO

DEVELOPMENT OF TECHNIQUES

CHAPTER 3: Review of Techniques in Tephra Correlation:

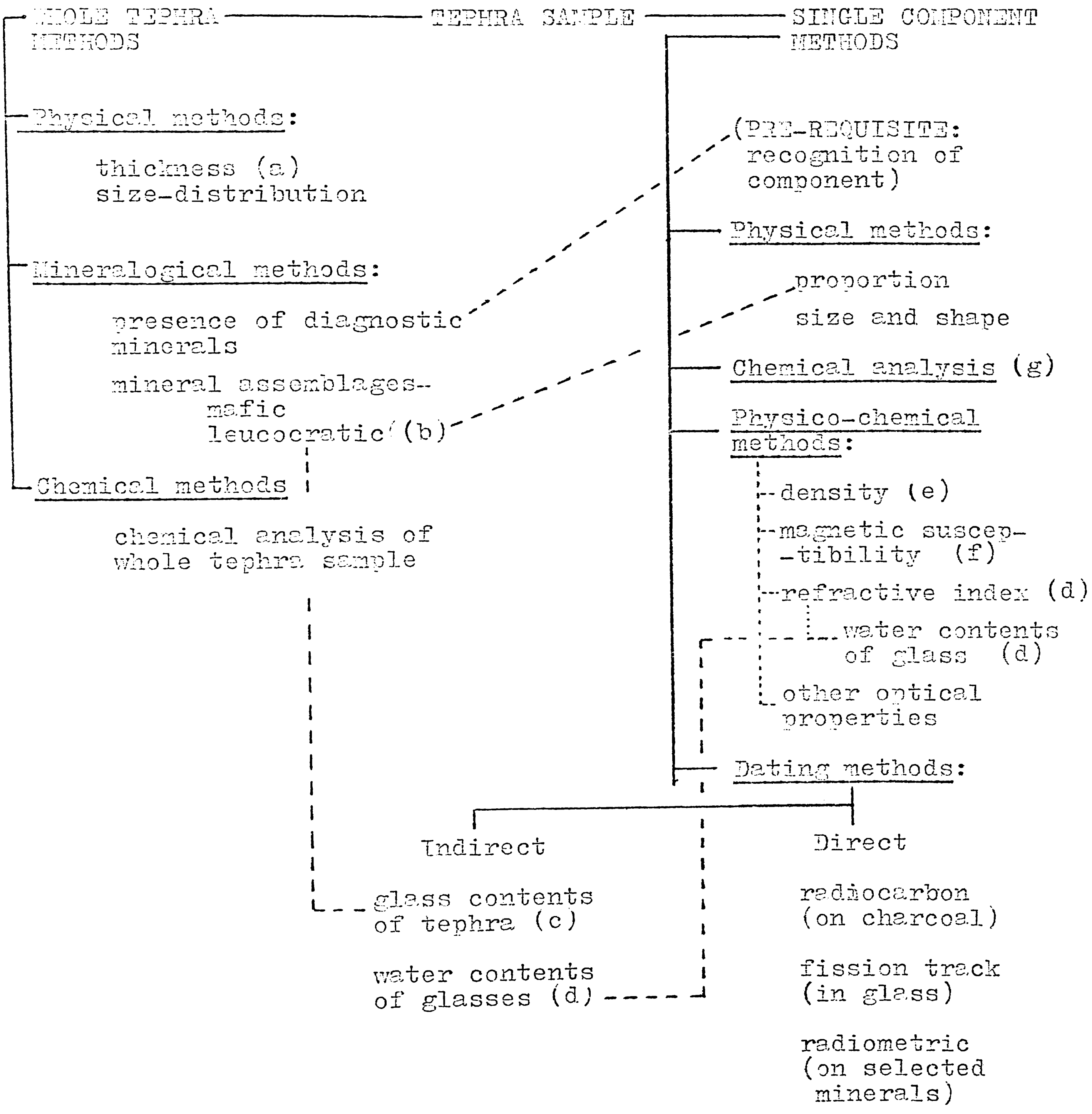
S3-1: Introduction:

Much tephra correlation has been achieved in the past by field data. The presence or absence of certain mineral components or lithologic features has been the principal criterion used in identification. From these in situ observations the distribution of the tephra have been computed on the basis of observed thickness. From such data the areal extent, volume, and source may be determined. However such a method requires that the tephra unit is, in fact, identifiable in the field, and thus in its strict applicability usually is restricted to regions sufficiently close to the source that the thickness of tephra is at least 15 cm, unless there is some specific diagnostic criterion which persists even in very thin deposits (as, for example a dramatic difference in colour). As has been shown in the previous section, the technique can be extrapolated to predict thicknesses of tephra in regions where they are not easily identified. This is, however, certainly no proof of the existence of these tephra in such localities since, as Wilcox (1965) indicates, there may be "major irregularities caused by local rainscavenging of the eruptive cloud and by water re-working of the original deposit."

This section, (Part II), then is devoted to describing, and developing techniques by which tephra may be characterised, and specifically this chapter describes and reviews techniques that have been previously applied. In fact the techniques fall into two broad categories, those that involve characterisation of the whole tephra and those that involve the separation of specific components and characterising the tephra on the basis of the presence of such components or on the basis of some physical or chemical parameter associated with that component. The relationships of such methods are indicated in Fig. 301 below, and are discussed in some detail in subsequent sections of this chapter.

FIG. 301

Techniques for characterising tephras



Cross reference to discussions in text:

(a), Chapter 2; (b), Chapter 5; (c), Chapter 6; (d), Chapter 9; (e), Chapter 7; (f), Chapter 8; (g), Chapter 10.

S3-2: Whole Tephra Methods:

The mapping of tephra by isopach mapping is of course a whole tephra method. Such a method implies some other criterion is available to identify the tephra. An example of this is how the presence of chalatoidites is used as a diagnostic indicator of Oruanui Ash, as described by Vucetich and Pullar (1969). In a more general way the presence and proportion of specific minerals has been used as an indicator for tephra. Ewart (1966) and Cole (1969) have found that in New Zealand the mafic mineral assemblages of tephras are usually distinctive near the source, although Wellman (1962) found such an approach less useful at greater distances. Generally, however, such investigations are based more on field evidence, and rely on the presence of certain diagnostic minerals rather than the assemblage. For mafic minerals, Pryor (1969) and Nelson and Cochrane (1970) have described a "fingerprint" method using x-ray diffraction. While this does not employ the complete tephra unit, in that the method does not involve the separation of a specific component, it is included here. An analogous method could be suggested for the felsic minerals (feldspar, quartz, etc) but is complicated by the presence of glass. This renders the use of x-ray diffraction impracticable but infra-red spectroscopy is a viable proposition. Infra-red spectroscopy has been used to study whole soils (Fieldes et al. (1972)) effectively by consideration of the different clay minerals formed from tephra of various ages.

Certain techniques are applicable because of the specific nature of the deposit: flow deposits have been characterised on the basis of their bulk porosities (Ross and Smith, 1961) and pumices have been characterised on the basis of their ferromagnetic minerals (Momose et al., 1968).

Chemical analysis of whole soils and tephra units has been used (Jack, Lajole and Carmichael, 1967) but is unlikely to be useful over a wide area, because as Wilcox (1965) points out:

> "Chemical analysis of whole samples of ash deposits are generally not helpful for correlation purposes because variations within the same deposit resulting from differing amounts of primary phenocrysts may be greater than the variation between separate ash deposits."

This is, in fact, the essence of difficulty with all whole tephra methods: that there may be significant mineralogical differences over the geographical extent of the ash. This objection may be lessened by the use of single-component methods as outlined in the next section.

S3-3: Single Component Methods:

Attention is being increasingly focussed on the physico-chemical properties of particular minerals, but there has been little attempt to extend already-known techniques or to apply techniques from other fields of study in such characterisation. A particularly useful component of tephra for this purpose is volcanic glass; and in this thesis techniques used for characterising this material are reviewed and extended. In some cases these techniques are improved to the point where the error associated with the technique is less than the mean discrepancy of the parameter obtained by replicate determinations.

It should be noted that, in attempting identification and correlation of tephra by the use of parameters affecting one particular component, the assumption is made that the component is invariant of site. Wilcox (1965) in this regard, notes:

> "..... if one constituent can be concentrated in sufficiently pure form ..... its chemical analysis is comparable from one sample to the next."

While this may be true for some chemical elements and physico-chemical properties, it is not universally true, particularly those for which leaching and hydration effects may be important. Of particular note in this regard are the iron contents and refractive indices of glass, which may be expected to be dependent on conditions prevailing at the site since deposition. Such effects will be described in detail in subsequent chapters.

One further note of caution needs to be sounded. The identity of two samples may be apparent rather than real, being simply due to the lack of precision in experimental technique rather than in an inherent identity. Again, an appropriate example of this is refractive index. Steen and Fryxell (1965) claim that glasses may be identified on the basis of identity of refractive index, measured to three decimal places (i.e. ±0.003). However, by so doing, the effect of hydration of the glass which changes the refractive index by up to 0.002 is neglected, and fallacious correlations would thus be possible.

However, the success claimed in correlation by compositions of minor and trace elements in glass (Rankin, 1973) and titanomagnetites (Kohn, 1970) suggests that "lateral" variation in the physico-chemical parameter is usually of secondary importance, and likely to be obstructive in tephra correlation only where compositional differences between the minerals involved are exceptionally small. To this extent, glasses reflecting as they do the magmatic composition at the time of eruption are probably likely to show significant differences between various eruptions, these differences being sufficiently great to render as minimal the post -eruptive effect on composition.

Since it is usual for any radiometric date to be achieved by analysis of a specific mineral, it is useful to consider dating techniques that may be applied to volcanic glass, and attention is now turned to this.

S3-4: Dating Techniques:

Most dating of Pleistocene and Holocene tephra in New Zealand has been done by radiocarbon methods. Such a method is only of use where the thickness of material erupted is sufficiently great to overwhelm trees. Of this Vucetich and Pullar (1969) write:

> "The degree of agreement between the ages of the ^{14}C samples and the deposits varies considerably. Dated materials giving best agreement are wood charred by the ash or peat immediately below the ash-bed."

Accordingly, except in areas where thin tephra beds are underlain by peat, the thinly bedded deposits cannot be reliably dated by radiocarbon techniques. Other radiometric methods are available, but in the N.Z. literature few dates from these techniques are mentioned. Conceivably, such dating techniques could be applied successfully to N.Z. glasses, as in fact has been done elsewhere (for example, Robinson and Marvin (1967)). Some interest has been shown recently in fission track dating of Pleistocene volcanic eruptions recorded in deep sea sediments (Ninkovich, 1968; Fisher, 1969; McDougall, 1971).

Nevertheless much dating has and, undoubtedly, will continue to be done by indirect correlating methods. An example of such is the identification and dating of late Pleistocene tephra in turbidites off Hawke Bay on the east coast of the North Island of New Zealand (Lewis and Kohn, 1973). Here identification and dating was achieved on the basis of titanomagnetite compositions. Another indirect method involves the amount of glass that remains after weathering. Ruxton (1968) noted that there was a relation, analogous to first order kinetics between glass contents and radiometric age. This technique is modified and extended to give tentative dates for the formation of the Tirau and Mairoa Ashes. Such a technique, of course, requires reference to dated tephra where the glass can be similarly extracted, just as do methods mentioned above that involve correlation by composition.

S3-5: Conclusion:

The purpose of this chapter has been to review the principal approaches that have been used to identify and correlate tephra. The remaining chapters in this part of the thesis will critically examine some of these techniques and assess their usefulness with particular reference to the problem of the Tirau and Mairoa Ashes.

CHAPTER 4: The Identification and Removal of Glass from Tephras and Soils

S4-1: Introduction:

As indicated previously, a particularly useful component in tephrostratigraphy is volcanic glass. The presence of glass in the field is usually taken as indicative of the bed's volcanic origin, but in order to be of use the glass must be removed and cleaned of impurities. The glass in tephra is of two types, a low density glass and one of a higher density. As will be shown, the former can be removed without significant difficulty, whereas the latter is intimately mixed with the felsic minerals, and, in particular, with quartz and feldspar. In this chapter techniques are described for the isolation of the low density (rhyolitic) glass and for the identification and estimation of the higher density (andesitic) glass.

S4-2: The Recovery of Rhyolitic Glass from Soils:

The first stage in the isolation of this glass is the liberation of the primary mineral grains from the surrounding matrix of allophanic clay. Chemical techniques for this process are described elsewhere (1) but ultrasonic cleaning is also effective. To safeguard against the possibility of the differences in a physico-chemical parameter being a function of cleaning procedure, as was claimed of the refractive index by Steen and Fryxell (1965) it is important that this process be as standardised and reproducible as possible.

For the present purpose a Kerry ultrasonic probe was used at maximum frequency and intensity settings on a slurry of about 100 grams of dried ash crushed through a sieve of opening 250 microns in some 100 ml of water. The slurry was normally subjected to ultrasonic vibration for about five minutes during which the slurry was kept agitated with a magnetic stirrer. (2).

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(1) By this means some of the magnetite was lost, and the mafite fraction of the sample is therefore slightly underestimated.

(2) This is purely on the basis of appearance: these "less weathered" samples usually gave a pale brown or yellow slurry when mixed with water, whereas the "more heavily weathered" sample gave a dark brown slurry usually of higher viscosity.

The precise time needed to remove the allophane adhering to the mineral grains depends on the amount of these present: lesser weathered samples with larger mineral grain content taking rather less time than the more strongly weathered soils. The grains were then allowed to sink to the bottom of the container and recovered from the overlying allophanic suspension by repeated washing with warm water and decantation. The grains were finally washed in acetone and set to dry under a heat lamp. The loss in weight during this extraction procedure is largely that of allophane, although inevitably small amounts of finely divided non-allophanic mineral grains are lost. It would be expected that samples that have been subjected to active soil-forming processes would show a lower yield of non-allophanic material than that tephra protected by rapid burial. This can be demonstrated in the profile at Whaka Forest (site 11) where the yields are lowest at the top of the recognised paleosol and higher at the base. This data is presented in Table 4-1. A similar effect is observed in the Oruanui beds at Tapapa Road (samples 905 and 906).

TABLE 4-1: Yield of Non-Clay Material as a Function of Position in Stratigraphic Sequence.

Sample	Yield (%)	Stratigraphic Relationship
1101	28	
1102	50	top of Paleosol
1103	75	
1104	73	parent lapilli
1105	57	'A' horizon of paleosol
1106	46	
1107	51	
1108	63	
1110	59	'A' horizon of paleosol
1111	71	
1112	65	
1113	57	) reverse trend may be due to differing
1114	51	) weathering regimes, ground-water flow, etc

As can be seen in the lower part of the Whaka Forest profile, other factors may modify the effect of burial, specifically a change in the weathering regime, and changes in the ground water flow (particularly if lateral flow becomes appreciable). These effects are discussed more fully subsequently in Chapter 6.

The yields for the samples making up the Tirau and Mairoa Ash sequences are given in Table 4-2. It will be clear that there are marked differences between sites, if the yields for the Oruanui and Rotoehu beds are compared. Also shown are scaled yields on the basis of Oruanui being 1.0.

TABLE 4-2: Yields of Non-Clay Material in Sequences of Tirau and Mairoa Ashes

Sample	Yield (%)	Scaled Yield	Sample	Yield (%)	Scaled Yield
901	24	0.65	401	16	0.94
902	20	0.54	402	11	0.65
903	17	0.47	403	7	0.41
904	14	0.38	404	11	0.65
(905	28	0.76	405	20	1.17
(a)(906	45	1.21	(a)406	17	1.00
			407	16	0.94
201	16	(c)	408	24	1.41
202	8		(b)409	58	3.40
203	5				
204	5		501	8	1.14
205	10		502	6	0.86
206	4		(a)503	7	1.00
			504	8	1.14
301	21	0.41	(b)505	12	1.71
302	20	0.38			
303	12	0.33	601	37	1.12
304	9	0.24	602	38	1.15
305	26	0.50	603	37	1.12
306	9	0.24	(604	42	1.28
(a)307	52	1.00	(a)(605	24	0.73
308	22	0.42	606	34	1.00
(b)309	43	0.82			

Notes: (a) field correlation: Oruanui Ash

(b) field correlation: Rotoehu Ash

(c) sequence not accessible to Oruanui and Rotoehu, so scaled yields not determined.

It is of interest that the scaled yields for Mairoa Ash appear to be larger than those for the samples from the Tirau Ash sequence, and that in spite of the higher rainfall at most of the sites for Mairoa Ash, it has a low clay content. The low yields for the samples at Tirau (site 2) and Kakepuku (site 5) can probably be linked with lateral ground water flow (see Chapter 6); since the yields are all lower than expected, even sample 503 (which is believed on field evidence to be Oruanui Ash).

After the separation of allophane, various mineral classes were separated by density flotation in heavy liquids assisted by centrifugation. Various modifications of the basic ideas have been made, as discussed by Marshall and Jeffries (1945) and Mueller (1967); in the present case constricted centrifuge tubes have been used, employing a rubber stopper attached to the end of a glass rod to close the constriction to facilitate the separation of floating and sinking grains. Initially a 78% solution of acetone in bromoform of density 2.42 gm/ml was used, in which rhyolitic glass floated and all other minerals sank. These latter grains, upon recovery, were subjected to the same treatment but using bromoform itself (of density 2.86 gm/ml). In this case the mafic minerals sank and felsic minerals such as quartz and feldspar floated. The recovered fractions were all washed with acetone to remove any remaining bromoform and were then set to dry under heat lamps.

Such techniques have the inevitable result of generating large volumes of bromoform-acetone mixtures of density too low for regeneration as a density separating reagent by adding further bromoform. The most effective means of recovery appears to be to wash the bromoform with water, thereby removing the acetone and subsequent drying of the product with fused calcium chloride (Muller and Burton, 1965). The recovery of bromoform can be enhanced by using a sweat-box, modified after Woo (1964), to recover the bromoform from the calcium chloride. The purity of the recovered bromoform can be assessed by its density, or more rapidly by its refractive index. The apparatus used in this thesis to recover bromoform is shown in Fig. 401.

The rhyolitic glass was subsequently purified magnetically to remove any iron-bearing weathered products of low density. For this a Frantz magnetic separator was used, with a forward slope of 20°, a side-slope of 10°, and a magnet current of one amp. On the basis of a nomogram of Hess (1966), the pure glass, invariably white or pale yellow in colour, is essentially non-magnetic. With some samples, particularly of Mairoa Ash from Mairoa itself, considerable brown magnetic material was removed in this way. This material gave no significant x-ray diffraction peaks (A.G. Hogg, pers. comm.), but differential thermal analysis curves were suggestive of gibbsite (N.B. Milestone, pers. comm). This last possibility is inconsistent with the material's magnetic properties unless it is contaminated with hydrous iron oxides.

S4-3: The Identification and Estimation of Andesitic Volcanic Glass:

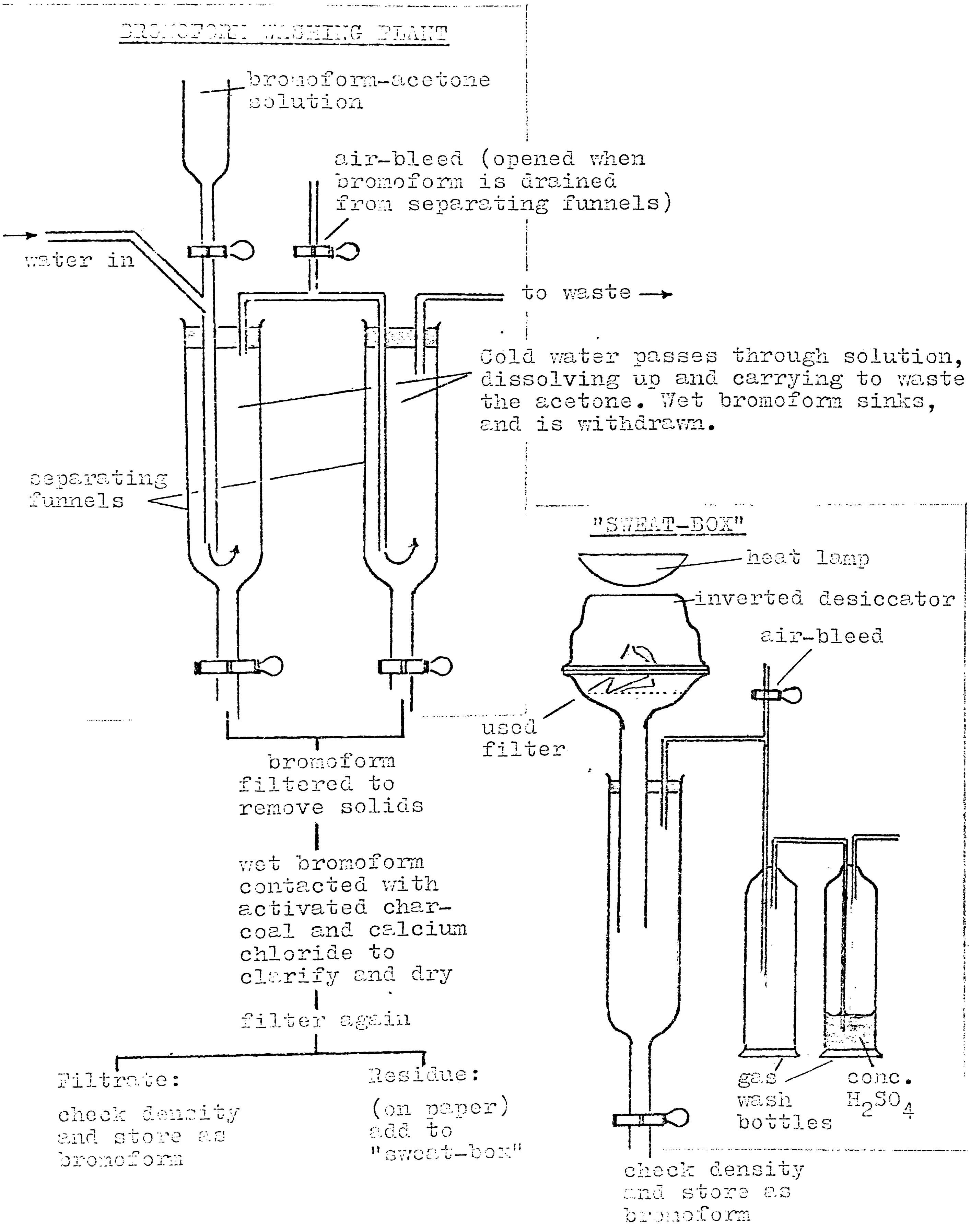
An andesitic glass would be expected to resemble in composition the plagioclase feldspar andesite. On this basis a silica percentage of some 60% is expected (Deer, Howie and Zussman, 1967). A comparison of plots of density and refractive index as a function of silica content (for example that of George, 1924) with similar data for quartz and feldspar (van der Plas, 1966) suggests that this material would be hard to separate physically. An instrumental method for confirming the presence of this glass and for its quantitative estimation was sought: infra-red spectroscopic investigation proved feasible and is now described.

The use of infra-red spectroscopy in studies of vitreous material has long been recognised. Simon and McMahon (1953) wrote:

> "One of the most significant uses of the infra-red method is its ability to analyse for amorphous materials such as glasses, whether these are natural volcanic glasses like obsidian or synthetic glasses like pyrex."

FIG 401

Apparatus for bromoform recovery



In mineralogical studies, infra-red spectrscopy was applied in the determination of properties of quartz and vitreous silica (Gaskell, 1966; Yanagase and Sugionhara, 1970), and also in the determination of structural analogues of glass (Wong and Angell, 1970). Of greater significance, mineralogically, however, was the application of the technique to clay minerals (Fieldes, 1955). Fieldes, Furkert and Wells, (1972) subsequently gave the infra-red spectra of "glassy rocks and primary minerals" and "amorphous and crystalline clay minerals" and these are reproduced in Fig. 402. From this diagram it is clear that in order to use infra-red absorption to identify glass it is necessary to pretreat the sample to remove clay minerals. Further in order to determine andesitic glass, it is necessary to ensure that the sample is free of rhyolitic glass.

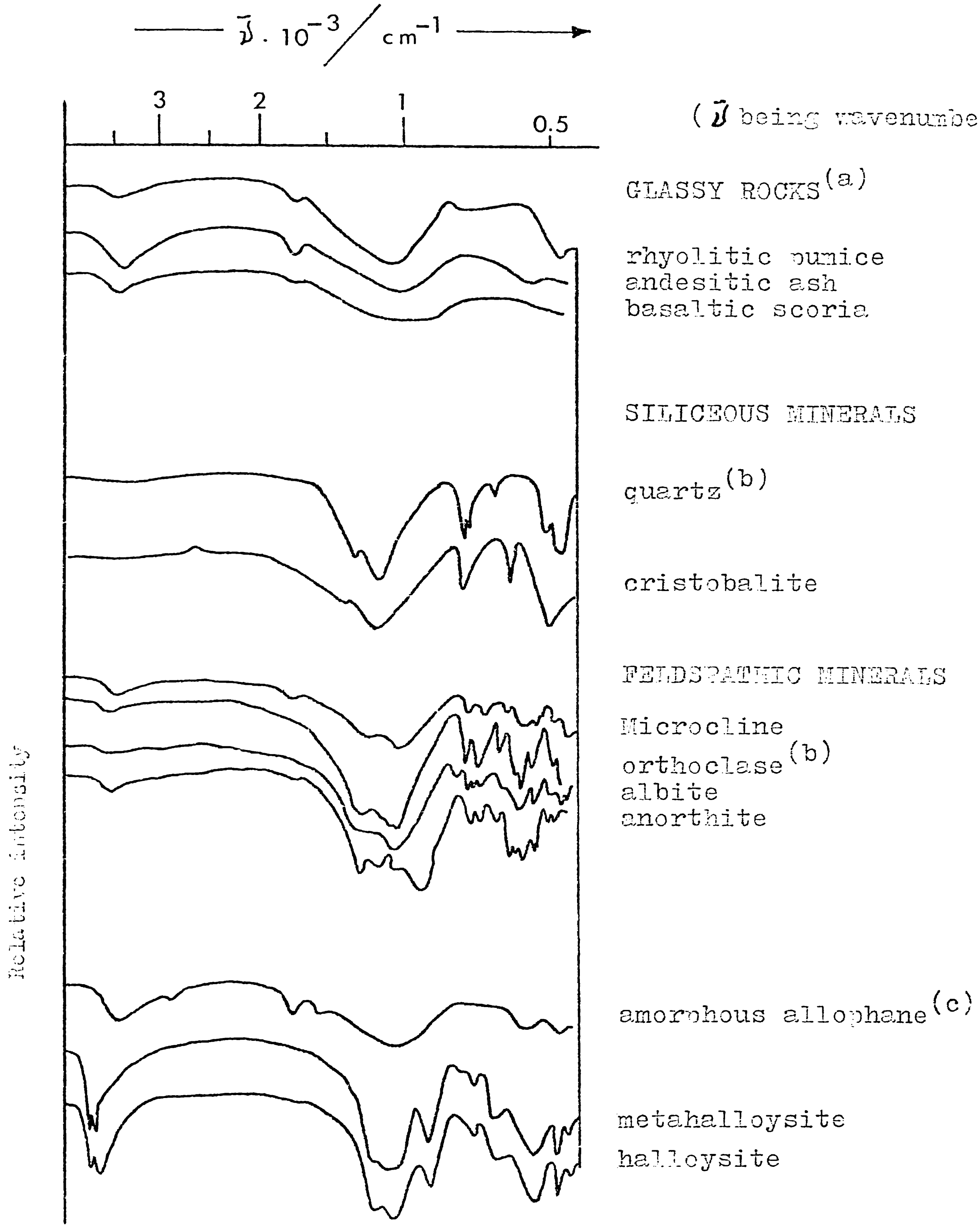
The technique of separation of mineral grains as described thus far has separated the rhyolitic glass, the clay (allophane) and the mafic minerals, thereby leaving in one fraction feldspatic and siliceous minerals and such andesitic glass as may be present. This glass would be expected to show an absorption spectrum similar to that of rhyolitic pumice on Fig. 402. Infra-red spectra of representative felsic fractions (Fig. 403) show this similarity suggesting that glass is present, but this is more readily appreciated once the quantitative aspects of the spectra are recognised.

The quantitative nature of the infra-red absorption pattern has been described by Lyon (1967) as:

> "Glasses possess 'molecular' structure and thus show infra-red spectra where patterns change with composition and progressive ordering (as in the beginning of crystallisation). Glasses can often be treated, therefore, as separate phases where infra-red spectra appear in addition to those of any crystalline material present."

FIG 402

Infra-red spectra of "glassy rocks and primary minerals" and "amorphous clay minerals"



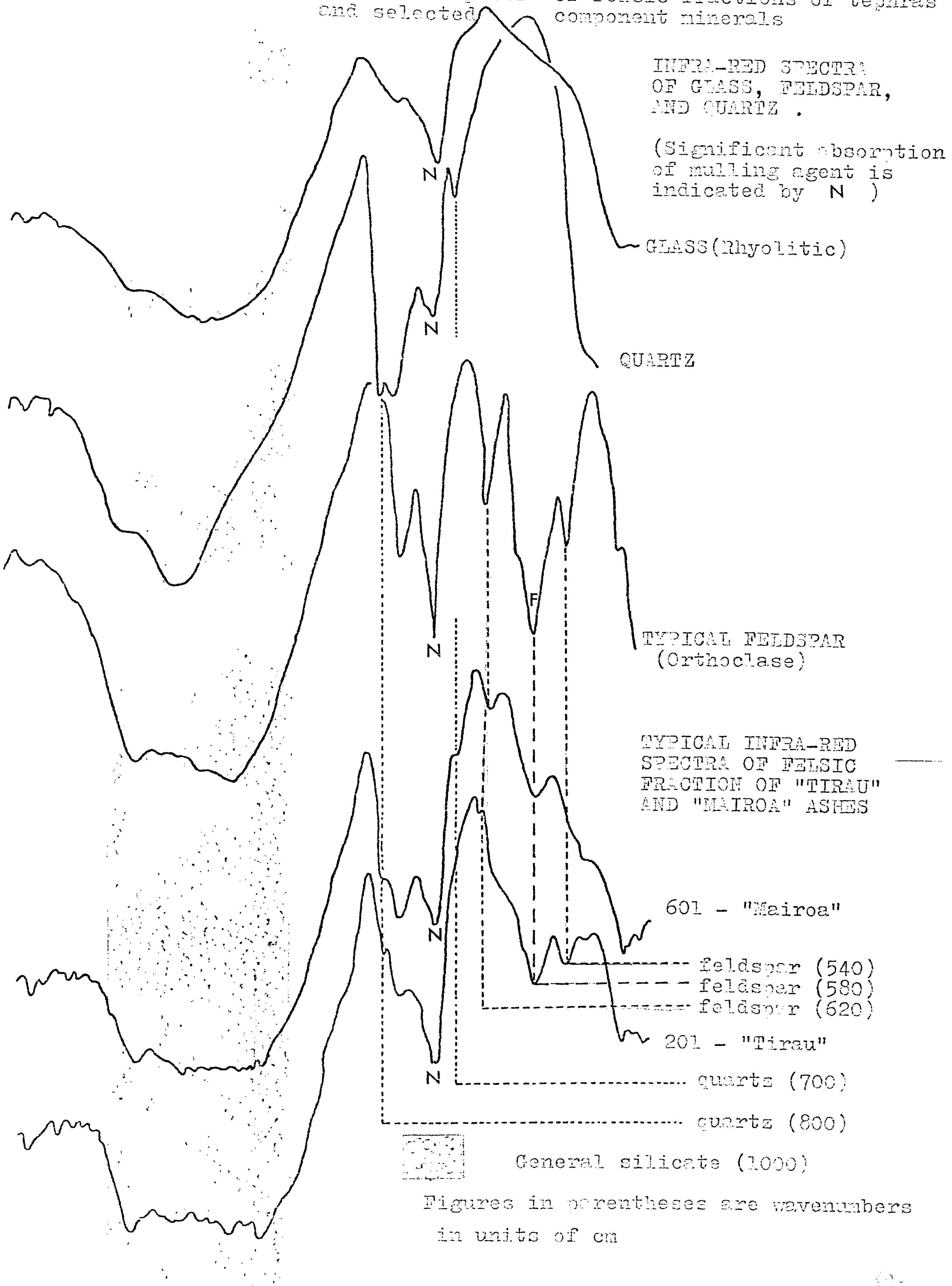
(a) undoubtedly incorporates elements of spectra of siliceous and feldspathic minerals

(b) minerals used in combination with glass for calibration

(c) Note the similarity to the spectra for glassy rocks. This demonstrates the necessity for removing such material before infra-red analysis of glass-bearing samples

FIG. 403

Infra-red spectra of felsic fractions of tephras and selected component minerals



Figures in parentheses are wavenumbers in units of cm

More specifically it has been stated that "from standard calibration curves obtained by using individual pure minerals, and with the aid of synthetic mixtures of the diagnostic minerals, the quantities and types of minerals present in the unknown samples can be rapidly determined" (Lyon, 1963).

The difficulties of quantitative analysis by infra-red spectroscopy are practical rather than theoretical. Most authors make use of potassium bromide discs, using a standardised preparative technique to ensure reasonable reproducibility (Lyon, Tuddenham and Thompson, 1959; Duychaerts, 1959). Reference is frequently made in studies of this kind to the difficulties in reproducibility, arising from the grinding of the sample. It is claimed by Fieldes, Furkert and Wells (1972), for example, that the absorption peaks of quartz become more pronounced with grinding. More typical, however, in the observations of Fieldes and Furkert (1966) that peak heights become less marked with increased grinding. This is usually attributed to a loss of crystal structure. Clearly this grinding problem becomes even more significant when mixtures of minerals of differing hardness are involved. In the present study synthetic mixture of borosilicate glass or rhyolitic volcanic glass were required to be mixed with quartz or feldspar. The glasses are much harder than the latter minerals, and it was found that unless the mixture was heavily ground, the potassium bromide disc contained inhomogeneities presumably caused by the glass. If the mixture was ground sufficiently to produce satisfactory discs without such inhomogeneities, much of the feldspar absorption was lost. For this reason, and also for reasons of time, recourse was made to the use of nujol mulls. This technique has not been widely used in mineralogical work but has been employed quantitatively in organic chemistry, as for example by Barnes (1947) in a study of the structure of penicillins.

Quantitative analysis using the disc preparative method is usually achieved by interpolating the sample's absorbance on diagnostic wavelengths on curves derived from standard spectra. Frequently it is sufficient to compare relative intensities of appropriate absorptions, (Fieldes, Furkert and Wells 1972; Lyon, Tuddenham and Thompson, 1959). In either case the method of preparation is such as to produce discs of consistent thickness. Thus, if the incident infra-red radiation is considered to conform to the Beer-Lambert law:

$$\log (Io/I) = \epsilon c d$$

where Io and I are baseline and peak intensities respectively, ϵ is the extinction coefficient and d the thickness of the disc, then a plot of absorbance, A, as a function of concentration, c, should be linear. For mulls however there is the added complication that the mulls may vary in thickness. Barnes (1947) suggested the use of an internal standard whence it could be shown that:

$$(\log (Io/I) \text{ sample})/(\log (Io/I) \text{ standard}) = \text{const.} \times \text{concentration}$$

This is to say that the concentration of a particular component was the ratio of the absorbances of the component and of the internal standard, whose proportions are known by setting up appropriate standards. The difficulty in mineralogical applications of this analytical technique is finding an internal standard whose principal absorption differs significantly in wavelength both from the silicates being determined and from the mulling agent, and whose subsidiary absorptions are such as to negligibly complicate the spectra of silicates by absorbing at their diagnostic wavenumbers. As can be seen from Table 4-3 and in the typical spectra of feldspathic and siliceous minerals reproduced in Figs. 402 and 403, such a standard would conveniently need to have its only significant absorption at a wavenumber higher than 1500 cm^{-1}. There was found to be no suitable compound to use in this way and thus it was decided to use an absorption given by all silicates (namely the Si-O 'stretch' absorption) as an internal standard.

TABLE 4-3: Principal Absorption Wavenumbers for Feldspathic and Siliceous Minerals

Mineral	Diagnostic wavenumber for quantitative analysis ($\bar{\nu}$ /cm^{-1})(a)	Diagnostic wavenumber (not quantitative) ($\bar{\nu}$ /cm^{-1})(b)	Other absorptions ($\bar{\nu}$ /cm^{-1})(c)
rhyolitic glass andesitic glass	spectrum characterised by absence of absorptions other than at		800, 1050
quartz	690, 795	<u>ca</u> 500	1080
feldspar	580	540, 620	980, 720-780

(a) These wavenumbers used in the calibration curves described in Sec. 4-4.

(b) These wavenumbers are diagnostic for the mineral but the absorbances are usually too low to be used quantitatively.

(c) Note that all silicates absorb in the regions 800 cm^{-1} and 1000 cm^{-1}.

From Table 4-3 it is clear that since all silicates absorb at around 100 cm^{-1}, the absorbance for this broad peak can be considered, at least to a first approximation, as representative of the total silicate. Thus the ratio of the absorbance of feldspar and quartz at their respective diagnostic frequencies to the total silicate absorbance is expected to be a linear function of the concentration of feldspar and quartz relative to the total silicate. The calibration curves subsequently described are based on this premise.

That all silicates absorb in the region of 1000 cm^{-1} is a property that lends itself to semi-quantitative interpretation. In general, the lower the proportion of quartz and feldspar the broader is the absorption. There is some tendency for the wavelength associated with this peak to be slightly composition-dependent. This was established by comparing the spectra from various synthetic mixtures of silicates. However, there is a secondary absorption at 1130 cm^{-1}, which is independent of composition and it is at this wavenumber that the absorbances for the total silicate absorption have been calculated.

§4-4: Calibration Curves for Infra-Red Analysis of Felsic Minerals:

Mixtures of glass and orthoclase were prepared by weighing out appropriate amounts of the materials, followed by intimate mixing and grinding. A mull was prepared of the whole specimen, and then the infra-red spectra of the mull contained between potassium bromide windows was obtained. For the glass portion of the mixture, rhyolitic volcanic glass (extracted as previously described) was used. Although this differs compositionally from the andesitic glass the technique seeks to determine, the infra-red spectra are taken to be the same, infra-red spectra being rather more a function of structure than chemical composition. Typical of the spectra of these synthetic mixtures are those presented in Fig. 404. From such spectra the intensities are evaluated and hence the absorbances obtained. In the analysis the background intensity is taken to be that intensity at which the line joining the upper regions of the peak intercepts the wavenumber in question. This is shown diagrammatically in Fig. 405. The ratio of the absorbances of the feldspar to total silicate absorptions are plotted as a function of proportion feldspar in Fig. 406 wherein it is seen that the nature of any other silicates present is of no consequence: in that there is no systematic bias or clustering of points corresponding to a particular type of synthetic mixture. When linear regression statistics are applied to the data the results given in Table 4-4 are obtained.

The same analytical procedure can be applied to infra-red analysis for mixtures containing quartz. In this case the procedure is complicated by the nature of the diagnostic absorptions, whether the absorptions should be considered as peaks in their own right or as shoulders to neighbouring absorptions (see Fig. 406). The results of linear regression analysis of spectra of standard mixtures, the spectral intensities of which have been modified as previously described are given in Table 4-4.

TABLE 4-4: Linear Regression Statistics for Determination of quartz and feldspar in synthetic mixtures.

lineral analysis (M):	feldspar	quartz	quartz	quartz	quartz
Wavenumber ($\bar{\nu}$ /cm^{-1}):	540	780	780	690	690
Absorption character:	peak	peak	shoulder	peak	shoulder
Parameter: Correlation coeff * (r)	0.977	0.862	0.751	0.861	0.955
Intercept (b)	-0.0026	0.064	0.002	0.055	-0.0094
Slope (m)	0.004	0.004	0.002	0.001	0.0009

* r is the correlation coefficient for the straight line $Y = mx + b$, where Y is the absorbance ratio and X is the mineral proportion.

Clearly for best results a relationship of high correlation coefficient and high slope is desirable. It is apparent from Table 4-4 that for the 780 cm^{-1} peak, the calibration curve of absorbance ratio versus concentration has a slope comparable to that obtained for feldspar analysis. The higher correlation coefficient that results from treating the absorption as a peak in its own right indicates that this is the preferable analytical method. For the 690 cm^{-1} peak, the correlation coefficient for the peak treated as a shoulder is much higher than when treated as a peak in its own right, but the low slope of the curve indicates that such analysis is of low sensitivity.

FIG. 404

Gradation of infra-red spectra for various mixtures of glass and feldspar. The spectra given are for synthetic mixtures of orthoclase and rhyolitic glass.

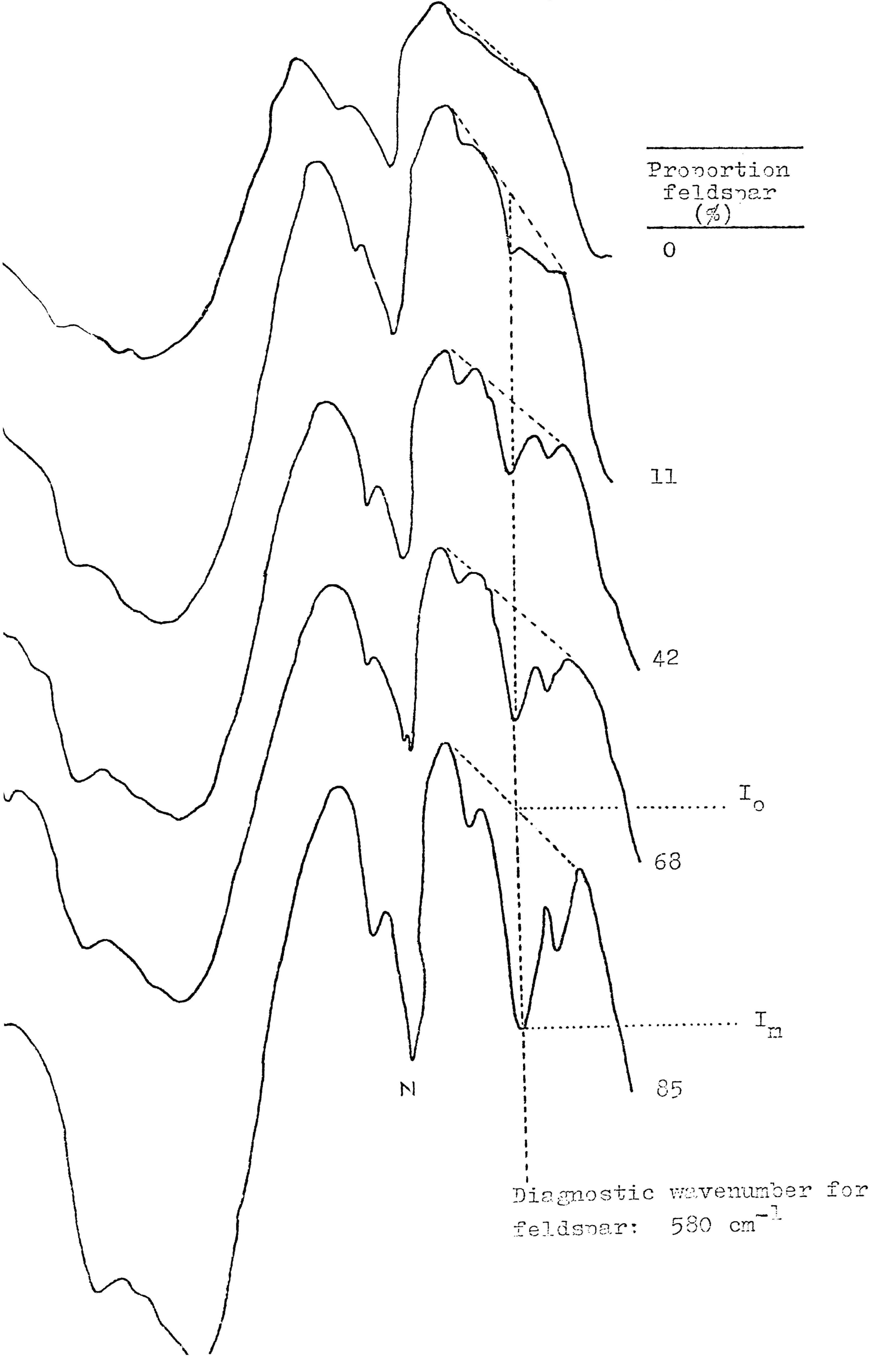
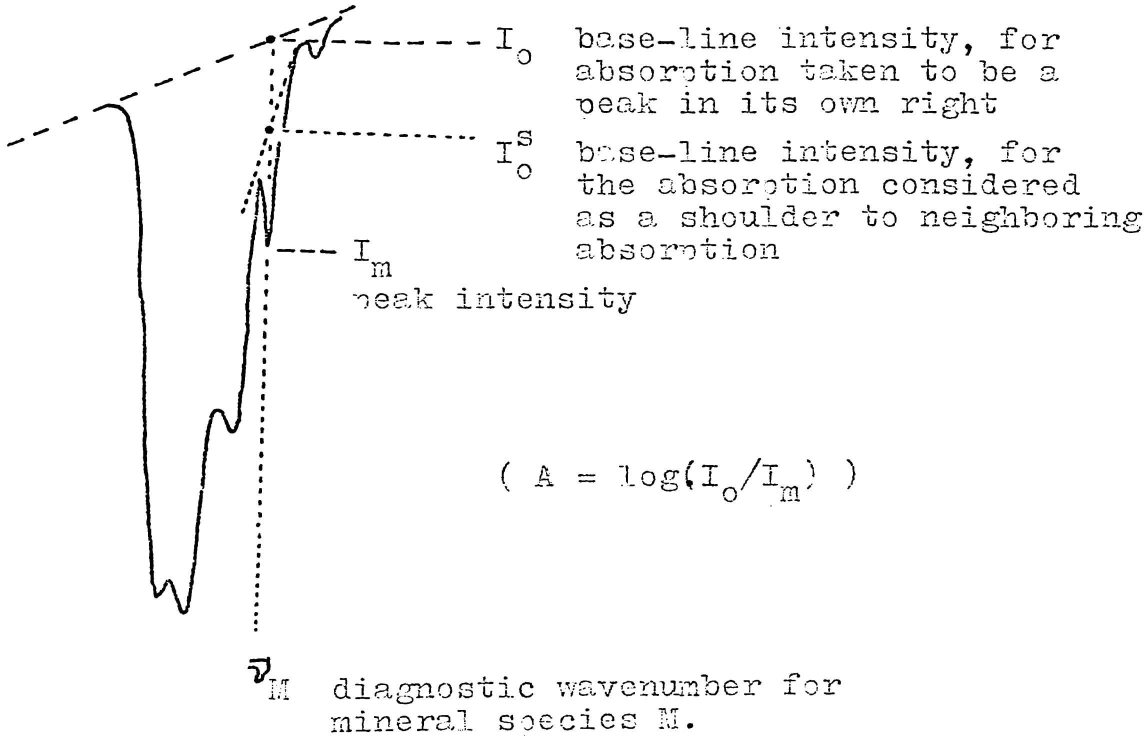


FIG. 405

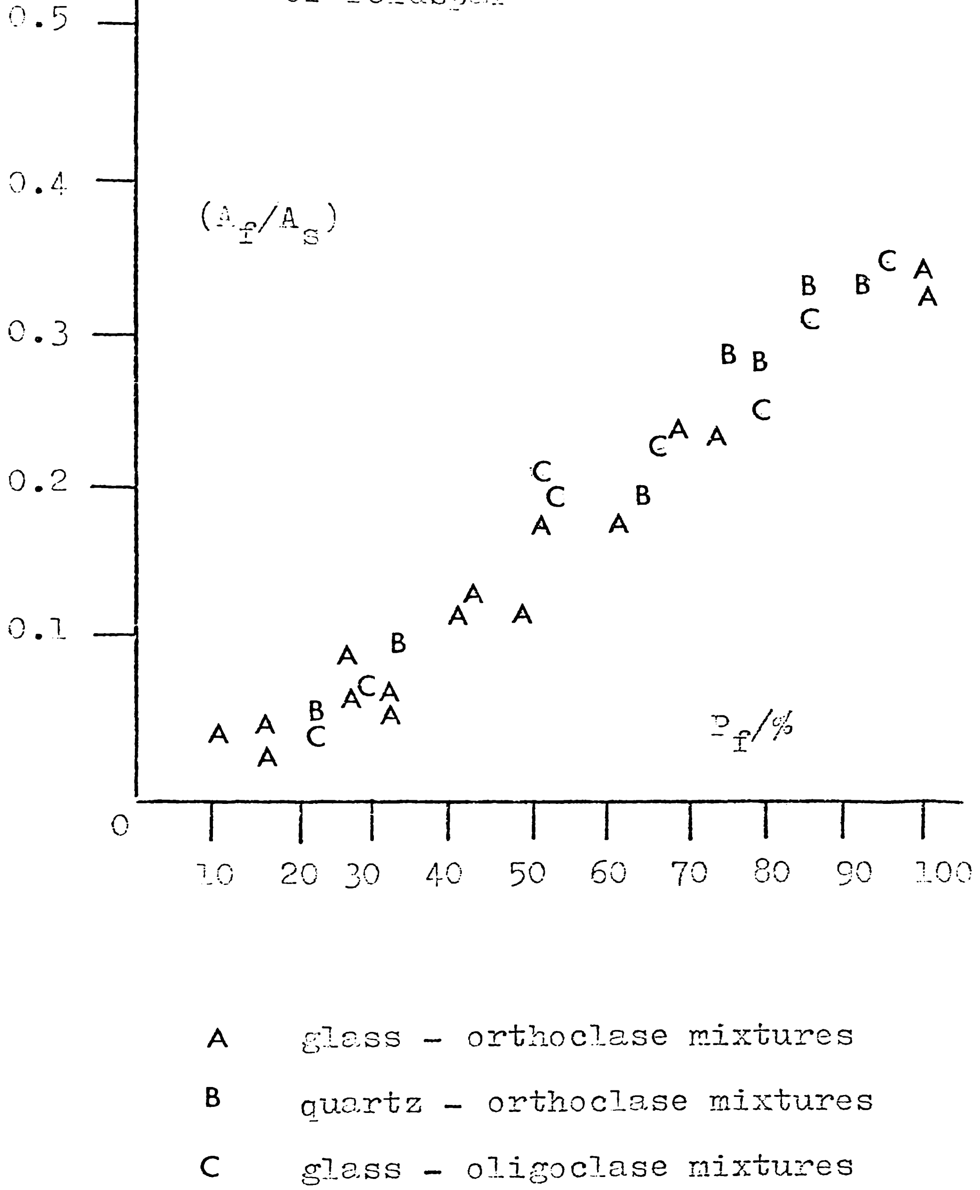
Terminology for the identification of base and peak intensities for diagnostic absorptions



$$(A = \log(I_o/I_m))$$

FIG 406

Calibration curve for infra-red determination of feldspar



(There is an essentially linear relationship between the absorbance ratio, feldspar to total silicate (A_f/A_s) and the proportion of feldspar (P_f) in synthetic mixtures of feldspars and other silicates)

S4-5: Conclusion:

In this chapter procedures have been described for the recovery of rhyolitic glass and for the determination of vitreous components in the felsic fraction, being those minerals of density greater than rhyolitic glass (ca 2.42 $gm.cm^{-3}$) and less than that typical for mafic minerals (> 2.8 $gm.cm^{-3}$). Infra-red spectroscopy has been shown to be a suitable technique for the identification and determination of quartz and feldspar in this fraction; the andesitic glass being taken to be the balance of the felsic minerals. In the next chapter the relative proportions of these felsic minerals and rhyolitic glass (herein referred to as the leucocratic mineral assemblage) are considered and in Chapter 6 the relative proportions of the two vitreous components are interpreted in terms of a kinetics model for weathering.

CHAPTER 5: Mineral Assemblages in Tephra Identification:

S5-1: Introduction:

The recognition of mineral assemblages has long been used to differentiate tephra, particularly where different sources are implicated and preferably where different tephra are envisaged. In effect correlation of tephra on this basis makes the implicit assumption that identity of characteristic assemblage indicates identity of strata. While such an approach is at risk of being prey to the Neptunist fallacy (Eicher, 1968) concept is undoubtedly reasonable over a limited area, wherein it is claimed (Fieldes and Weatherhead, 1968) that in spite of possible comminution and redistribution of the original material:

> "in general sufficient material remains associated in sand fractions to permit identification of the principal source rocks."

In this chapter mineral assemblages are considered on the basis of density and on the basis of the relative proportions of the leucocratic minerals. Because of the doubts cast by Wellman (1962) on the use of mafic mineral assemblages little investigation has been made of these in this research.

S5-2: Mineral Assemblages on the Basis of Density:

Fieldes and Weatherhead (1968) give typical mineral assemblages for rhyolitic and andesitic parent ashes, and these together with typical densities are grouped in Table 5-1 in terms of glass, felsic minerals, and mafic minerals. In this table it is assumed that the glass present in andesitic tephra is largely andesitic and thus of a density consistent with that of felsic minerals, while it is taken that the glass of rhyolitic tephra is taken to be rhyolitic and therefore of lower density.*

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* These density relationships are considered in great detail in Chapter 7.

TABLE 5-1: Mineral Assemblages of Rhyolitic and Andesitic Tephras:

Mineral	Typical Density /gm.cm^{-3} (a)	Rhyolitic Tephra: Mineral Proportion	Rhyolitic Tephra: Class	Rhyolitic Tephra: Class Proportion	Andesitic Tephra: Mineral Proportion	Andesitic Tephra: Class	Andesitic Tephra: Class Proportion
glass (Rhyolitic)	2.30(b)	60(c)	GLASS L	60	-	GLASS L	0
glass (andesitic)	2.60(d)	-	FELSIC M	30	30(3)	FELSIC	70
quartz	2.65	V.L.			V.L.		
andesine	*ca* 2.69	-			40		
alkali feldspar	2.56 - 2.63	30			-		
biotite	2.7 - 3.3	-	MAFIC H	5	5	MAFIC H	30
hornblende	3.0 - 3.5	1			10		
hypersthene	3.96	1-3			5		
augite-diopside	2.96 - 3.22	1			5		
ilmenite	4.70 - 4.78	-			1-5		
magnetite	5.20	1			1-5		

Mineral and class proportions are expressed in percent whole tephra.

(a) unless otherwise stated, densities from Deer, Howie and Zussman (2)

(b) evaluated by technique described in Chapter 7.

(c) all glass in rhyolitic ash assumed rhyolitic.

(d) If andesitic glass reflects the plagioclase composition of andesine, then its SiO_2 proportion is expectedly some 60%. By the plot of George (1924) of density versus SiO_2 content, this gives a density of some 2.60 gm/ml. (See also Chapter 7).

(e) all glass in andesitic tephra assumed andesitic.

In Table 5-2, the proportions of minerals given are of the material retained after ultrasonic cleaning and for comparison with the literature values given, it is assumed that the ultrasonically cleaned material is comparable to the sand fraction of Fieldes and Weatherhead (1968). As is shown on the literature-derived plots the proportion of mafic minerals shows a relative increase with age and weathering presumably due to the faster weathering of glass and feldspar. From the plots of data, Fig 5C2 derived in this study it is seen that the marker bed, Oruanui Formation, shows a greater proportion of mafic minerals in some of the more westerly sites. This is probably a result of more intense weathering at these sites. Thus, a strongly weathered rhyolitic tephra may tend

TABLE 5-2: Density Assemblages of Sand Fractions(a) of Sequences of Tirau and Mairoa Ashes

Sample	P_L (%)	P_M (%)	P_H (%)
201	64	29	7
202	62	29	7
203	75	20	5
204	65	27	7
205	68	29	3

TABLE 5-2: continued

Sample		P_L (%)	P_M (%)	P_H (%)
206		35	55	10
301		68	24	8
302		70	24	6
303		57	32	11
304		43	52	5
305		11	73	16
306		44	48	8
307		60	34	6
401		52	34	14
402		45	41	14
403		45	44	11
404		59	35	7
405		57	37	6
406	(b)			
407		35	53	12
501		52	30	19
502		40	41	19
503		30	50	20
504		28	47	24
505		33	53	14
601	(c)	40	49	11
602	(c)	55	40	5
603	(c)	40	55	5
604		65	29	5
605		73	23	4
606		7	87	4

TABLE 5-2: continued

Sample	P_L (%)	P_M (%)	P_H (%)
901	56	37	7
902	53	41	6
903	62	33	5
904	73	23	4
905	75	23	2
906	36	53	11

(a) the allophanic content of the ashes is thereby ignored.

(b) not available.

(c) strongly weathered, abundant brown glass.

to the same region of the ternary diagram as an adesitic one. Thus density assemblages can distinguish with certainty fresh rhyolitic tephra from other material, but is less able to resolve between an andesitic tephra and a weathered rhyolitic one.

A clearer distinction between tephra types is likely if allowance is made for there being two types of glass in differing proportions and this is described in the next sections.

S5-3: Leucocratic Mineral Assemblages in Tephra Identification:

Using the analytical procedure described in the previous chapter the proportions of quartz, feldspar and andesitic glass the leucocratic mineral fraction may be found. This can be converted to proportions of andesitic glass, rhyolitic glass, quartz, and feldspar in terms of the ultrasonically cleaned material (the sand fraction) or to the original ash. These proportions are shown in Table 5-3.

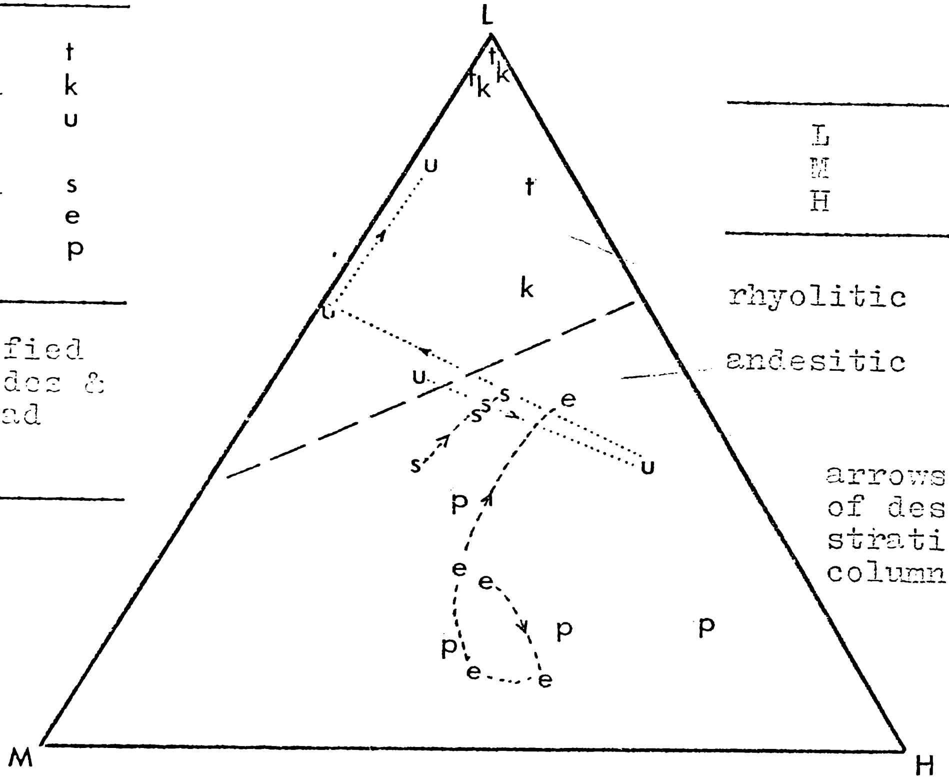
FIG. 501

Ternary diagram of density fractions for sand fractions of the soils derived from various tephras

Soils	
Taupo	t
Kaingaroa	k
Tirau	u
Stratford	s
Egmont	e
Patua	p

Data modified from Fieldes & Weatherhead (1968)

Fraction	Density range $\rho/\mathrm{gm.cm}^{-3}$
L	< 2.4
M	$2.4 - 2.8$
H	> 2.8



arrows in direction of descent of stratigraphic column

Parent rocks and tephras	
rhyolitic tephra	R
andesitic tephra	A
basaltic scoria	B
rhyolite	r
andesite	a
basalt	b

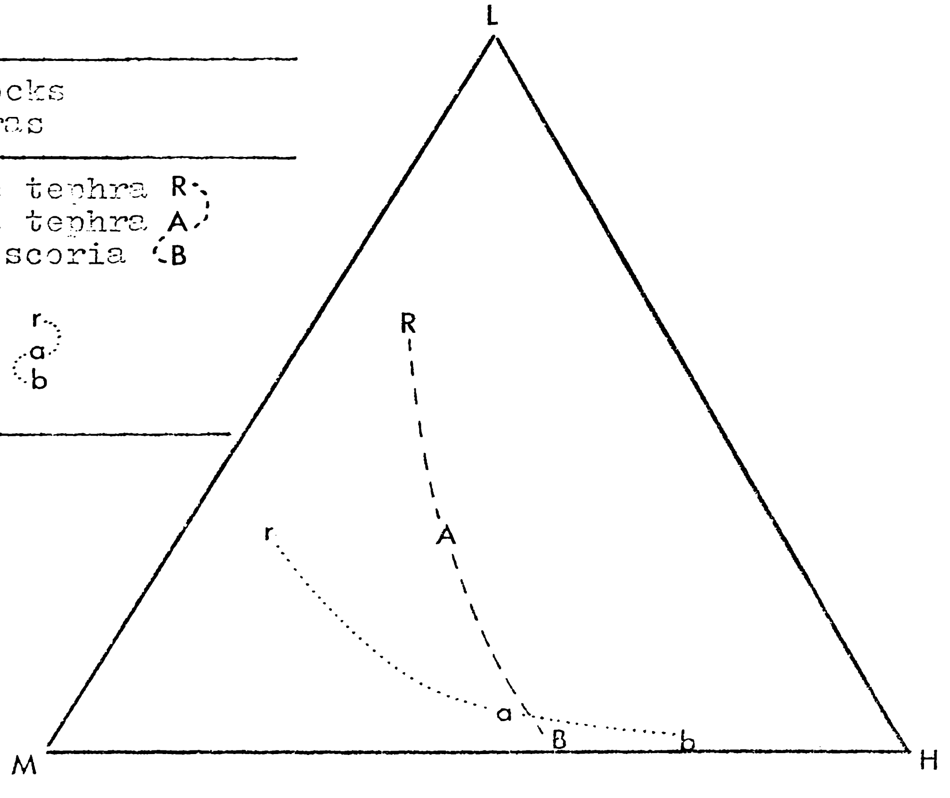
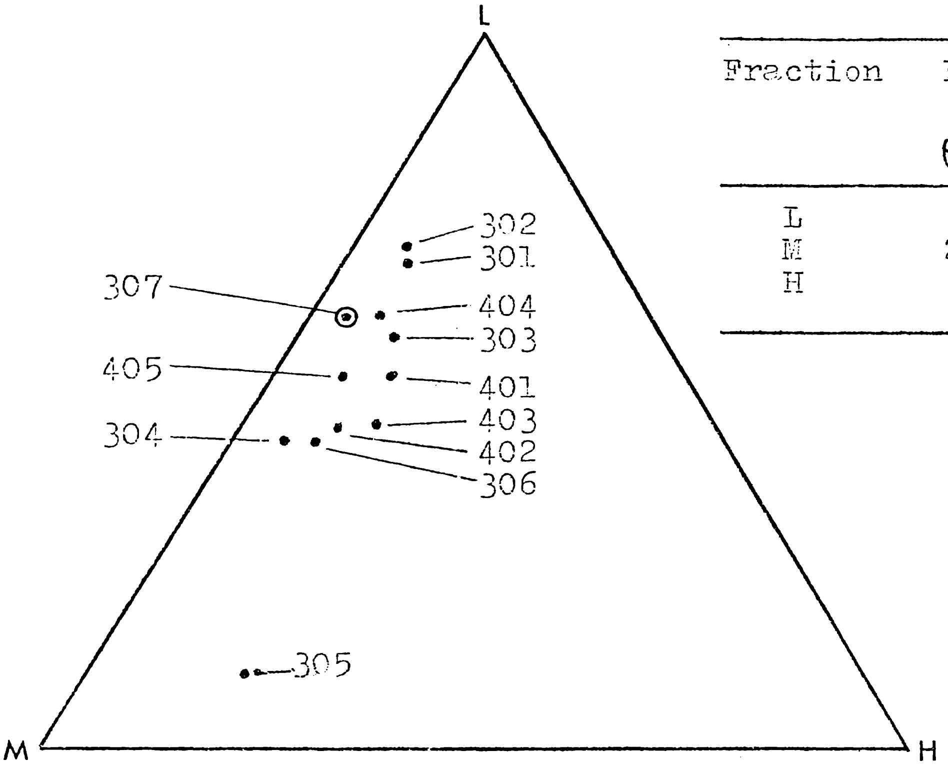


FIG. 502

Ternary diagrams of density fractions for non-clay fractions of samples from sequences of Tirau Ash and Mairoa Ash



Fraction	Density range ρ/gm.cm^{-3}
L	< 2.4
M	2.4 - 2.8
H	> 2.8

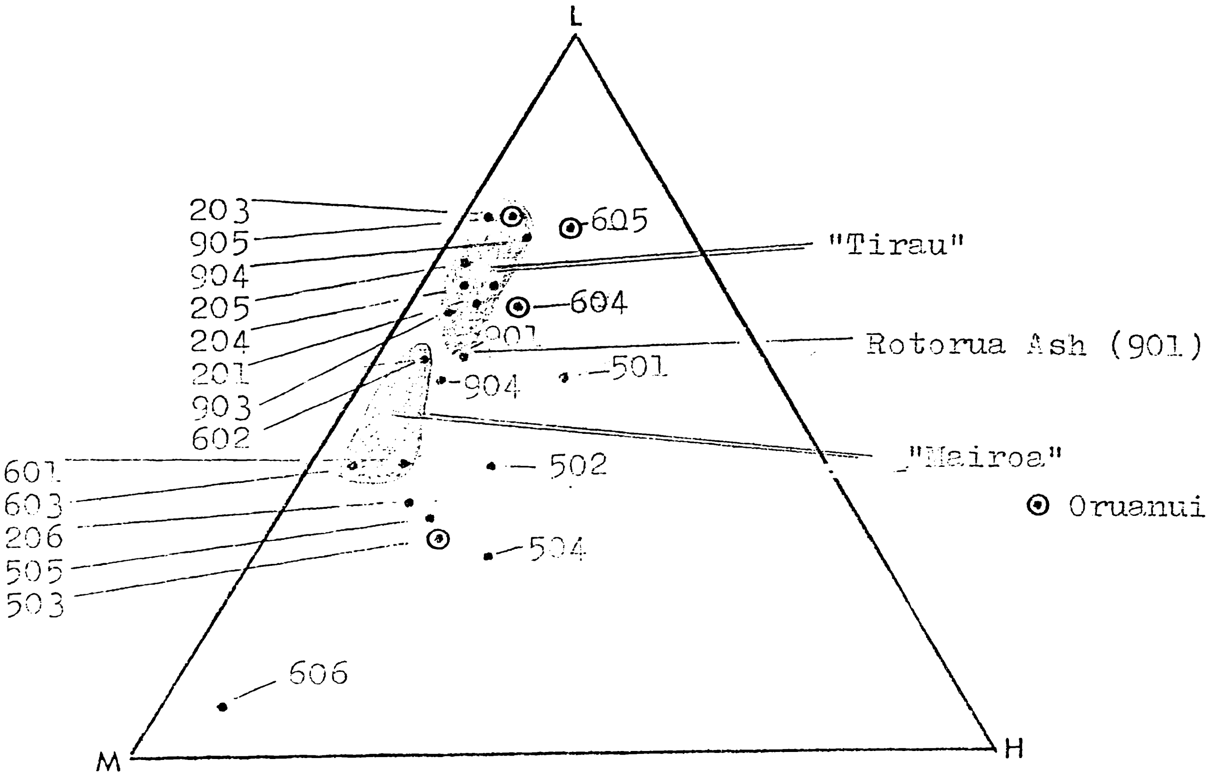


TABLE 5-3: Proportions of quartz, feldspar, andesitic glass, and rhyolitic glass in the ultrasonically cleaned product (sand fraction) and the whole sample for sequences of Tirau and Mairoa Ashes.

Sample	Ultrasonically Cleaned Product				Original Ash			
Proportion	Quartz (P_Q/%)	feldspar (P_F/%)	Andesitic glass (P_{G_a}/%)	Rhyolitic glass (P_{G_r}/%)	Quartz (P_Q/%)	Feldspar (P_F/%)	Andesitic glass (P_{G_a}/%)	Rhyolitic glass (P_{G_r}/%)
201	8	20.5	0	46.2	1.3	3.3	0	7.75
202	6.7	14.3	5.6	43.7	0.6	1.2	0.47	3.70
203	7.0	11.9	0	62.0	0.4	0.6	0	3.26
204	7.5	14.1	3.2	54.3	0.4	0.7	0.15	2.57
205	9.0	14.5	2.9	53.6	0.9	1.4	0.29	5.20
206	16.3	22.9	11.6	24.8	0.8	1.1	0.57	0.12
301	5.0	11.0	5.6	36.0	1.0	2.3	1.2	7.6
302	3.8	9.3	8.2	32.5	0.8	1.9	1.6	6.5
303	7.1	14.2	8.3	35.6	0.9	1.7	1.0	4.2
304	8.9	10.4	25.5	29.6	0.8	1.0	2.4	2.7

TABLE 5-3: continued.

Sample	Ultrasonically Cleaned Product				Original Ash			
Proportion	Quartz (P_Q/%)	Feldspar (P_F/%)	Andesitic glass (P_{G_a}/%)	Rhyolitic glass (P_{G_r}/%)	Quartz (P_Q/%)	Feldspar (P_F/%)	Andesitic glass (P_{G_a}/%)	Rhyolitic glass (P_{G_r}/%)
305	19.0	32.3	19.0	6.7	4.7	8.0	4.7	1.6
306	5.4	20.3	12.6	47.5	0.5	2.0	1.2	4.6
307^{OU}	5.5	11.9	13.2	45.8	2.9	6.2	7.1	2.4
308^{RE}	10.3	30.8	27.2	9.1	2.3	6.9	6.1	2.0
309^{RE}	4.8	5.6	16.2	17.3	4.0	4.7	13.5	14.4
401	5.9	17.4	7.8	30.3			1.29	4.98
402	8.3	17.8	13.6	23.0			1.43	2.44
403	10.9	19.2	10.1	32.8			0.73	2.35
404	9.3	15.6	7.5	46.5			0.84	5.20
405	9.0	19.2	7.9	47.0			1.60	8.35
406^{OU}	-	-	-	-			-	-
407	13.8	24.4	12.7	15.2			2.41	2.87

TABLE 5-3: continued

Sample	Ultrasonically Cleaned Product				Original Ash			
Proportion	Quartz (P_Q/%)	Feldspar (P_F/%)	Andesitic glass (P_{G_a}/%)	Rhyolitic glass (P_{G_r}/%)	Quartz (P_Q/%)	Feldspar (P_F/%)	Andesitic glass (P_{G_a}/%)	Rhyolitic glass (P_{G_r}/%)
408^{RE}	-	-	-	-	-	-	-	-
409^{RE}	8.7	17.2	0	14.6			0	7.7
501	10.0	13.2	4.4	24.8			0.32	1.83
502	7.6	19.4	10.9	20.0			0.63	1.15
503^{OU}	15.2	25.3	6.6	16.5			0.48	1.21
504	16.9	19.8	8.0	12.5			0.70	1.09
505^{RE}	21.3	18.3	6.0	6.6			0.69	0.75
601	24.7	14.0	6.1	3.5	9.30	5.28	2.3	1.3
602	15.4	13.1	10.1	3.7	6.00	5.05	3.9	1.4
603	18.6	12.2	22.3	13.4	4.02	2.64	4.9	2.9
604^{OU}	8.2	18.1	11.0	56.5	3.43	7.6	0.5	23.6
605^{OU}	5.3	10.8	5.1	70.0	1.30	2.6	1.3	15.7
606	22.3	9.9	5.5	2.5	7.65	3.4	1.8	0.9

TABLE 5-3: continued.

Sample	Ultrasonically Cleaned Product								
	Proportion	Quartz $(P_Q/\%)$	Feldspar $(P_F/\%)$	Andesitic glass $(P_{G_a}/\%)$	Rhyolitic glass $(P_{G_r}/\%)$	Quartz $(P_Q/\%)$	Feldspar $(P_F/\%)$	Andesitic glass $(P_{G_a}/\%)$	Rhyolitic glass $(P_{G_r}/\%)$
901		16	2	18	56	3.7	0.48	4.1	13
902		19	3	18	53	3.8	0.60	3.6	10.6
903		16	5	12	62	2.7	0.83	2.0	10.3
904		12	7	14	73	1.7	0.98	2.0	10.4
905^{OU}		* 8	2	9	71	2.3	0.57	2.6	20
		3	2	5	83				
906^{OU}		16	5	32	36	7.2	2.30	1.4	16.2

Sample numbers superscripted OU are considered to be Oruanui Ash on the basis of field evidence, those superscripted RE are believed to be representative of the Rotoehu ashes.

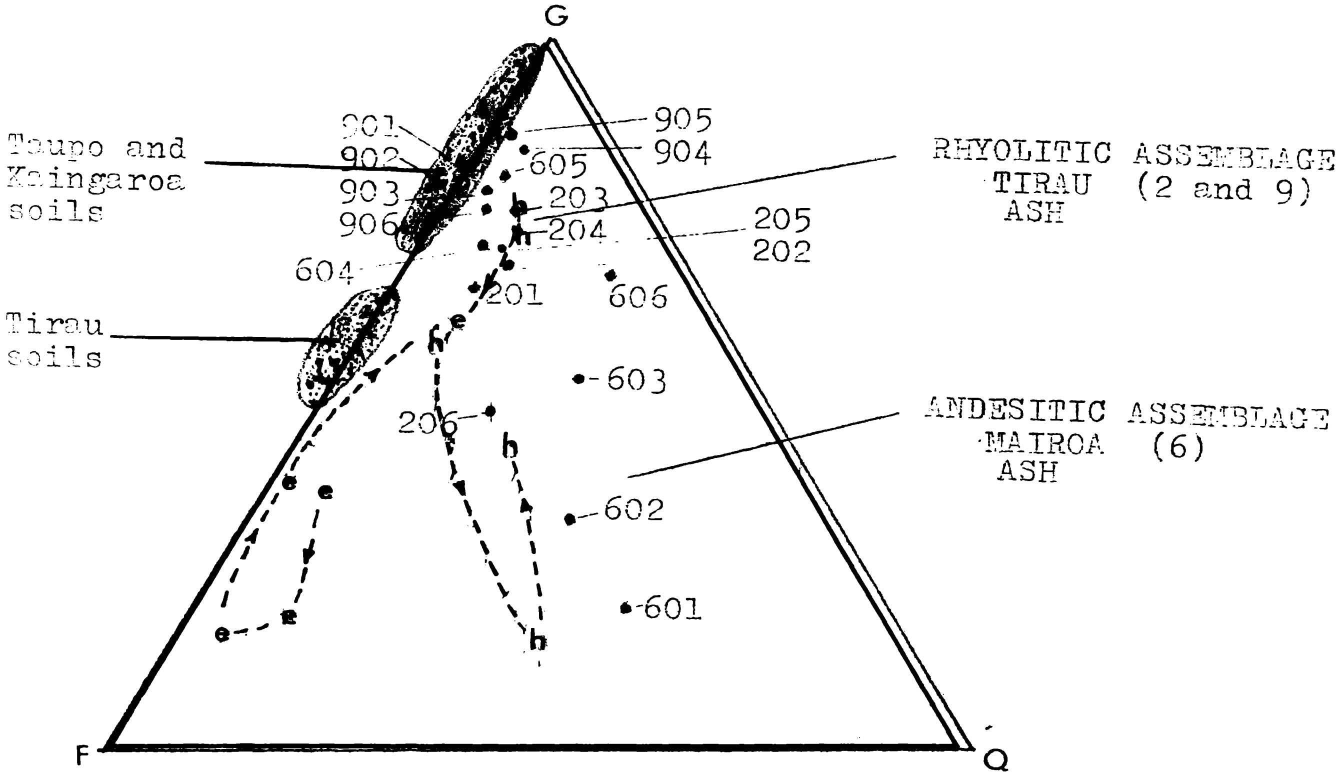
Fieldes and Weatherhead (1968) give "mineral frequencies" for soils derived from various tephra types, but do not distinguish between rhyolitic and andesitic glass. However the data suggest that the sand fractions from soils of andesitic origin tend to have higher quartz and feldspar relative to their total glass content, than those of rhyolitic origin. This can be illustrated by means of a ternary diagram; for which the proportions of quartz, feldspar and glass for Table 5-3 are scaled so that their total is 100%; and compared with the correspondingly scaled data of Fieldes and Weatherhead (1968). This is shown in Fig. 503, wherein it is clear that the samples of Mairoa Ash, especially that sampled at Mairoa itself (samples 601 - 603) plot in the same region of the diagram as the andesitic tephra from the literature, and that the other ashes resemble the rhyolitic tephra from the literature.

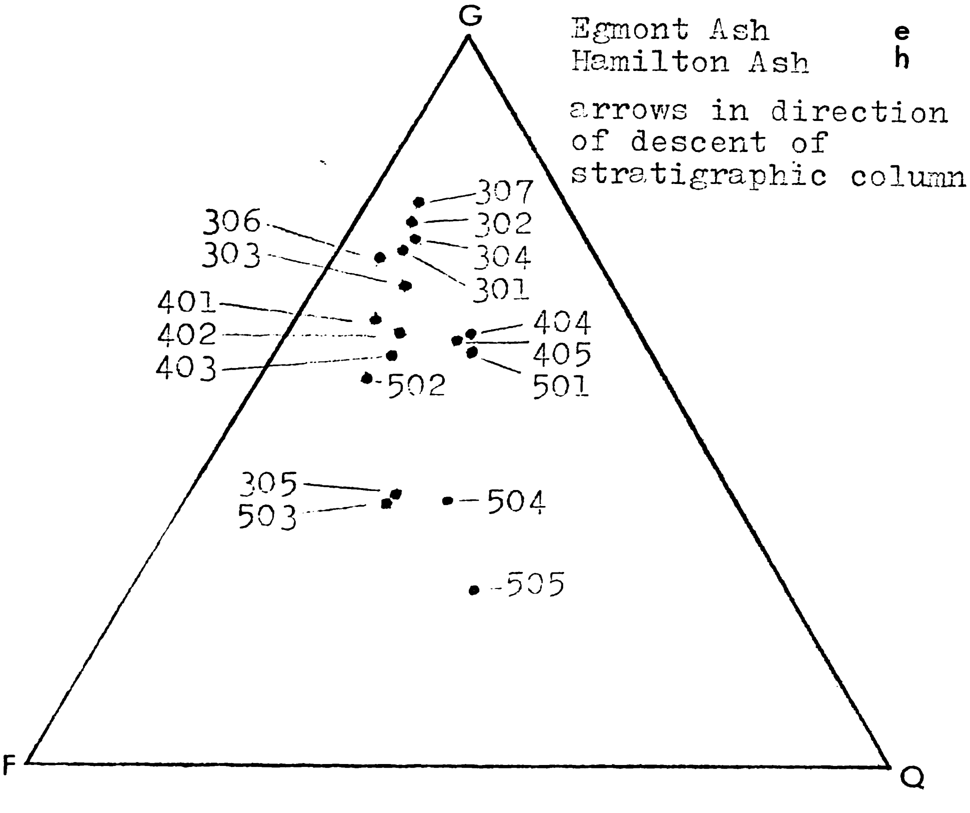
An alternative representation is to plot the system: quartz, feldspar, ando-glass, and rhyo-glass as an orthogonal projection of a tetrahedron (Ricci, 1966). On this projection each vertex represents one of the four components. If, as previously, andesitic tephras are taken to contain andesitic glass as the principal glass, and rhyolitic tephra, rhyolitic glass, the literature data used earlier can be again employed to demonstrate the different parts of the diagram to which different tephra-types plot. This is shown in Fig. 504, the arrows indicating the direction of increasing age. When the scaled data of Table 5-3 is similarly plotted (Fig. 505), it is again seen that the Mairoa Ash appears to be andesitic, the Tirau Ash and members of the Oruanui Formation rhyolitic, and many samples from the Waikato region, as for example 303 - 306, 402 - 405, and 501 - 502 appear to be composite. As an indication of the present-day composition of the remnants of the tephra, the ratio of the rhyolitic to andesitic glass contents (R) is useful. Probably preferable is the parameter α defined by the equation: $\alpha = R/(1 + R)$

FIG. 503

Ternary diagram: felsic assemblage (quartz, feldspar, and glass) for samples of Tirau Ash and Mairoa Ash

Overlay: Corresponding data for selected soil-forming tephras





soils developed on:

Egmont Ash e
Hamilton Ash h

arrows in direction of descent of stratigraphic column

FIG. 503

Ternary diagram: felsic assemblage (quartz, feldspar, and glass) for samples of Tirau Ash and Mairoa Ash

Overlay: Corresponding data for selected soil-forming tephras

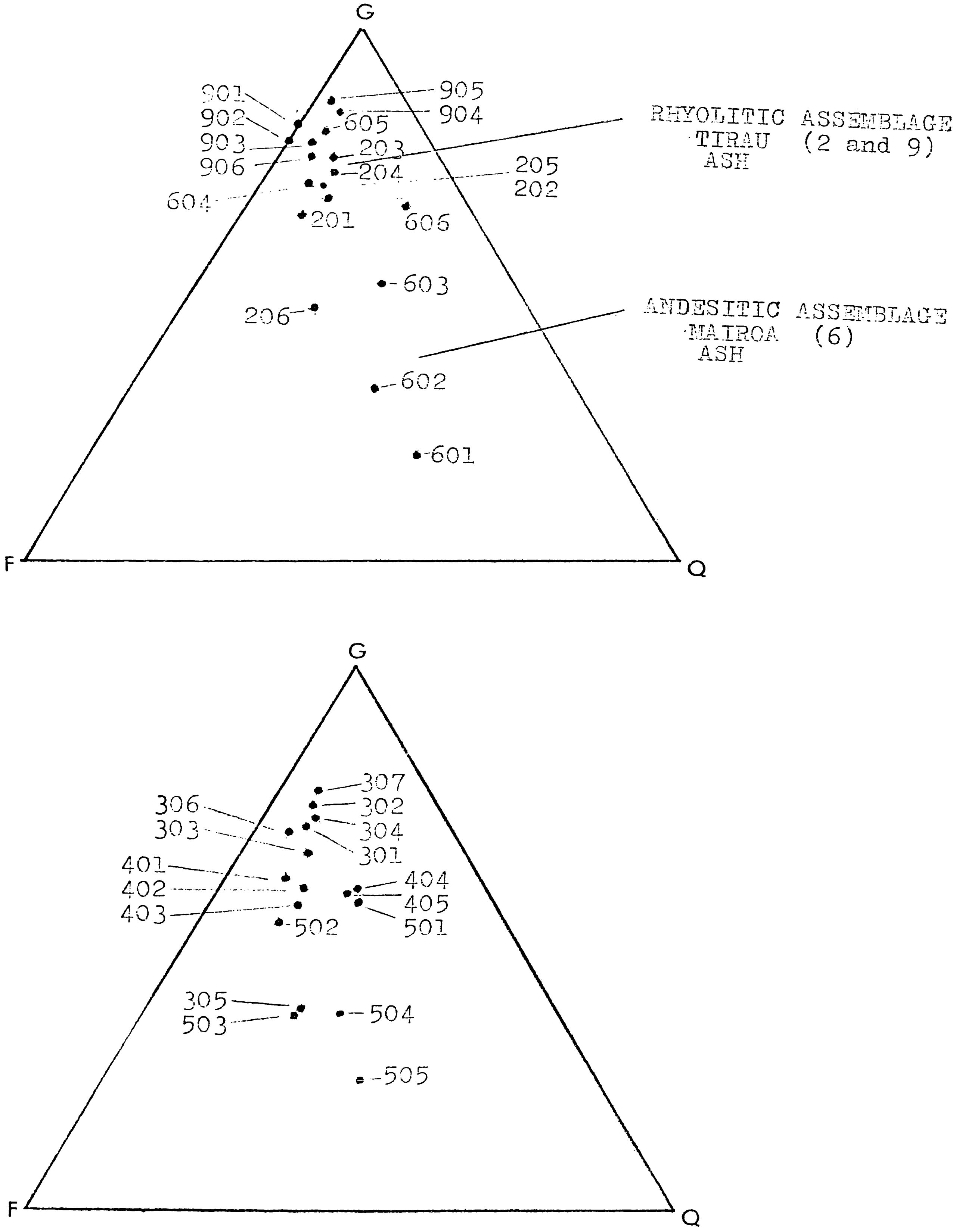
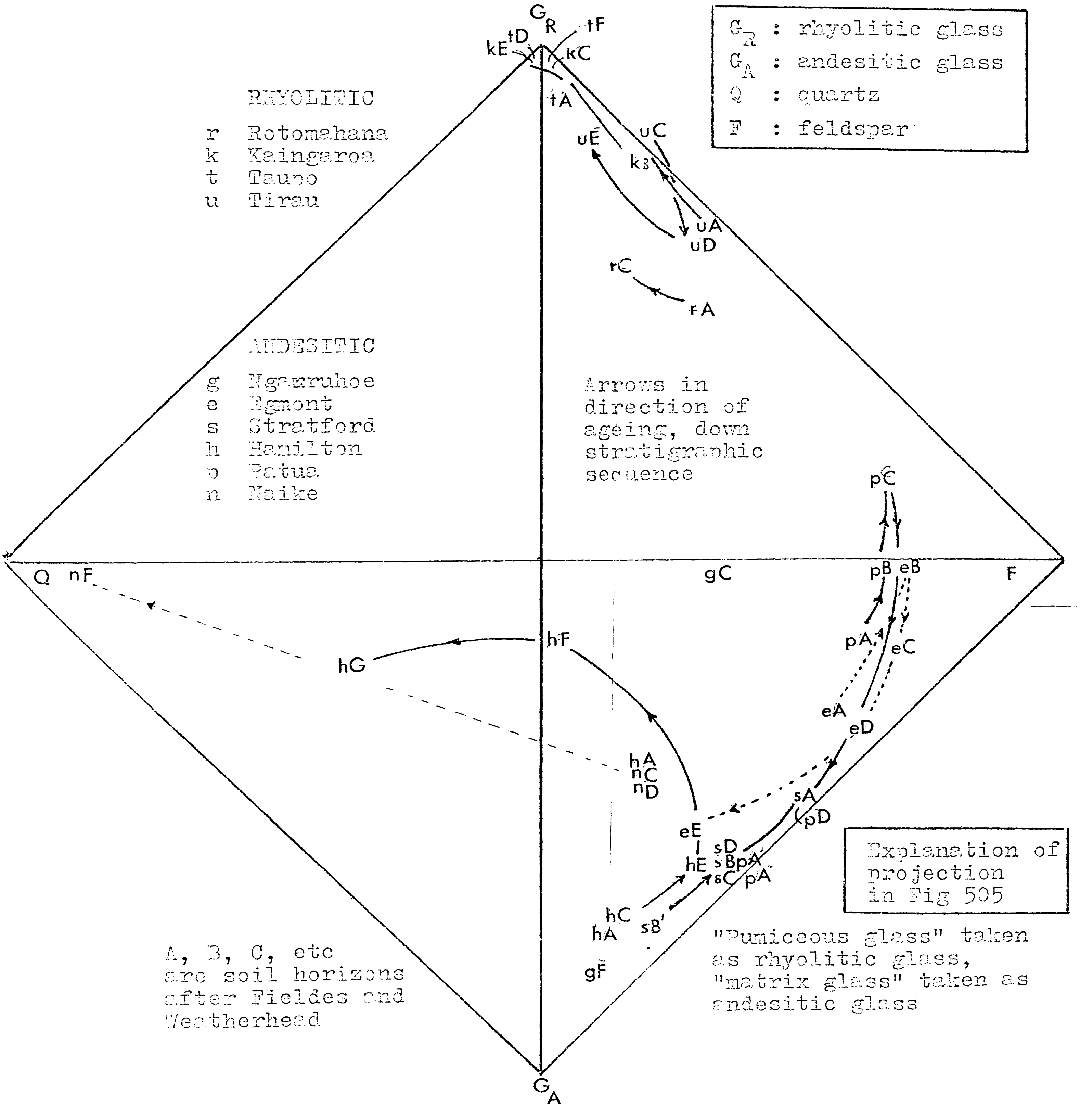


FIG. 504

Orthogonal projection of the tetrahedron defined by the 4-component system quartz, feldspar, rhyolitic glass, and andesitic glass for selected soil-forming tephras

(Data modified from Fieldes and Weatherhead (1968))



G_R : rhyolitic glass
G_A : andesitic glass
Q : quartz
F : feldspar

RHYOLITIC

r Rotomahana
k Kaingaroa
t Taupo
u Tirau

ANDESITIC

g Ngaurruhoe
e Egmont
s Stratford
h Hamilton
p Patua
n Naike

Arrows in direction of ageing, down stratigraphic sequence

Explanation of projection in Fig 505

A, B, C, etc are soil horizons after Fieldes and Weatherhead

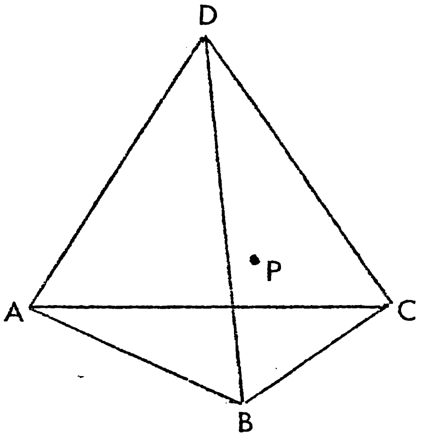
"Pumiceous glass" taken as rhyolitic glass, "matrix glass" taken as andesitic glass

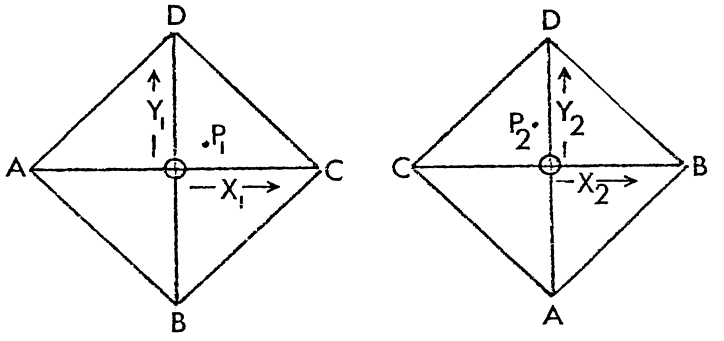
FIG. 505

Orthogonal projection of the tetrahedron defined by the 4-component system quartz, feldspar, rhyolitic glass, and andesitic glass for samples from Tirau Ash and Mairoa Ash

Insert: Representation of a tetrahedron by orthogonal projection

The corners of the tetrahedron represent the pure components A, B, C, and D.
P is a point of known composition





The projection shown is "square orthogonal", being a projection on a plane drawn parallel to two edges of the tetrahedron that do not intersect one another The projection plane is now a square with two edges of the tetrahedron as its diagonals.

For the purpose of plotting the projection, these edges are taken as rectangular axes, with the intersection of their projections, 0, as origin. With AC as the X-axis, and with the length AC still representing 100%, X is plotted as (%C - %A)/2, while Y = (%D - %B)/2.

While one such projection suffices to represent known data, to use the projections for interpretation both are needed, since for a given "unknown" point, %A is $(50 - X_1 + Y_1 - 2Y_2)/2$, whereupon the other percentages follow immediately: C from X_1 and D from Y_2.

(modified from Ricci (1966))

FIG. 505 (cont.)

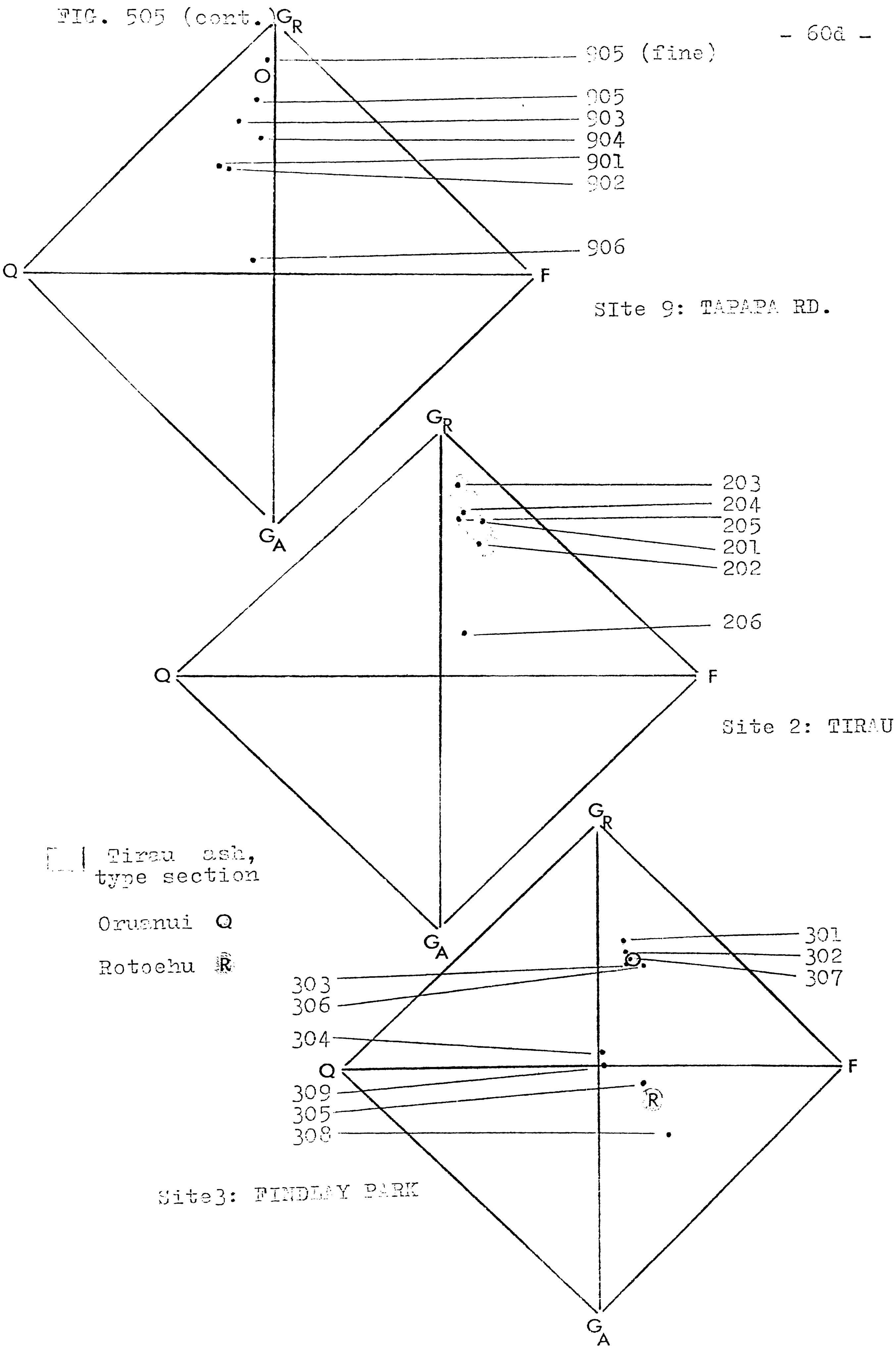
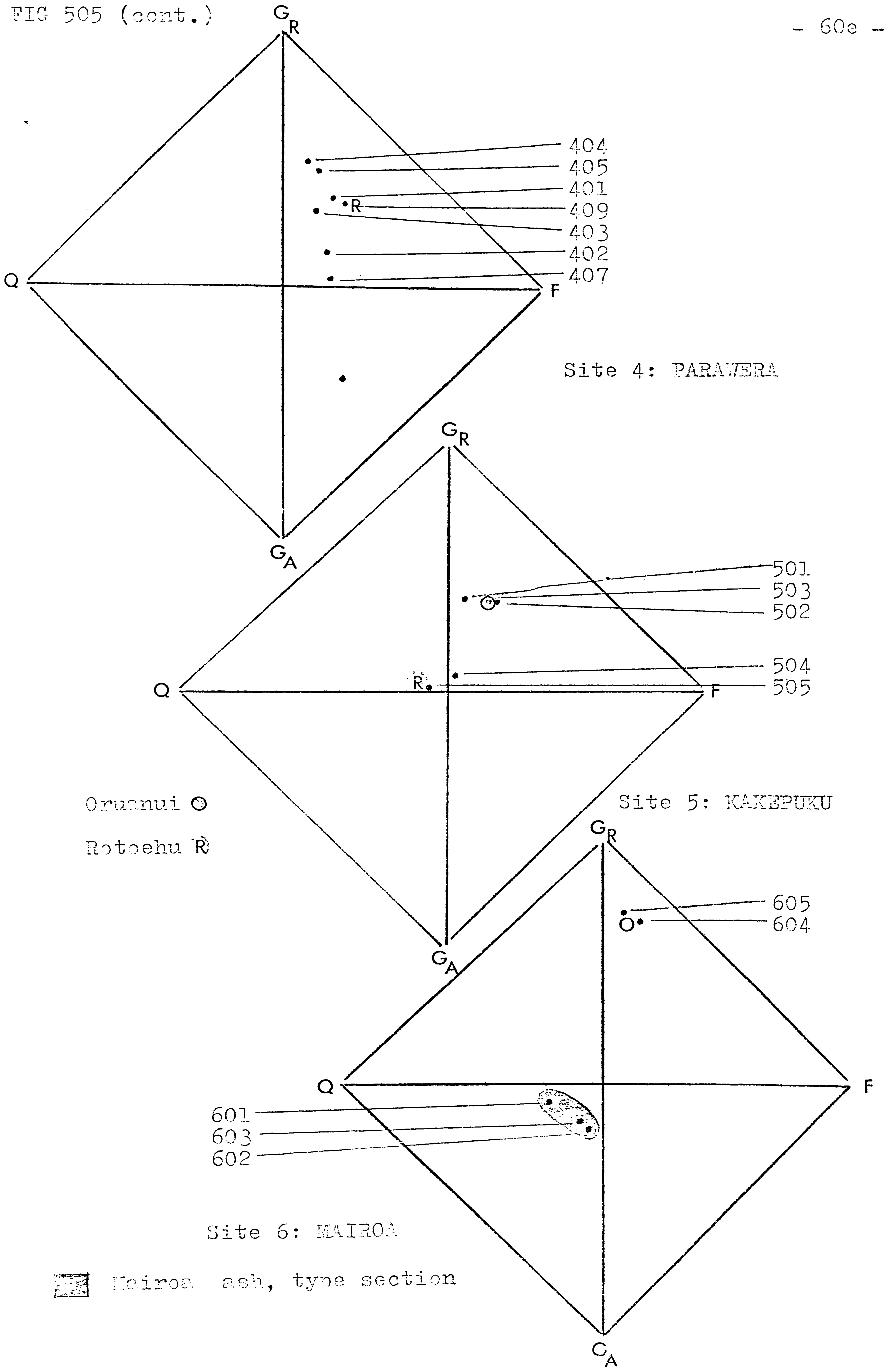

G_R
905 (fine)
905
903
904
901
902
906
Q
F
G_A
SIte 9: TAPAPA RD.
G_R
203
204
205
201
202
206
Q
F
G_A
Site 2: TIRAU
Tirau ash, type section
Oruanui Q
Rotoehu R
G_R
301
302
307
303
306
304
Q
F
309
305
308
G_A
Site3: FINDLAY PARK

FIG 505 (cont.)



Site 4: PARAWERA

Site 5: KAKEPUKU

Oruanui ⊙

Rotoehu Ⓡ

Site 6: MAIROA

▨ Mairoa ash, type section

since it takes the value 0 for a tephra that is totally andesitic and 1.0 for one that is rhyolitic. This "rhyolitic parameter" is presented as a function of position in the stratigraphic sequence in Fig. 506 and in tabular form in Table 6-4. From this data the following conclusions emerge:

(i) that the Tirau Ash has a high value of α , suggestive of its being a rhyolitic tephra

(ii) that the Mairoa Ash has a low value of α , suggestive of its being an andesitic tephra

(iii) that at the sites in the Waikato region, for samples above the Oruanui Formation there tends to be a gradation from lower to higher values of α as the stratigraphic column is ascended.

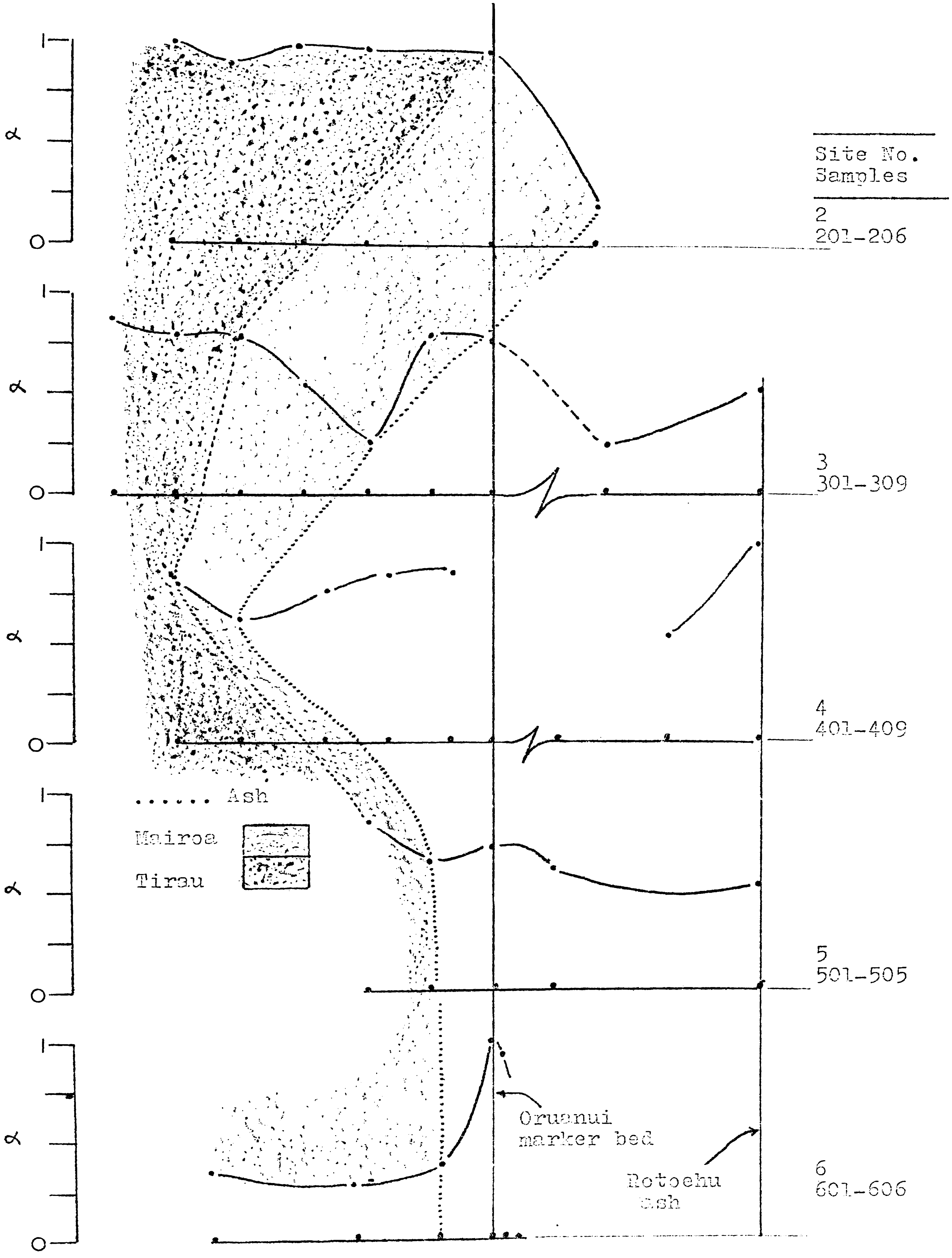
In using α as a correlating parameter, the assumption is implicitly made that the rate of weathering of the two glass types is comparable, and further that the mode of weathering in each locality has been similar. These aspects will be discussed in detail in Chapter 6.

Andesitic components of Tirau Ash have been recognised by Birrell and Pullar (1973) on the basis of examination of rhyolitic tephras "by andesitic or basaltic constituents of the sand fraction such as andesine feldspar and augite," but they do not give any quantitative estimate of the extent of this contamination.

Thus the conclusion is reached, on the basis of present-day mineral assemblages that the Mairoa Ash has a significant andesitic component, that the Tirau Ash is dominantly rhyolitic, and that samples from localities in the Waikato region lying geographically between these sequences at their type localities are composite in character.

FIG. 506

Rhyolitic character of tephra as a function of stratigraphic position for samples of Tirau Ash and Mairoa Ash



CHAPTER 6: Dating of Soils on the Basis of Glass Contents:

S6-1: Introduction:

As the primary minerals of which a tephra is composed become involved in soil-forming processes, there is a progressive decrease in these minerals and an increase in the amount of secondary minerals. Principal among the latter are allophane and halloysite. Fieldes (1955) showed a sequence of tephra of different age may display different infra-red spectra of their derived soil depending upon whether glass, allophane, or halloysite were present, see Fig. 601, and in fact, proposed a reaction sequence whereby glass weathers to allophane and thence to halloysite. Unfortunately, in the present case, the tephra are not sufficiently old to give appreciable halloysite and the spectra of allophane and glass are not really distinctive enough to use the infra-red spectra of the soils as parameter indicative of age. However, there are sufficient primary minerals, in particular, glass, to consider reaction models for the loss of these minerals during weathering. In this chapter, such models are developed for various relative weathering rates and initial compositions of tephra and ages are evaluated by reference to samples of known radiometric age.

It should be stressed at the outset that the method aims to provide an estimate of the age of the tephra without the necessity of relying on inference from stratigraphic relationships. Because of the nature of this model and its attendant assumptions, the dates provided should be regarded as tentative and representative of the first attempts at dating of the samples of Tirau and Mairoa Ashes themselves.

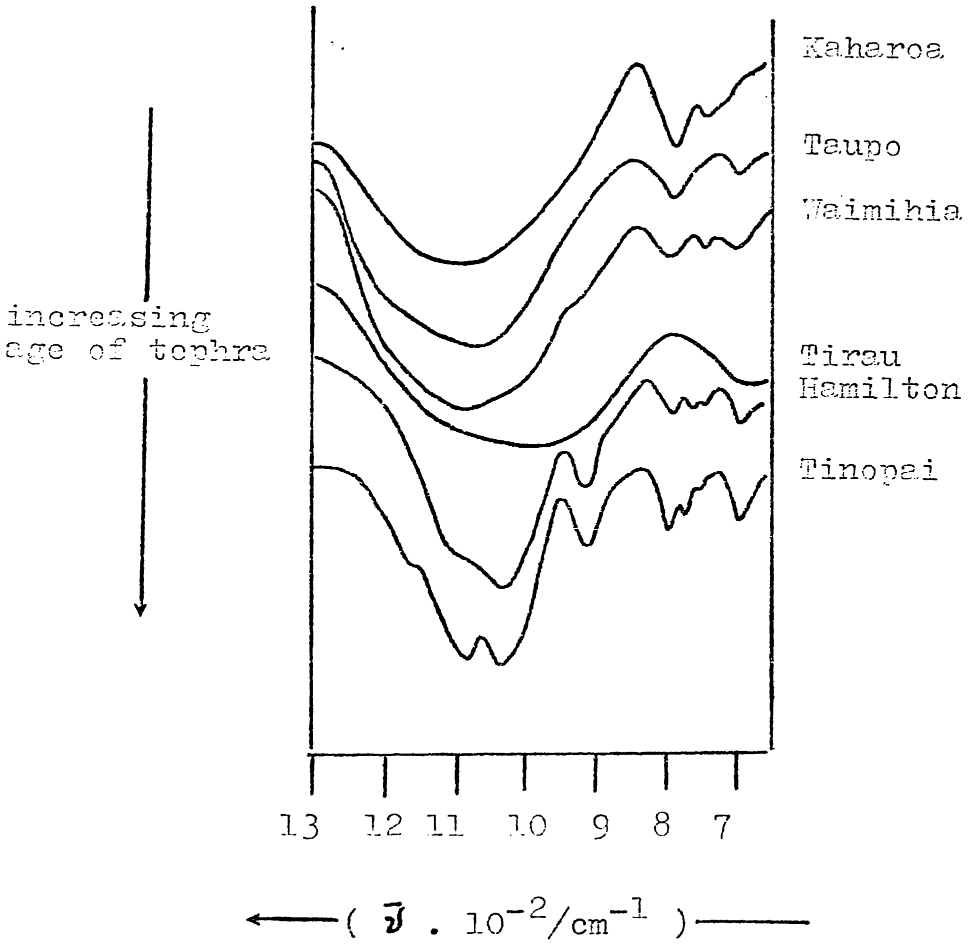
S6-2: First-Order Weathering of Volcanic Glass:

Ruxton (1968) has claimed that the weathering of volcanic glass can be represented by the reaction:

$$\underset{\text{(with gas and acids)}}{\text{Glass + water}} \longrightarrow \underset{\text{(silica and cations)}}{\text{allophane + solutes}}$$

FIG. 601

Infra-red spectra of whole soils, as a tool in characterising tephras



This figure has its basis in the formation of different clays depending on the time available for soil development between deposition and subsequent burial of the parent tephra.

after: M.Fieldes: Clay mineralogy of New Zealand soils, Part 2: Allophane and related mineral colloids, N.Z. Jnl. Sci. Tech., B37, 336, (1955) He asserts that since water is added at a relatively constant rate, and the solutes are similarly removed, the rate of reaction is proportional to the concentration of glass in the deposit, and there is thus an analogy with first-order reaction kinetics. His data on glass contents for dacitic tephras of known age yield a relationship of the form:

$$c = c_o e^{-kt}$$

or equivalently: $\ln c_o - \ln c = kt$

where c is the concentration of glass by weight at time t, c_o is the initial concentration of the glass (at the time of the eruption) and k is a constant. In this case c_o may be readily determined since it is considered that all the ashes of the sequence initially had the same composition, and further that this composition resembled closely that of recently erupted material. That a first order kinetic relationship is observed over the last 24,000 years, implies that the weathering rate constant k has been constant throughout this period.

Ruxton (1968) suggests that the weathering constant is primarily a function of infiltration, or available water and thus for the sites and tephra he considers there has been little change in climate over the past twenty thousand years. In New Zealand, there is evidence of climatic changes in the last 20,000 years associated with the end of the last glaciation. Accordingly, the rate constant k is not expected to be invariant with time. Also there is the difficulty of assigning a value to the initial concentration of glass, since this is dependent on the value of α, the rhyolitic parameter. This is discussed in Sec. 6-4. Before proceeding to this, however, the relative ease of weathering of andesitic and rhyolitic glasses will be considered.

S6-3: The Relative Weathering Rates of Volcanic Glasses:

There appears to be a conflict in the literature over the relative weathering rates of glasses and their relationship to feldspars and mafic minerals. Aomine and Wada (1966) give proportions of minerals in differentially weathered ash-beds. From this data relative-rate constants can be evaluated if it is assumed that first order kinetics apply in all cases. This data is presented in Table 6-1, and from this it is seen that the rate constant for glass is significantly higher than for feldspars which are in turn greater than for mafic minerals.

TABLE 6-1: Differential Weathering: Interpretation in Terms of Relative Rate Constants.

Mineral	Weathering Regime Allophanic ash-derived soil to halloysitic soil (a)				Allophanic pumice derived soil to halloysitic soil (a)			
	c_o	c	$\ln[c_o/c]$	k_{rel}(b)	c_o	c	$\ln[c_o/c]$	k_{rel}(b)
magnetite	2.7	2.7	0	0	1.2	1.2	0	0
hypersthene-augite (c)	11	8.9	0.21	0.15	3.7	2.2	0.51	0.27
feldspar (d)	23.8	8.1	1.08	0.75	24.5	14.8	0.50	0.26
volcanic glass (e)	54	13	1.43	1.00	59	8.9	1.90	1.00

(a) on basis of Fieldes clay format. sequence see Sec. 6-1.

(b) relative to rhyolitic glass $k_{rel} = 1.0$

(c) includes all non-magnetic mafic minerals

(d) being andesine-labradonite

(e) being both rhyolitic and andesine glass

This result supports the statement by Ruxton (1968) that "the total element loss is from the glass." Aomine and Wada (1966) consider that the weathering of glass proceeds by a "desilication together with a remarkable loss of bases although the amount of iron oxides and alumina remain essentially constant." If the weathering of other minerals were to occur by a similar process then there might be expected to be some relationship between the rate constant for weathering and composition.

Data for this is given in Table 6-2 and plotted in Fig. 602 for the minerals that Aomine and Wada describe.

TABLE 6-2: Potential Desilication and Base Loss of Minerals as a Function of Relative Rate Constant.

Mineral	Relative rate constant (a)	Desilication (b)		Base loss (c)		
		Potential	Reduced Potential (d)	Potential	Reduced Potential (d)	Ratio
		S	Sr	B	Br	S/B
quartz	0	100	00	0	0	0
magnetite	0	0.27	0.003	0	0	0
hypersthene-	0.15	50.1	1.59	0.07	0.002	0.0013
augite		48.9	1.54	0.78	0.024	0.016
andesine	0.75	58.1	2.18	6.48	0.29	0.13
labradorite		53.0	1.74	4.34	0.15	0.08
glass	1.00	72.4	4.38	7.98	0.52	0.12

(a) relative to glass

(b) being the total SiO_2 content

(c) being the sum of the Na_2O and K_2O contents

(d) relative to the oxide sum: $FeO + Fe_2O_3 + Al_2O_3$

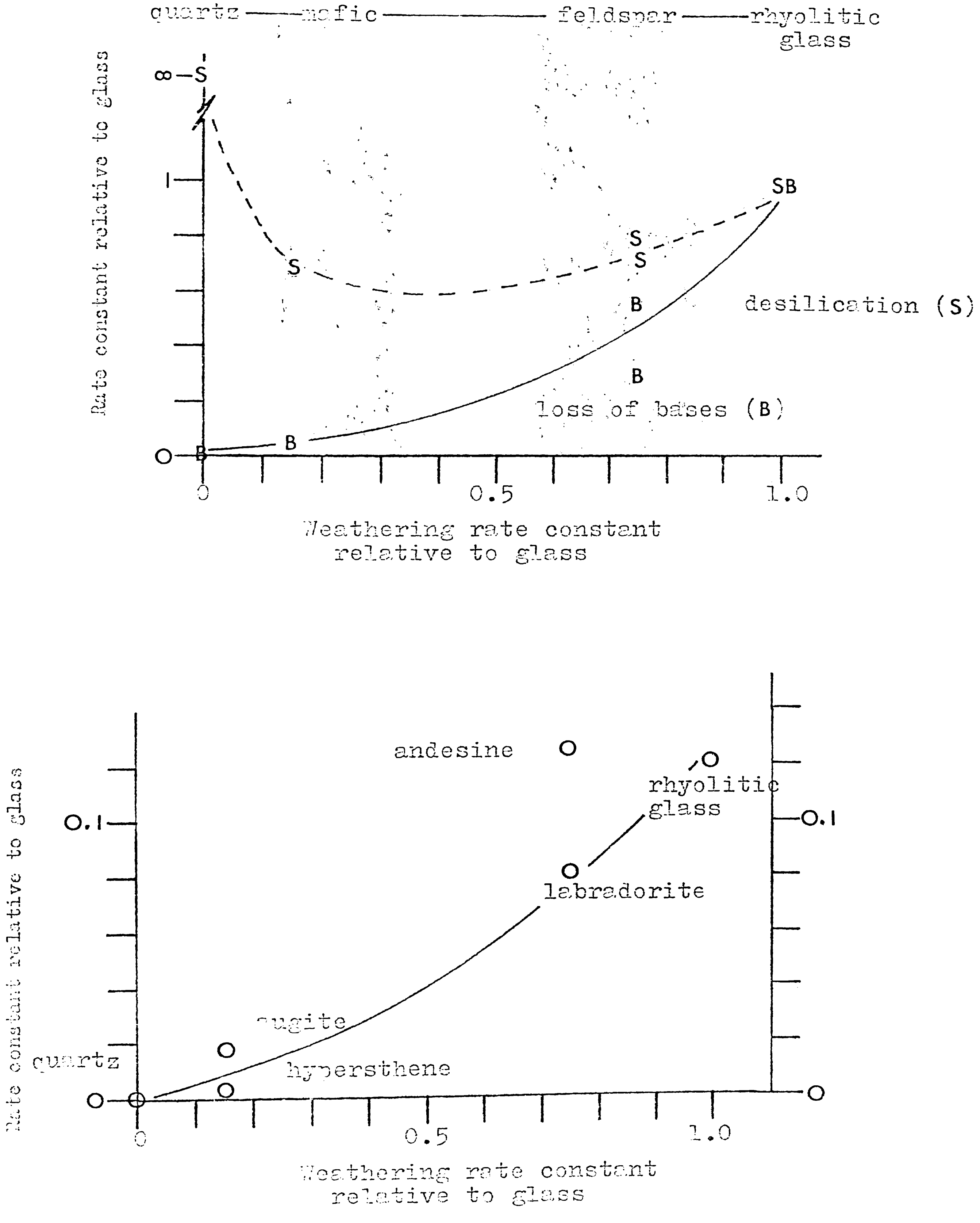
From this it is clear that an increased rate constant is associated with a higher basic oxide content, and in particular with a higher basic oxide to silica ratio. If like other first order reactions, the rate constant is related to terms involving the frequency of successful molecular collisions (A) and the activation energy (E^*) by the so-called Arrhenian relationship

$$k = A \exp(-E^*/RT)$$

it may be that the composition is related to the frequency factor. Further, from what has already been assumed about the similarity of weathering processes, the values of the activation energy E^* for the

FIG. 602

Compositional relationships for minerals of known relative rate constants



various minerals are probably fairly similar. Since the constant A is related to the number of effective "collisions" that result in reaction it may well be dependent on the concentration of basic oxides in the structure, and thus the empirical relationship between a kinetic parameter (k) and a thermodynamic parameter (composition) has theoretical justification.

Accordingly, the less silicic a glass, or in fact a mineral, the more slowly should it weather, provided that the decreasing silica content is paralleled by a decrease in basic oxide contents and a consequential rise in the mafic oxides. Thus it would be expected on this argument that basaltic glass should weather but slowly and might thus remain even after prolonged weathering. Of this Fieldes and Weatherhead (1968) write:

> "in soils from basaltic parent materials, glass persists strongly in the sands after andesine is no longer detected, suggesting that any stable soil of considerable age .... may contain forms of glass resistant to weathering."

From the kinetic interpretations described in this section, it would seem that andesitic glass (which may be taken as compositionally resembling the plagioclase andesine) may be predicted as having a rate constant some 0.75 times that of rhyolitic glass. Thus, the relevant kinetic relationships are:

$$\ln\,(c_o^r/c^r) = k_r t$$

$$\text{and} \quad \ln(c_o^a/c^a) = k_a t = 0.75\, k_r t$$

whence on eliminating $k_r t$, reduce to:

$$\frac{(c^r)^{0.75}}{c^a} = \frac{(c_o^r)^{0.75}}{c_o^a}$$

In these expressions c and c_o are the present and initial concentration of the respective glasses in the tephra samples and the superscripts a and r indicate andesitic and rhyolitic glass respectively. From this it can be shown that the relationship between the rhyolitic parameter observed (R) and initially, at the time of deposition, (R_o) is given by:

$$R = R_o \exp(-0.25\, k_a t) = \bar{R}_o \exp(-0.19\, k_r t)$$

This is to say that the rhyolitic character is itself a function of time. Using the previously described relationship between α and R, and considering the above expression in terms of a logarithmic series, neglecting all higher order powers the equation:

$$\alpha_o - \alpha = 0.05\, k_r t$$

is achieved. Since the product $k_r t$ may not be negative, this requires that:

$$\alpha_o > \alpha$$

This relationship reflects the observation noted when discussing mineral assemblages that it is difficult to distinguish older rhyolitic tephras from possibly younger andesitic tephras on the basis of glass contents. It can be seen from this last equation that there are too many unknown parameters to enable dating of members of the stratigraphic sequences under study. Assistance in overcoming this difficulty can be effected by considering the climatic dependence of the rate constant and the variation of the rate constant with time, both of which are dealt with in subsequent sections.

The order of ease of weathering proposed by Aomine and Wada (1966) differs significantly from those of Fieldes and Swindale (1954) and Jackson and Sherman (1953). Their sequences in order of increasing stability to weathering with the minerals used in Aomine and Wada underlined are given below:

——— increasing stability ———>

Jackson and Sherman: basic volcanic glass, olivine, hypersthene, biotite, augite, amphibole, anorthite, epidotite, bytownite, andesine, oligoclase, muscovite, garnet

Fieldes and Swindale: olivine, augite, hypersthene-basic volcanic glass, zeolite-biotite, muscovite-volcanic glass (acidic), feldspar-quartz

Fieldes and Swindale (1954) postulate that acidic (rhyolitic) volcanic glass weathers at a rate comparable to that of feldspar and more slowly than basic volcanic glass. This conclusion is inconsistent with the observed persistence in the field of basaltic glass but does concur with an unsubstantiated statement by Ross and Smith (1955) that there is but "a small tendency for basaltic magmas to form glasses and (there is) ready alteration of such glasses." It is interesting that, while Fieldes and Weatherhead (1968) indicate that basaltic glasses seem stable to weathering they do note that olivine weathers readily. Thus it would seem that the rate may be not only compositionally, but structurally dependent, and the stability series indicated above suggest that framework structures are less easily weathered than simpler silicates. The members of the sequence are plotted as a function of the silicon to oxygen ratio (effectively a structural parameter) in Fig. 603 wherein it is readily seen that the more complex structures are usually less readily weathered. Also given in Fig. 603 is a plot of the minerals of these sequences showing the variation of the ratio of basic oxide and silica content.

Thus there appear to be two competing aspects of the ease of weathering: that the ease of weathering increases for increasing ratio of basic oxide to silica, and that the ease of weathering increases with decreasing structural complexity of the mineral. It is probably a fortuitous combination of these factors for the minerals. Aomine and Wada (1966) give, that the structural effect is outweighed by the effects of composition. As a consequence of this, it may be reasoned that, for minerals of comparable structural complexity, compositional relationships dictate the relative rate constants. Such an interpretation does not alter the calculated relative rate constants for rhyolitic and andesitic glasses previously given and supports the observed persistence of mafic volcanic glass.

FIG. 603

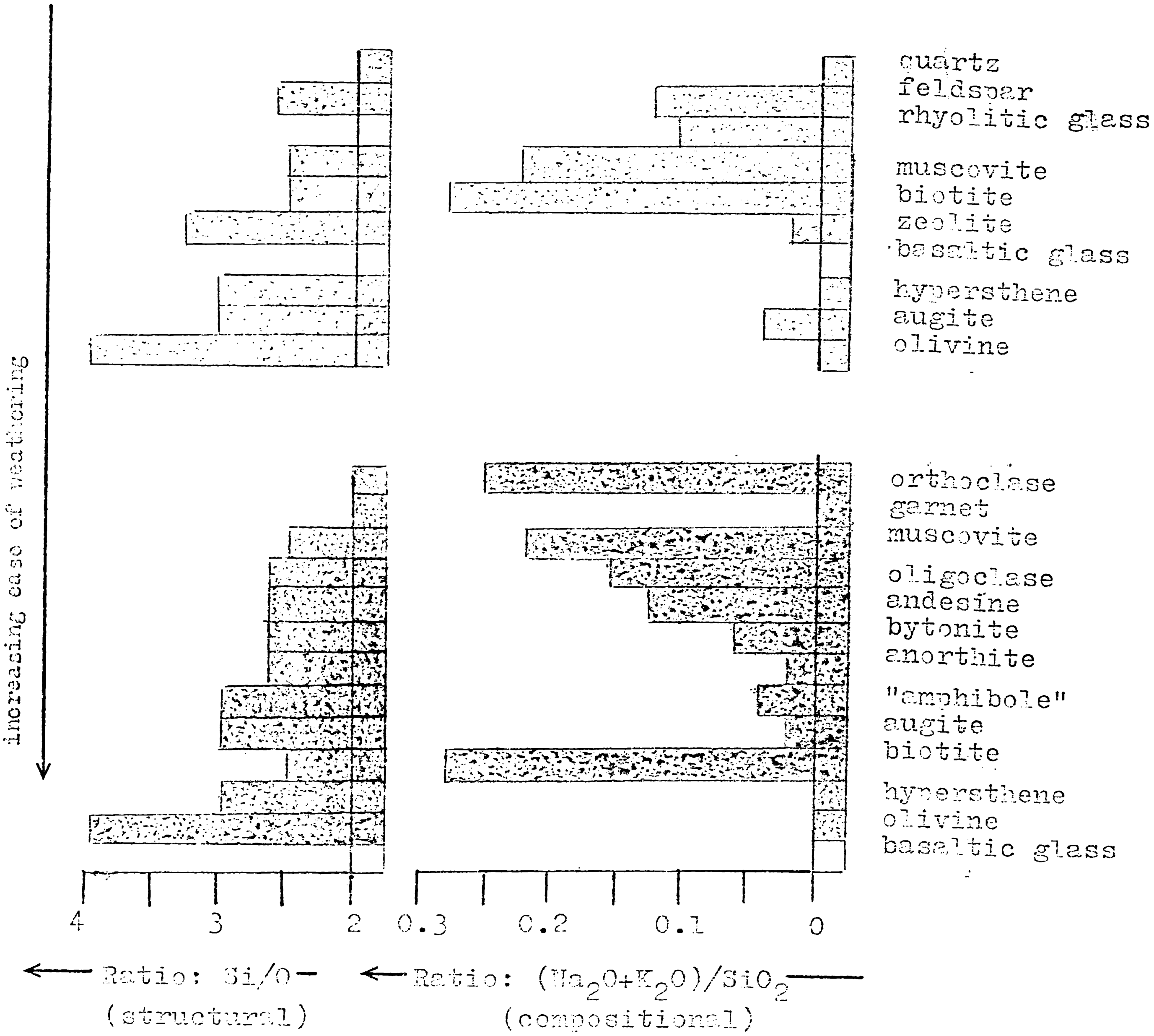
Sequences of minerals in order of stability to weathering as a function of compositional and structural parameters

The minerals are listed in order of relative ease of weathering. The two sequences are from

Jackson and Sherman ▓

and -

Fieldes and Swindale ░



S6-4: Ruxton's Weathering Model Modified for a Mixed Tephra Deposit:

It has already been shown (Ruxton, 1968) how if the concentration of andesitic and rhyolitic glasses are respectively c_o^a and c_o^r at the time of eruption, and are observed subsequently to be c^a and c^r, and further that the appropriate rate constants for weathering are k_a and k_r then the appropriate rate equations are:

$$\ln (c_o^a/c^a) = k_a t \quad \text{and} \quad \ln(c_o^r/c^r) = k_r t$$

It may be shown that the variation of the rhyolitic parameter with time is small and can to a reasonable approximation, be neglected. This is tantamount to neglecting the difference in rate constant between the two glass types. If this is taken to be the case, then the initial concentrations of the vitreous components of a mixed tephra can be derived from estimates of the initial concentrations of glass in tephras either entirely rhyolitic or entirely andesitic.

Various suggestions for the value of c_o for different ash types have been made as given in Table 6-3 and plotted as a function of in Fig. 604.

TABLE 6-3: Estimation of Initial Glass Contents for Various Types of Tephra

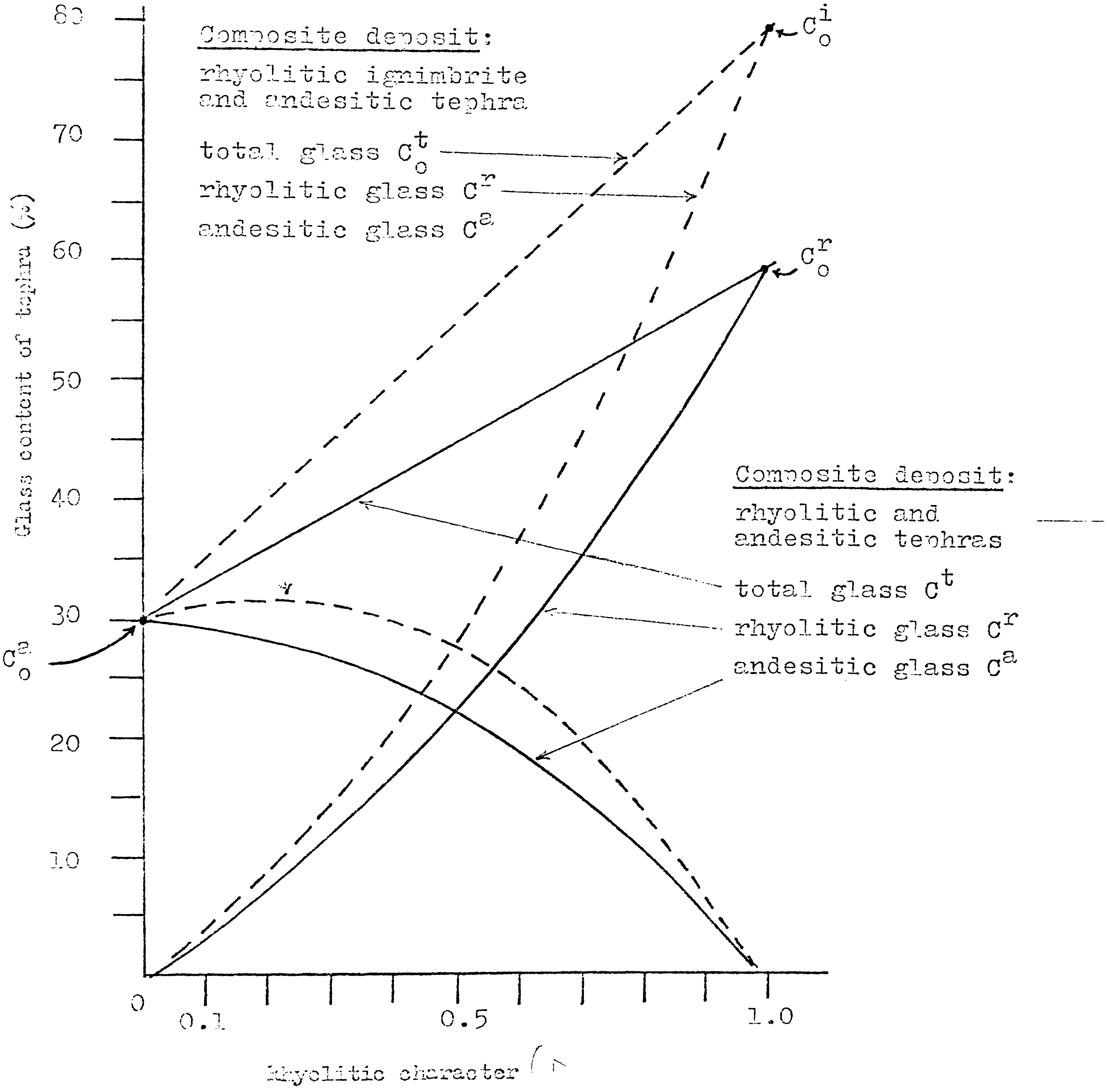
Consideration*	Initial Concentrations			Reference
	rhyolitic glass c_o^r/o/o	andesitic glass c_o^a/o/o	ignimbritic glass+ c_o^i/o/o	
(a)	30	30	-	Fieldes (1966)
(b)	60	30	-	Fieldes and Weatherhead (1968)
(c)	-	30	90	Ewart (1963)∓

* correspond to similarly labelled data columns in Table 6-4.

\+ ignimbritic glass is rhyolitic in composition, but because of the

FIG. 604

Glass contents of tephras as a function of rhyolitic character



nature of the eruption that gives rise to it, it may be more pumiceous and certainly representa greater proportion of the volcanic ejectamenta.

∓ The estimate for ignimbrite taken to be that for Taupo Pumice after Ewart (1963), andesite taken as 30% as for the other considerations.

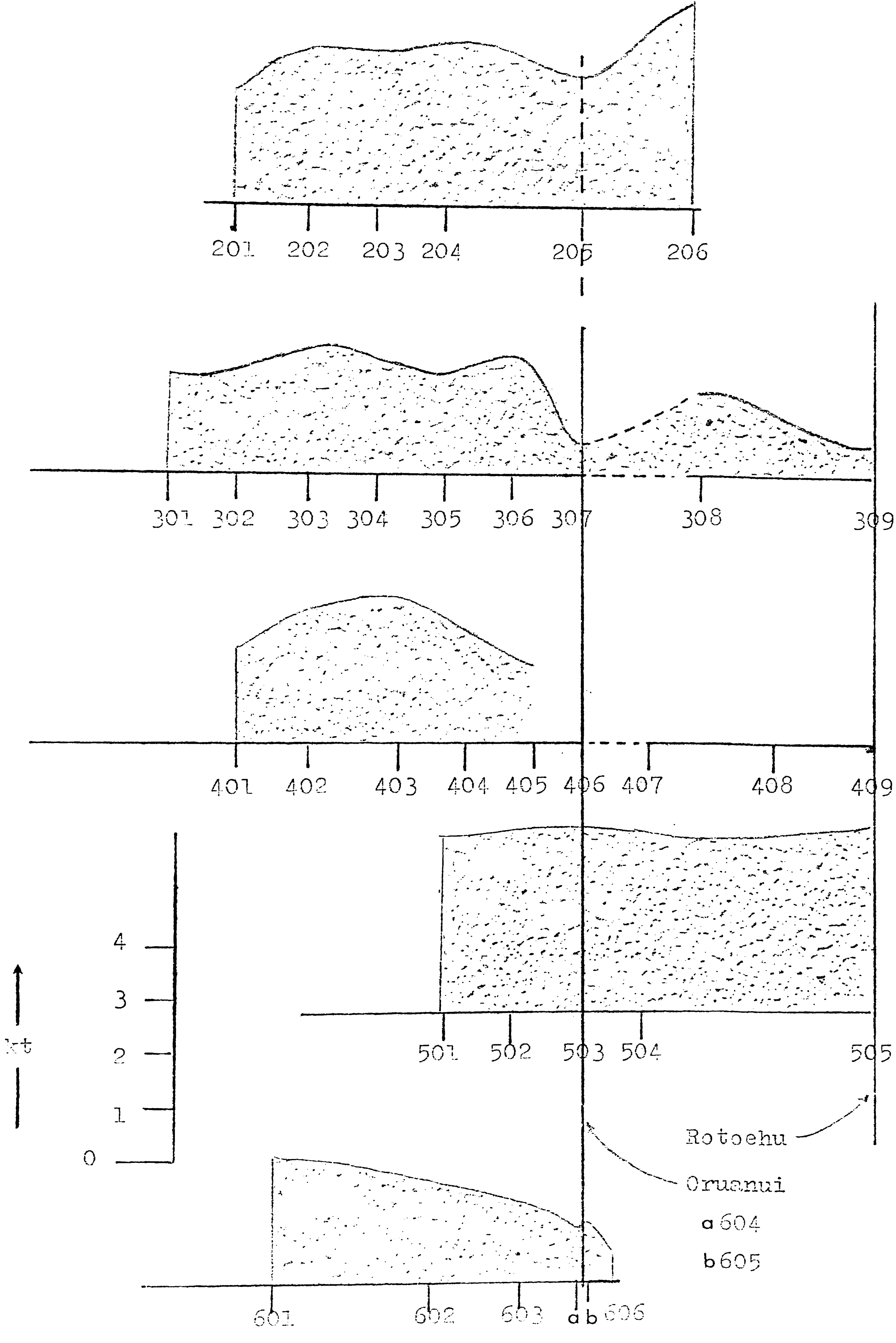
If values of c^r and c^a are small, errors in the ratio and hence the parameter kt is subject to appreciable error. One way of circumventing this difficulty is to use the ratio of total glass observed to the total glass estimated as existing initially, this initial value being determined by the rhyolitic parameter, α . The plot of total glass content as a function of α is of course linear in all cases. Since this is not so for plots of c_0^a and c_0^r versus α (see Fig. 604) errors are further reduced by this procedure.

Values of the kinetic parameter kt are evaluated in Table 6-4 for the various considerations. In that the ratio c_0^t/c_0 exceeds unity for the Oruanui Formation samples under consideration (a) suggests that this may be unreasonable. Consideration (c) was included to determine whether the assignment of ignimbritic character reduced the considerable difference between the values of Oruanui Formation and Rotoehu Ash and the remaining ashes in the sequence, but the effect is marginal.

Plots of kt versus position in the stratigraphic sequence (Fig. 605) show that for Tirau Ash sequence, the parameter rises to a maximum: in the case of the Tapapa Road site, the maximum is reached just above the Oruanui Formation. At Mairoa it is noteworthy that the upper portion of the curve is missing, there being only the function from near the projected maximum to the Oruanui Formation. This attests either to erosion of upper members or to the non-deposition at Mairoa of the material that gives rise to the rising part of the curve at other sites. A less distinct but similar trend is evident for the Kakepuku (Site 5) samples.

FIG. 605

Kinetic parameter (the product kt) as a function of stratigraphic position for samples from sequences of Tirau Ash and Mairoa Ash



That the parameter kt shows a maximum is highly suggestive of climatic variations within the last 20,000 years and is similar to the plot based on soil formation data of Vucetich to be discussed in Sec. 6-8

TABLE 6-4: Evaluation of Kinetic Parameter (kt) on Basis of α and Values of c_o.

Sample	c^t (%)	α	c_o^t (a)	c_o^t (b)	c_o^t (c)	$\ln(c_t^o/c^t)$ (a)	$\ln(c_o^t/c^t)$ (b)	$\ln(c_o^t/c^t)$ (c)
201	7.75	1.0	30	60	80	1.355	2.048	2.330
202	3.17	0.89	30	57	74.5	1.244	2.882	3.158
203	3.26	1.0	30	60	80	2.216	2.919	3.202
204	2.72	0.95	30	59	78	2.408	3.071	3.352
205	5.59	0.95	30	59	78	1.682	2.354	2.631
206	0.69	0.17	30	35	38.5	3.772	3.912	4.017
301	8.8	0.87	30	56.5	73	1.228	1.858	2.112
302	8.1	0.80	30	54	70	1.309	1.897	2.154
303	5.23	0.81	30	54.5	70	1.749	2.333	2.594
304	5.10	0.54	30	46.5	57	1.772	2.207	2.408
305	6.29	0.26	30	38	43	1.565	1.796	2.805
306	5.86	0.79	30	54	69	1.635	2.216	2.465
307 *	31.05	0.77	30	53.5	68	-	0.536	0.781
308	8.12	0.25	30	37.5	42.5	1.306	1.533	1.656
309+	27.83	0.52	30	46	56	0.076	0.503	0.703
401	6.27	0.80	30	54	70	1.565	2.153	2.414
402	3.87	0.63	30	49	62.5	2.048	2.538	2.781
403	3.08	0.76	30	53	67.5	2.273	2.847	3.088
404	6.04	0.86	30	56	72.5	1.605	2.226	2.489
405	9.95	0.84	30	55.5	72	1.103	1.720	1.981
407	5.28	0.54	30	46.5	57	1.737	2.172	2.375

TABLE 6-4 cont.

Sample	c^t (%)	$\propto$	c_c^t (a)	c_o^t (b)	c_o^t (c)	$\ln(c_t^o/c^t)$ (a)	$\ln(c_c^t/c^t)$ (b)	$\ln(c_c^t/c^t)$ (c)
409+	7.70	1.0	30	60	80	1.363	2.048	2.333
501	2.15	0.85	30	56	72	2.631	3.260	3.507
502	1.78	0.64	30	49.5	62	2.882	3.324	3.547
503*	1.69	0.72	30	52	66	2.882	3.430	3.665
504	1.79	0.61	30	48.5	60	2.830	3.297	3.507
505+	1.44	0.52	30	46	56	3.037	3.461	3.657
601	3.61	0.36	30	41	47.5	2.120	2.436	2.577
602	5.33	0.27	30	38	43.5	1.726	1.959	2.104
603	7.75	0.38	30	42	49.0	1.355	1.687	1.845
604*	24.06	0.99	30	60	80.0	0.219	0.916	1.197
605*	17.04	0.92	30	58	76	0.566	1.228	1.492
606	18.85	0.05	30	32	32.5	0.465	0.528	0.545
901	13	0.76	30	53	68	0.837	1.406	1.654
902	10.6	0.75	30	52.5	67.5	1.040	1.601	1.853
903	10.3	0.84	30	55	72.5	1.072	1.694	1.953
904	10.4	0.84	30	55	72.5	1.061	1.686	1.946
905*	20	0.89	30	57	75	0.406	1.047	1.327
906*	16.2	0.53	30	46	57	0.615	1.044	1.258

(a) on Fieldes' (1966) criterion, the maximum glass contents of both rhyolitic and andesitic tephras is 20%

(b) based on Fieldes and Weatherhead (1968), 30% glass in andesitic tephra, 60% in rhyolitic

(c) as for (b), except assume rhyolitic tephra is ignimbrite and has a glass content of 80%

* field identified as Oruanui Ash + field identified as Rotoehu Ash

S6-5: An Alternative Method for Determining Initial Glass Contents:

Rather than the empirical method described in Sec. 6-4, the value of initial glass contents may be established on the basis of allophane contents. Fieldes (1966) gives an indication of the conversion of glass to allophane for the two principal tephra types and his data is presented in Table 6-5.

TABLE 6-5: Glass, feldspar and allophane contents of N.Z. tephra-derived soils (after Fieldes (1966)).

Parent ash type	Soil type	Feldspar (C_F/%)	Glass (C_G/%)		Allophane (C_A/%)
rhyolitic tephra	(fresh tephra)	60	30	G_R	-
" "	yellow-brown pumice soil	45	5		15
" "	yellow brown loam	35	15		12
andesitic tephra	(fresh tephra)	40	30	G_A	-
" "	yellow brown loam	15	15		50

From this table it is seen that in the formation of a yellow brown loam from rhyolitic tephra, 12 grams of allophane form for every 15 grams of rhyolitic glass that are lost, and similarly in the formation of the same type of soil from andesitic tephra 50 grams of allophane form from every 15 grams of andesitic glass lost. Thus:

$$0.3\, C_{G_A} = 1.24\, C_{G_R} = C_A$$

Now if an ash deposit is considered whose rhyolitic character is α, then: 15α grams of rhyolitic glass are lost to form 12α grams of allophane, and $15\,(1-\alpha)$ grams of andesitic glass are lost to form $(1-\alpha)\,50$ grams of allophane.

But the two "allophanes" are not distinguished so that 15α grams of rhyolitic glass appears to result in $(50 - 38\alpha)$ grams of allophane, as does $15\,(1-\alpha)$ grams of andesitic glass.

Hence the ratio of 'lost' rhyolitic glass to allophane is $\alpha/(3.3 - 2.5\alpha)$ and the ratio of lost andesitic glass to allophane is $(1 - \alpha)/(3.3 - 2.5\alpha)$. Thus the initial glass concentration can be expressed in terms of the present glass concentration and the allophane content by expressions of the form:

$C^r_o = C^r + (\alpha/3.3 - 2.5\alpha)A$ and $C^a_o = C^a + (1 - \alpha)/(3.3 - 2.5\alpha).A$

where A is the weight loss on ultrasonic cleaning and is assumed for the purposes of this calculation to be totally composed of allophane. On this basis, values of C^r_o and C^a_o may be calculated and hence the kinetic parameter $k_r t$ defined by the equation:

$$k_r t = \ln(C^r_o/C^r)$$

TABLE 6-6: Estimation of the Kinetic Parameter (kt) on Basis of Allophane and Glass Contents

Sample	α	A	C_{E_R}	$C^o_{E_R}$	$\ln(C^o_{G_R}/C_{G_R}) = kt$
201	1.0	83.8	7.75	112.50(a)	2.68
202	0.89	91.6	3.70	77.89	3.05
203	1.0	94.8	3.26	121.76	3.62
204	0.95	95.2	2.57	101.58	3.68
205	0.95	90.1	5.30	99.00	2.93
206	0.17	96.6	0.12	5.92(b)	3.89
301	0.87	77.0	7.6	65.1	2.15
302	0.80	80.0	6.5	53.5	2.10
303	0.81	88.5	4.23	58.23	2.63
304	0.54	90.5	2.74	28.1	2.33
305	0.26	75.5	1.64	9.19(b)	1.72
306	0.79	90.0	4.63	55.63	2.49
307*	0.77	44.7	24.0	48.3	0.70
308	0.25	77.7	2.03	9.02(b)	1.49

TABLE 6-6 cont.

Sample	α	A	C_{E_R}	$C^o_{E_R}$	$\ln(C^o_{G_R}/C_{G_R}) = kt$
309+	0.52	57.0	14.38	29.20	0.71
401	0.80	83.6	4.98	54.30	2.39
402	0.63	89.5	2.44	34.66	2.65
403	0.76	92.8	2.35	50.61	3.07
404	0.86	88.8	5.20	69.14	2.59
405	0.84	89.3	8.35	68.18	2.10
407	0.54	81.1	2.87	25.58	2.19
409+	1.0(c)	47.0	7.70	66.45	2.16
501	0.85	92.6	1.83	65.72	3.58
502	0.64	94.3	1.15	36.04	3.45
503*	0.72	92.7	1.21	44.78	3.61
504	0.61	91.3	1.09	32.13	3.38
505+	0.52	88.5	0.75	46.77	4.13
601	0.36	62.5	1.31	11.31	2.16(2.16)(a)
602	0.27	61.5	1.43	7.58	1.67(1.68)
603	0.38	62.8	2.90	12.90	1.49(1.47)
604*	0.99	57.8	23.60	93.60	1.38
605*	0.92	75.5	15.70	85.20	1.69
606	0.05	66.0	0.85	1.51(b)	0.58
901	0.76	77	13	54.6	1.44
902	0.75	80	10.6	53.2	1.62
903	0.84	83	10.3	68.3	1.89
904	0.84	86	10.4	70.4	1.91
905*	0.89	72	20	78	1.36
906*	0.53	55	16.2	30.7	0.64

(a) that G_R^o exceeds 100% indicates that not all the weight loss under ultrasonic cleaning is due to allophane

(b) low values of G_R^o are suggestive of loess, see Sec.

(c) This sample is supposed on field evidence to be correlative with 309 and 505

(d) evaluated from corresponding equation for andesitic component

Field recognition: * Oruanui Formation + Rotoehu Ash

It is clear from Table 6-6, in which this data is presented, that the trend of values down the stratigraphic sequences is the same as that previously established, although the absolute magnitude of the parameter differs a little. These variations may arise from an over-estimation of the allophane content, since, as has been previously pointed out, the weight loss in the ultrasonic cleaning may include primary minerals of fine grain size.

In order to use this technique to date tephra, it is necessary to consider the nature of the rate constant k. Clearly the constant is related to climatic variables and this correlation is explored in the next section. Subsequently the rate constants obtained on the basis of present-day climate are compared with the product kt for identified Oruanui Ash samples, and the variation of rate constant over the last twenty thousand years considered.

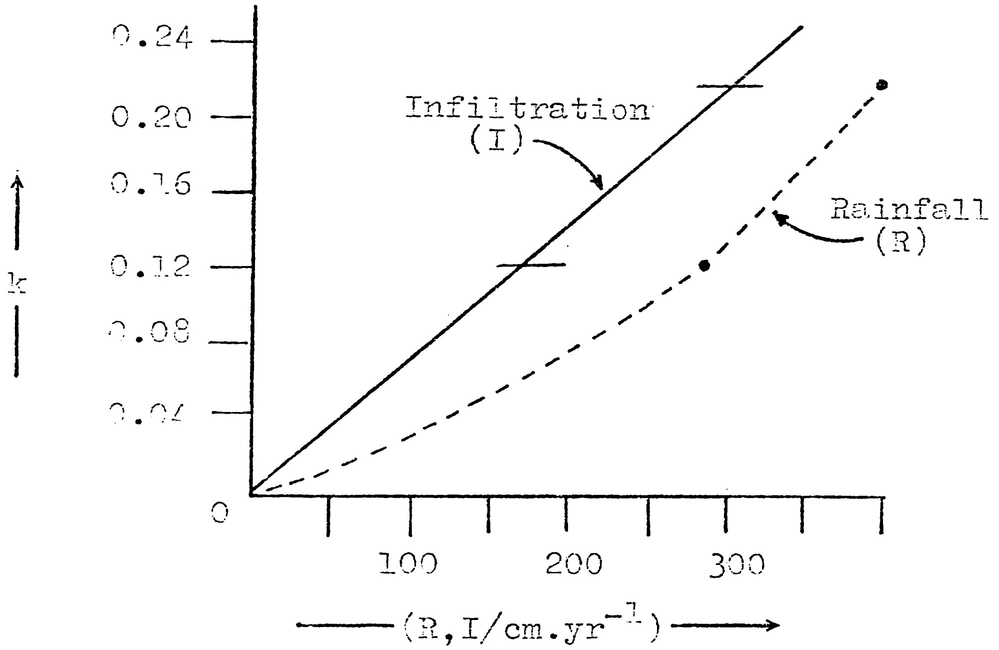
S6-6: Climatic Dependence of the Rate Constant for Weathering:

Ruxton (1968) noted that the weathering rate constant was primarily dependent on rainfall, or more strictly, infiltration. This is shown from his limited data on Fig. 606. By reference to the temperature dependence of the hydration of glass (to be discussed in Chapter 9) he concluded that temperature was less significant in determining the rate.

Rainfall data for the Waikato-Hauraki and King Country regions may be estimated from a map by de Lisle (1967), shown in Fig. 607 and

FIG. 606

Weathering rate constant (k) for dacitic ash as a function of rainfall (R) and infiltration (I); data after Ruxton (1968)



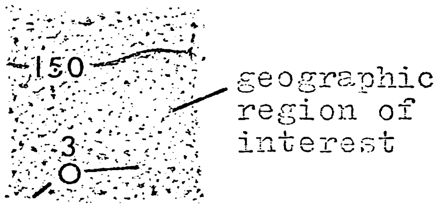
(Rate constant k in units of per thousand years)

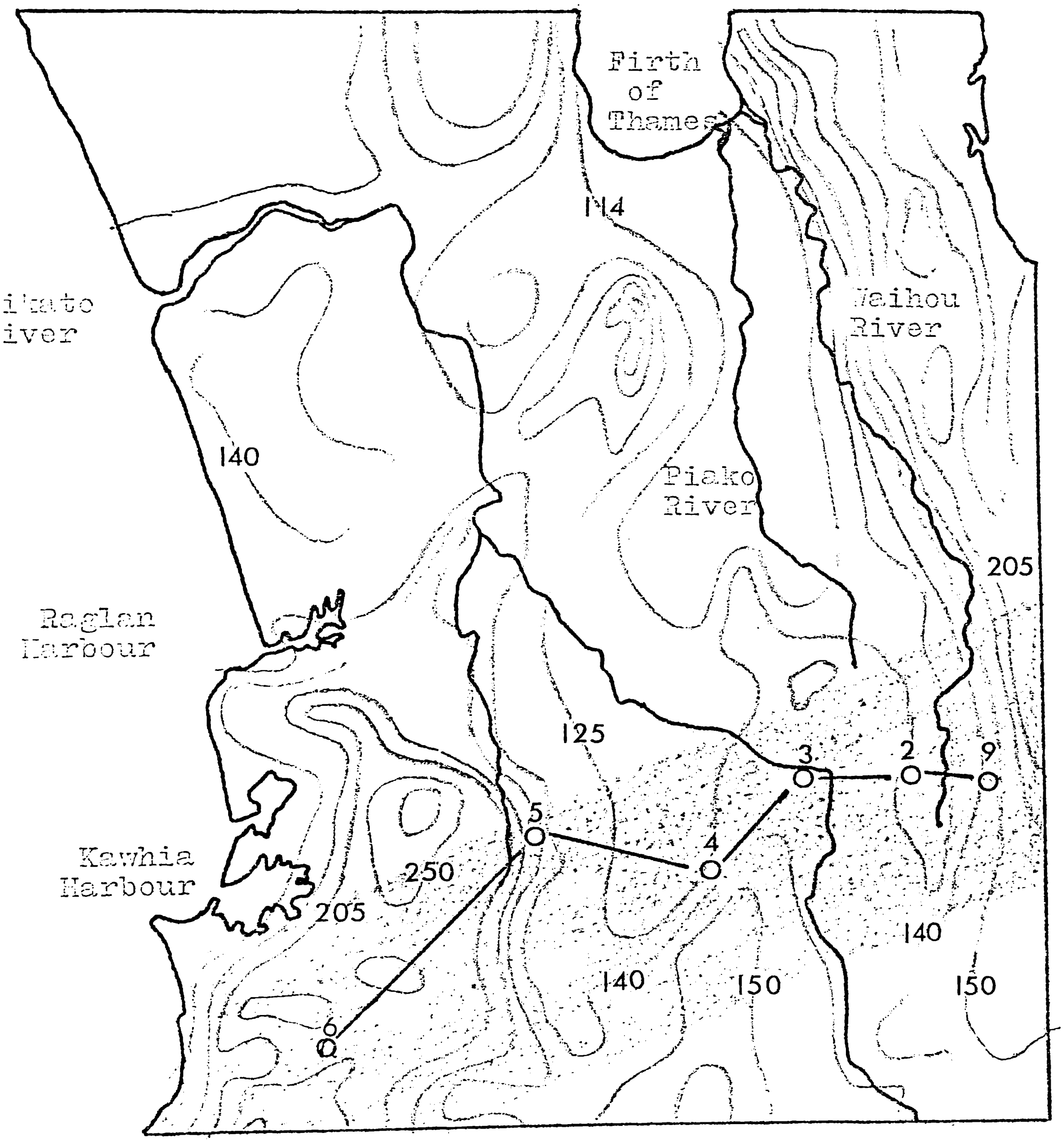
FIG. 607

Distribution of rainfall in the Waikato-Hauraki and King Country regions, based on a map by de Lisle (1967) and over-printed with the localities from which samples were taken for resolving the problem of the Tirau Ash and Mairoa Ash beds.

Rainfall in $cm.yr^{-1}$ shown thus:

Sampled localities shown thus:





overprinted with site localities for this thesis. Infiltration can be assessed as the difference between rainfall and evapotranspiration. This latter parameter is difficult to estimate on empirical grounds, although Thornthwaite (1948) proposed a relationship between evapotranspiration (PE) and temperature (T) of the form:

$$PE = cT^a$$

where a and c are constants which vary geographically. Since there is a decrease in temperature with altitude a relationship between potential evapotranspiration and altitude might be expected of the form:

$$PE = c(T_o - kh)^a$$

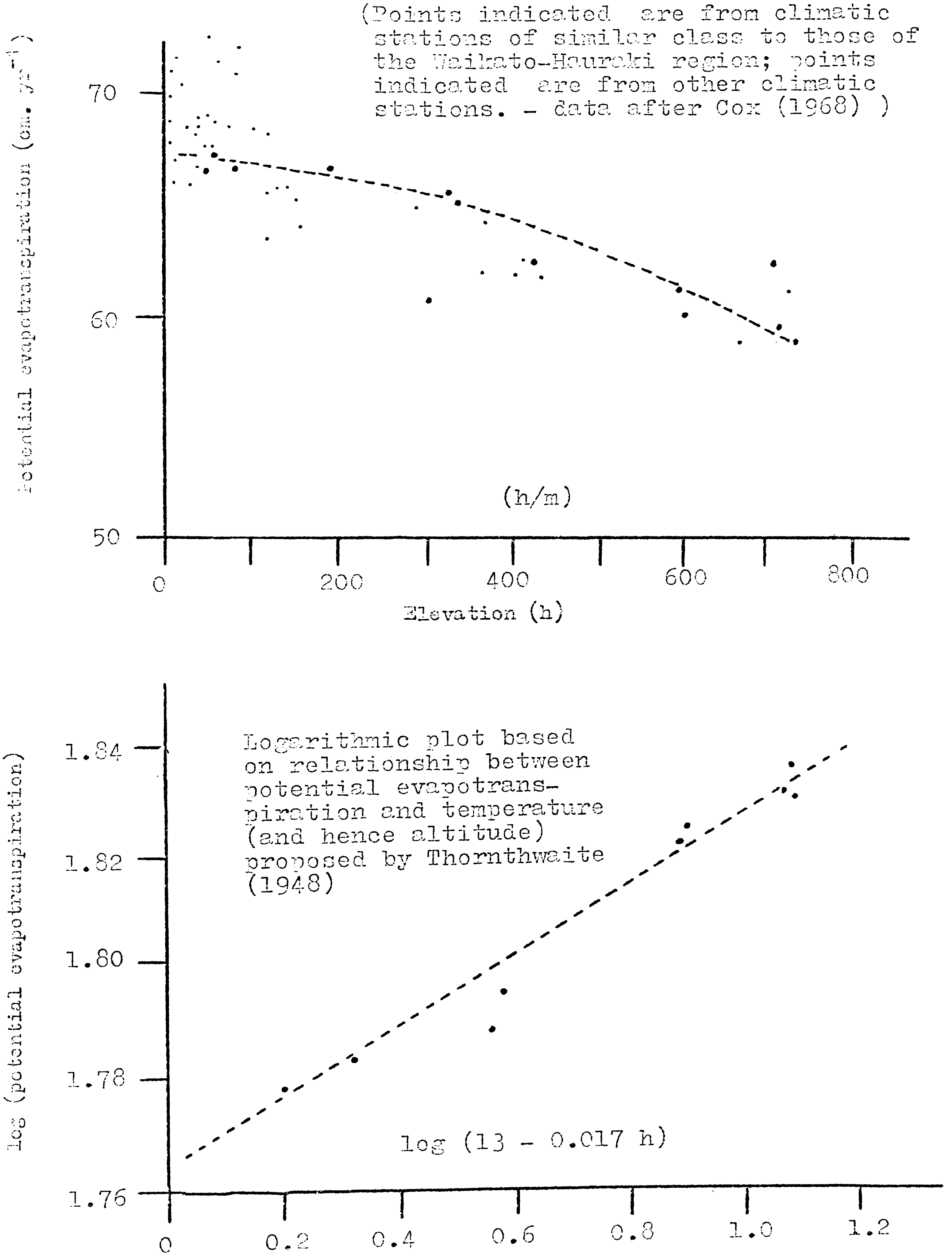
where T_o is the sea level temperature of the site in question, h is the altitude, and k the altitude coefficient of temperature. For the Waikato district, this becomes:

$$PE = c(13 - 0.017h)^a$$

A logarithmic plot shown in Fig. 608 indicates a value of 'a' of 0.8. A direct plot is also given in this figure which as expected from the value of 'a' is almost linear. From such an estimate of potential evapotranspiration and the rainfall data, estimates of infiltration and thus of rate constants may be made on the basis of present climate for the sites under study. Such constants are given in Table 6-7.

FIG. 608

Potential evapotranspiration as a function of altitude, linear and logarithmic plots.


(Points indicated are from climatic stations of similar class to those of the Waikato-Hauraki region; points indicated are from other climatic stations. - data after Cox (1968))

Logarithmic plot based on relationship between potential evapotranspiration and temperature (and hence altitude) proposed by Thornthwaite (1948)

TABLE 6-7: Calculated Weathering Rate Constants for Sites of Tirau and Mairoa Ashes:

Site	Elevation (h/cm)	Potential evapotranspiration $(PE/(cm.yr^{-1}))^{(a)}$	Rainfall $(R/(cm.yr^{-1}))$ (b)	Infiltration $(I/(cm.yr^{-1}))$	Rate Constant $(k \times 10^3/yr^{-1})$ (c)	Rate constant $(k \times 10^3/yr^{-1})$ (d)
Tirau	110	67.7	126	58.3	0.040	-
Findlay Park (307)	166	67.5	139	71.5	0.048	0.13
Parawera	153	67.5	139	71.5	0.052	
Kakepuku (503)	67	68.0	152	84	0.060	0.18
Mairoa (604)	400	65.5	228	122.5	0.118	0.01
(605)						0.08
Tapapa Rd (905)	300	64.0	254	190	0.132	0.11
(906)						0.47?

(a) Interpolated from Fig. 608

(b) after de Lisle, Fig. 607

(c) interpolated from Fig. 606, being the present-day rate constant calculated for dacitic ashes after the method of Ruxton (1968).

(d) being $(1 - \alpha)$ for Oruanui glasses, the mean rate constant over the last twenty thousand years

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It is of interest that the present-day rate constants rise with increasing altitude. Under these conditions the glass contents of correlative ashes would be expected to be less at higher altitudes. As is indicated in the next section, this does appear to be the case for some sites, and enables the comparison of data for sites at which the Oruanui Formation was not available for analysis of glass content.

S6-7: Correlation of Kinetics between Tephra Sequences:

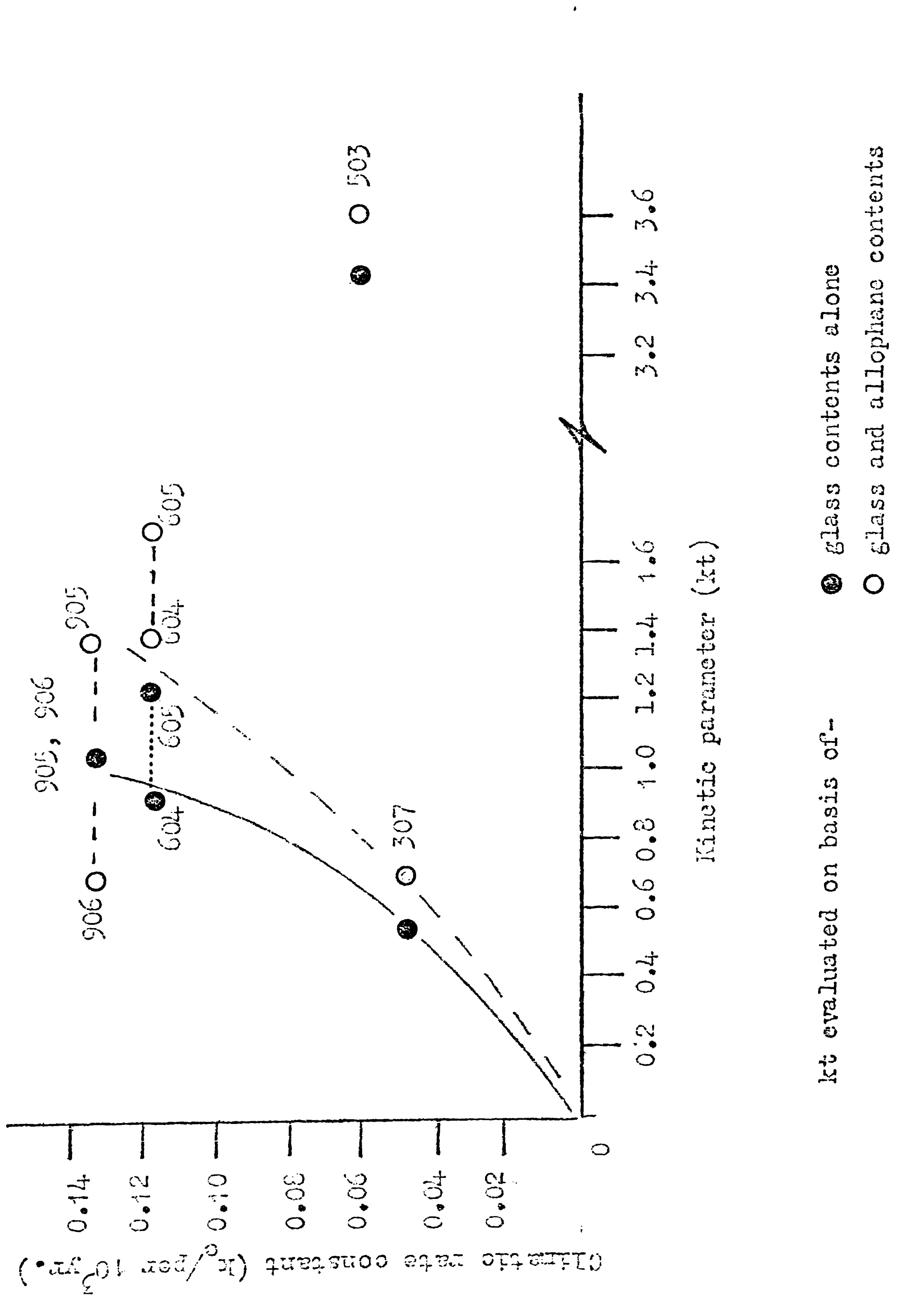
From Table 6-4 and Table 6-7, it will be seen that the estimates of the kinetic parameter for the samples of Oruanui Formation differ from site to site. As is evident in Table 6-8, this does bear some relationship to the present climatic differences. This data is plotted on Fig. 609 whereon it is seen that the correlation is better between

TABLE 6-8: Comparison of Rate Constants Evaluated on Climatic Basis and on Basis of Glass Content of Oruanui Formation:

Site	Rate constant from present-day climate k_c	Sample No. (Oruanui Formation)	Kinetic parameter k x t	
			(1)	(2)
2	0.040		(0.50)(3)	(0.60)(4)
3	0.048	307	0.54	0.70
4	0.052		(0.57)(3)	(0.74)(4)
5	0.060	503	3.43	3.61
6	0.118	604	0.92	1.38
		605	1.23	1.69
9	0.132	905	1.05	1.36
		906	1.04	0.64

FIG. 609

Variation of weathering rate constant evaluated from present-day climatic data with the kinetic parameter based on glass contents of the Oruanui Formation sampled at various localities



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(1) on basis of glass contents - plotted as closed circles on Fig. 609 from Table 6-5.

(2) on basis of glass and allophane contents - plotted as open circles on Fig. 609 from Table 6-7.

(3) interpolated from solid line, Fig. 609 (see text).

(4) interpolated from broken line, Fig. 609.

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the present-day rate constant and the kinetic parameter of Oruanui Formation evaluated on the basis of glass contents than with the parameter evaluated on the basis of glass and allophane contents. The deviation from linearity for samples in series 6 and 9 could be interpreted as caused by the reduction of the effective rate constant by there being a greater depth of burial. It is noteworthy that for samples from site 5, the kinetic parameter is much larger than would be expected on the basis of the climatic rate constant and is suggestive of lateral ground-water flow. On the basis of this diagram, and assuming no lateral ground-water flow, the kinetic parameters for sites 2 and 4 can be interpolated: the values obtained are given in parentheses in Table 6-8.

Reducing the kinetic parameters to that for Oruanui, kt = 1.0, the parameters for the samples may be correlated from sequence to sequence and this provides the basis of a crude method of geologic dating, provided the variation of rate constant with temperature is known.

S6-8: The Variation of Rate Constant with Time:

Vucetich (1968) has estimated the rates of soil development for soils derived from volcanic ashes over the past twenty thousand years. His "degree of soil development" are evaluated on pedological criteria, and may be expected to relate primarily to processes that occur prior to subsequent burial. Since the diminution of glass contents is the principal contribution to soil development from tephra, there is a certain correlation between glass contents and soil development.

If Vucetich's data is plotted as in Fig. 610, it is seen that the function shows a maximum, reminiscent of that obtained at the Findlay Park and Parawera sites for the "kinetic parameter" from glass contents of tephra of this maximum. Vucetich (1968) wrote:

> "..... it is inferred that the rate of soil development increased rapidly about 14.7 thousand years ago, which corresponds to the end of the last glaciation. The increase in the rate of soil development is attributed to the temperature becoming warmer at that time."

This is an interesting conclusion in that it conflicts with the proposal for a cold stadial at about 15 thousand years ago by Brodie (1957) and Suggate (1965) for more southern areas of New Zealand, and the postulated cold period in the Waikato region between 12,000 and 16,000 years ago, during which the final deposition of the Hinuera Formation might have occurred (Vucetich and Pullar, 1969). Vucetich, in fact, made the implicit assumption that the increased weathering rate of the soil-former (glass) can only be due to increased temperature. Reference has already been made to the fact that weathering of glass is more dependent on available water than temperature, and it may be that the post-glacial warming proposed by Vucetich (1968) is in fact a pluvial.

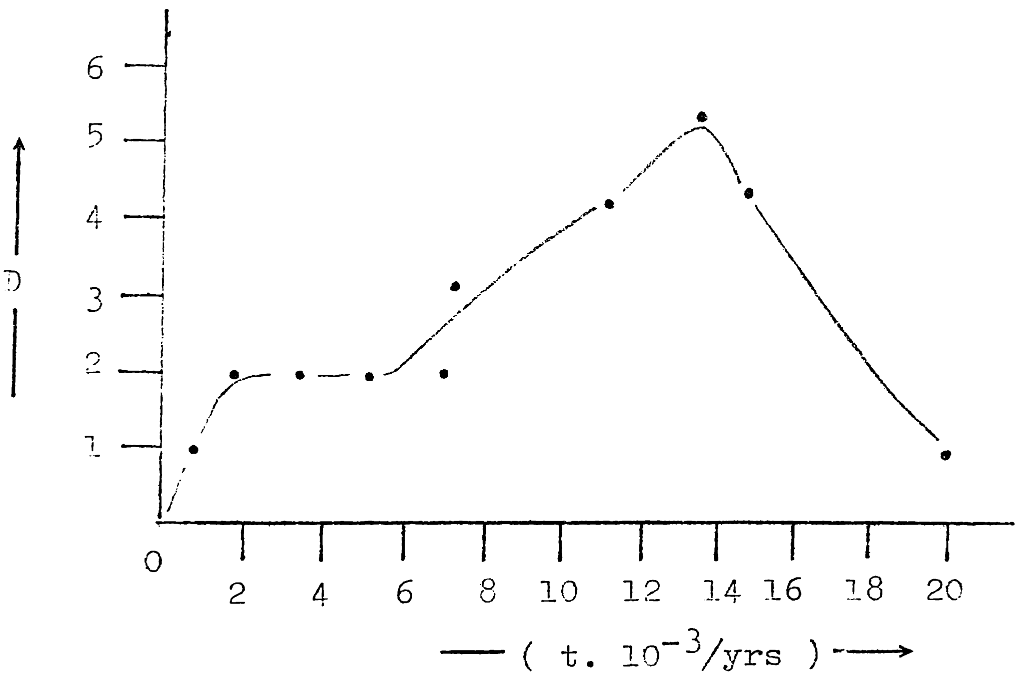
The "degree of soil development" needs to be incorporated into a kinetic framework if quantitative comparisons are to be made with the kinetic parameters based on glass contents, and attention is turned to this in the next section.

S6-9: Degree of Soil Development - a Kinetic Interpretation:

For the reference site described by Vucetich (1968), sufficient data is provided to calculate the present-day weathering rate constants on the basis of altitude and assessed infiltration by the methods previously described. This data is shown in Table 6-9. Assuming that

FIG. 610

Degree of soil development (D) as a function of the age of the parent tephra - data after Vucetich (1968)



for Kaharoa ash the age of the tephra is also the effective time for weathering, the kinetic parameter (kt) can be evaluated as the product of the age and the present-day rate constant, making the implicit assumption that the present-day rate constant has been effective over the last thousand years.

Now Frost and Pearson (1961) indicate that "a general equation can be derived for relating a measured physical quantity with concentration if a linear relationship exists." If such a relationship exists between Vucetich's degree of soil development and the concentration of glass in tephra-derived soils, then the equation:

$$kt = \ln\ (d_\infty - d_o)/(d_\infty - d) \quad = \ln(C_{g,o}/C_g)$$

holds, were d is the degree of soil development of the tephra being dated, d_o being the degree of development at deposition and d_∞ the degree if the tephra remains unburied for infinite time.

TABLE 6-9: Evaluation of Weathering Rate Constant for Vucetich Site X

Parameter	Value	Reference and Notes
Elevation (h/m)	360	Vucetich (1968)
Potential evapotranspiration (P.E./cm.yr^{-1})	66	Fig. 608
Rainfall (R/cm.yr^{-1})	127	Vucetich (1968)
Infiltration (I/cm.yr^{-1})	61	being R - P.E.
Weathering const. (k/10^{3}yr^{-1})	0.044	Fig. 606
Age of Kaharoa Ash (t/10^{3}yr)	0.9	
Product kt	0.0396	

On such a basis, if the original degree of soil development is taken as zero, d_∞ is evaluated as 26. Accordingly, from the degrees of formation, kinetic parameters can be evaluated. Further to this, using estimates of the time for weathering of the respective tephras before subsequent burial, weathering rate constants can also be evaluated.

The results of these calculations are shown in Table 6-10.

TABLE 6-10: Kinetic Parameters and Weathering Rate Constants for Various Tephras

Formation or member	Estimated degree of soil development at top of formation (d) Note (a)	Age of formation ($t/10^3$yr) (b)	Kinetic parameter kt (c)	Time for weathering ($t/10^3$yr) (b)	Rate Const. k (d)
Tarawera	-	0.08			
Kaharoa	1	0.93	0.0392	0.86	0.045
Taupo Pumice	2	1.82	0.077	0.89	0.086
Taupo subgrp. 9 - 13	1		0.039		
Waimihia Ash	2	3.40	0.077	1.58	0.049
Whakatane Ash	2	5.18	0.077	4.25	0.018
Mamuku Ash	2	7.05	0.077	1.87	0.041
Rotoma Ash	3	7.33	0.122	0.30	0.4
Taupo subgrp. 16 - 18	3.5		0.148		
Waiohau Ash	4	11.20	0.167	3.9	0.043
Rotorua Ash	5	13.5	0.215		
Rerewhakaiitu Ash	4	14.7	0.167	3.5	0.048
Okareka Ash	1	20.7	0.039	6.0	0.006
Te Rere Ash	1	<u>ca</u> 20	0.039	? nil	
Oruanui Ash	1	20.5	0.039	? nil	

Notes: (a) after Vucetich (1968)

(b) after Birrell and Pullar (1973)

(c) being defined by the equation: $kt = \ln(26/(26 - d))$
i.e. taking $d_o = 0$ and $d_\infty = 26$

(d) evaluated from the product kt where t is the effective time for weathering of the tephra

Of particular note is that, while the kinetic parameter goes through a maximum in relation to the tephra's age, the rate constant shows no such variation, being relatively constant except for the Rotoma and Whakatane Ashes and the late Pleistocene tephra, the latter of which were probably little weathered before burial. This is suggestive that the kinetic parameter, besides being dependent on the climate at, and subsequent to, deposition is also highly dependent on the lapse of time between deposition and burial, a factor which Vucetich's kinetic analysis appears to overlook.

It will be noted too that the values for the kinetic parameter obtained by this method are considerably lower than those obtained by the glass contents technique. This undoubtedly arises because the weathering constant evaluated for site X relates strictly to glass loss rather than soil formation. This difficulty is easily overcome by plotting the kinetic parameter (kt) as a function of time, scaling the parameters such that that for Oruanui Ash is unity. Such a plot may be demonstrated to be identical to Fig. 610 and forms the basis of the assignment of dates for the members of the Tirau and Mairoa Ashes.

S6-10: Assignment of Dates to the Tirau Ash and Mairoa Ash:

If the kinetic parameters of Table 6-4 are reduced so that the kinetic parameter for Oruanui Formation is unity, the results given in Table 6-11 are obtained. Interpolation of this on Fig. 610 enables the assignment of approximate dates. For sequences in which the Oruanui Ash was not identified with certainty, values of the kinetic parameter for Oruanui Ash required for scaling purposes were inferred from the relationships between kinetic parameter and rate constant shown in Fig. 609 and Table 6-8, assuming in all cases that the Ash is rhyolitic. Also given in Table 6-11 are the corresponding reduced parameters where the parameters were initially determined from both glass and alleged allophane contents of the soils.

TABLE 6-11: Reduced Kinetic Parameters and Derived Ages:

Sample	Reduced kinetic parameter (1)	Assigned Age (2)	Reduced kinetic parameter (3)	Assigned Age (2)
201	4.09	10.6	4.46	11.5
202	5.75	ca 13	5.10	12.5
203	5.85		5.90	ca 13.5
204	6.18		6.15	
205	4.70	14.4	4.90	14
206	7.80			
301	3.45	8.5	3.07	7.5
302	3.51	8.5	3.00	7.5
303	4.30	11.0	3.75	9.5
304	4.10	15	3.33	16
305	3.33	16	2.46	17
306	4.10	?	?	
307	1.00	(20)	1.00	(20)
401	3.80	10	3.26	7.5
402	4.43	11.5	3.60	8.5
403	5.01	12.5,14(4)	4.15	10.5, 15.5
404	3.96	15	3.50	16
405	3.03	16.5	2.84	16.5
501	ca 1.0	See Note (5)	ca 1.0	See note (5)
502				
503				
601	2.66	7.17	1.66	18.5

TABLE 6-11 (continued): Reduced Kinetic Parameters and Derived Ages:

Sample	Reduced kinetic parameter (1)	Assigned Age (2)	Reduced kinetic parameter (3)	Assigned Age (2)
602	2.13	18	1.21	18.5
603	1.82	18.5	1.08	20
604*	1.00	(20)	1.00	(20)
605*	0.75	(20)	1.22	(20)
606	-		-	
901	1.34	(13)	2.25	6.5
902	1.52		2.37	7
903	1.62	See note (5)	2.95	7.5
904	1.60		3.00	8,16
905*	1.00	(20)	2.13	17.5
906*	1.00	(20)	1.00	(20)

Notes: (1) kinetic parameter reduced relative to Oruanui, the kinetic parameters being those established on the basis of glass contents alone.

(2) from Fig. 610.

(3) reduced kinetic parameter as in (1), the initial kinetic parameters being those established on the basis of both allophane and glass contents.

(4) value obtained depends on the 'side' of the maximum considered appropriate

(5) negligible variation suggests post depositional mixing of beds

(6) anomalously low ages obtained, may be related to greater depth of burial.

Ages of tephra established by radiocarbon dating shown: ( )

Such a technique of dating makes the inherent assumption that the depositional sequence is the same or at least comparable in each case, as both between the sequences and between a given sequence and Vucetich's site X for which the time dependence was derived. To this extent the estimation of ages between 14.7 and 20 thousand years is of lower reliability, since Vucetich gives no tephra of this age - since at site X, this is sufficiently far from the Egmont centre to have received negligible amounts of the Mairoa material. Nevertheless, it would appear that the Tirau ash beds span between some 11 and 15 thousand years and the Mairoa sequence predates this but post-dates the Oruanui Formation of 20,000 years age.

Of interest is the observation that material recognised in the field as Mairoa ash is younger than the uppermost bed sampled at Mairoa itself. This might suggest that some of the upper members at the Mairoa locality might have been eroded, or alternatively that the bed may be contaminated with tephra of greater age. That the direction of thinning of the Mairoa ash is to the east suggests that the latter possibility is more likely. The most likely contaminant is the underlying Oruanui Formation; such incorporation is likely to be the reason for the failure of this dating technique to resolve the stratigraphy at Kakepuku (site 5). Results from physico-chemical and chemical analyses confirm the likelihood of the inclusion of Oruanui glass in these samples.

S6-11: Conclusion:

In this chapter procedures for obtaining an estimate of the age of tephra on the basis of glass contents has been described. In so doing it has been assumed that the rate of loss can be assessed on the basis of the weight loss of glass extracted and that for a given weathering regime this weight loss may be adequately described in terms of a first-order reaction. This model, previously proposed for dacitic eruptives was modified to render it applicable to mixtures of glass types. It was however necessary to propose a semi-empirical method of achieving the initial glass concentrations, and in order to reduce the variables, such that an ultimate solution might be possible, the weathering rates of andesitic and rhyolitic glass were assumed the same. Actually the rates do differ a little, as was shown by considering the rates of weathering of minerals comparable in composition to the two glass types.

For the New Zealand case, the model is further complicated by the variation of the rate constant with time. This has been assessed with reference to pedological criteria which gave a curve from which approximate ages could be interpolated. In so doing, the tacit assumption is made that the weathering of glass is the principal contribution to soil development. As a consequence of this dating, the Tirau Ash would seem to be not older than about 13 thousand years, and the Mairoa Ash older than this. That at Mairoa itself the youngest member of the Mairoa Ash sequence is some 17 thousand years suggests either erosional loss of the upper portion of the sequence, reworking of the material and incorporation of older material into the tephra bed.

It should be noted that the dates obtained by this method are but approximate. Apart from the limitations described above, the assumption is also implicitly made that there is negligible movement of clay minerals within the profile and an insignificant loss of minerals by means other than chemical weathering. However, in spite of such limitations, the technique has enabled assignment of dates to these ashes on the basis of an inherent property of the material itself rather than by inferred stratigraphic relationships.

CHAPTER 7: THE DENSITY OF VOLCANIC GLASS AS A TEPHRA CORRELATION PARAMETER

S7-1: Introduction:

The density of a glass shard reflects its bulk composition, and may therefore find application as a parameter in tephra correlation. Not a great deal of work has been done on the density of glasses in geology although the parameter is widely used in forensic work. Wilcox (1965) epitomised the reluctant approach of geologists with regard to density measurements:

> "The intrinsic specific gravity of the glass of the shards would be a useful characteristic, but unfortunately no convenient method of measurement is available in the presence of the many inclusions and bubbles."

Ross indicates that volcanic glass exhibits three principal habits which are described by Ewart (1963) as:

> "One type being composed of glass which originally enclosed rounded bubbles, consists of curved fragments of the bubble wall and may be Y-shaped where three bubbles were in close contact .... A second type is made up of almost flat glass plates, formed by the fragmentation of the walls which enclose large, flattened, lens shaped vesicles ..... A third type is fibrous and represents pumice fragments."

Although there is a complete gradation between these types, it is clear that the disquiet of Wilcox is only of significance for the third type, and there is in fact no justifiable reason for condemning density as largely unsuitable in tephra correlation.

Since much of the expertise in density measurements of materials, and glass in particular, has developed under the auspices of forensic science it is appropriate to review its usefulness and the techniques developed in this field before attempting tephra correlations on the basis of density.

S7-2: Techniques in the Determination of Density of Glass:

The correlative value of a technique is obviously of great importance in forensic work, and over thirty years ago statistical experiments described by Nelson (1965) showed that the chance of two randomly chosen glass samples being identical is very small, this chance of identity decreasing as the accuracy of the determination is increased, as is indicated in Table 7-1. In order to achieve this degree of accuracy, sensitive methods of density measurement are required, the most widely used of which are density gradient techniques and techniques that take advantage of the variation of density of a liquid with temperature.

Nelson (1965) describes the latter technique as enabling the separation of glasses differing in density by 0.000024 $gm.cm^{-3}$. The principle of the method is to heat a suitable liquid, the density of which is such that the immersed chips of glass rest on the bottom of the container, until they just rise. He notes that it is preferable not to arrange the procedure so that measurement is made when the glass chip sinks since a floating chip may be held at the surface in spite of its having a greater density than the liquid because of surface tension effects and convection currents. In such determinations a bromoform-xylene mixture of density 2.5 gm/ml was used in a water bath controlled to $\pm 0.01^{\circ}C$. Similar procedures are described by Kind and Summerscales (1966).

TABLE 7-1: Indications of Accuracy in Determinations of Density in Forensic Applications

Glass Sampled	No. of samples	Density Range	Reference
non-optical glasses	100	2.2447 - 3.1278 (96 within range of 0.4887)	1
bottles	30	0.0225	2
headlights	50	2.4658 - 2.4970	3
Lucas headlights	6	0.0005	4

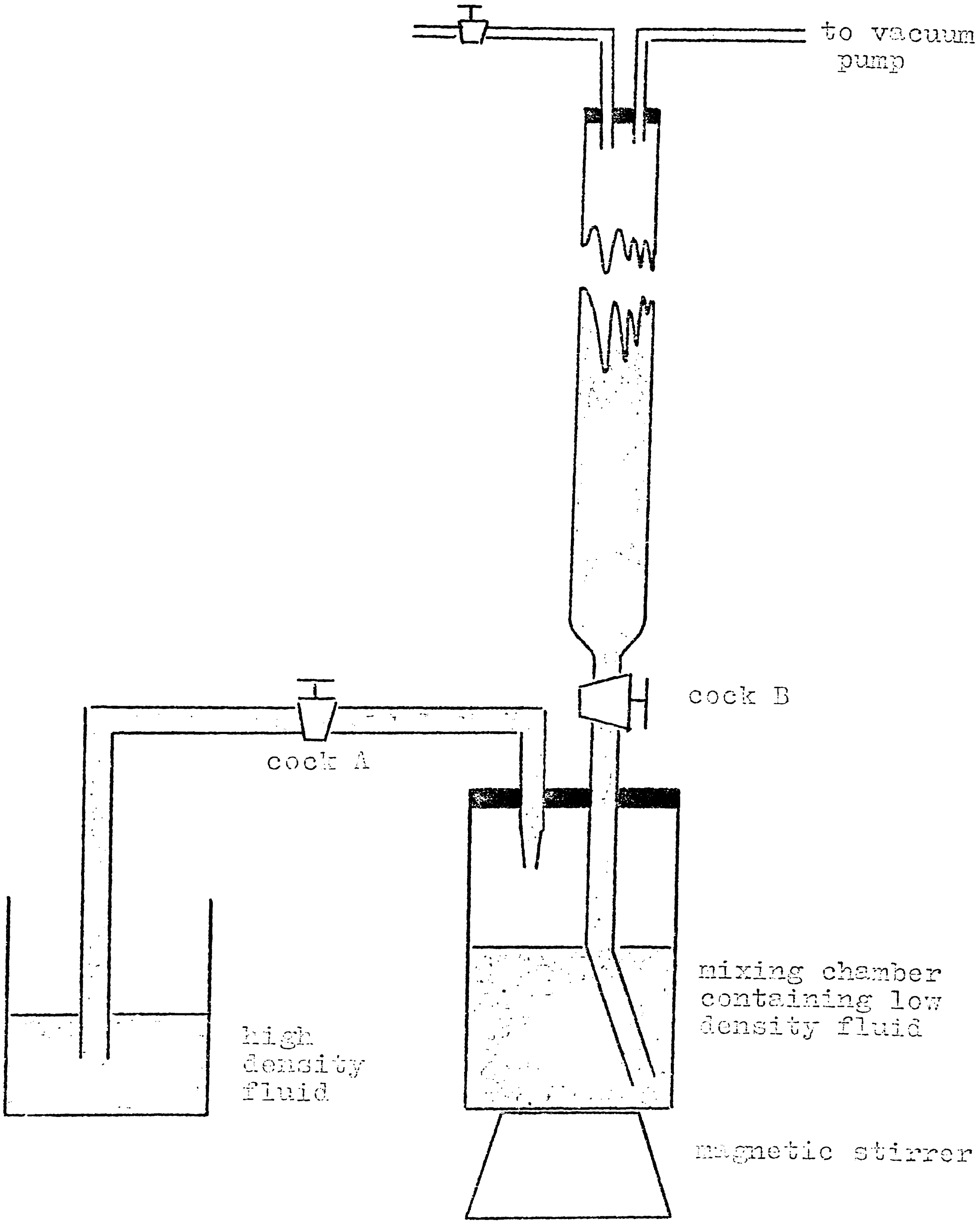
References: (1) Gamble, Bird and Roche (1943)
(2) Finch and Williams (1958)
(3) Green and Burd (1949)
(4) Nelson (1959)

A procedure such as this is likely to be time-consuming, although very accurate, and is therefore perhaps not be favoured for routine density determinations. By contrast density gradient methods are more easily set up and,because the result can be photographed, the densities of the glasses can be more readily compared, especially if they encompass a range of values. Nelson (1965) described the formation of a graded density column for forensic work stating that the sensitivity of the technique was proportional to the length of the column and the densities of the constituent heavy liquids. This column was made by successive addition of progressively dilated heavy liquids, having a rather larger volume of the end-member than of the intermediate members so as to "enable the full range of the gradient to be maintained for a considerable time."

Density gradient columns have been in use for many years, for example, Sollas (1891) and in general can be divided into two categories, one whereby the gradient is formed by mixing techniques and the other in which it is formed as a result of diffusional processes. The former have the advantage in the rapidity with which the gradient can be set up and the capability of modification to give different gradient profiles. Various methods are described by Anderson (1955). One such method (Jones, 1961) is illustrated in Fig. 701. The way in which"this simple apparatus, which enables the rapid establishment of a column of liquid graded in density and having controlled characteristics" works is described:

FIG. 701

A mechanical device for setting up a density gradient column; the method of Jones (1961), described for setting up a gradient over the density range 1.2 to 1.5 gm/ml



> "Upon subjecting the empty column to reduced pressure the low density liquid is drawn through cock B and replaced in the chamber by high density solution from the beaker. A gradual and even increase in the density of liquid in the chamber and therefore of the liquid drawn into the column, is ensured by continuous mixing with an electromagnetic stirrer. The liquid rises steadily up the column, there being little disturbance by the inflow at the base. When the vertical tube is filled, cock B is closed and the column is ready for use ....."

The technique as illustrated is for 'light' and 'heavy' liquids which differ in density by only a small amount. When such an apparatus was constructed, difficulties were encountered if there was a large density difference between the high and low density fluids, since under these conditions a considerable volume of the low density fluid is withdrawn before the high density fluid enters the chamber. Thus the rate of ascent of the mixed solution up the column appears to be a function of density. Add to this the difficulties of evaporation of the diluent (usually acetone or alcohol is used as the diluent, with bromoform as the heavy liquid) and it is appreciated that such mechanical devices probably have little application in mineralogical work where gradients over a wide density range are usually required. Muller and Burton (1965) describe similar apparatus for mineralogical application which operates under gravity rather than under vacuum and thus does not suffer from the density dependence of solution velocity. However, the apparatus requires special equipment and for the present investigation it was considered that comparable results would be obtainable by diffusional techniques which, as has been shown, has sufficed in accuracy-demanding forensic applications.

The original method for establishing a gradient of density was simply to allow diffusion to occur at the interface of two miscible liquids of differing density (Galileo (1665); Fick (1855). While such a system is impracticable in the present situation in that the time to set up a column in this way would be inordinately long, and much of both the heavy liquid and the diluent would have evaporated, the principle is fundamental to all diffusional columns. In order to reduce the time for diffusion to render suitable column characteristics, diffusional columns are usually made by laying aliquots of progressively decreasing density (Goin and Kirk, 1947), or by a "slip-under" method in which each layer is introduced through a capillary tube and slipped under the preceding layer (Fortuin, 1960). The procedure followed in the present study was that of Woolson and Axley (1969), using 1 ml. aliquots added slowly from a syringe tube (without needle attached) to a 10 ml graduated centrifuge tube held in a slanted position. Some mixing of the layers as the aliquot is added is inevitable but this has been claimed, in fact, to be desirable (Boyer et al., 1946; Linderstrom, Lang 1937). The tubes were generally prepared in batches of four, loaded with sufficient material to give clearly defined bands and then centrifuged gently to facilitate the settling of the added material into bands. Low and Richards (1952) claimed that the gradient characteristics of the column are not affected by centrifugation; and this has the further advantage of reducing the time that any iron-bearing mineral is in contact with the heavy liquid. Following this the positions of the bands were then noted and the column is characterised.

S7-3: The Characteristics of Density Gradient Columns:

Woolson and Axley (1969) do not indicate how they characterised their columns. It is possible that they did not do so since they consider that:

> "a possible error equal to or less than the difference between two adjacent heavy liquid layers is inherent in the system."

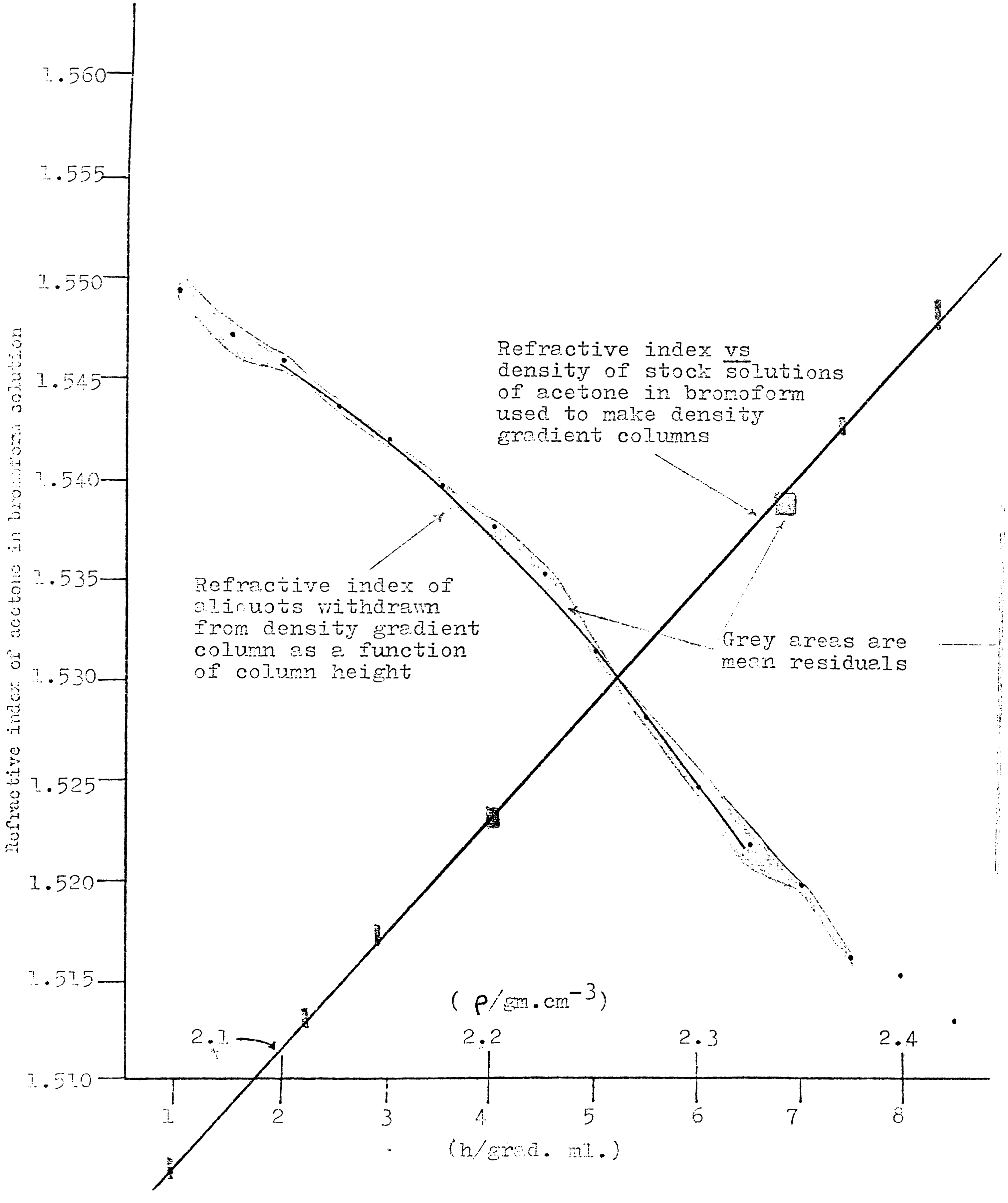
In the present case the added aliquots differ by about 0.05 gm/ml in solution density and further, on this basis only, a step-wise gradient can be drawn and the effect on the density characteristics of diffusion can only be estimated. A suitable method of characterising the column is by withdrawing small aliquots from various levels in the column and determining their refractive index. Twenty microlitre portions removed with a syringe causes minimal disturbance to the gradient, but it is necessary to work progressively down the column since there is a significant overall volume diminution. If the refractive indices of the stock liquids are determined as a function of their densitites, then the relationship between density and column height can be established. A typical curve for solution refractive index as a function of column height is shown in Fig. 702, the grey bounds representing the mean residual of refractive index at the particular height. Typically the mean residual is some 0.00005 units of refractive index. The relationship between refractive index and density is also shown in Fig. 702 for which the slope $\Delta n / \Delta \rho$ is 0.116. From this the error in density corresponding to the mean residual of refractive index is 0.004 gm.cm^{-3}. As will be seen subsequently this is considerably less than the natural variation in glass density.

Both the density and refractive index of liquids are functions of temperature. On the basis of their coefficients of expansion, acetone and bromoform have a temperature coefficient of density of - 0.0011 and - 0.0029 (gm.ml^{-1}K^{-1}) respectively (Chemical Rubber Co., 1972). Temperature coefficients of refractive index are not tabulated for these two liquids, but typically this parameter is of the order of - 0.0004 to - 0.0007 (K^{-1}) (Hinnawi, 1966). The effect of this on the relationship between refractive index and density is such that if the temperature of the stock solutions used to generate the refractive index-density curve differed by 1 K from the temperature of the column, there would be an error of some 0.003 gm.ml^{-1} introduced in the density assigned a given band. Of course it matters not that the refractive index and density determinations are made at different temperatures, providing that for a

FIG. 702

Characteristics of density gradient column over the density range 2.0 to 2.5 gm/ml

being plots of solution refractive index as a function of column height, and density of stock solution as a function of its refractive index



given batch, the determination of refractive index of the samples removed from the column and of the stock solutions are made at the same temperature, and that the determination of density of the stock solutions and the recording of band positions are also made at the same temperature (but not necessarily the same as that for refractive index).

It will be noted for Fig. 702 that the gradient is not linear; the system is like that described by Oster and Yamamoto (1963) as a "diffusion system without reservoirs" for which "one cannot achieve a linear gradient by diffusion and furthermore the gradient achieved is unstable and eventually disappears." The disappearance of the gradient was investigated by sampling columns of the same batch after allowing them to stand for differing lengths of time. Typically, the column "collapses" around the mid-point of the column, and eventually a liquid column of nearly uniform density is obtained, as is shown in Fig. 703. The collapse occurs primarily because of diffusional processes, but is probably aided by the evaporation of the diluent (acetone) from the top of the column, and photochemical dissociation of the bromoform.

S7-4: The Dependence of Density on Particle Size:

To determine the effect that particle size has on the observed density of the glass, batches of columns were loaded with various sieve fractions of identical glasses. Typical of these is sample 110 (Rotoehu Ash) shown in Plate 71 for which the sizes are, from left: greater than 250 microns, between 125 and 250 microns, between 75 and 125 microns and less than 75 microns. The differences that are obvious on Plate 71 arise because the grains in the larger size fraction are not "liberated." Muller and Burton (1965), who use this term do not indicate whether the non-"liberation" of grains arises because of an inherent dependence of density on particle size or because of buoyancy effect in the column that prevent the larger grains from settling. In any event the mean density is the same for all sized particles although the range tends to be greater for larger particles. This is in an interesting comparison

FIG. 703

Effect of time on characteristics of density gradient column over density range 2.0 to 2.5 gm/ml

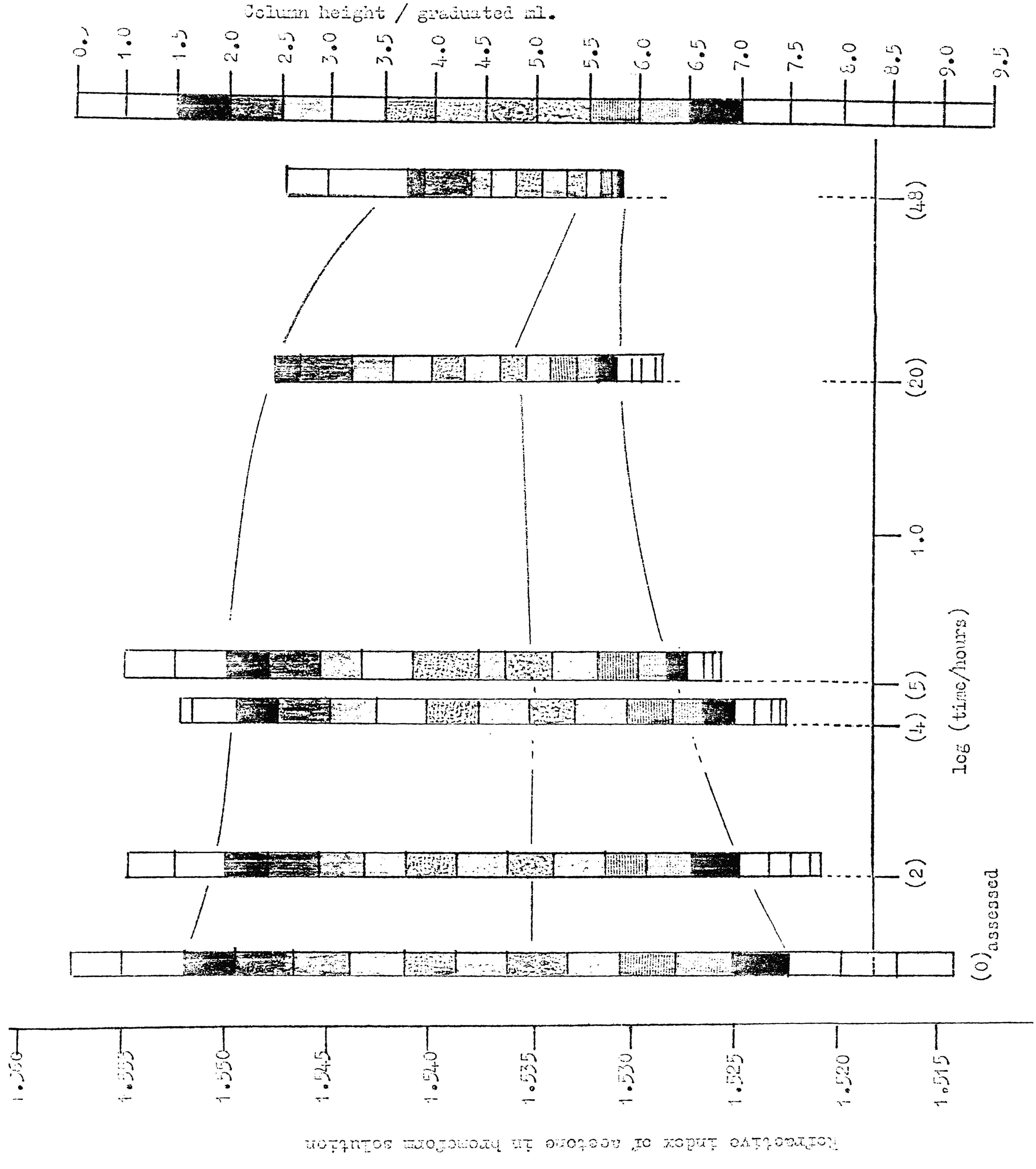
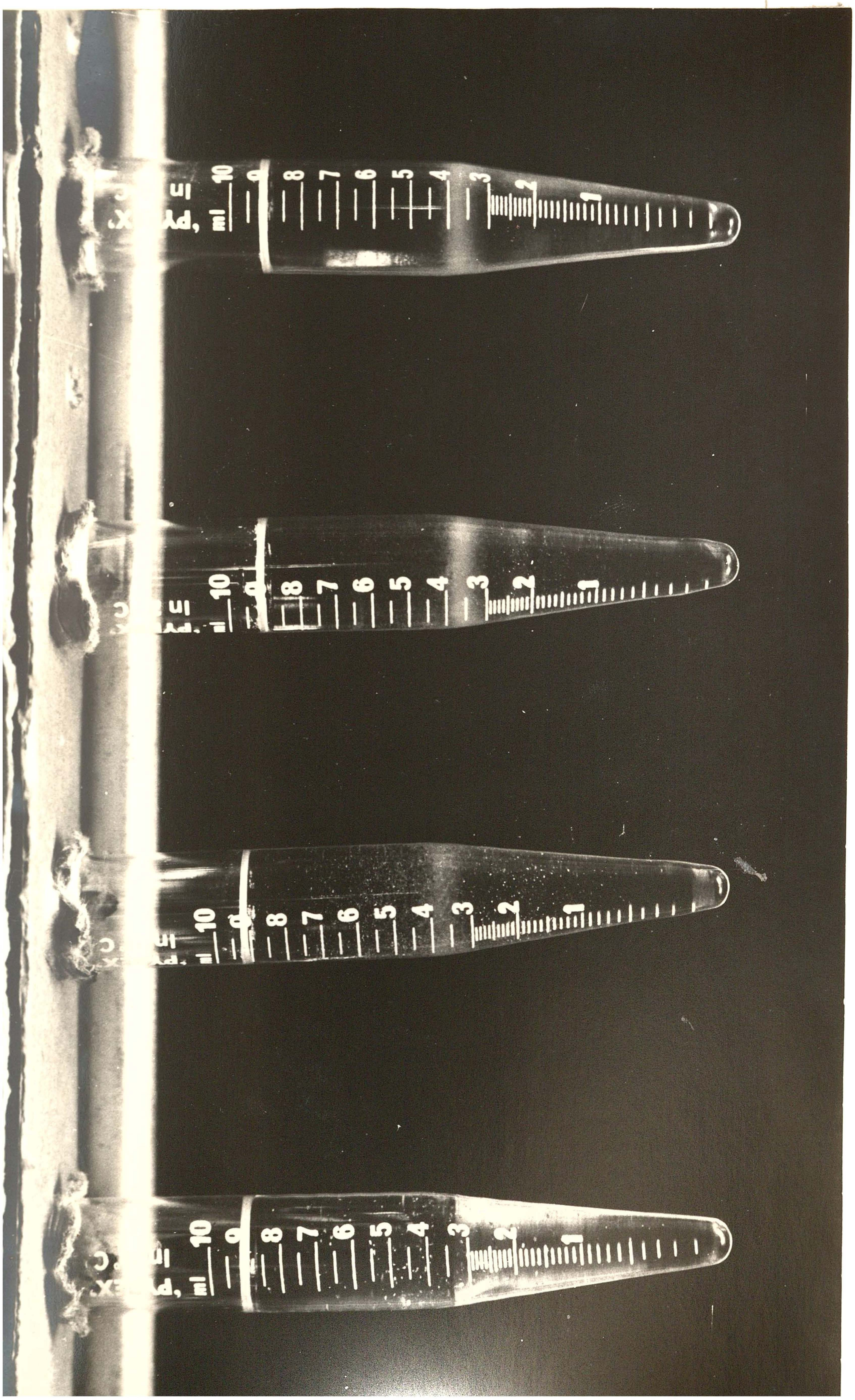


PLATE 71

Dependence of density of rhyolitic glass shards with particle size

(Sample: glass from Rotoehu Ash (110))



Particle size

less than 75 microns

75 - 125 microns

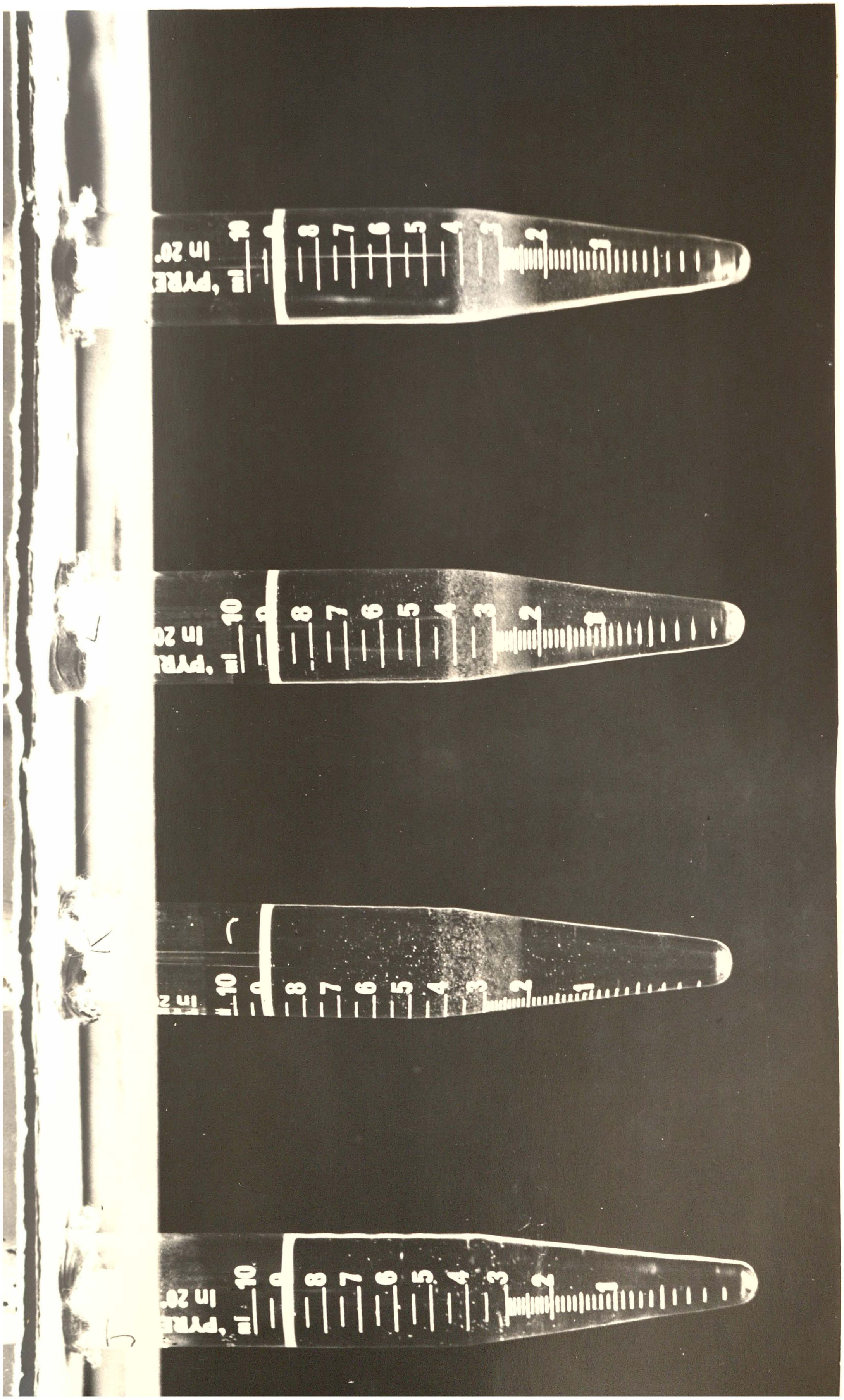
125 - 250 microns

greater than 250 microns

PLATE 72

Density of glass from Okareka Ash (sample 101)

Note the two bands of particles in the column



Particle size

less than
75 microns

75 - 125
microns

125 - 250
microns

greater than
250 microns

since the mesh of liberation appears to be 125 microns in that the band character is clear for particles of this and smaller size, and since most of the glass particles are of comparable size (see Table 7-2) it is adequate to use unsieved samples of glass for density determinations.

TABLE 7-2: Proportions of Glass of Various Size Fractions for Representative Samples

Sample No.	Representative of	Particle size (μ)			
		less than 75	(75-125)	(125-250)	greater than 250 *
		Proportion (% by weight)			
301	Tirau Ash	37	38	23	2
304	Mairoa Ash	56	36	10	0
307	Oruanui Formation	65	33	42	8

* This proportion should be very small, since dried ash was crushed through a 250 micron sieve prior to ultrasonic cleaning.

S7-5: Lateral Variation of Glass Density:

Wilcox (1965) suggests that there should be an averaging effect at distances far from the projected source:

> "Variations in the composition of erupted material can take place during the course of the eruption and have been demonstrated in some historic eruptions...... But in many cases original variation appears to be averaged out in transit by turbulence and shearing in the ash cloud and locally by mild reworking immediately after initial deposition, so that the makeup of the resulting bed is remarkably uniform throughout its geographic extent. It is hardly to be expected that a particular ash-fall deposit would have one set of primary constituents at one locality, and another

set at another locality, and although variations occur from place to place in the size of particles and in the proportions of the constituents, rarely is any primary constituent totally lacking in a sample. Likewise there may be a range of composition of the glass, but most of this range is present in almost every sample of the ash......"

This is indicated in Table 7-3 which compares the densities of the glasses in the Oruanui Formation and Rotoehu Ash as recognised in the Waikato district with those of the same tephra units on the Mamaku Range (Hauraki District).

Such correlations assume that the density of the glass is not significantly affected by weathering. The principal weathering effect, at least, initially is hydration, as is discussed in Chapter 9. Ross and Smith (1955) note that the addition of 4% water causes an increase in density of Arroyo Hondo glass from 2.34 to 2.37. Thus density discrepancies of the order of 0.04 $gm.cm^{-3}$ may be explained on the basis of weathering. Unfortunately, this is very nearly the same as the maximum variation of glass density between known tephras, and this may limit the use of glass density in heavily weathered soils. For the present case, this probably means that samples from the Kakepuku site cannot be reliably correlated by this technique. A correlation is attempted for the three sites in the Waikato district in Table 7-4, wherein it will be noted that glass from samples from Findlay Park, tentatively recognised as Tirau Ash, have slightly higher densities than those glasses from samples prepared as Mairoa Ash at Mairoa. At Parawera, the samples from immediately above the marker bed, (Oruanui Formation) which are un-named on field evidence, bear closer density relationships to Mairoa Ash at Mairoa than does the alleged Mairoa Ash higher in the stratigraphic sequence at Parawera.

TABLE 7-3: Lateral Variation of Glass Density (in gm/ml^{-1}):

	Mamaku Plateau	Findlay Park	Parawera	Kakepuku	Mairoa
TE RERE ASH (104):	2.29 - 2.32	(306):2.28 - 2.29(a)			
ORUANUI FORMATION: (105)	2.27 - 2.29	(307):2.28 - 2.29	(406):2.27 - 2.31(b)	(503):2.30 - 2.31(c)	(604):2.28 - 2.30
MANGAONE LAPILLI: (109)	2.30 - 2.33 ?	(308):2.31 - 2.32 (d)	(408):2.29 - 2.31		
ROTOEHU ASH (110):	2.27 - 2.30	(309):2.30 - 2.32	(409):2.31 - 2.33	(505): *ca* 2.31	
(112):	2.30 - 2.33				
(116):	2.27 - 2.32				

Correlation: on basis of density; — — — — on basis of field evidence. ————

(a) on field evidence is possibly Te Rere Ash but on a density basis is possibly Oruanui Formation.

(b) all densities in this sequence seem lower than expected.

(c) density higher than expected.

(d) Comparing sample 308 with the Rotoehu Ash samples from Mamaku Range and Mangaone Lapilli suggests that it might be Mangaone Lapilli since density does not concur with that of glass of upper Rotoehu Ash.

TABLE 7-4: Densities of Glass Shards from Tirau and Mairoa Ashes

Findlay Park		Parawera		Mairoa	
Sample	Density (ρ/gm.cm^{-3})	Sample	Density (ρ/gm.cm^{-3})	Sample	Density (ρ/gm.cm^{-3})
301 T	2.30 - 2.32	401 T-M	2.30 - 2.31		
302 T	2.30 - 2.32	402 M	2.31 - 2.32	602 M	2.28 - 2.30
303 M	2.30 - 2.32	403	2.31 - 2.32	603 M	2.28 - 2.30
304	2.30 - 2.33	(404 M?	2.27 - 2.33	604 OU	2.28 - 2.30
305	2.30 - 2.31	(405	2.28 - 2.30		
306	2.28 - 2.29	406 OU	2.27 - 2.31		
307 OU	2.28 - 2.29				

Key: M: Mairoa Ash
T: Tirau Ash
OU: Oruanui Formation

It seems that the density of rhyolitic glass shards is not as useful a correlative parameter as might be hoped because of the large natural variation in glass density. This is presumably the result of weathering and tends to mask any inherent differences in the initially erupted glass.

S7-6: An Attempt to Isolate Andesitic Glass with a Density Gradient Method:

It has already been noted that andesitic glass is not easily separated: one way that was attempted was to see whether it would show up as a band in a density gradient over the appropriate range of solution density. Thus columns were set up with a density range from 2.4 -2.9 gm.ml^{-1}, for which plots analogous to those described earlier are shown:

Characteristics of density gradient column over density range 2.4 - 2.9 $gm.cm^{-3}$: Fig. 704.

Effect of time on characteristics of density gradient column over density range 2.4 - 2.9 $gm.cm^{-3}$: Fig. 705.

Because of the rather lesser amounts of the diluent (acetone) used, the columns are rather more stable with time and the mean residuals from characterising the column are smaller than those for the 2.0 - 2.5 gm/ml range.

Since it has been demonstrated that Mairoa Ash contains andesitic ash, the felsic fractions of samples 601 and 602 were added to prepared columns. It might have been expected that there would be three bands, but as Plate 73 shows there are but two. In order to determine in which band the andesitic glass was concentrated, a bromoform in acetone solution of density 2.57 $gm.ml^{-1}$ was used to separate the components of the felsic fraction by the method described in Chapter 2 for separating rhyolitic glass, mafic minerals and the felsic fraction. This particular density value of 2.57 $gm.ml^{-1}$ was that mid-way between the observed bands. The fractions recovered by this technique were then mulled and their infra-red spectra determined. From the quantitative analysis of these spectra the proportion data given in Table 7-5 were derived.

From Table 7-5, it is clear that the lower band observed in Plate 73 is primarily composed of glass and quartz, while the upper band is largely feldspar. At this stage it is appropriate to compare the felsic assemblage estimated by the combination of density techniques with infra-red analysis of the components of the observed bands with that obtained by infra-red analysis of the entire felsic fraction as described earlier. From the data of Table 7-5, and the proportionate weights of the various density fractions (Table 7-6) the proportions of

FIG. 704

Characteristics of density gradient column over the density range 2.4 to 2.9 gm/ml

being plots of solution refractive index as a function of column height, and density of stock solutions as a function of refractive index

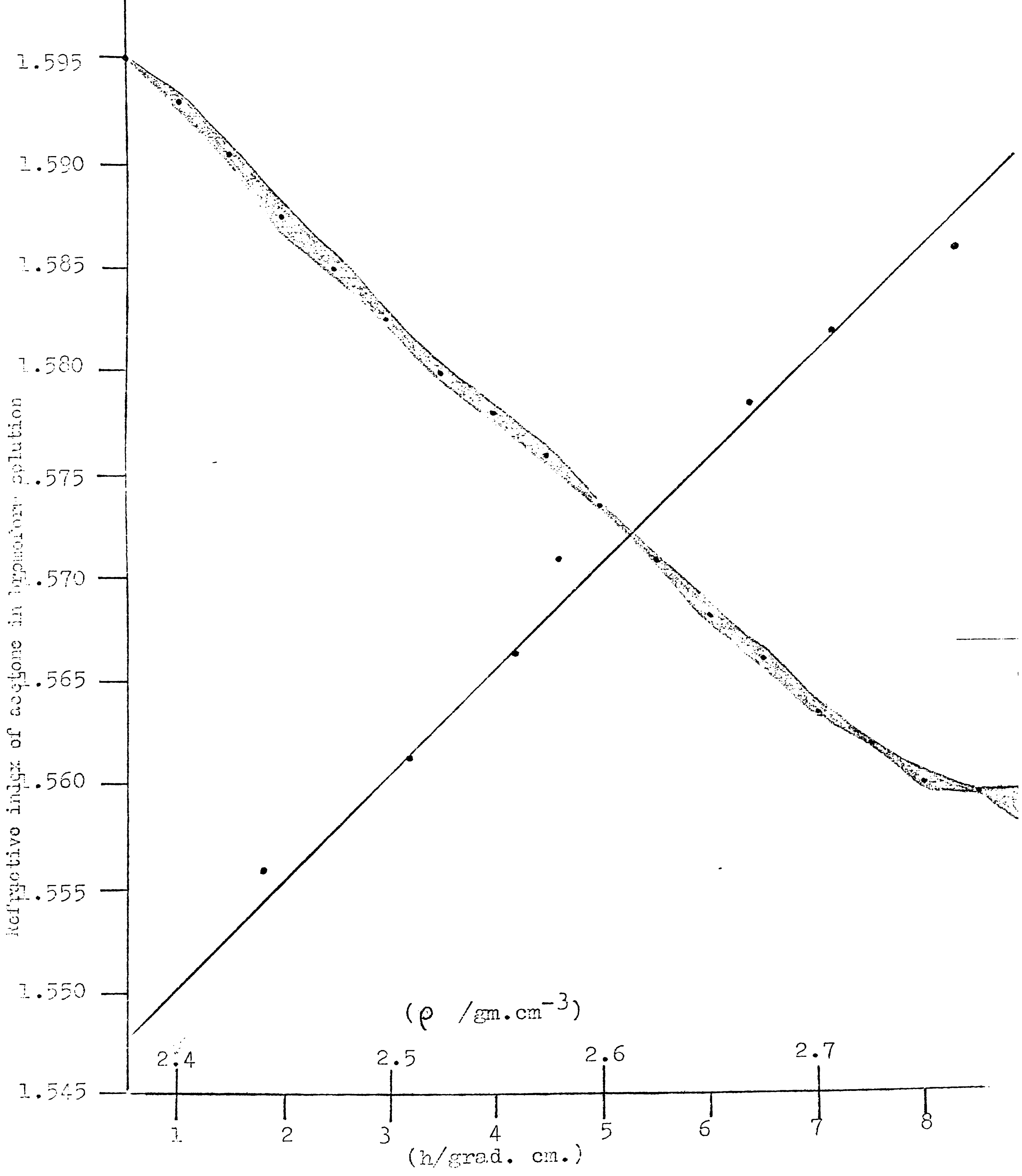
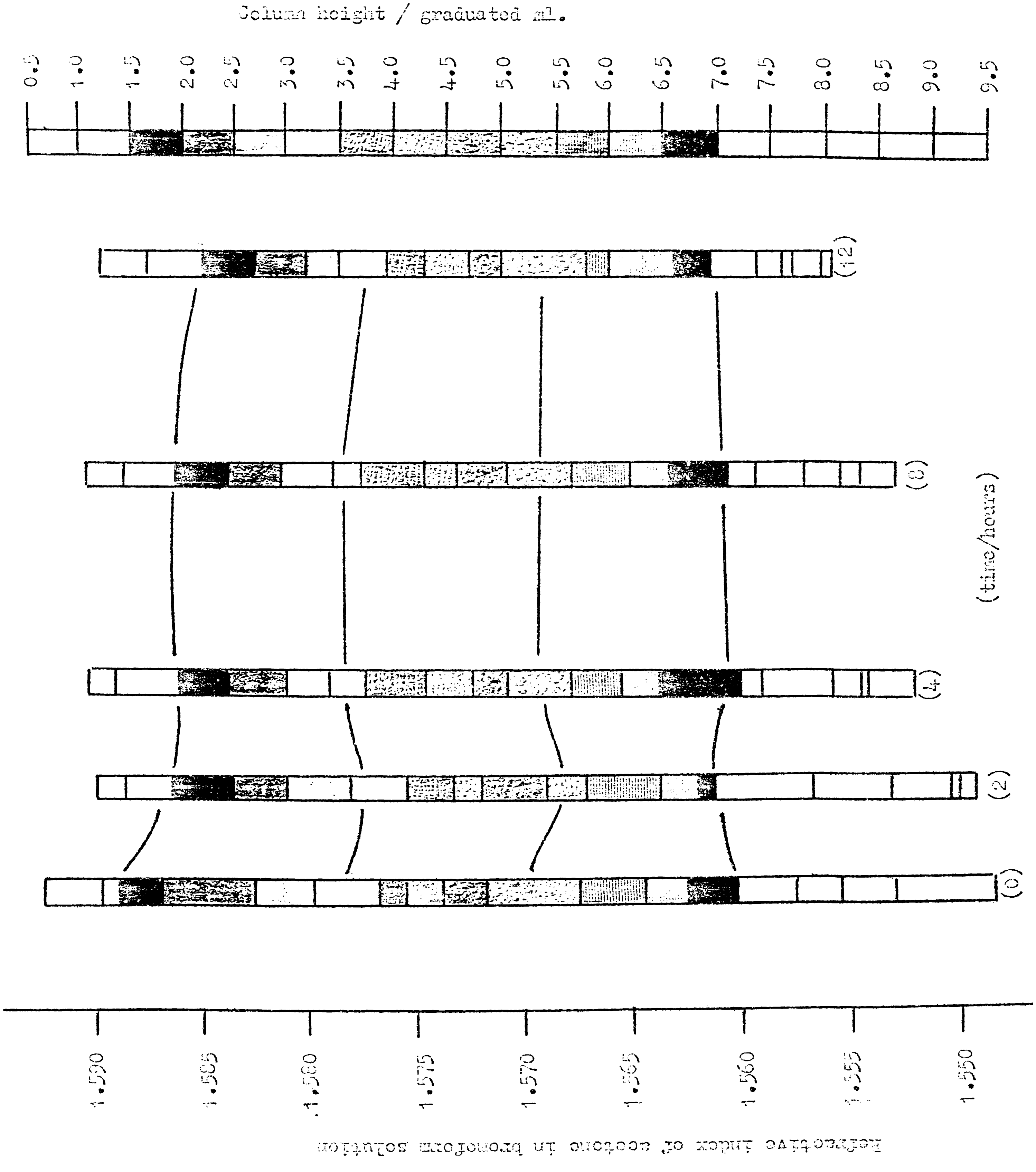


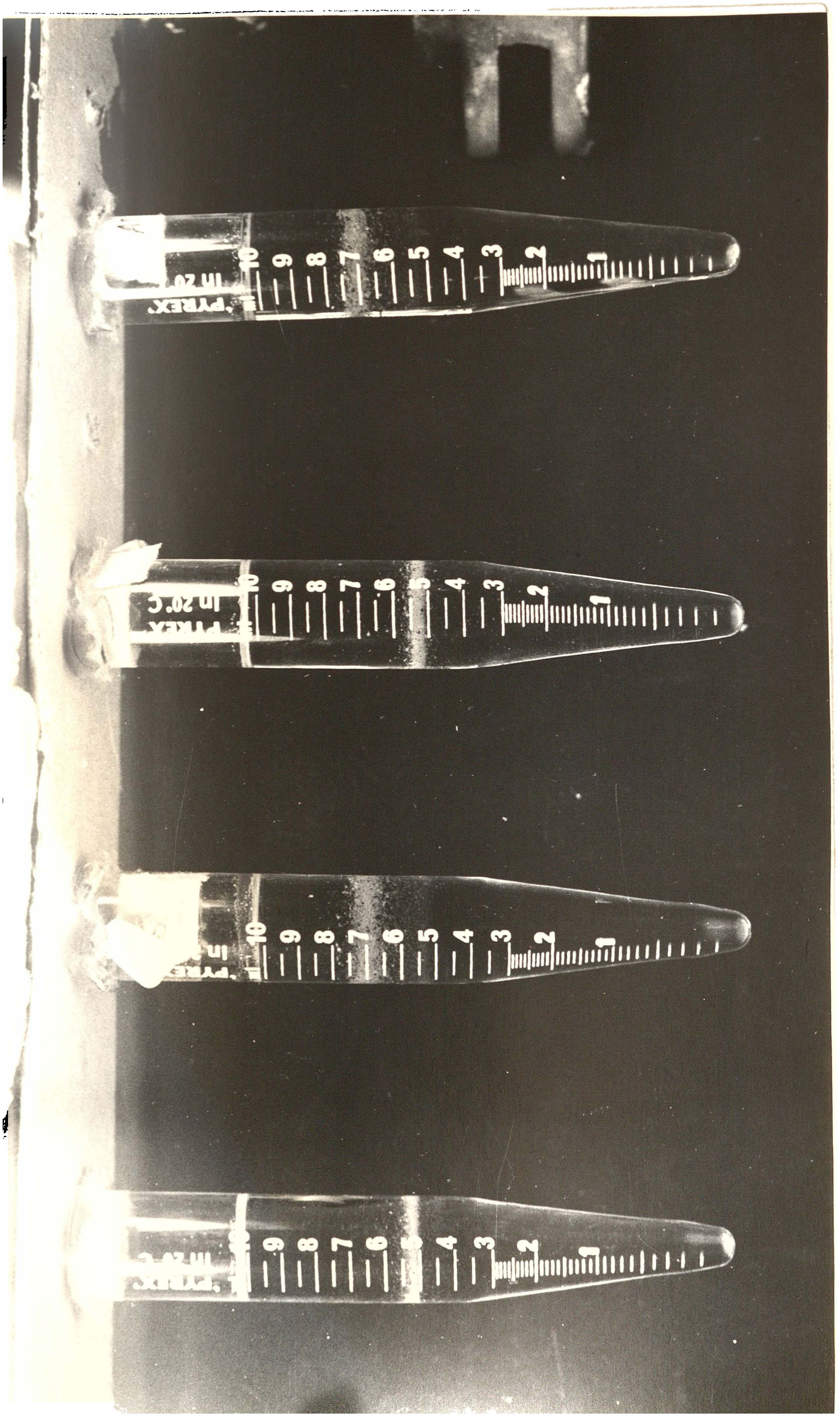
FIG. 705

Effect of time on characteristics of density gradient column over density range 2.4 to 2.9 gm/ml



Density of components of felsic fractions of samples of Mairoa Ash (601, 602)

The whole fraction shows a density distribution like that shown for sample 603 (Plate 74). Here the bands have been separated physically prior to addition to gradient column



Sample 602

this band shown by i.r. spectrum to be feldspar, by density is alkali feldspar

this band shown by i.r. spectrum to be feldspar, quartz, & glass; by density the feldspar is plagioclase

Sample 601

upper band (alkali feldspar)

lower band (quartz, andesitic glass, plagioclase)

TABLE 7-5: Determination of Andesitic Glass Concentration in Felsic Fraction

Proportion of X in fraction	Sample					
	601			602		
	Density of recovered material /gm.cm^{-3}					
X	2.52-2.54^{+}	2.57*	2.60-2.61^{+}	2.52-2.54	2.57	2.60-2.61
quartz	4±5	35±13	54±9	0	35±7	57±6
feldspar	86±12	21±7	9±2	88±8	20±4	3±2
glass$^{\pm}$	10±17	44±20	27±11	12±8	45±11	40±8

* density of separatory reagent: a fraction of suspended material was also retained.

\+ ranges of density are of bounds in density gradient column

± proportions are 100% - proportion of quartz and feldspar

quartz, feldspar and andesitic glass in the total felsic assemblage can be established. This data and that obtained earlier are given in Table 7-7 in which it may be seen that the proportions of quartz and feldspar agree to within 10%. The discrepancy for the proportion of andesitic glass is greater because its proportion is evaluated by difference.

TABLE 7-6: Proportions of Felsic Fraction of Various Density for Mairoa Ash Samples

Density /gm.cm^{-3}	Sample 601	Sample 602
	Proportionate weight (%)	
2.52 - 2.54	18	19
<u>ca</u> 2.57	9	10
2.60 - 2.61	73	71

TABLE 7-7: Comparison of Proportions of Quartz, Feldspar, and Andesitic Glass for Two Determinative Methods

Sample	Method	Proportion Quartz (%)	Proportion Feldspar (%)	Proportion Andesitic Glass (%)
601	A	53	30	17
	B	44	24	32
602	A	40	34	26
	B	44	23	33

A: Infra-red analysis of whole felsic fraction (the felsic fraction being of density 2.4 - 2.8 $gm.cm^{-3}$).

B: Infra-red analysis of material separated as bands in a density gradient column (from 2.5 - 2.8 $gm.ml^{-1}$ solution density).

Van der Plas (1966) gives a series of density limits for the separation of plagioclase, alkali feldspar and quartz and these are:

less than 2.59 $gm.cm^{-3}$	alkali feldspar
2.59 - 2.63	albite and quartz
2.63 - 2.67	quartz and plagioclase
2.67 - 2.89	basic plagioclase

On this basis the upper band, which encompasses the density range 2.52 - 2.55 $gm.cm^{-3}$ (corresponding to a position in the gradient column of 6.5 - 7.0 grad. mls) would be identified as alkali feldspar and the lower band of density 2.63 $gm.cm^{-3}$ (5.0 grad. mls) would be identified as quartz. Accordingly, the andesitic glass, which infra-red analysis suggests is concentrated in the lower band has a density near to that of quartz. It should also be noted that Fieldes and Weatherhead (1968) note that plagioclase feldspar, which are of comparable density to andesitic glass, are common in rhyolitic tephra in New Zealand.

Accordingly the lower band in the gradient column is expected to be prominent in all samples: in andesitic samples it being composed of quartz and glass in rhyolitic samples it probably being plagioclase with some quartz[†]. The occurrence of alkali feldspar with abundant glass is considered by Fieldes and Weatherhead (1968) to be indicative of accretion of rhyolitic tephra and implies rhyolitic contamination of the Mairoa Ash, since it is in clear evidence in those samples.

S7-7: Conclusion:

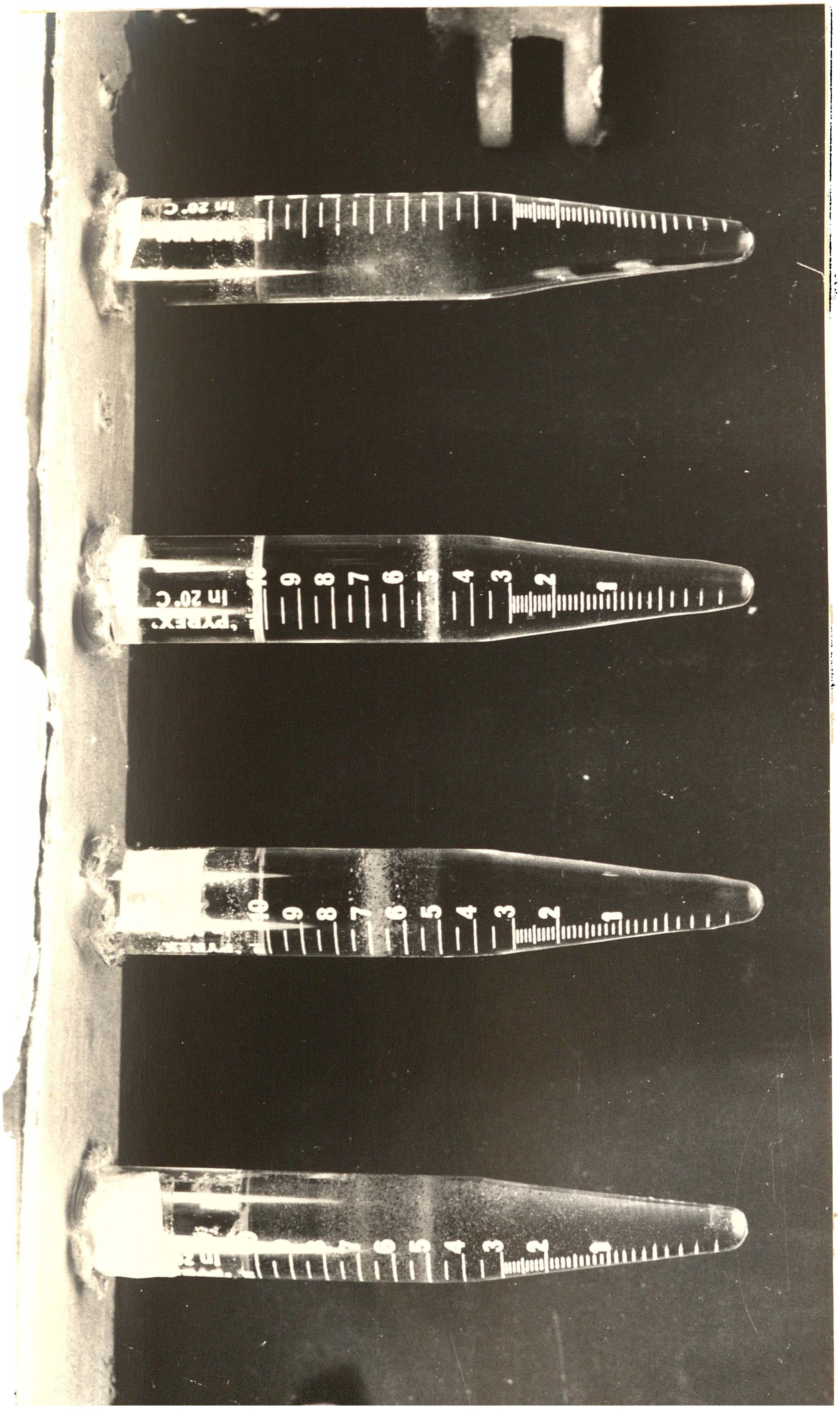
In this chapter the use of density and in particular density gradient techniques has been assessed as a possible means of correlating tephra. With rhyolitic glass, the technique is limited not so much by the accuracy of determination, but rather by the wide natural variation. This distribution of densities is probably related to minor differences in chemical composition or to differing hydration effects. Nevertheless certain tephra possess associated glasses of sufficiently diagnostic density to enable this property to be used, in particular the glass of the Oruanui Formation, which has a lower density than is typical for rhyolitic glasses, and the glass of the Okareka Ash, for which there appear to be two co-existing glasses of marginally differing density.

Density gradient techniques may be useful in obtaining further information about the felsic mineral assemblage. Specifically, such techniques coupled with quantitative infra-red analysis confirm that andesitic glass is of the same density as quartz and plagioclase. In fact, andesitic glass may be referred to as vitric plagioclase, since plagioclase is inferred to be present in samples not containing significant andesitic glass because the corresponding band is still evident in the gradient column. The existence of alkali feldspar in all samples whether of considered rhyolitic or andesitic origin strongly suggests that rhyolitic material is present in all tephras studied in this work.

[†] see Plates 74 and 75

PLATE 74

Density distributions for felsic fractions of Mairoa Ash



Mairoa Ash in the Waikato district, sample 403

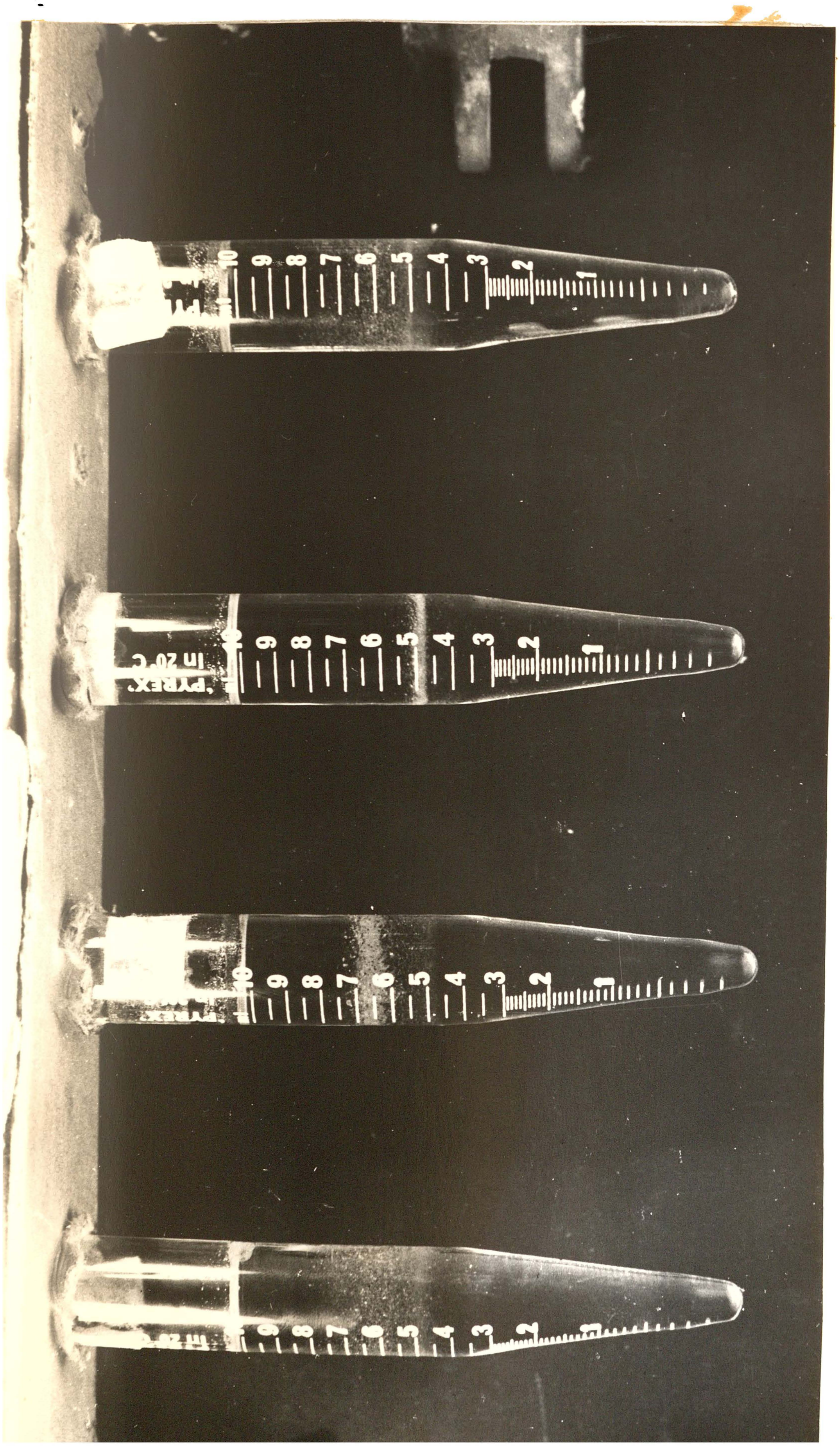
lower band (601) primarily quartz and andesitic glass

upper band (601) alkali feldspar

Mairoa Ash in King Country sample 603

PLATE 75

Density distributions for felsic fractions of samples representative of Tirau and Rotoehu Ashes



Rotoehu Ash
(sample 409)

This tephra is said to be dacitic

---

lower band (601) primarily quartz and andesitic glass

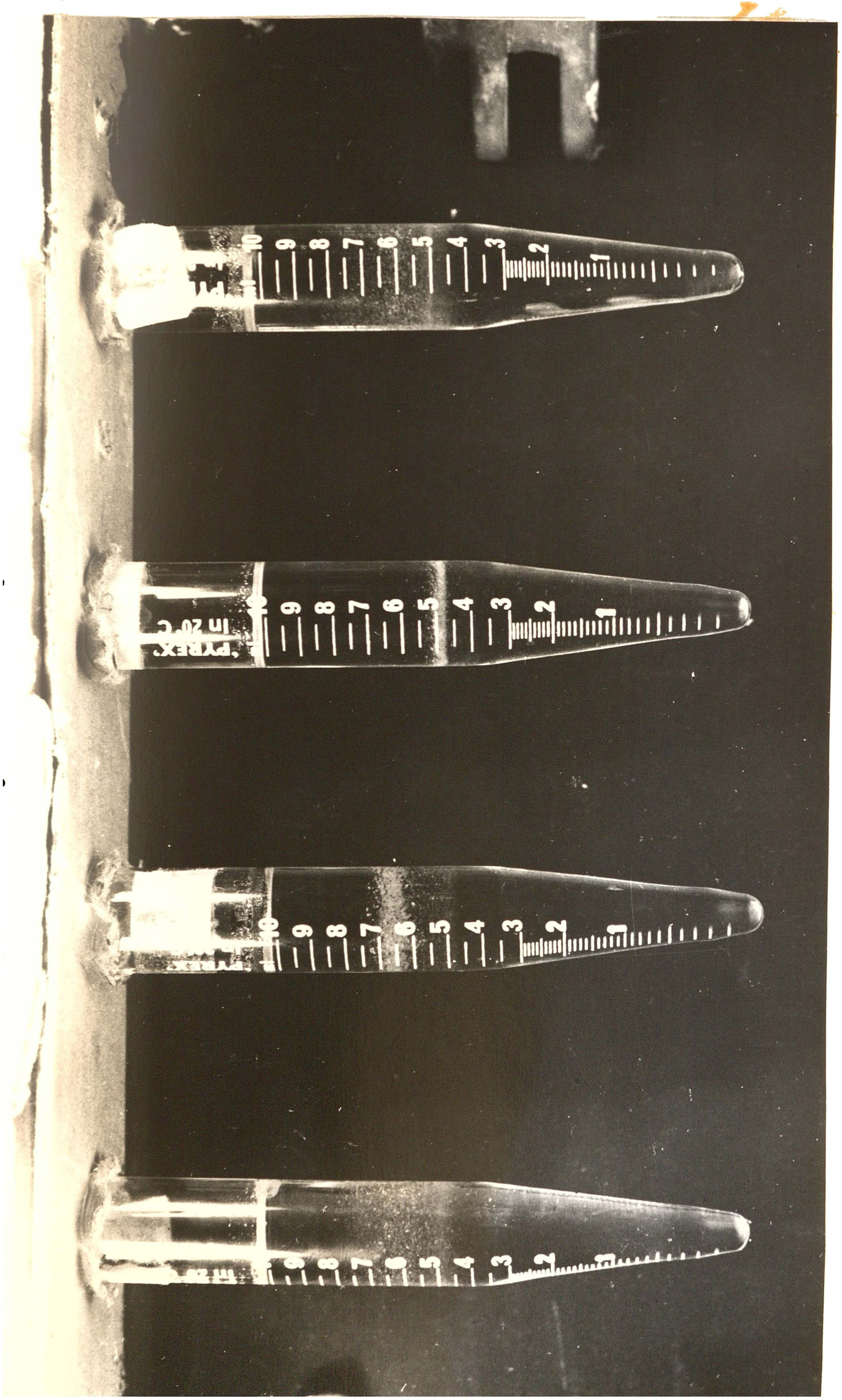
upper band alkali feldspar

Tirau Ash
(sample 202)

rhyolitic tephra

PLATE 75

Density distributions for felsic fractions of samples representative of Tirau and Rotoehu Ashes



Rotoehu Ash
(sample 409)

This tephra is
said to be
dacitic

---

lower band (601)
primarily quartz
and andesitic
glass

upper band
alkali feldspar

Tirau Ash
(sample 202)

rhyolitic tephra

CHAPTER 8: MAGNETIC STUDIES AND IRON CONTENTS OF VOLCANIC GLASSES:

S8-1: Introduction:

Of bulk properties of glass, Chao (1963) wrote:

> "The index of refraction is an excellent clue to ..... chemical composition. It varies inversely with silica content and directly with the ferrous ion content. Since the ferrous ion content reflects the magnetic susceptibility of the glass, the index of refraction and the magnetic properties are useful to predict or check the chemical data."

This statement made in respect of tektite glasses provided the impetus for development of suitable techniques for studying magnetic properties and refractive index, the latter of which is considered in detail in Chapter 9. In this chapter, the techniques of determination of magnetic susceptibilities are described and then the resulting ferrous contents and the term of ferric ratio is considered in terms of their being correlative parameters for tephra identification.

S8-2: Magnetic Susceptibility and Ferrous Content of Glass:

Chao (1963) gave a plot of magnetic susceptibility * versus FeO content in tektites which is effectively a straight line. Linear regression statistics on his data yield the equation:

$$X = (1.5692(\mathrm{FeO}) - 0.339) \times 10^{-6}$$

for which the correlation coefficient is 0.98. The value of the intercept $-\ 0.339 \times 10^{-6}$ (e.m.u./gm) is close to the values given by Hurd (1966) for pyrex glass and thus seems a reasonable estimate of the susceptibility of the iron-free glass.

Senftle and Thorpe (1959) indicate that the total susceptibility is related to the susceptibility of its constituents by a relation of the form: $X = X_{Fe}(ii)\ C_{Fe}(ii) + X_{Fe}(iii)\ C_{Fe}(iii) + X_g$,

---

* strictly mass susceptibility (of units e.m.u.gm^{-1})

where $X_{Fe}(ii)$ and $C_{Fe}(ii)$ are the susceptibility and proportion of the ferrous species, with $X_{Fe}(iii)$ and $C_{Fe}(iii)$ being the corresponding parameters for ferric species, and Xg the susceptibility of the base (i.e. iron-free) glass since tektites contain only a small amount of ferric oxide the term $X_{Fe}(iii)\ C_{Fe}(iii)$ is negligible and accordingly:

$$X_{Fe}(ii) = 1.5692 \times 10^{-4} \text{ e.m.u./gm}$$

where the species referred to is ferrous oxide in glass. As expected this differs somewhat from the value for free ferrous oxide ($X = 1.00 \times 10^{-4}$ e.m.u./gm), (Chemical Rubber Co., 1972).

Glass extracted from the Taupo sequence of ashes was sufficiently iron-rich to be separable on the Frantz magnetic separator. On the basis of measurement techniques and the nomogram relating instrumental settings to mass susceptibility (Hess, 1966) the mass susceptibility is 1.8×10^{-6} e.m.u./gm. Ewart (1963) gives the ferrous oxide content of lapilli from Taupo Pumice as 1.35% and the ferric oxide as 0.75%. Substituting this into the last-given equation yields a susceptibility of Fe_2O_3 in glass of 1.2×10^{5} e.m.u./gm. This confirms that the magnetic susceptibility can be wholly ascribed to ferrous oxide. The glasses extracted from all other samples were too feebly magnetic to be separated on the Frantz separator and an alternative method was sought.

S8-3: Determination of Susceptibilities by the Guoy Method:

In this technique susceptibility is determined by rating the difference in sample weight in the presence and absence of an inhomogeneous magnetic field whose strength is greatest at the base of the sample and least at the top. For the present study, use was made of a modified Mettler balance which had been fitted with a movable permanent magnet in its base.

The experimental arrangement causes there to be a balance of magnetic and gravitational forces. Mulay (1972) indicates that this relationship may be represented by the equation:

$$g\Delta W_s = \tfrac{1}{2}A.H^2(K_s - K_{air})$$

where g is the gravitational constant, ΔW_s is the change in weight of the sample when the magnetic field is applied and removed, A is the cross-sectional area of the tube, H is the magnetic field strength, K_s is the magnetic susceptibility (the susceptibility per unit volume) of the sample, and K_{air} is the corresponding parameter for air. Now the magnetic susceptibility K (of units e.m.u.cm^{-3}) is related to the density d and the mass susceptibility X (of units e.m.u.gm^{-1}) by the equation:

$$K = X.d.$$

whence the original expression becomes, in terms of the magnetic field strength:

$$H = \left\{ 2g\Delta W_s / A(X_s d_s - K_{air}) \right\}^{\frac{1}{2}}$$

This equation is directly applicable to liquids, and using acetone as a calibrant, the magnetic field strength can be determined as a function of the height of liquid in the tube. This data is given in Table 8-1. From the above equation:

$$dH/d\Delta W_s = H/2\Delta W_s$$

$$\text{i.e.} \quad dH = (H/2\Delta W_s)\, d\Delta W_s$$

where dH and $d\Delta W_s$ are the errors in magnetic field strength and weight change respectively. Typically, in the case of acetone, the weight difference is comparable to its associated error and thus:

$$dH \approx H/2$$

which gives a typical error of ± 1000 Oe.

TABLE 8-1: Calibration of Data for Guoy Balance I: Evaluation of Magnetic Field Strength as a Function of Height of Liquid in the Tube.

Materials constants: Calibrant : acetone

X : $- 0.5081 \text{ e.m.u.gm}^{-1}$

d : 0.787 gm.cm^{-3}

Filled height (h/cm)	Magnetic field strength (H/Oe)
2.00	1530
3.95	2640
4.45	2260
5.45	3450
6.45	4050
7.15	3450

For the experimental set-up used, therefore, the use of liquid calibrants was not satisfactory.

The determinate of the susceptibility of powdered solid is more difficult than that of liquids because:

> "..... it is almost impossible to powder solids to the same particle size and to pack them uniformly up to a mark in the tube: this introduces variations in the volume of paramagnetic air held in the pockets of the sample. Hence a correction must be made for the susceptibility of air pockets in the powdered sample by including the contribution:
>
> $$K_{air} (1 - W_s/v.d_s)$$
>
> due to the air entrapped per cubic centimetre of the solid-air mixtures....." - Mulay (1972).

With such modification, the original expression becomes:

$$g \Delta W_s \quad + \quad \tfrac{1}{2} A H^2 \ (K_s - K_{air} + K_{air} \ (1 - \bar{W}_s / v.d_s)$$

whence:

$$H \quad = \quad \left\{ 2g \Delta W_s / (AK_s - K_{air} \ (\bar{W}_s / h) / d_s) \right\}^{\frac{1}{2}}$$

This expression is evaluated in Table 8-2, using glass from Taupo Pumice (sample 1104) as a standard.

TABLE 8-2: Calibration Data for Guoy Balance II: Evaluation of Magnetic Field Strength at Various Values of Packed Height using a Glass Sample of Known Mass Susceptibility.

Materials Constants: Sample: 1104 (Taupo Pumice)

Mass susceptibility: $X_s = 1.8 \times 10^{-6}$ e.m.u.gm^{-1}

Density: $d_s = 2.3$ gm.cm^{-3}

Nature (1)	Packed Height (h/cm)	Magnetic Field Strength H/Oe
+	1.2	850
+	1.9	2260
+	2.7	3580
+	3.5	3900
+	4.6	4140
+	5.4	4060
+	5.5	3940
+	6.1	3940
o	1.35	850
o	2.10	2370
o	2.7	3240
o	3.1	3380
o	4.2	3580
o	4.9	3520
o	5.5	3450

Notes: (1) + indicates material that passes a 75-micron sieve, o indicates whole glass. Both were considered to have the same susceptibility.

(2) The packing ratio (h/W_s) is much larger for 1104 than in other samples, although the density of the material is the same as that of other glasses.

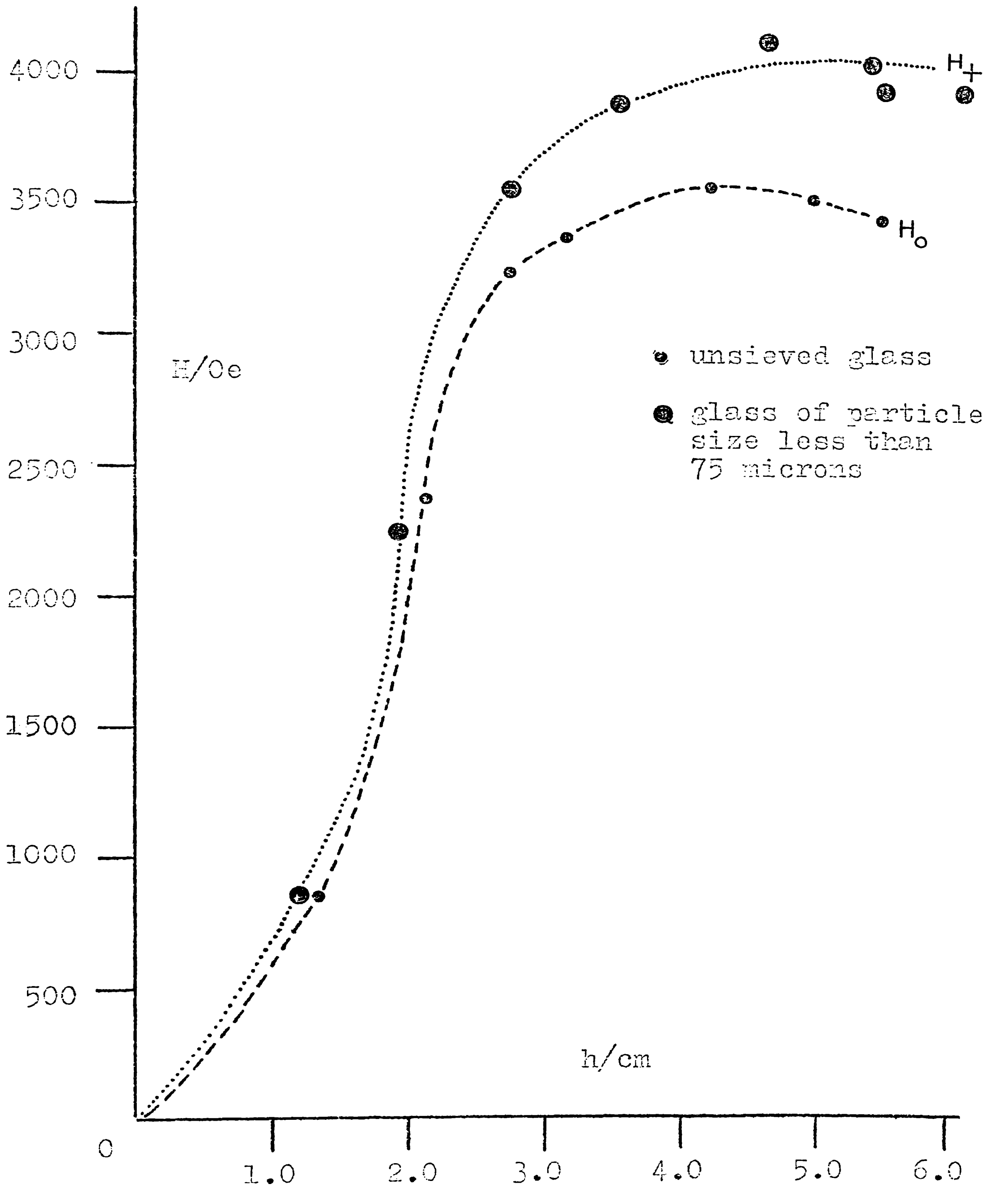
Plots of magnetic field strength as a function of height (h) are given in Fig. 801. It is noteworthy that the derived value of H is greater for smaller particle size. This is probably the preferred interpretation to one that says that the susceptibility is itself a function of particle size. The latter argument would suggest that fine particles might have a lower ferrous iron content because of greater proportionate leaching, and this would be reflected in a lower value for X and thus a higher value for H than might be expected. If this were the case, larger particles would have been preferentially attracted in the magnetic separator, and this was not observed. From an empirical point of view, also, this possibility seems unlikely in that if, for

TABLE 8-3: Comparison of Iron Contents for Different Determinative Methods

Sample	Total Fe as FeO_t (%) (1)	$X_{(o)}^{(2)}$	$FeO^{(3)}$	FeO/FeO_t	$X_{(+)}^{(4)}$	$FeO^{(3)}$	FeO/FeO_t
201	1.25	1.63(5)	1.20	0.96	1.23	0.90	0.72
202	1.23	1.89	1.33	1.08	1.56	1.10	0.90
203	1.26	1.83	1.25	0.99	1.38	1.00	0.79
204	1.31	1.28	0.95	0.73	1.03	0.80	0.61
205	1.37	1.23	0.90	0.66	0.94	0.75	0.55
901	1.23	1.60	1.13	0.92	1.05	0.80	0.65
902	1.13	1.48	1.05	0.93	1.08	0.83	0.73
903	1.28	1.95	1.35	1.05	1.42	1.03	0.80
904	1.37	1.46	1.05	0.76	1.07	0.80	0.58

FIG. 801

Magnetic field strength (H/Oe) as a function of packed height (h/cm) of glass tube in calibration of Guoy balance for determination of mass susceptibility



(1) total analysis by atomic absorption, see Sec. 10-2.

(2) using H_o as a function of h (Fig. 801).

(3) evaluated from the relationship: $X = (1.5692.FeO - 0.339) \times 10^{-6}$; $(X/e.m.u.gm^{-1})$. (FeO/%).

(4) using H_+ as a function of h (Fig. 801).

(5) mean value, usually of duplicate determinations.

example, the magnetic susceptibility for fine glass from the Tirau sequence is calculated using values of magnetic field strength obtained from the lower curve of Fig. 801, the corresponding ferrous iron content is comparable to the total iron content, as is demonstrated in Table 8-3, whereas ratios of ferrous to total iron is expected to be less than unity. Such ratios are obtained on the basis of the upper curve of Fig. 801 and it is on this basis that the ferrous contents shown in Table 8-4 were determined. The ratio of ferrous to total iron content (both expressed as FeO) is also given in Table 8-4. Typically, the error in the susceptibility measurements is some ± 0.02 $e.m.u.gm^{-1}$ which yields an error in the ferrous content of some ± 0.013 %FeO.

TABLE 8-4: Mass Susceptibilities and Ferrous Contents of Glasses from Tephra Sequences in Localities 2, 3, 4, 5, 6, 9 and 10, and selected members of the sequence at Site 11.

Nature(1)	Sample No.	Mass susceptibility $(X/e.m.u.gm^{-1})$	Ferrous Content(2) (FeO/%)	Total Iron(3) $(FeO_T/\%)$	Ratio: Ferrous to total iron (FeO/FeO_T)
+	201	1.23	1.00	1.25	0.80
+	202	1.56	1.21	1.23	0.98
+	203	1.38	1.10	1.26	0.87
+	204	1.03	0.87	1.31	0.66
+	205	0.94	0.82	1.37	0.60
+	301	1.04	0.88	1.12	0.78

TABLE 8-4: continued

Nature(1)	Sample No.	Mass susceptibility (X/e.m.u.gm^{-1})	Ferrous Content(2) (FeO/%)	Total Iron(3) (FeO_T/%)	Ratio: Ferrous to total iron (FeO/FeO_T)
o	303	1.02	0.86	1.22	0.70
o	304	1.20	0.98	1.24	0.79
o	305	0.69	0.65	1.11	0.58
+	306	1.02	0.87	1.29	0.67
+	307	0.86	0.76	1.34	0.57
+	308	0.56	0.57	1.06	0.54
+	309	0.75	0.70	0.99	0.71
+	401	0.98	0.84	1.06	0.79
+	402	0.96	0.83	1.08	0.77
+	403	0.87	0.77	1.24	0.62
+	404	1.05	0.89	1.23	0.72
+	405	1.29	1.04	1.23	0.84
+	406	0.57	0.58	1.24	0.47
o	407	1.15	0.95	1.23	0.77
+	409	0.63	0.61	1.04	0.58
o	501	0.98	0.84	1.15	0.73
o	502	0.98	0.84	1.17	0.71
o	503	1.22	0.99	1.18	0.84
o	504	0.99	0.85	1.19	0.71
o	505	0.83	0.75	1.15	0.65
o	601	0.69	0.65	1.09	0.60
o	602	0.56	0.57	1.16	0.49
o	603	0.40	0.47	1.33	0.35
+	604	0.81	0.73	1.36	0.53
+	605	0.88	0.78	1.38	0.56
o	606	0.53	0.55	1.37	0.40

TABLE 8-4: continued

Nature(1)	Sample No.	Mass susceptibility (X/e.m.u.gm^{-1})	Ferrous Content(2) (FeO/%)	Total Iron(3) (FeO_T/%)	Ratio: Ferrous to total iron (FeO/FeO_T)
+	901	1.05	0.89	1.23	0.72
+	902	1.08	0.91	1.13	0.80
+	903	1.42	1.12	1.28	0.87
+	904	1.07	0.90	1.37	0.66
+	905	0.74	0.69	1.46	0.47
+	906	1.14	0.88	1.44	0.61

Notes: (1) + indicates particles of glass are smaller than 75 microns,

o denotes unsieved glass.

(2) from relationship $X = (1.5692\ FeO - 0.339) \times 10^{-6}$;

(X/e.m.u.gm^{-1}), (FeO/%).

(3) by atomic absorption.

This data is plotted for the stratigraphic sequences described in this thesis in Fig. 802. On these diagrams it is seen that the glass from samples considered to be Mairoa Ash have a lower iron oxide content and a slightly lower $(Fe^{(ii)}/Fe^{(iii)})$ ratio than those representative of Tirau Ash. There are two possibilities to explain this:

(i) the FeO content decreases with increasing age,

(ii) the glass from Mairoa Ash is of substantially different initial composition.

These possibilities can be checked by plotting the ferrous to ferric ratio as a function of age, using the dates previously tabulated, and by plotting the ratio as a function of the rhyolitic character of the whole ash, and these are presented in Figs. 803 and 804 respectively. In general, there is a tendency for the ferric to ferrous ratio to increase with time. There is a wide scatter in Fig. 803 because of the differing protection of the various samples from oxidation afforded

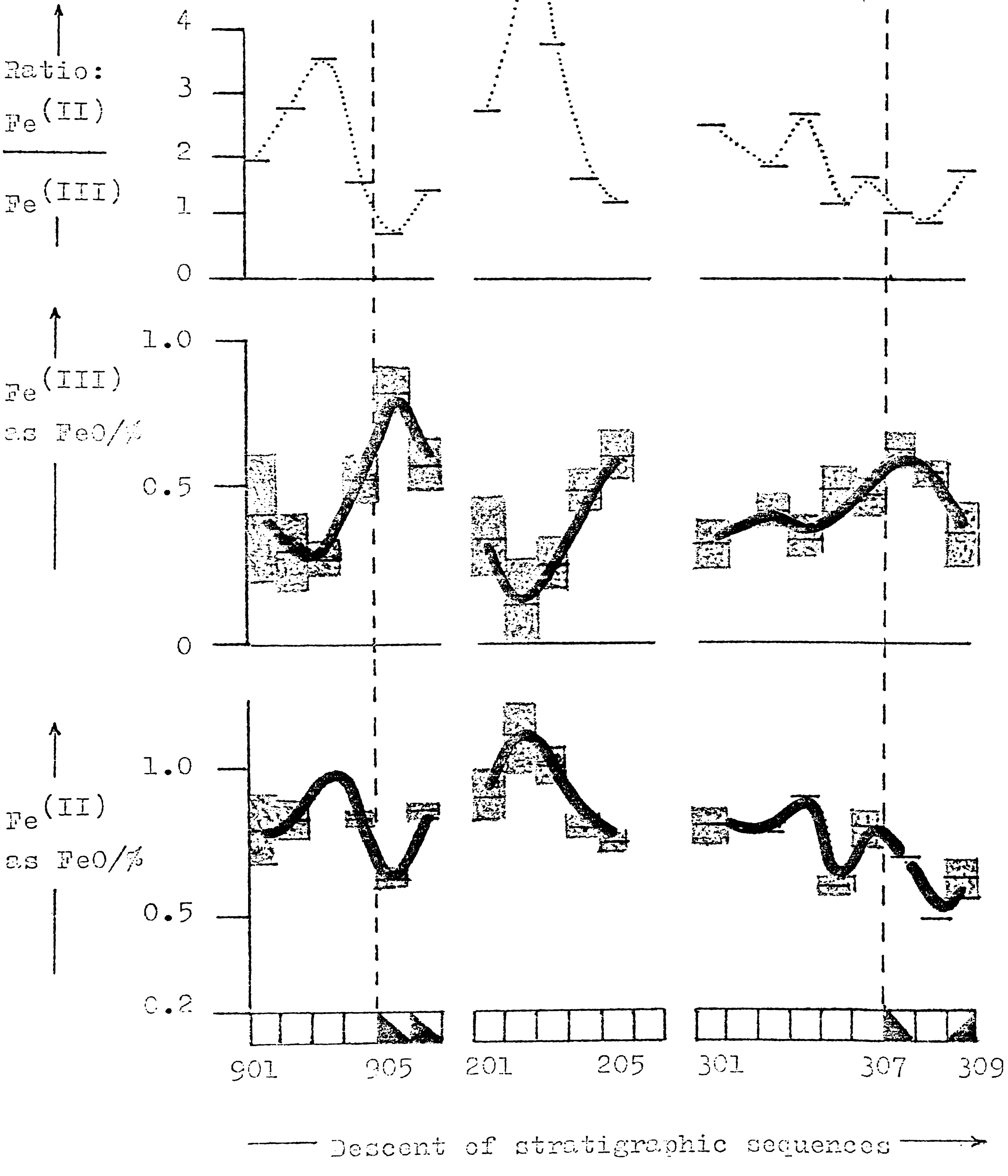
FIG. 802

Ferrous and ferric contents and ratios for rhyolitic glasses from sequences of Tirau Ash and Mairoa Ash

Part I:	Tapapa Road	site 9	sequence	(901 - 906)
	Tirau	2		(201 - 205)
	Findlay Park	3		(301 - 309)

Tirau and Mairoa Ashes to left of broken line. Underlying marker beds are:

Oruanui Formation ◪ Rotoehu Ash ◪



(Grey areas denote mean residual associated with mean)
▨ —

FIG. 802 (continued)

Ferrous and ferric contents and ratios for rhyolitic glasses from sequences of Tirau Ash and Mairoa Ash

Part II: Parawera site 4 sequence (401 - 409)
Kakepuku 5 (501 - 505)
Mairoa 6 (601 - 606)

Tirau and Mairoa Ashes to left of broken line. Underlying marker beds are:

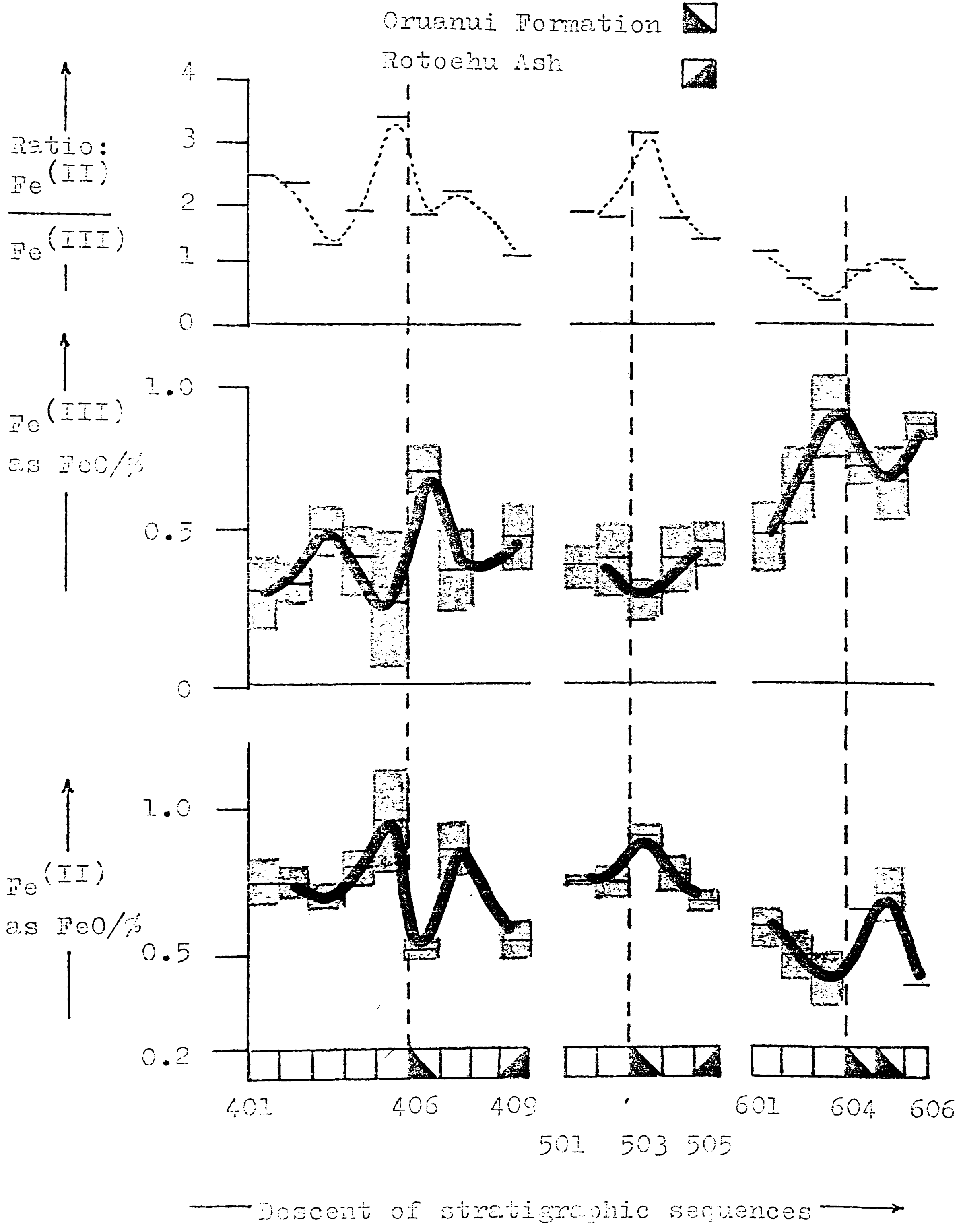


FIG. 803

Ratio of ferrous to ferric contents of rhyolitic glass as a function of estimated age of the tephras.

(Ferrous and ferric contents are evaluated as percent ferrous oxide)

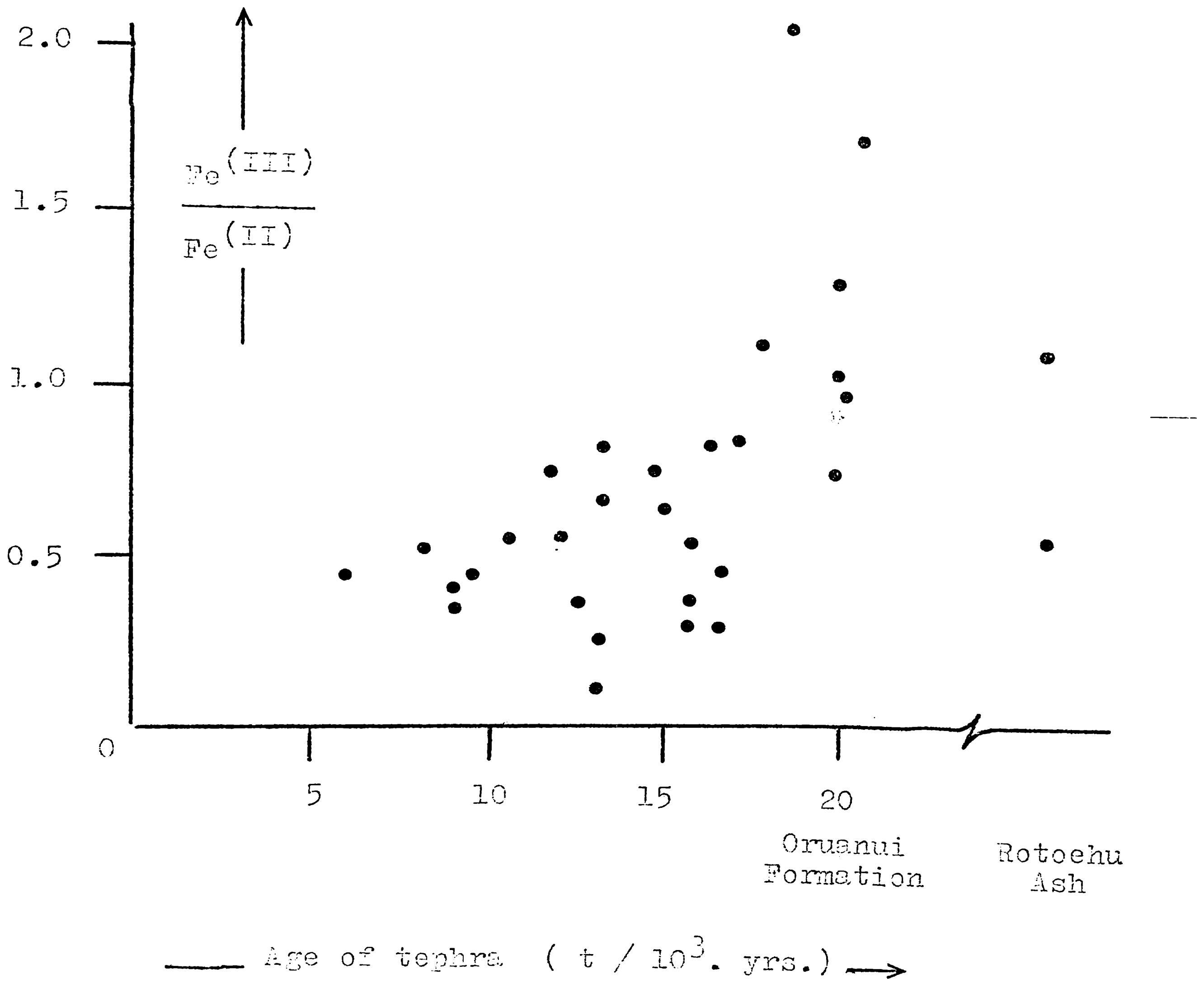
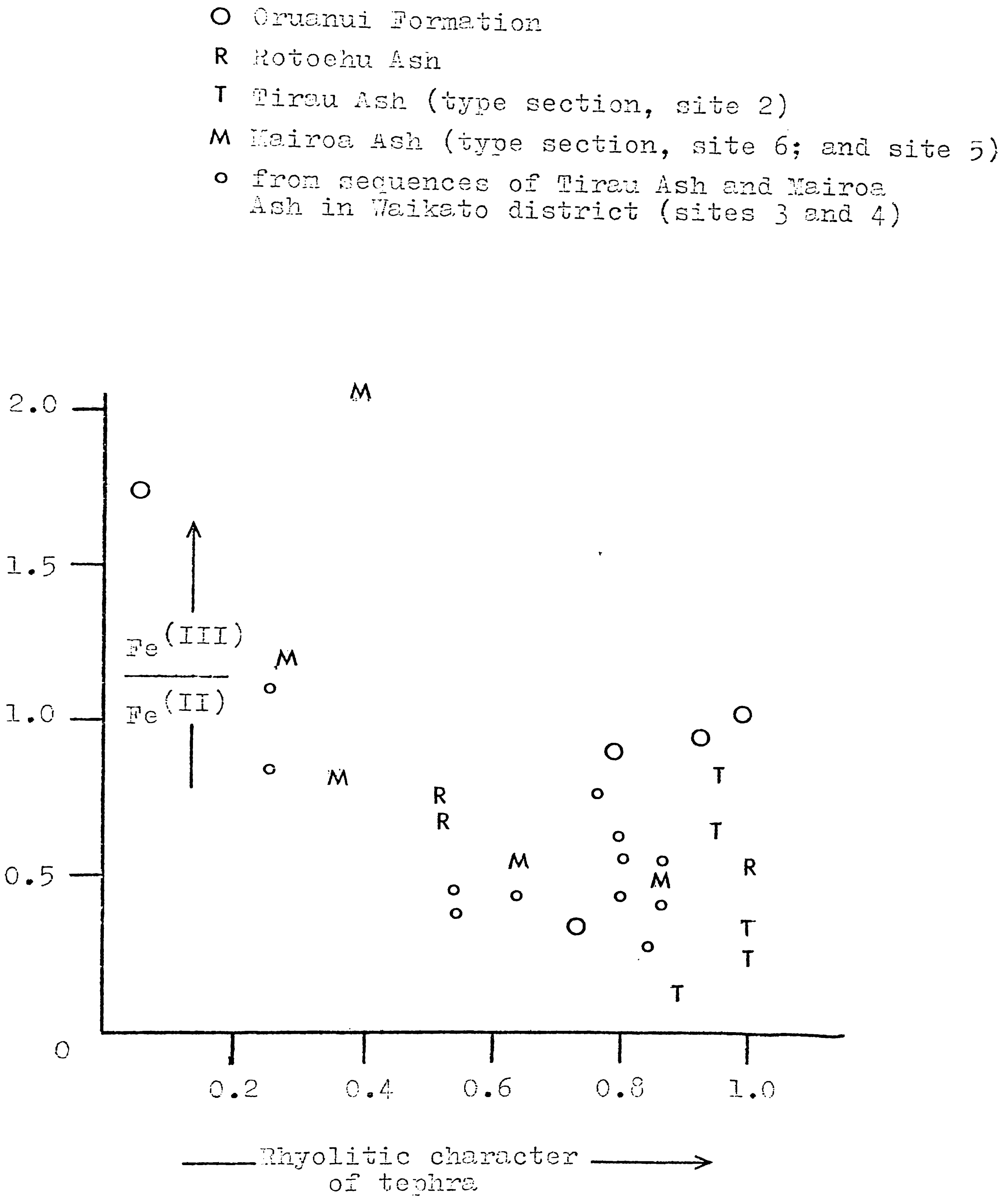


FIG. 804

Ferric to ferrous ratio in rhyolitic glass as a function of the rhyolitic character of the tephra



by various depths of overburden and by variations in climate. Fig. 804 shows a decrease in the ferric to ferrous ratio with increasing rhyolitic character. The worth of this latter relationship is a little dubious, because for the ash samples chosen in this study, there tends to be a relationship between rhyolitic character and age; the older tephras being more andesitic. The ratio of the ferric to ferrous oxide in the glass has kinetic implications which will now be discussed.

S8-5: Kinetic Relationships of Iron Oxides in Glass:

If it is envisaged that the iron is itself not leached from the glass, but is only lost after oxidation, the following sequences of reaction may be envisaged:

$$2\ FeO_{(glass)} \longrightarrow Fe_2O_{3(glass)}$$

$$Fe_2O_{3(glass)} \longrightarrow Fe_2O_{3(leached)} \quad \text{(with structural breakdown)}$$

Thus the ferric oxide contained in the glass is effectively the intermediate in the sequence. These reactions are undoubtedly diffusion controlled and accordingly may be considered as first order. Subject to time independence of rate constants the values of these oxide contents may be evaluated on the basis of series kinetics from equations given by Frost and Pearson (1961) as in Table 8-5.

TABLE 8-5: Concentration Dependence with Time for Series First-Order Reaction.

Species	Symbol	Kinetic Relationship
$FeO_{(glass)}$	A_o	(initial concentration of FeO in glass)
	A	$A_o e^{-\tau}$
$Fe_2O_{3(glass)}$	B	$(A_o/K - 1)(e^{-\tau} - e^{-K\tau})$
$Fe_2O_{3(leached)}$	C	$(A_o \{1 + (Ke^{-\tau} - e^{-K\tau})/(1 - K)\})$

Relative concentrations, α β γ, defined by

$$\alpha = A/A_o \qquad \beta = B/A_o \qquad \gamma = C/A_o$$

In this table K is the ratio of rate constants of the first to the second step of the reaction series and $\overline{\tau} = k_1 t$ where k_1 is the rate constant for the first process and t is the time. Combining the first two of these equations yields:

$$B/A = \beta / \alpha = \frac{1}{(K - 1)} \; 1 - \alpha^{K}$$

As the reaction proceeds α decreases so that the ratio of ferric to ferrous contents would be expected to show an increase with time, provided $K > 1.0$, the exact rate being dependent on the relative values of α and K. There is inadequate data to evaluate the relative rate constant with certainty, since the initial iron oxide content is not known. However, if the glass from the Taupo sequence, of Ewart (1963), is assumed to be but little altered, and further that the glasses in the sequences were initially similar to Taupo glasses, then the relative rate constant (K) is about 3.0. This is to say that the oxidation of ferrous oxide is rate determining.

S8-6: Conclusion:

Magnetic susceptibility measurements on rhyolitic volcanic glass are a good, but not universally applicable, parameter for correlating tephra. Glass from the Taupo sequence of eruptions can be separated readily by magnetic methods and such techniques could be used to determine its presence in localities wherein it has not been thus far sought. Such a method, depending primarily on the ferrous content of the glass, is likely to be useful only for comparatively unleached glasses (which implies either young tephras or tephras protected from weathering processes) or from glasses having an initially high ferrous content.

For other glasses the magnetic susceptibility may be of rather more limited use in correlation, although the variation within a stratigraphic sequence may give some indication of likely identifications.

Similarly, the ferrous to ferric ratio may be diagnostic, and since it generally rises with increasing exposure to the effects of weathering, it may be indicative of the age of the glass. The ferrous to ferric ratio can be considered on a kinetic basis which suggests that the oxidation of ferrous ion within the glass rather than the loss of ferric ion from the glass is the rate determining process in the achievement of a given ferrous to ferric ratio.

CHAPTER 9: REFRACTIVE INDEX OF VOLCANIC GLASS AS A TEPHRA CORRELATION PARAMETER.

S9-1: Introduction:

As was the case with density, refractive index is a good guide to bulk composition. In a review of techniques, Wilcox (1965) observes that the refractive index of the glass is likely to be "one of the features expected to be consistent throughout the extent of the ash-fall deposit," but adds a note of caution:

> "The refractive index of the glass increases with hydration and the general agreement in refractive index of ash shards of a particular fall over a wide range of climatic environments may therefore rest on a generally similar degree of hydration....."

Thus refractive index cannot be usefully discussed without reference to the water contents of the glass, since this affects not only the value of the index, but also the accuracy with which the determination needs to be made. In this chapter, techniques used for the measurement of refractive index are critically examined prior to their application to glasses from the samples under study. From the data obtained from the samples, a method of geologic dating based on the water contents of rhyolitic glasses is examined.

S9-2: The Accuracy of Refractive Index Determinations:

In most petrological work refractive index determinations are carried out on the stage of an ordinary petrological microscope by successive trials in immersion media of slightly differing refractive index. Dodge (1949) estimated that for such a technique with crushed mineral grains using a set of liquids of interval 0.002 units of refractive index gives an accuracy in refractive index of ±0.001. Ross and Smith (1955) have noted in their determination of the effect of water on refractive index that this changes the fourth decimal place. They note the difficulties of preparing a set of liquids accurate to four decimal places, and certainly they need to be checked more frequently than is routinely done in petrology laboratories. The liquids can of course be mixed and when a liquid of appropriate refractive index is obtained, then its refractive index can be determined on an Abbe refractometer. This is a clumsy procedure and further requires that the refractometer and microscope stage be at the same temperature. This last requirement usually necessitates the stage being cooled by circulating water, which also passes through the refractometer, since the temperature of the stage has been shown by Micheelson (1957) to increase significantly with time.

All of these difficulties can be circumvented by the use of a hot-stage method. Although this method is referred to in many texts on microscopy (for example Chamot and Mason (1958) and Hinnawi (1966)) it seems to have found little acceptance in petrology. It has, however, found application in forensic work (Rees, 1968).

Nelson (1959), for example, in a study of headlight glasses, found it possible by this technique to distinguish glass shards over a refractive index range from 1.5100 to 1.5220 to an accuracy of ±0.0001. Earlier work by Finch and Williams (1958) enabled the distinguishing of refractive index of glass chips from bottles whose refractive indices varied between 1.5120 and 1.5170 (a range of 0.005) and a similar study on fifty headlamp glasses by Green and Burd (1949) enabled similar determination of glass chips over a 0.003 unit range. Clearly, then this technique seems best able to achieve the accuracy required if water contents are to be considered in relation to refractive index, and it will now be described in detail.

S9-3: Determination of Refractive Index by Thermal Variation Methods:

The hot-stage method, first described by Gaubert (1927) and Emmons (1928), involves heating the sample, immersed in a suitable liquid whose refractive index varies with temperature in a known manner, until equivalence of refractive index is achieved. The temperature at which this occurs will be referred to as the coincidence temperature. Any of the well-known optical techniques can be used, although the Becke line technique is usually adequate. In principle it is possible to establish the temperature at which the Becke line disappears and reappears, in which case the coincidence temperature, from which the refractive index is determined may be taken as the mean. However, this is not always practicable, sometimes because of the temperature involved (see Sec. 9-4) or because of the high optical dispersion of either the mineral or of the liquid. This latter difficulty can be overcome by using monocromatic light or by a "double variation method" described by Grabar and Principe (1963) whereby the variation of refractive index with both temperature and wavelength of light is employed.* One of the advantages of the thermal variation method is that unless much of the immersion medium has been lost, either by the expansion of entrapped air bubbles, or by heating the specimen such that the liquid is near its boiling point, the determinative process can usually be repeated many times with the same specimen or even the same grain.

The principal requirement for this technique is of course the hot-stage. Heated stages that may be attached to biological-type microscopes (i.e. microscopes without revolving stages) are available but the sample holder can usually only take very small samples crushed between two cover slips, and, of great disadvantage, the position of the sample cannot be altered while heating is in progress. Much to be preferred is a hot-stage microscope with provision to move the slide about the stage even while heating is in progress (see Fig. 901). Hot-

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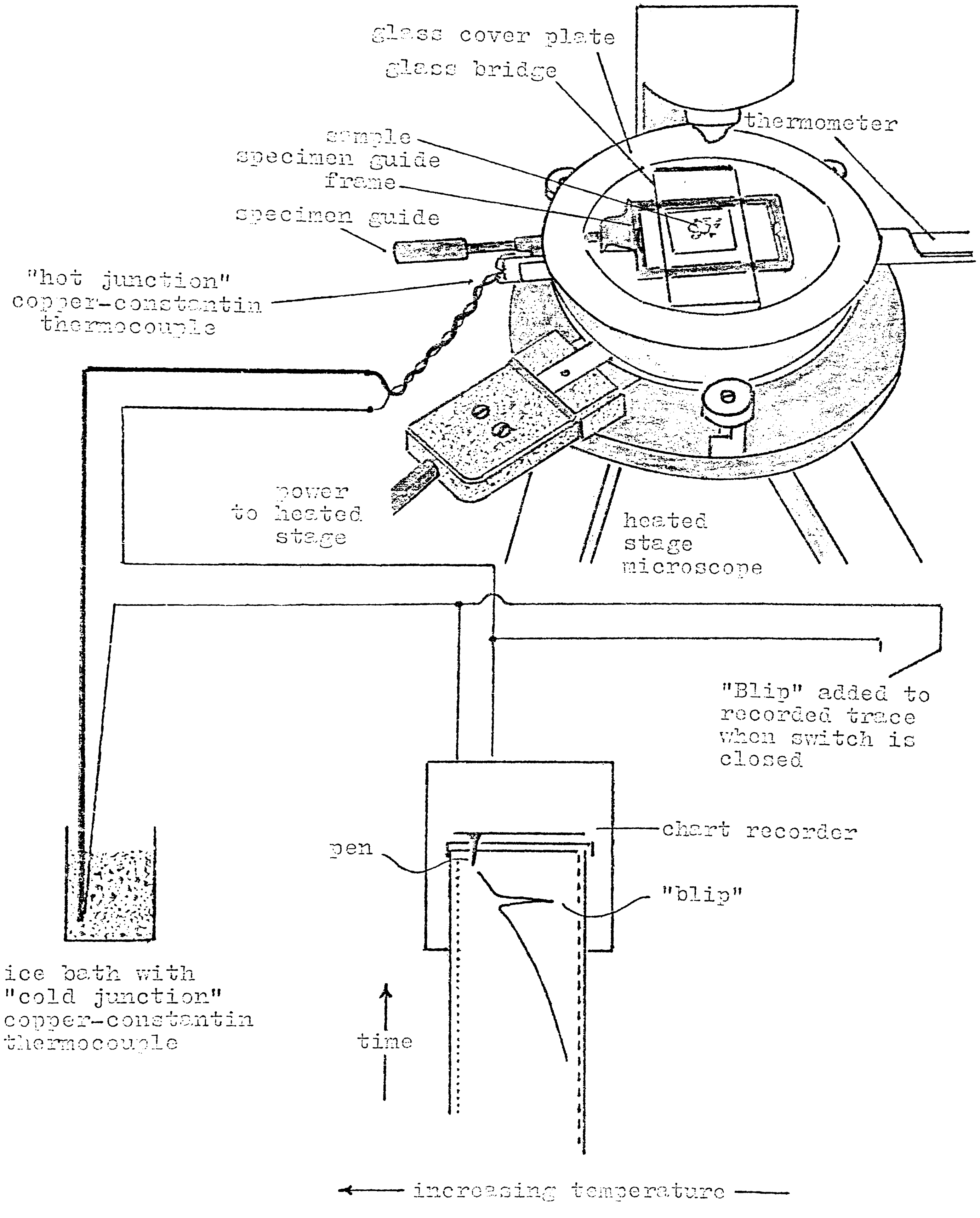
* It is an interesting comparison with the forensic work given earlier that these latter authors estimated an experimental error of ±0.0016, but consider that if two glasses were present in the same sample, a dispersion difference of 0.0008 could be observed.

FIG 901

Apparatus for determination of refractive index of glass shards by a thermal variation method



stages that are heated electrically are probably preferable to those heated by circulating hot water, in that although the latter can be coupled to a refractometer for determining the refractive index of the liquid at the particular temperature, equilibrium of the circulating water needs to be established between readings, thereby inordinately increasing the determination time.

Clearly in this technique, the estimation of temperature is of paramount importance. The usual errors in this regard arise because the microscope slide may not be at the same temperature as the heated block in which the thermometer is usually placed and because of the time-lag between observing the mineral and noting the temperature. An estimation of the magnitude of the first of these can be made by using thermocouples to monitor the temperature difference between the top of the slide and the heated block. This is negligible for the Kofler model used (see Fig. 901) but is significant for the modified microscope type earlier mentioned. The overall effect of the two sources of error can be determined by establishing a calibration curve of thermometer temperature versus slide temperature, the slide temperature being defined by the observed melting points of known organic compounds, or by the refractive index of standard glasses or minerals. A very effective method of removing the time-lag error is a simple pulse arrangement in a thermocouple monitoring circuit as shown in Fig. 901. With this arrangement the operator simply depresses a switch when he observes the coincidence temperature and this action is registered on the temperature-time trace scribed by a recorder.

S9-4: The Choice of Immersion Media for the Thermal Variation Method:

The most suitable liquids for this technique are those whose refractive index varies in a regular, and preferably linear, manner with temperature. If the latter is the case, then the temperature at which the refractive index of the immersed solid equals that of the liquid is given by the expression: $n_s = n_\theta - (dn/dT).(T - \theta)$ in which n_s is the refractive index of the solid, T is the temperature at which there is coincidence of refractive index, n_θ is the refractive index of the liquid at temperature θ , and dn/dT is the temperature coefficient of refractive index for the liquid, generally between 0.0004 and 0.0007 K^{-1} (Hinnawi, 1966). It is desirable that the liquid chosen should have a low vapour pressure over the temperature interval corresponding to the refractive index range of interest to minimise evaporation of the specimen preparation as the determination proceeds. Vapour pressures of liquids have been tabulated (Chemical Rubber Co., 1972) on the basis of equations of the form:

$$\log p(v) = - 0.2185\ A/T + B$$

where p(v) is the vapour pressure and A and B are constants. Atmospheric pressure, being the vapour pressures of a liquid at its boiling point, can be analogously expressed as:

$$\log p(a) = - 0.2185\ A/T(b) + B$$

where T(b) is the normal boiling point. From these two expressions, the reduced vapour pressure π may be expressed:

$$\log \pi = 0.2185\ A \quad 1/T(b) - 1/T.$$

Now the refractive index of a pure liquid varies with temperature by the relation:

$$n = n(\theta) - (dn/dT)(T - \theta)$$

where n and $n(\theta)$ are the refractive indices of the liquid at temperatures T and θ respectively. Combining these last two equations yield an expression for π in terms of the refractive index:

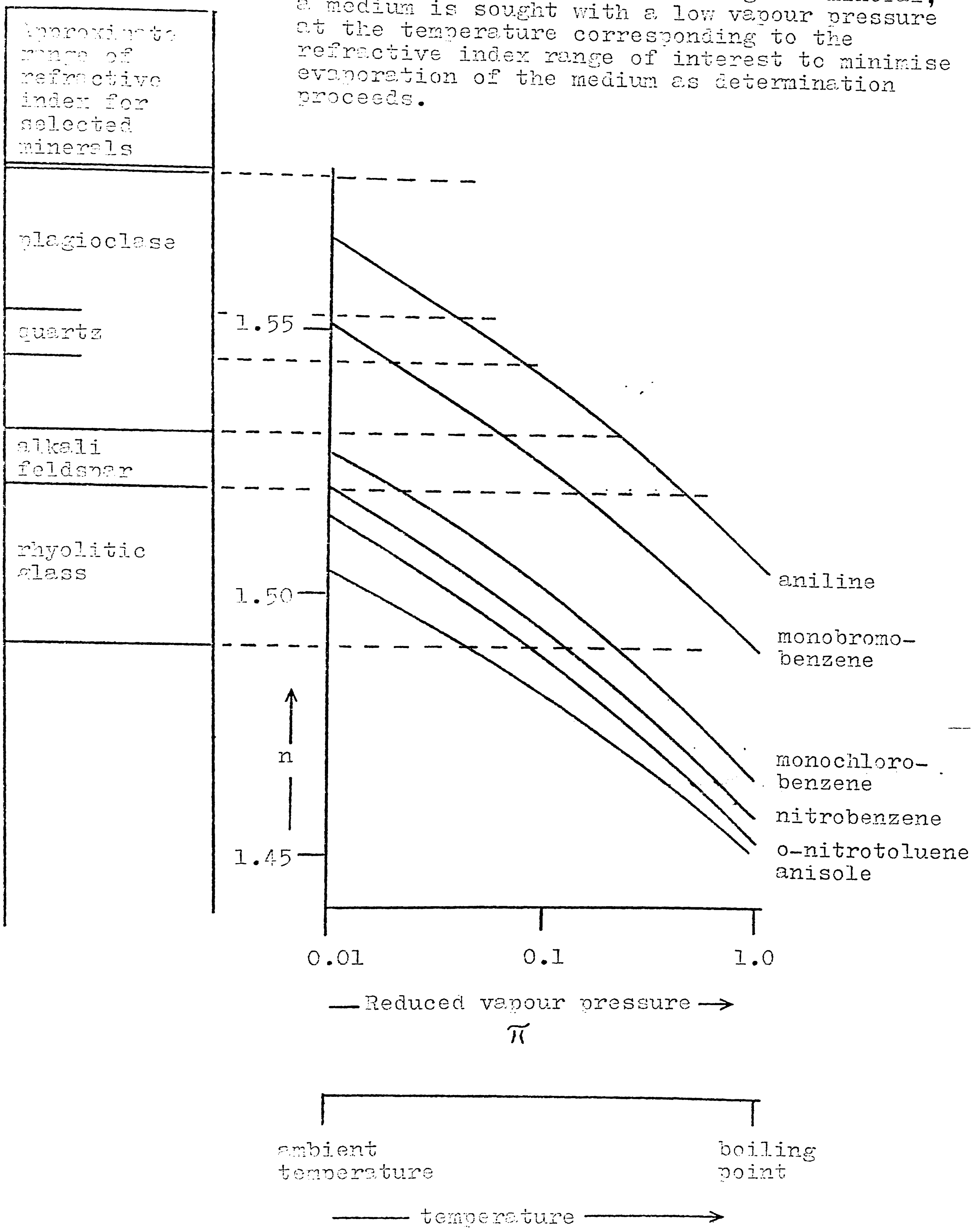
$$\log \pi = 0.2185\ A.\left\{(1/T(b) - (dn/dT))/(n_\theta - n + (dn/dT)\ )\right\}$$

This function is plotted for selected liquids in Fig. 902. The liquids deemed to be most suitable for determining minerals of low refractive index (such as rhyolitic glass) are shown as broken lines, liquids suitable for minerals of rather higher refractive index (quartz, feldspar and andesitic glass, for example) are shown as solid lines. Attention is drawn to the particularly low vapour pressures of nitrobenzene and

FIG. 902

Refractive index (n) as a function of reduced vapour pressure for selected immersion media

For determining the index of a given mineral, a medium is sought with a low vapour pressure at the temperature corresponding to the refractive index range of interest to minimise evaporation of the medium as determination proceeds.



o-nitrotoluene over the refractive index range 1.49 - 1.53, which would make these media particularly suitable for the successive determination of a suite of leucocratic minerals in one specimen preparation of the sample. It would be possible in fact to use either of these liquids in the determination of the refractive index of rhyolitic glass but their high toxicity by comparison with anisole makes the latter preferable.

A further consideration in the choice of immersion media is the value of the coincidence temperature in relation to ambient. Heat loss effects and clouding of the cover plates become greater at elevated temperatures and as a general rule, if the coincidence temperature exceeds 350 K it is wise to seek an alternative medium.

S9-5: Temperature Coefficients of Refractive Index:

One of the criticisms of the technique of thermal variation refractive index determinations is that the assumption needs to be made that the refractive index of the solid changes by an insignificant amount with changing temperature (Chamot and Mason, 1958). Most proponents of the technique refute the criticism, but do not offer any guide as to how the viability of the criticism may be tested. An empirical estimate of this effect can be achieved using the coefficients of expansion and the refractivity of the material under consideration. Now, the expression for the temperature dependence of refractive index may be written as the differential equation:

$$dn/dT = -\mu$$

where μ is the temperature coefficient of refractive index. The relationship between density (ρ) and volume coefficient of expansion (α) may be expressed in terms of a differential equation:

$$d\rho/dT = -\alpha.\rho$$

Now density and refractive index can be related using the Lorenz-Lorentz formula (Partington, 1953):

$$\left(\frac{n^2 - 1}{n^2 + 2}\right)\frac{1}{\rho} = R$$

where R is the refractivity, a constant dependent on structure type or molecular arrangement, M is the molecular weight and K a constant. From these relationships it can be shown that:

$$\mu = \alpha \left\{ (n^2 + 2)(n^2 - 1)/6n \right\}$$

The predictive value of this relationship is demonstrated in Table 9-1 for various liquids and solids, and the temperature coefficient of a typical glass is evaluated. From this it may be seen that the temperature coefficient of the glass is some 40 times less than that of the liquids used. For the medium, anisole, the coincidence temperature for volcanic glass is about 320K (some 30K above ambient temperature). For such a temperature rise a reduction of some 0.0005 units of refractive index is expected and it thus appears that there may be a consistent discrepancy of 0.0005 magnitude. This would of course have no bearing on the refractive index relationships in forensic work in that such studies involve the determination of glasses over temperature ranges sufficiently small to negate this effect and also because interest is centred on relative values between samples rather than on absolute values.

TABLE 9-1: Evaluation of Temperature Coefficients of Refractive Index by an Empirical Method and Comparison with Literature Values.

Substance	State	Refractive index (n)	Coefficient of cubical expansion $-(\alpha/\mathrm{K}^{-1})$	Temp.coefficient of refractive index (calculated) $-(\mu/\mathrm{K}^{-1})$	Temp. coefficient of refractive index (μ/K^{-1}) (literature)
aniline	liquid		85×10^{-5}	6.2×10^{-4}	5.0×10^{-4}
water	liquid	1.331	21×10^{-5}	7.8×10^{-4}	8×10^{-4}
polystyrene	solid	1.587	$3 \times 8.6 \times 10^{-5}$	18.6×10^{-5}	*ca* 14×10^{-5}
perspex	solid	1.491	$3 \times 8.5 \times 10^{-5}$	14.7×10^{-5}	
glass	solid	*ca* 1.50	2.55×10^{-5}	1.5×10^{-5}	-

Data on refractive index is that near 20°C (293 K). All literature data and materials constants are from Kaye and Laby (1966).

The same may be said when volcanic glasses are being compared one to another. However, in studies wherein the glass is being related to some external variable, as for example when water contents are being considered, allowance should be made for this effect, although the error of the determination is usually of comparable magnitude.

S9-6: The Dependence of Refractive Index on Particle Size:

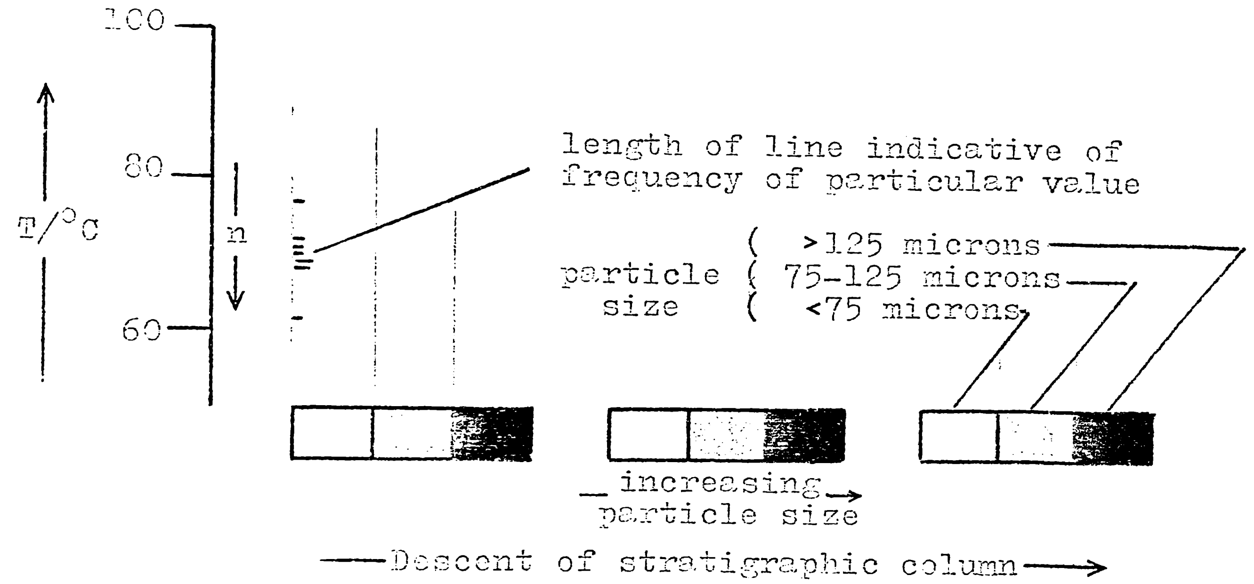
It will be recalled from the discussion of densities that there did appear to be some variation of density with particle size, although there were doubts whether this phenomonen was real or apparent. One way of assessing this is by determining refractive indices of various size fractions for glasses. For comparison with the density data, the same sieve fractions were used and representative data is presented in Fig. 903. In this diagram, it is seen that the coincidence temperature at which the refractive index of liquid and glass concur generally rises with increasing particle size. This is to say that the refractive index is higher for smaller shards. This effect is particularly marked in glasses from tephra that have been subjected to prolonged soil processes, as for example, samples 302 and 304. The effect is less obvious in glasses of tephra buried shortly after deposition, as for example, the Oruanui Formation and Rotoehu Ash. This size dependence is probably related to the greater susceptibility of smaller shards to show hydration effects than their larger counterparts. The only exception to the size dependence encountered was the upper portion of Okareka Ash in which the trend of refractive index with size is reversed; this may be related to the double-band density character of the glass previously referred to.

The range of values of refractive index is comparable for all the size fractions, and this suggests that the increasing density distribution for larger sized particles previously noted is related to the problem of grain "liberation" rather than being a function of the material. The variation of refractive index with particle size

FIG. 903

Dependence of refractive index of glass shards on particle size

Refractive index (n) represented as temperature at which the refractive index of the immersion medium is the same as the glass (T)



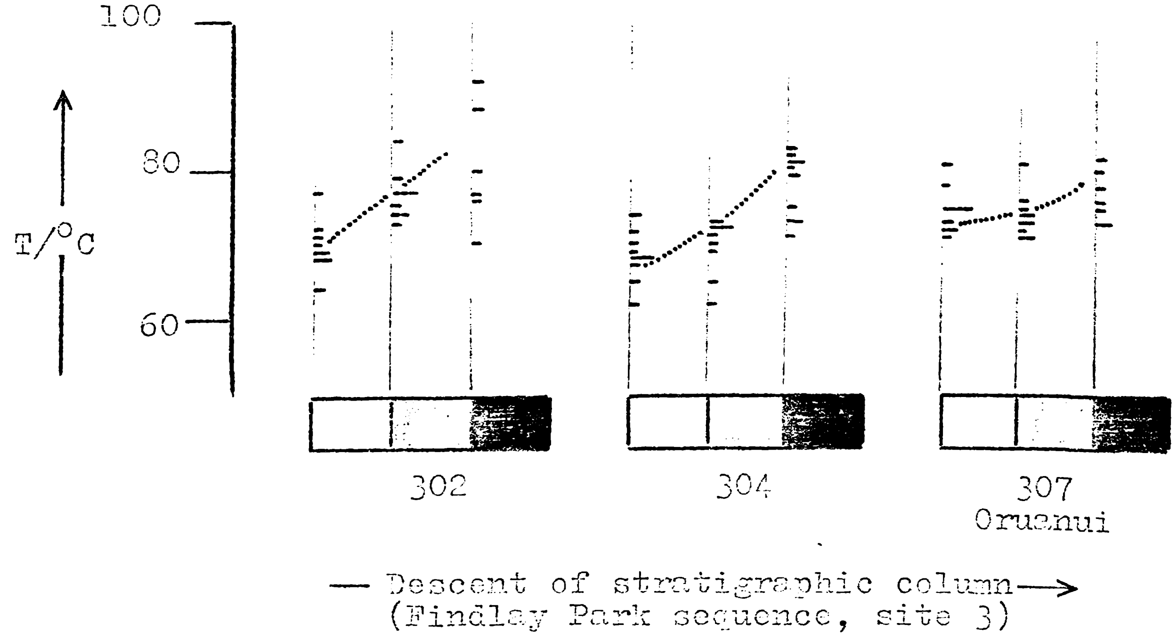
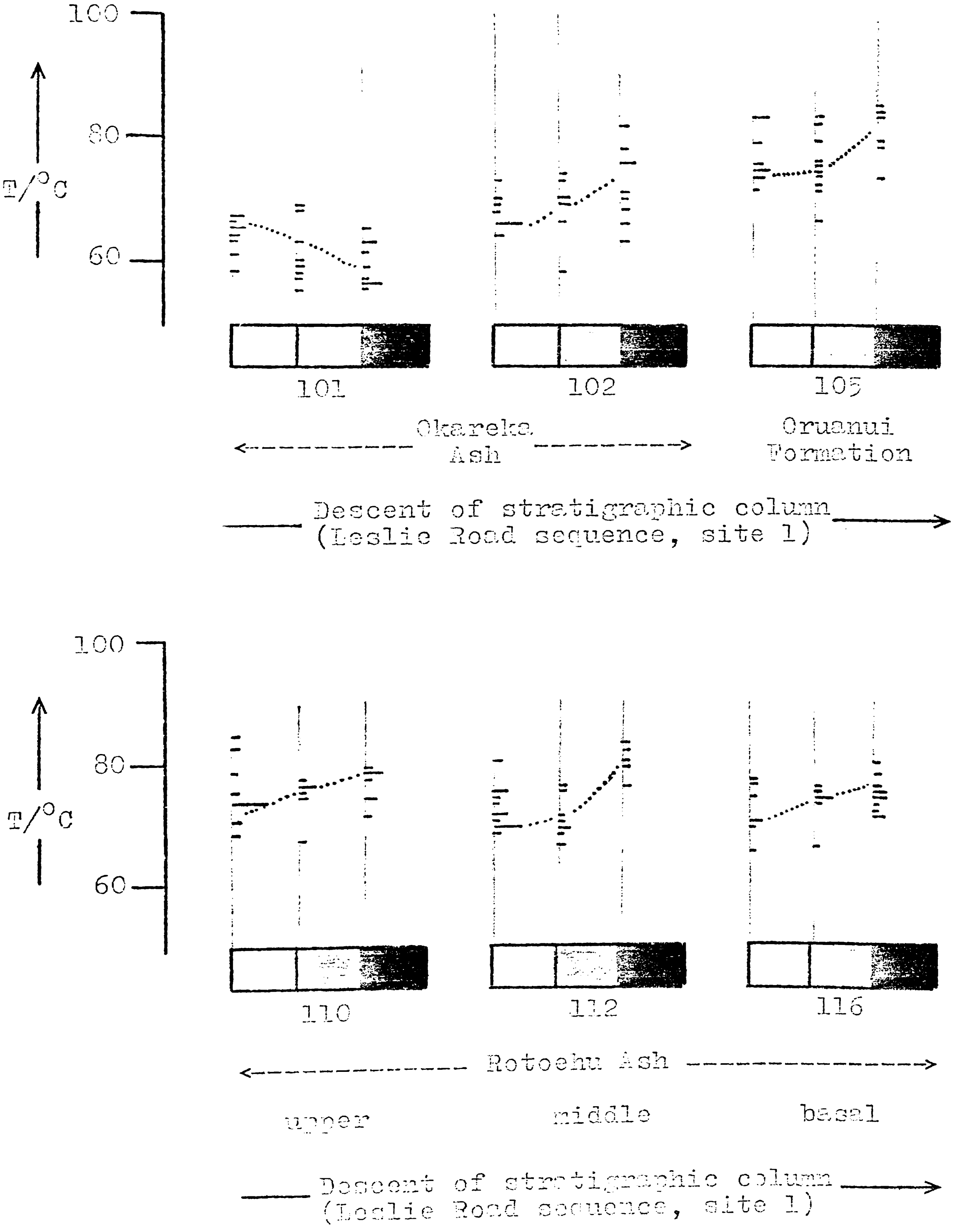


FIG. 903 (continued)

Dependence of refractive index of glass shards on particle size



indicates the need to specify the size of particle being determined, in this thesis the size fraction determined hereafter is that whose constituents are of less than 75μ diameter.

S9-7: The Use of Statistics in Refractive Index Determinations:

The refractive index of a glass was generally determined about six times, or more until consistent results were obtained. The values obtained were averaged, as were the mean residuals (the mean difference between the mean and the constituent values). The mean residual is taken to be the determinative error, and is typically some 0.003 units of refractive index.

When the refractive index of the glass of the Mairoa Ash sampled at Mairoa itself was determined, the upper members were found to have a higher mean residual than was typical. A closer examination of the contributing data indicated clusters of readings around two values. Thus the Mairoa Ash contains two rhyolitic glasses of differing refractive index, which indicates that either the one source erupted two types of rhyolitic glass, or that more than one source was involved. The refractive indices for the Mairoa Ash sequence are given in Fig. 904. The lower valued glass is not found in other localities where Mairoa Ash is suspected, but as is discussed in the next section, these refractive indices are nevertheless lower than is the case for rhyolitic glasses associated with the Tirau Ash sequence. This may be evidence for the interdigitation of the tephra units, although at these localities the mean residuals for the Mairoa Ash glasses are not significantly greater than their Tirau Ash analogues.

S9-8: Refractive Indices of Glasses From Mairoa Ash and Tirau Ash:

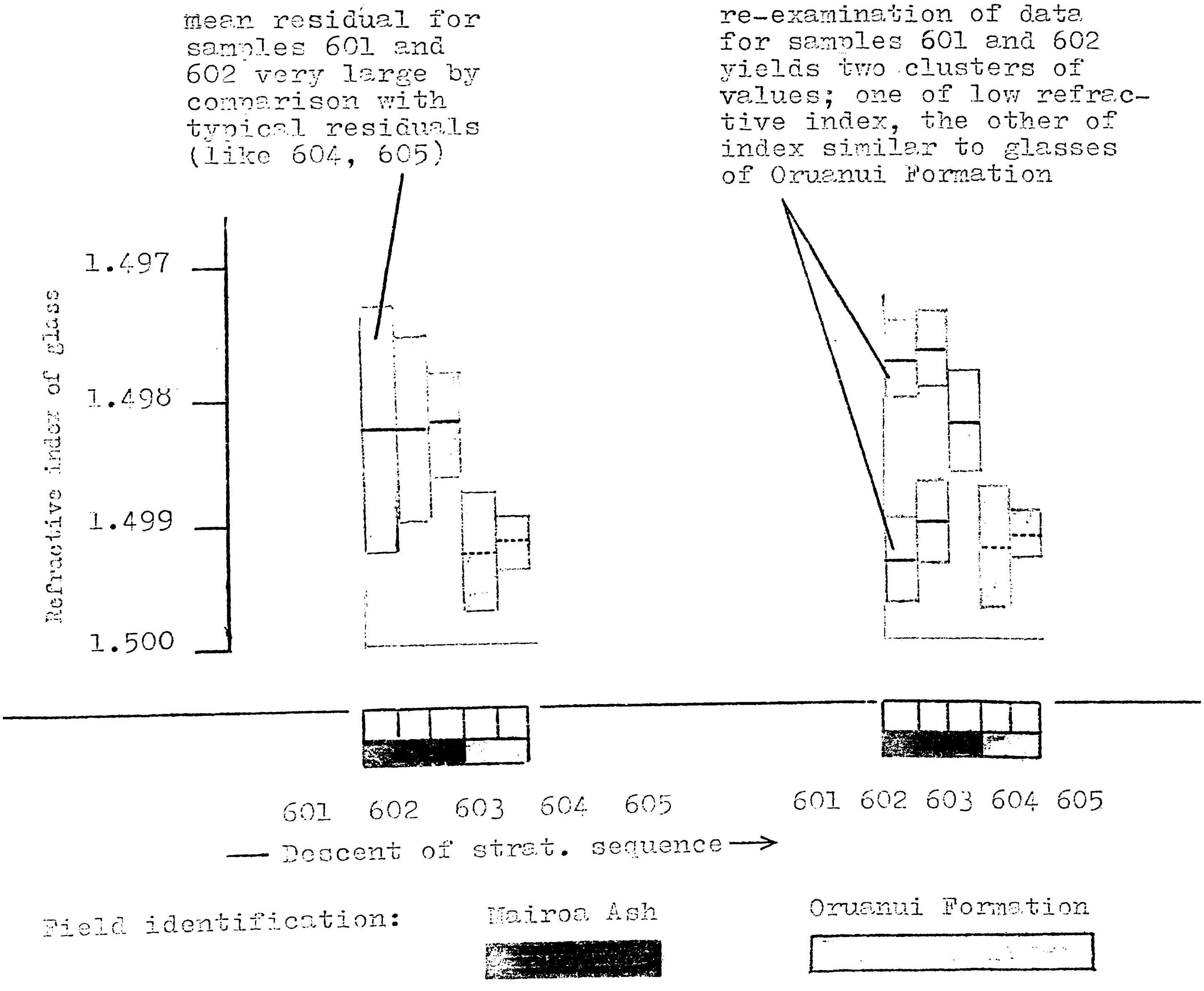
For the sequences of ashes previously described, the refractive indices of the associated rhyolitic glasses are given in Fig. 905. Of particular significance is the fact that the glasses of the Tirau Ash sequence of ashes have a higher refractive index than their Mairoa

FIG. 904

Recognition of two rhyolitic glasses in a particular tephra by consideration of the residuals associated with the values of refractive index

Grey areas on the diagram denote mean residual, being the mean difference between the mean refractive index and the values of refractive index that contribute to the mean

— / - - - Mean refractive index indicated by heavy solid (Mairoa glasses) or broken (Oruanui glass) lines



mean residual for samples 601 and 602 very large by comparison with typical residuals (like 604, 605)

re-examination of data for samples 601 and 602 yields two clusters of values; one of low refractive index, the other of index similar to glasses of Oruanui Formation

FIG. 905

Refractive indices of rhyolitic glasses from sequences of Tirau Ash and Mairoa Ash

(Upper plots are the difference in refractive index between when the Becke line disappears and when it reappears; for details, see text)

Part I: Tapapa Road, site 9; Tirau, site 2.

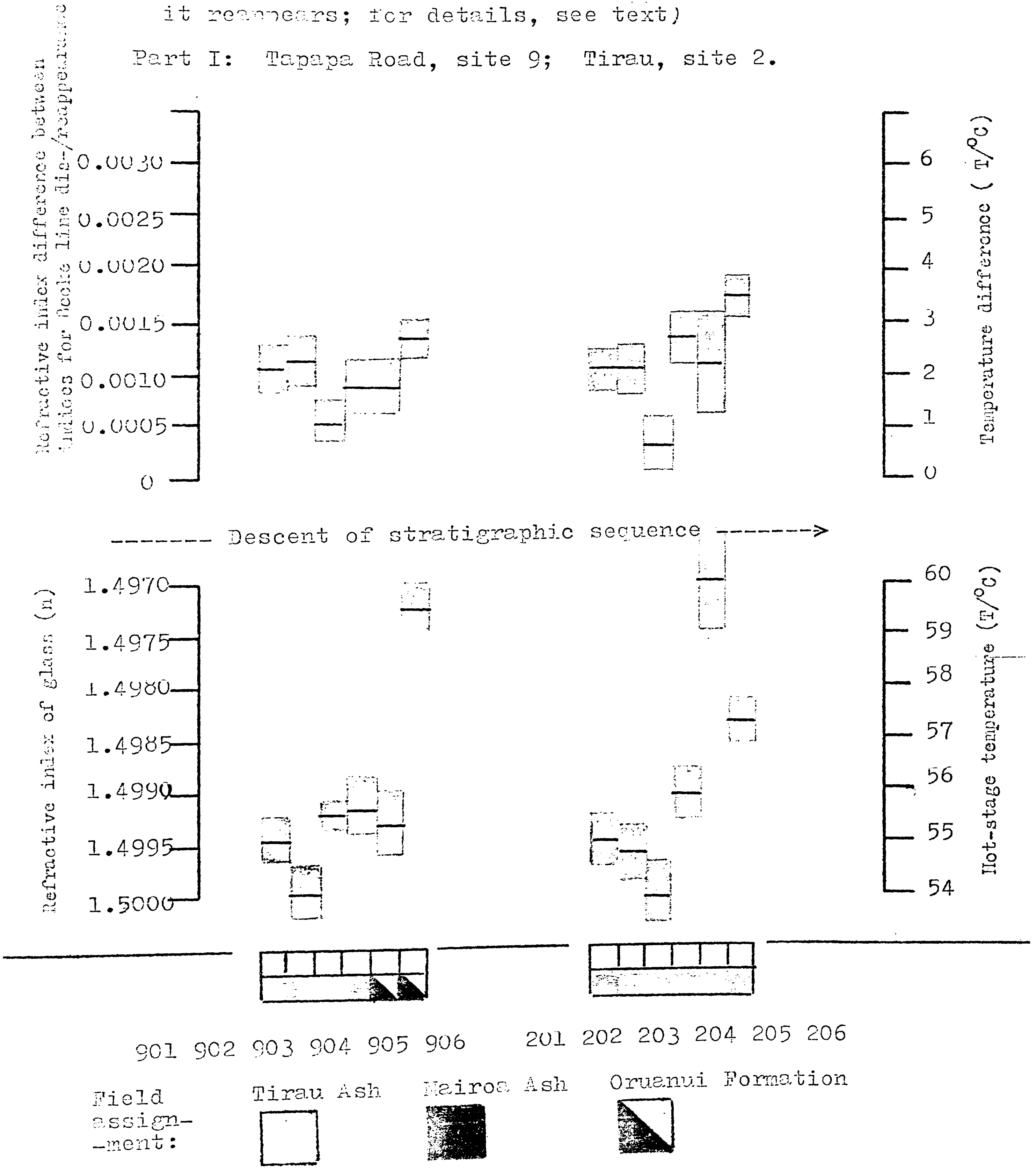


FIG. 905 (continued)

Refractive indices of rhyolitic glasses from sequences of Tirau Ash and Mairoa Ash

Part II: Findlay Park, site 3; Parawera, site 4.

(Samples given in numeric sequence 301-309, 401-409)

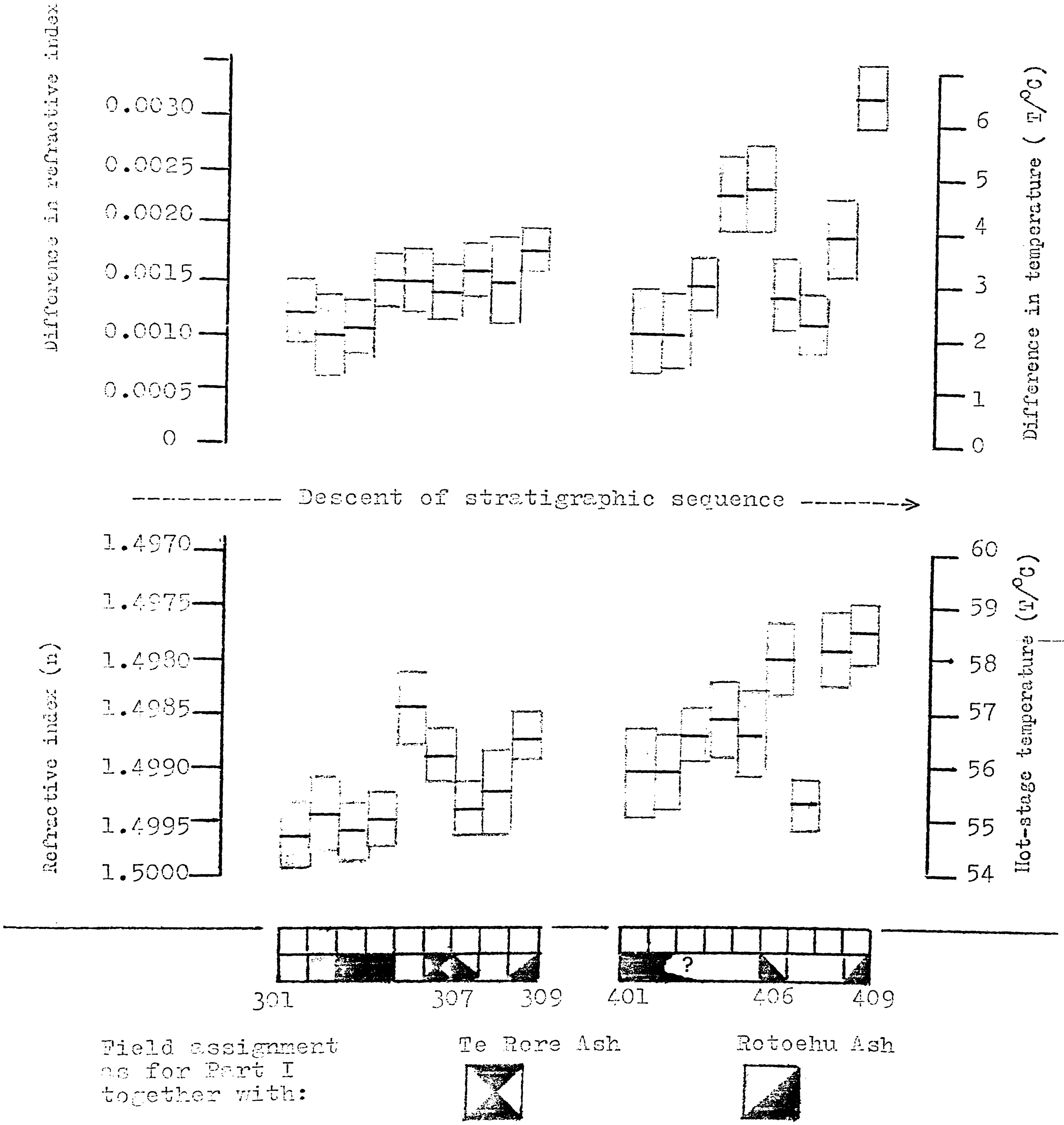
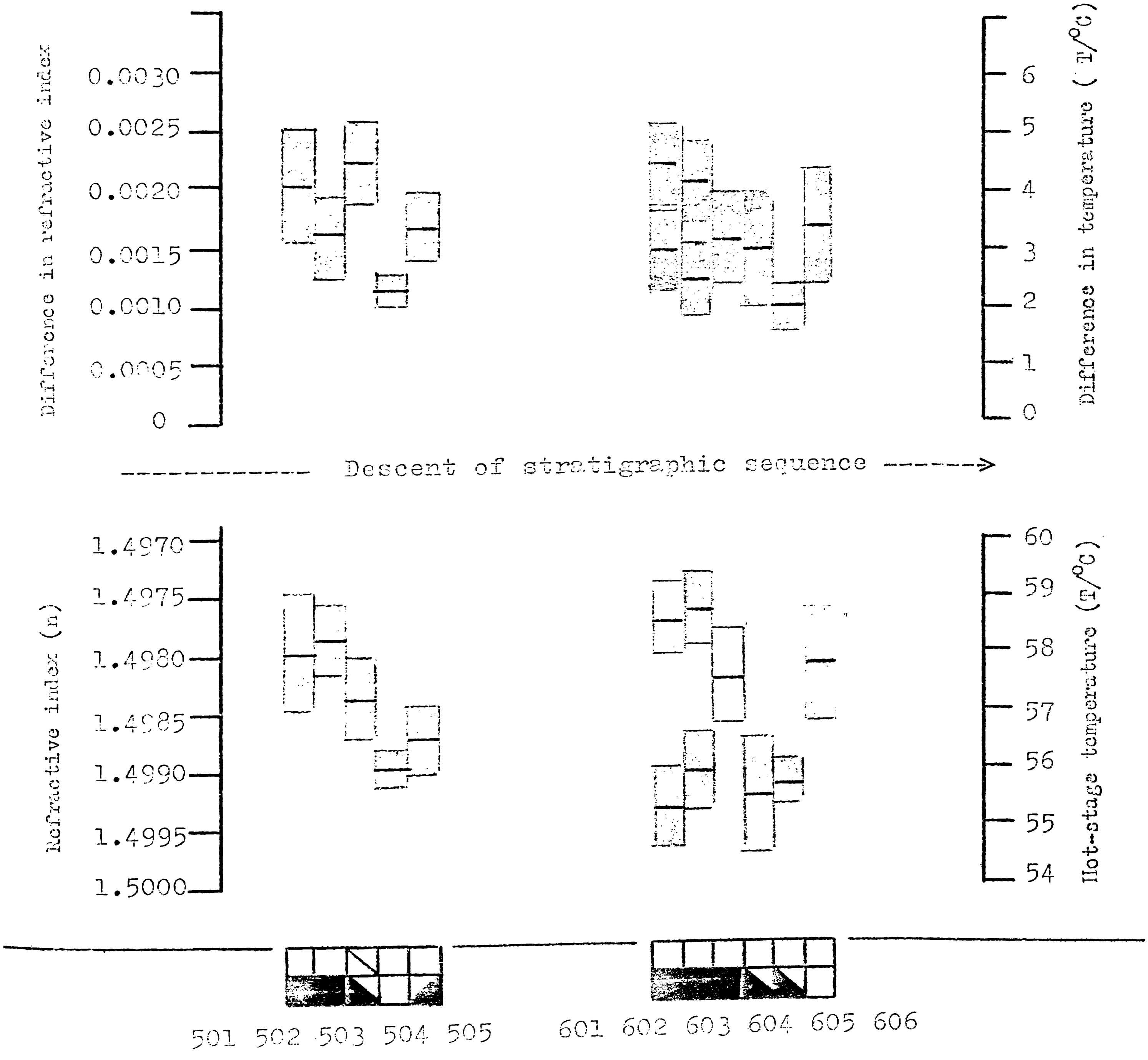


FIG. 905 (continued)

Refractive indices of rhyolitic glasses from sequences of Tirau Ash and Mairoa Ash

Part III: Kakepuku, site 5; Mairoa, site 6.



analogues. Accordingly, a sequence showing a gradation (on field criteria) from Tirau Ash to Mairoa Ash and thence to Oruanui Formation would be expected to show a minimum in the profile. This is, in fact, observed. As will be shown subsequently, increasing age may be expected to increase the refractive index because of hydration effects, if the weathering regime and chemical composition of the originally erupted glass have been invariant with time. That there is a minimum in the curve is suggestive that either or both of these factors are involved.

It is noteworthy, however, that the refractive index that defines this minimum varies from site to site, as does the value of the refractive index of glass considered in the field to be from the Oruanui Formation. The variation in this latter case may be due either to the effect of its being mixed with the overlying Mairoa glass or to weathering effects. It has already been noted that glass weathers initially by hydration. In Section 9-9, this hydration process will be treated in more detail; suffice it here to say that hydration increases the refractive index. Accordingly, one might expect that the refractive index might rise with increasing infiltration for a given glass. Such a variation is shown for Oruanui glass in Fig. 906. On first appearances such a correlation would appear to be sustained, but curiously, sample 307 deviates from the correlation line while 503 lies on it. This is curious because on the basis of glass contents, the empirical estimate of infiltration for the Kakepuku site (503) is rather too low, whereas that for Findlay Park (307) would seem to be reasonable. Since, in fact, the refractive index values of samples 406 and 503 are close to the lower values associated with the Mairoa Ash sequence, it may be that these samples are Oruanui glass contaminated with glass of the Mairoa Ash, and that the refractive index of Oruanui glass itself is largely independent of the locality in which it is found. Such a conclusion is in agreement with the conclusion reached by Steen and Fryxell (1965),

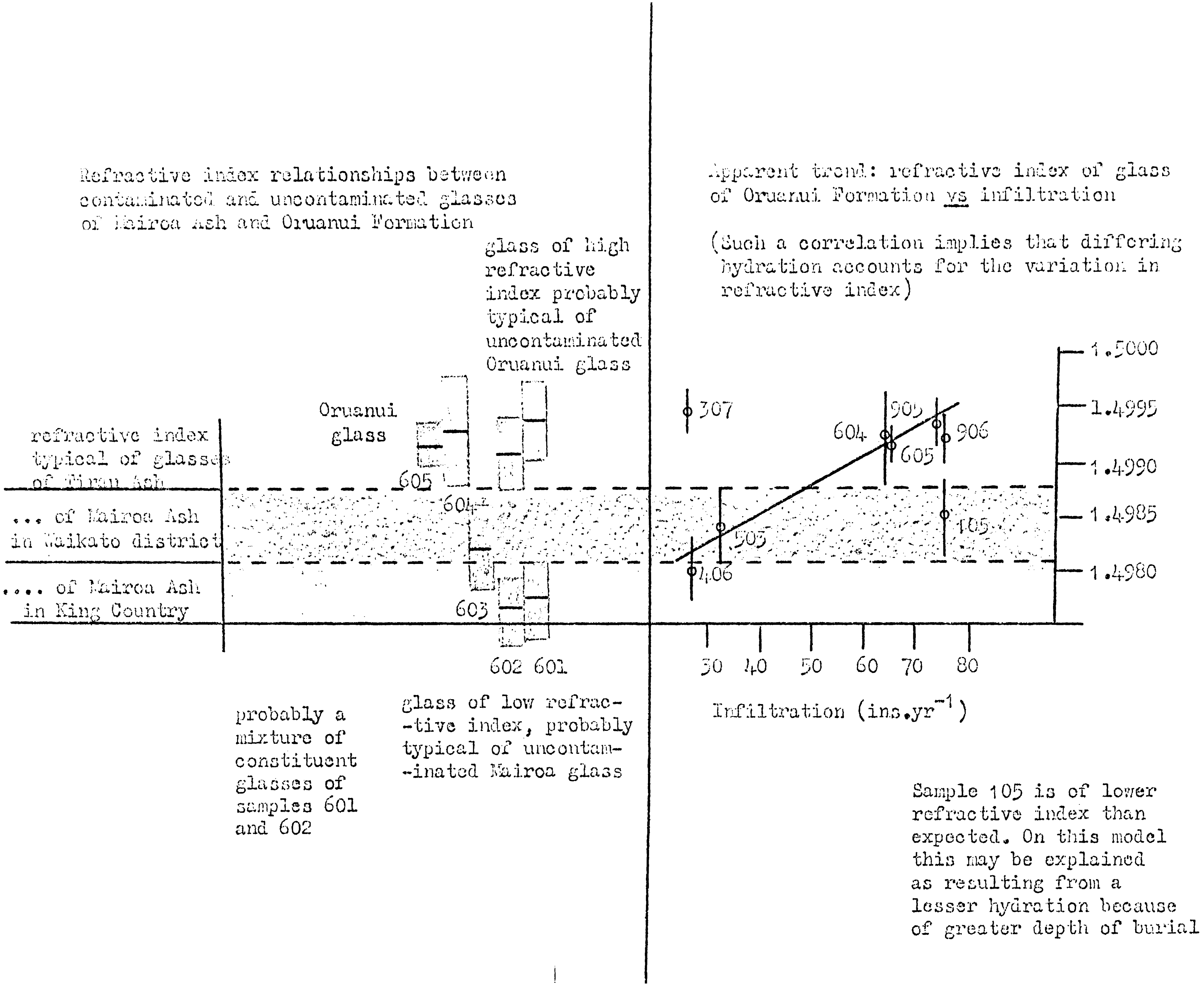


FIG. 9C6

Refractive index relationships between rhyolitic glass extracted from Oruanui Formation at various sites, at some of which this tephra is contaminated with Mairoa Ash on glasses from late Pleistocene ashes in the United States, although their experimental technique was such that all but the largest differences in refractive index due to variability in hydration would be masked by the determinative error.

It will be recalled that two rhyolitic glasses were found in the Mairoa Ash glasses at Mairoa. If the glass of lower index (1.4977) is taken as the value for uncontaminated Mairoa Ash glass, and that of higher index (1.4992) as that of uncontaminated Oruanui, then, with the knowledge of the "average" refractive index the degree of contamination may be estimated. Such estimates are given in Table 9-2. Similar effects may be expected between the lower Mairoa and Oruanui glasses in other sites; corresponding data for the Kakepuku site are included in Table 9-2.

TABLE 9-2: Estimation of Contamination of Rhyolitic Glass from Oruanui Formation and Mairoa Ash.

Sample	Refractive index	Prop. Oruanui glass (%)	Prop. Mairoa glass (%)
Uncontaminated rhyolitic glasses:			
Mairoa[(a)]	1.4977	0	100
Oruanui	1.4992	100	0
Contaminated rhyolitic glasses:			
501	1.4980	20	80
502	1.4979	27	73
503	1.4984	47	53
601[(b)]	1.4983	35	65
602	1.4983	46	54
603	1,4983	47	53
406	1.4980	20	80
407	1.4993	100	0

Notes: (a) These values from the upper Mairoa sequence, two glasses recognised on basis of refractive index.

(b) mean determined value: this value is inherently weighted to allow for the proportions of the constituent rhyolitic glasses.

On the basis of this table, it is clear that there has been some reworking of the material that comprises the Mairoa Ash sequence. This of course has some bearing on the ages previously assigned, and these ages may be corrected by the use of the equation:

$$P_{g(OU)} \times 20 + P_{g(M)} \times t_M = \bar{t}$$

where P_g represents the proportion of Oruanui (OU) or Mairoa (M) glass in the rhyolitic glass, t_m is the age of the ash deposit allowing for the correction, and $\bar{t}$ is the age found in Chapter 6 (effectively a weighted mean age). Under these conditions the age of the Mairoa Ash sequence is between some 15 and 17 thousand years at Mairoa itself. This is in closer accord with the dates from the more easterly sites. Because of the uncertainty of the weathering rate constant for the Kakepuku site, such correction procedures do not give any more satisfactory estimates of the dates than have been given previously, in other words, for the purpose of the above equation $\bar{t}$ is uncertain.

The possibility exists of a similar kind of mixing between the Tirau and Mairoa ashes themselves, and such an effect may account for the tendency for the minimum in the refractive index versus stratigraphic position profiles to be at lower indices for the more westerly sites where the Mairoa Ash component is more prominent. Since, however, the deposition of the sequences is, by the correction procedure just discussed, rather more contemporaneous than would be suggested by Chapter 6, such mixing would have little effect on the assignment of age. Such interdigitation effects may however limit the usefulness of chemical analysis of bulk samples of glass: this is described in Chapter 10.

It will be recalled from when the technique of the refractive index determination was being described, that the temperatures could be noted whereat the Becke line disappeared and where it re-appeared. These temperature differences are indicated on the upper curve of Fig. 905. From this plot it is seen that there is a tendency for glasses associated with the Mairoa Ashes to have higher values of this parameter than those of the Tirau Ash. It is difficult to ascribe a reason for this, but it probably represents differing strains set up in the glass because of different eruptive mechanisms in the ejecting of rhyolitic glass from rhyolitic vents and andesitic vents. The recognition that rhyolitic glasses are associated with andesitic eruptives is a fact of itself worth noting.

Correlation of the refractive index of the glasses comprising the two sequences with possible parent glasses is difficult because of the contamination of the tephras. The glass from the Rotorua ash (sampled at the Tapapa Road site for Tirau Ash) and the Rotoma Ash (sampled rather nearer to source) are similar to those comprising the Tirau Ash sequence as far as refractive index is concerned. This does not conclusively prove their inclusion in the sequences, but they are certainly more likely to be present than the glass from the Taupo Pumice eruption which has a significantly higher refractive index.

Mention has already been made of the effect of hydration on refractive index, and it is to a discussion of this that the remainder of this chapter is directed.

S9-9: Water Contents of Volcanic Glasses and their Effect on Refractive Index.

Water contents can be experimentally determined by heating the specimen and measuring the loss in weight of the sample or by measuring the volume of water quantitatively absorbed. The former, which may be considered a "physical" method, suffers from the drawback that:

"the value obtained will represent the water content only in the absence of similarly volatile constituents such as CO_2, F, S, Cl and to some extent the alkali metals, it also requires the absence of constituents that are readily oxidised or reduced during ignition, chief among which is ferrous ion." - (Maxwell, 1968).

This last objection is not removed by "chemical" methods, since the sample is still heated - the difference being that the water content is determined by quantitative absorption. Under these conditions the only augmentation on diminution of water content is that arising from oxidation or reduction processes. In the case of ferrous ion this process may be written:

$$H_2O + 2FeO \longrightarrow Fe_2O_3 + H_2$$

From the stoichiometry of this equation, each percent change in the FeO content changes the water content by only 0.1% (by weight). Experiments by Drysdale et al.(1963) confirm that this effect can be ignored except for those glasses in which the ferrous content is exceptionally high. The equation is probably better represented by:

$$H_2O + Fe^{(ii)}_{(glass)} \longrightarrow Fe^{(iii)}_{(glass)} + OH^-_{(glass)} + \tfrac{1}{2}H_2$$

The existence of hydrogen in bubble cavities as required by such an equation has been disputed by Friedman (1958), and it may be that attributing variations of water content to this process is unnecessary.

It is usual to tabulate the values of water contents at two temperatures, generally at 105°C (H_2O^-) and near 1000°C (H_2O^+). In fact, water is lost at all temperatures and the precise water content is said to be as dependent upon the duration as the temperature of dehydration (Butler, 1961; Carmichael, 1960) and it has been further suggested that weight loss data should be interpreted in collaboration with data from differential thermal analysis (Chalmers, 1964). It is interesting to compare the various water contents for different determinative methods and this is done for some literature data on pumice glasses in Table 9-3. In general the weight loss at red heat is very nearly the value H_2O^+, and, as expected, since the pumice glasses are vesicular, the results from the physical determinations are usually marginally higher than those chemically determined. The relationship between the weight loss at 105°C and H_2O^- is more erratic. For the investigation of the samples for this thesis, the good agreement of values for a weathered glass of low vesicle content (member 19 of Table 9-3) suggests that water contents of glasses may be useful in correlating tephras.

For rhyolitic glass, Ross and Smith (1955) note that there appear to be two different types of water present as far as the structure of the glass is concerned: one which is initially present when the glass is first erupted, amounting to some tenths of a percent and removed only with difficulty; and another which is acquired as a result of post-eruptive weathering. Glasses with water of the first type only are termed "obsidians," those which have both are "perlites." These authors showed that on dehydrating a perlite an obsidian could be formed. On the basis of the temperatures required to expel these two water types, it would seem that the "obsidian" water should be identified with part of the H_2O^+ and the "perlitic" water with the sum of the H_2O^- and the balance of the H_2O^+.

Ross and Smith (1955) also observed that the ratio of the change in refractive index on dehydration to the water loss was essentially constant for each of perlitic and obsidian glasses. A plot of refractive index versus water contents thus had two distinct parts as is shown in Fig. 907, the short steep portion being associated with the loss of "obsidian" water, and the flatter portion with the loss of perlitic water. By plotting values of the change of refractive index on dehydration as a function of water contents for other data given by these authors, it is seen that these lie close to the line for Arroya Hondo glass (plotted as the solid line on Fig. 907).

FIG. 907

Variation of refractive index with water contents of rhyolitic glasses

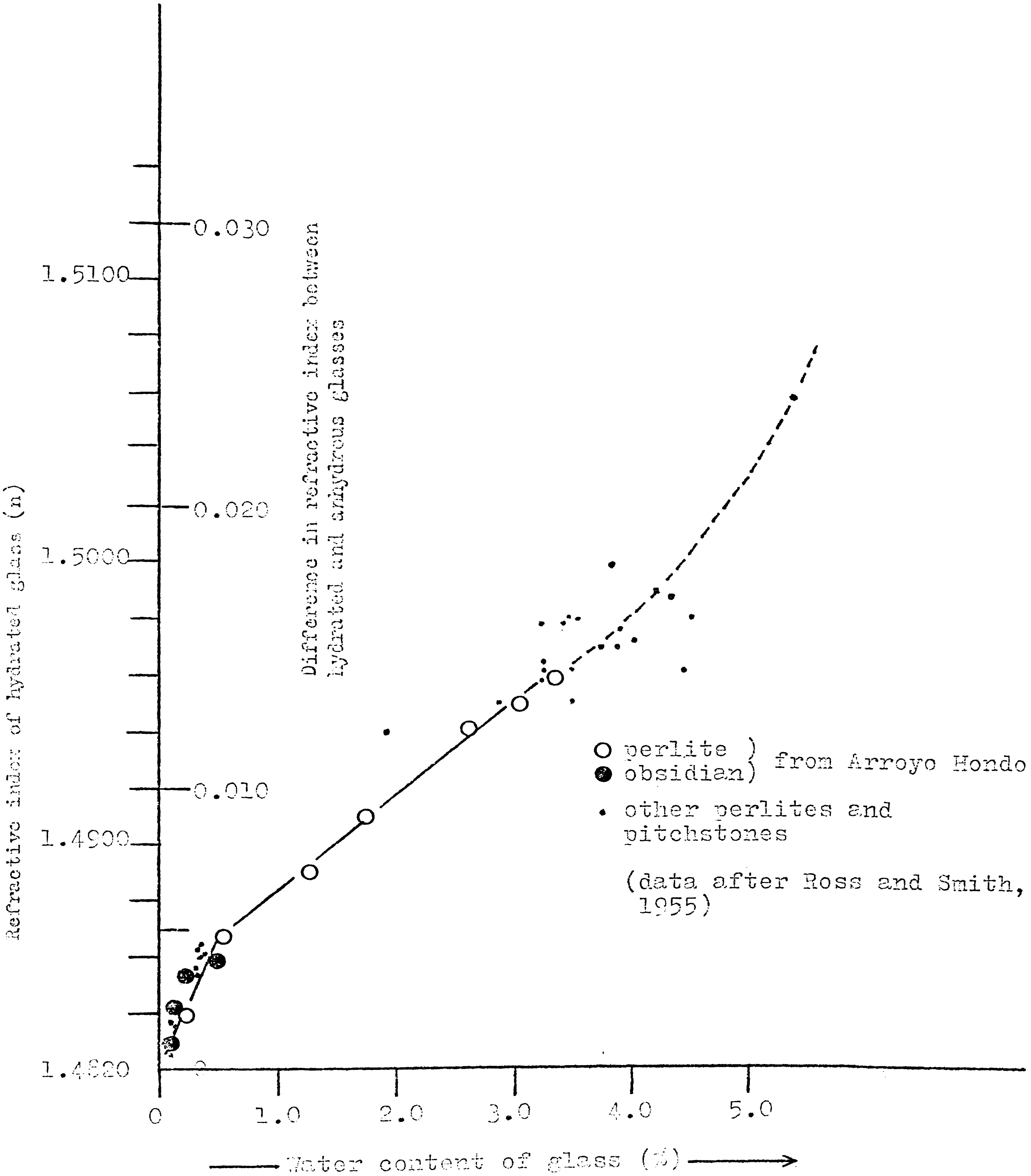


TABLE 9-3: Comparison of Water Contents of Rhyolitic Glasses Determined "Physically" and "Chemically."

Glass Sample(a)	Vesicle content of associated pumice	Physical determination			Chemical determination			Ratios		
		at 105°C(b) W_1/%	at red heat(c) W_2/%	total W_3/%	H_2O^- W_4/%	H_2O^+ W_5/%	Total W_6/%	$\frac{W_1}{W_4}$ (d)	$\frac{W_2}{W_5}$	$\frac{W_3}{W_6}$
Taupo Lapilli(3)	66	0.40	2.73	3.13	0.74	2.63	3.37	0.54	1.04	0.93
Member 5	60	0.40	3.31	3.71	0.86	3.20	4.06	0.46	1.03	0.92
Member 8	62	0.65	3.00	3.65	0.82	2.87	3.69	0.79	1.05	0.98
Member 14D (upper	63	0.61	3.22	3.83)	(f) 0.40	3.14	3.54	(1.53	1.02	1.08
(lower	70	0.60	3.18	3.78)				(1.50	1.01	1.07
Waimihia (15)	73	0.34	2.71	3.05	0.46	3.47	3.93	0.74	0.78	0.78
Member 19(e)	35	1.63	3.53	5.16	1.63	3.52	5.15	1.00	1.00	1.00
Member 24 (upper	55	0.67	2.76	3.43)	(f) 0.44	4.36	4.80	(1.53	0.63	0.72
(lower	50	0.62	4.45	5.07)				(1.41	1.02	1.06
Member 25 (upper	58	0.46	4.00	4.46)	(f) 0.48	3.92	4.40	(0.96	1.02	1.01
(lower	65	0.58	2.43	3.01)				(1.21	0.62	0.69

TABLE 9-3:

Notes: (a) from Ewart (1963); all samples of essentially the same bulk composition.

(b) Comparable to H_2O^- determinations from point of view of dehydration temperature.

(c) Comparable to H_2O^+ determinations from point of view of dehydration temperature.

(d) Differences are quite marked for water lost at low temperatures, rather less so for the other ratios.

(e) Although there is no definite correlation between vesicle content and the ratio, it does appear that the ratios tend to unity as the glass becomes less vesicular. It is also of interest that this sample should yield this result, since in spite of the similarity in chemical composition to the other glasses it is claimed by Ewart to be weathered.

(f) Ewart does not indicate whether this is a mean value, but in that it is not designated as "upper" or "lower" it may presumably be taken to be a mean value.

In order to determine the water contents of glasses on the basis of refractive indices rather than by direct determinations of water content, some other parameter is needed to define the refractive index of anhydrous glass. Only then can values of the change in refractive index of hydration, and hence the water contents, can be determined.

S9-10: Parameters Correlative with Refractive Index of Anhydrous Glasses

Examination of the data on refractive index and density of tektites from Chao (1963) and similar data for synthetic glasses (Kaye and Laby, 1966) yields a relationship given by the equation:

$$n_o - 0.103\rho_o + 1.251$$

Since both tektites and synthetic glasses have very low water contents, it is reasonable to assume that the plot obtained is of dry refractive index versus dry density, symbolised as n_o and ρ_o respectively.

Now the density of a glass does vary slightly with hydration. Tilley (1922) claims that the density of a glass was reduced for increasing water content, but Ross and Smith (1955) in the study, already referred to, suggested that the density was increased and their data is represented by the equation:

$$\rho = \rho_o + 0.0086\,W$$

where W is the water content. Now for the formation of perlitic glass from obsidian the relationship between refractive index and water content over the range AC can be expressed as:

$$n = n_o + 0.0039\,W \quad \text{(from Ross and Smith (1955))}$$

Combining these three equations yields:

$$W = 323n - 404 - 33.3\rho$$

The difficulty with this approach is the large error introduced because of the range of density values. Typically the principal band spans a density range of 0.02 gm.cm^{-3} and this would introduce an error of some ±0.6% in water contents. By comparison the mean residual for refractive index (about 0.0003) introduces an error of about 0.1%. Since on Fig. 907 a change of 0.6% in water content has an attendant change in refractive index of some 0.002, and this is considerably in excess of the differences in refractive indices of the various glasses, density is not a good parameter to use as indicative of "anhydrous" refractive index.

Another approach is to use the relationship between refractive index and the proportion of a constituent oxide. Since the refractive index is a bulk compositional parameter dependent on all oxide components such a procedure may be of doubtful value (Matthews, 1951), but nevertheless since composition data can be obtained to an accuracy comparable to that of the refractive index methods described the theoretical objections are outweighed by its practicality. The obvious compositional relationship is that between silica content and refractive index. The disadvantage of this choice, as shown in plots by George (1924), Matthews (1951) and Chao (1963) is that the relationship is not regular. By contrast the relationship of refractive index to ferrous oxide contents is essentially linear as is shown by the high correlation coefficient when linear regression statistics are applied to the raw data for tektite glasses. A similar relationship was assumed to hold for pumiceous rhyolitic glasses from Ewart (1963), for which the linear regression statistics are shown in Table 9-4. The correlation coefficient is lower in this case because of the fewer data points and because of the lower accuracy in the refractive index determinations.

TABLE 9-4: Linear Regression Statistics: Refractive Index (n) vs Ferrous Content (FeO/%).

Parameter	Tektites	Dehydrated Volcanic Glass*
Correlation Coefficient (r)	0.966	0.864
Intercept (b)+	1.4668	1.4757
Slope (m)+	0.00773	0.0057

* refractive indices of dry glass evaluated by subtracting from the measured refraction index the increment in refractive index determined from the water contents by Fig. 907.

\+ Intercept and slope those for the equation $n_o = m\,(FeO) + b$.

As indicated previously the ferrous oxide proportions can be conveniently determined from the magnetic susceptibilities, and thus it is possible for water contents to be determined indirectly, on the basis of physiochemical properties.

S9-11: Water Contents of Glasses as a Function of Site and Age:

It was deduced earlier that refractive index was effectively independent of site. To determine whether the water contents of volcanic glass are also independent of site, water contents of glasses from Oruanui Formation may be determined as in Sec. 9-11, and considered in relation to present conditions prevailing at the sites. Data for this is given in Table 9-5. If the water contents were temperature dependent they would be expected to decrease with increasing elevation of the site. In fact, if anything, the reverse trend is noted which suggests that the hydration process is more dependent on infiltration (which generally increases with altitude). Such a conclusion is of course consistent with the model of glass weathering previously mentioned (Ruxton, 1968), and it also concurs with the results of the experimental diffusion studies carried out by Friedman, Smith and Long (1966) who considered that the concentration of water in the hydrated glass is independent of the hydration temperature.

The low water content of sample 503 is surprising in that other evidence has suggested that the material at this site has been more heavily weathered than expected on the basis of climate, and that additional water, perhaps by lateral flow, has aided the weathering regime. There is also the possibility that some of the hydration shell of the glass has been removed, as is described in a later section. It is also of interest that glasses lower down in the depositional sequence of a given tephra have a lower water content than their counterparts higher up the sequence. This is shown clearly in samples 604, 605 and 905, 906 and is presumably attributed to the lower sample being protected from the rigours of climate and soil formation virtually since deposition, and is indicative of a very rapid deposition of the Oruanui Formation. It is of interest to compare this situation with that of Rotoma Ash and its basal lapilli. In this case glass of the lapilli bed has a higher water content than the overlying Ash (see Table 9-6). This suggests

TABLE 9-5: Water Contents of Oruanui Glasses from Various Sites : Comparison with Site Data.

	Water Content Data						Site Data		
Sample	FeO-content$^{(1)}$ (%) (±0.05%)	$n_o^{(2)}$ (±0.0003)	$n^{(3)}$ (±0.0003)	Δn $(n-n_o)$ (±).0806)	$\Delta n'^{(4)}$ (n-0.0008)	$W^{(5)}$ (%) (±0.1%)	(6) Elevation (h/m)	(7) Infiltration (I/cm)	Depth of Burial (d/cm)
307	0.70	1.4797	1,4994	0.0197	0.0149	4.15	150	66	121
406	0.53	1.4787	1.4980	0.0193	0.0145	4.03	138	69	121
503	0.90	1.4808	1.4984	0.0176	0.0128	3.55	60	84	61
604	0.65	1.4794	1.4993	0.0199	0.0151	4.20) (8))	360	162	(101
605	0.70	1.4797	1.4992	0.0195	0.0147	4.07)			(104
905	0.63	1.4793	1.4997	0.0204	0.0156	4.33) (8))	270	182	(101
906	0.85	1.4806	1.4998	0.0192	0.0144	4.00)			(114
105									

Table 9-5: Notes:

(1) on basis of magnetic susceptibility measurements, see Chapter 8.

(2) evaluated from relationship : $n_o = 0.0057\ \mathrm{FeO} + 1.4757$.

(3) as measured.

(4) allowing for the "obsidian water" in the perlite: an increase of 0.0048 units of refractive index over the "dry" value is attributed to the water content of the glass prior to eruption.

(5) being $\Delta n'/0.0036$, the slope of the refractive index-perlite water content relationship on Fig. 907 being 0.0036 $(\%\ \mathrm{water})^{-1}$.

(6) effectively a temperature dependent parameter; de Lisle indicates a decrease of some 0.5K for each 100 m increase in elevation.

(7) being the water surplus, evaluated as before as the difference between estimated rainfall and estimated evapotranspiration.

(8) values of samples of the same tephra lower in the stratigraphic sequence. These would be expected to have lower water contents because they have been protected by overburden since deposition.

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that there was a reasonable time interval between the deposition of these layers - sufficient for hydration of the basal lapilli to occur to a considerable degree before the rate of hydration was slowed down by subsequent burial.

Earlier in this section, it was noted that there was some tendency for higher values of water content of a given glass to be associated with higher infiltration rates. This is, however, but a minor feature and considering the small variation of water contents for the large variation in infiltration, it is probably a reasonable approximation that the water content is site independent. If this is the case, then

TABLE 9-6: Derived Water Contents of Glasses from Tephras of Known Age.

Parent Ash	Sample No.	FeO/%(1) Ferrous Content	n_o(2)	n(3)	Δn ($n-n_o$)	$\Delta n'$(4)	W/%(5) (±0.1%)	$t/10^3$yr
Rotomahana Mud	1101	0.90	1.4808	1.4970	0.0162	0.0114	3.16	0.1
Taupo Pumice	1002	0.45	1.4784	1.4930	0.0146	0.098	2.72	0.93
Kaharoa Ash	1103	1.45	1.4839	1.5020	0.0181	0.0133	3.57	1.75
Rotoma Ash	1110	0.65	1.4795	1.4995	0.0200	0.0152	4.23	7.33
Rotoma Ash (basal lapilli)	1115	0.45	1.4783	1.4997	0.0214	0.0156	4.60	7.33
Rotorua Ash	901	0.80	1.4802	1.4995	0.0193	0.0145	4.00	13.45
Oruanui Formation (see Table 9-5)							4.0 - 4.3	19.85
Rotoehu Ash	307	0.63	1.4793	1.4987	0.0194	0.0146	4.05	41.7
	409	0.55	1.4788	1.4977	0.0189	0.0141	3.93	
	505	0.67	1.4795	1.4987	0.0192	0.0144	4.00	

Notes: (1) - (5) as for Table 9-5.

the water content of glass should be a function of age.

Similar considerations to that in Table 9-6 can be applied to glass from the Rotoehu Ash with analagous results. Interestingly, the water contents of the glasses of the Rotoehu Ash and Oruanui Formation are similar despite their considerable difference in age. At this stage, it is appropriate to consider the variation of water content with age by reference to samples of glass of known age and data for this is presented in Table 9-6. This data, together with data on water contents of chemically analysed glasses of known ages from the literature is presented in Fig. 908.

From the diagrams it is clear that the function rises rapidly and then levels off. There appears to be a slight drop in water contents with increasing age above about 15 thousand years, although this is within the error of ±0.1% imposed by the determinative method. Because the function is effectively constant above ages of about 10,000 years, it is probably not particularly useful as a dating technique. However, that there is clearly a change in mechanism as hydration proceeds is of interest and it is to this that attention is now turned.

S9-12: Kinetic Aspects of the Variation of Water Content with Aged Glass.

Data given for water contents of very old glasses in the United States (Izett et al., 1970) show water contents comparable to those obtained here, suggesting that if the function is exhibiting a maximum it is at low values of age. Frost and Pearson (1966) describe series reactions wherein one component is the intermediate of a reaction sequence. For the hydration of glass, such a series of reactions can be envisaged as:

$$\text{glass (obsidian)} \xrightarrow{\text{I}} \text{hydrated glass(perlite)} \xrightarrow{\text{II}} \text{allophane.}$$

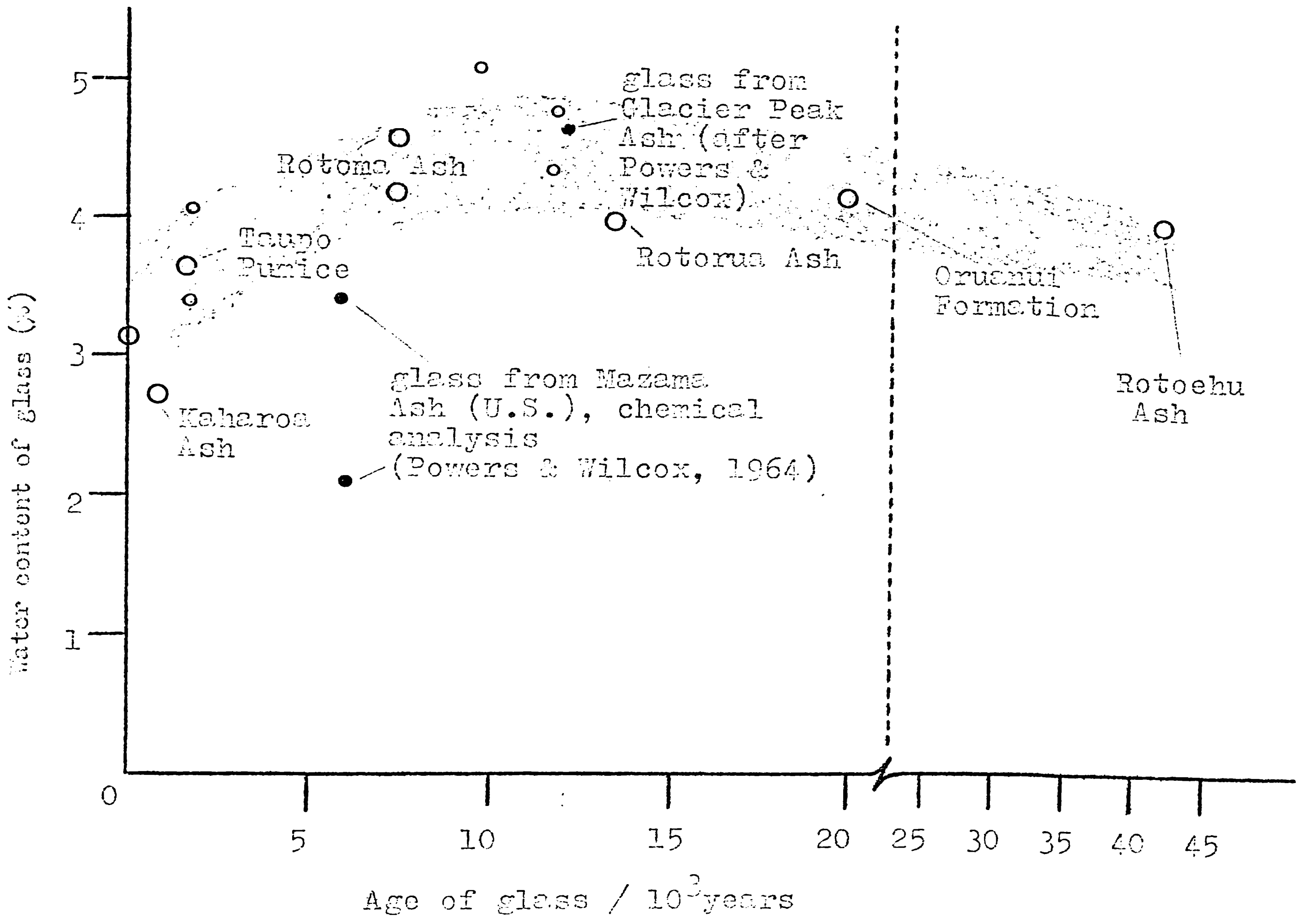
where reaction I is described by Ross and Smith (1955) and reaction II is that process of weathering of glass proposed by Fieldes (1955).

FIG. 908

Variation of water content of rhyolitic glasses with age of tephra

∘ data from chemical analysis of pumice glasses (Ewart, 1963)

○ data from indirect method of water content determination (this study)



If the water content is representative of the amount of perlite, it may be inferred that perlite is an intermediate in the process. The near constancy of the water content further implies that the reaction sequence may be considered to exhibit the kinetics of a chain reaction with a stationary state, which has as its criteria (Frost and Pearson, 1966):

> "..... that the intermediate (perlite, in this case) is very reactive compared with the original reactant and also results in the concentration of (perlite) being very low. The ..... condition (that $t >> 1/k_2$, where k_2 is the rate constant for process II) ensures that the induction period has been passed. Usually where the stationary-state approximation is applied the induction period is immeasurably short so that the method can be used with confidence."

This kinetic approach is similar to the mechanistic consideration of Friedman, Smith and Long (1966), who stated that since perlites typically contain some 3-4% water and have hydration shell thicknesses of some 20 microns, perlites do not attain greater hydration thicknesses, nor presumably water contents than this because:

> "..... the stress would be so great that a crack would form at the interface between the hydrated and unhydrated glass, and the process of hydration would start again."

This repeated process may account for the observation of Ewart and Fieldes (1962) of there being no systematic variation in strain for glasses of differing history. Such a hypothesis of the hydration process giving rise to strain is at variance with an earlier idea by Marshall (1961) that the strain features in perlites resulted from thermal strain during cooling, and that the high water contents are the result of absorption of water into the fractures. The other possible explanation, that of the glass becoming saturated so that no further hydration is possible, is satisfactory in that it explains the constancy of water contents in all but the youngest glasses, but it does not readily explain the occurrence of allophane as a weathering product of volcanic glass.

Friedman, Smith and Long (1966) described the hydration of obsidians to form perlites as conforming to the equation:

$$x^2 = k_D t$$

where x is the depth of hydration, t is the age and k_D is a constant, said to be related to the diffusion constant. An earlier paper by Moulson and Roberts (1961) followed the hydration and dehydration of silicate glasses by an infra-red method and showed that the optical density at the water absorption (2.7 microns) was related linearly to the square root of the time for which the glass was heated. They gave an expression for the diffusion coefficient as $D = (\pi l^2/16t)(d_1^2/d_2^2)$, where d_2 is the optical density at 2.7 microns of a saturated thin specimen of glass of thickness l and d_1 is the optical density of a thick, and presumably anhydrous, specimen. Now the ratio d_1/d_2 is a linear function of surface water content and l is a function of the depth of hydration. Accordingly, it would seem that the surficial water content is a function of the depth of hydration. Thus:

$$w^2 = c(D)t = c'(k_D)t$$

where c(D) is a constant, being a function of the diffusion coefficient. Now, such constants usually are related to the temperature by expressions of the form:

$$k_D \text{ or } D = A \exp(-E/RT)$$

In this expression, the so-called Arrhenian dependence, A is a pre-exponential factor, E is the activation energy for diffusion, and R and T are the gas constant and the temperature respectively. Thus for determinations of water contents at two differing temperatures:

$$D1/D2 = k_{D_1}/k_{D_2} = \exp\left[(E/R)(1/T_2 - 1/T_1)\right]$$

Consequently, $\left[(W_1^2/t_1)/(W_2^2/t_2)\right] = \exp.\left[\frac{E}{R}\cdot(1/T_2 - 1/T_1)\right]$

Estimates of the activation energy are around 20 kcal.mol^{-1} so that this relationship becomes:

$$\ln(W_1^2/t_1) + 10^4/T_1 = \ln(W_1^2/t_2) + 10^4/T_2$$

The values of temperature used in this equation are the effective hydration temperature of which Friedman, Smith and Long (1966) write:

> "The effective hydration temperature is not the average temperature but rather an estimated temperature at which hydration proceeds at the indicated rate if this temperature is maintained constantly. ..... In nature, the effective hydration temperature depends not only on the maximum temperature, but also on the length of time that the high temperatures are maintained. The hydration rate measured on objects hydrated under natural conditions is an integrated rate."

These authors do not however give the basis of how this 'integrated rate' might be calculated.

Hendy and Wilson (1968) gave the variation of temperature with time, on the basis of oxygen-isotope measurements in stalactites. Their curve is given in Fig. 909 where it will be seen that there is a maximum around 9,000 years. This means that the effective hydration temperature for glasses older than this is probably a little less than 13°C (286K). For glasses younger than this, the effective hydration temperature is adequately represented by:

$$T(^\circ C) = 0.223\ t + 11$$

Since there is only a two-degree rise in temperature between the present-day and the maximum this will have but little effect on the effective hydration temperature. Accordingly, all the glasses, at least as old as the Oruanui Formation, have hydrated under essentially similar effective hydration temperatures. This enables the conclusion to be reached that the plateau in the water-content age plot (Fig. 907) represents the end of the range of applicability of the relation:

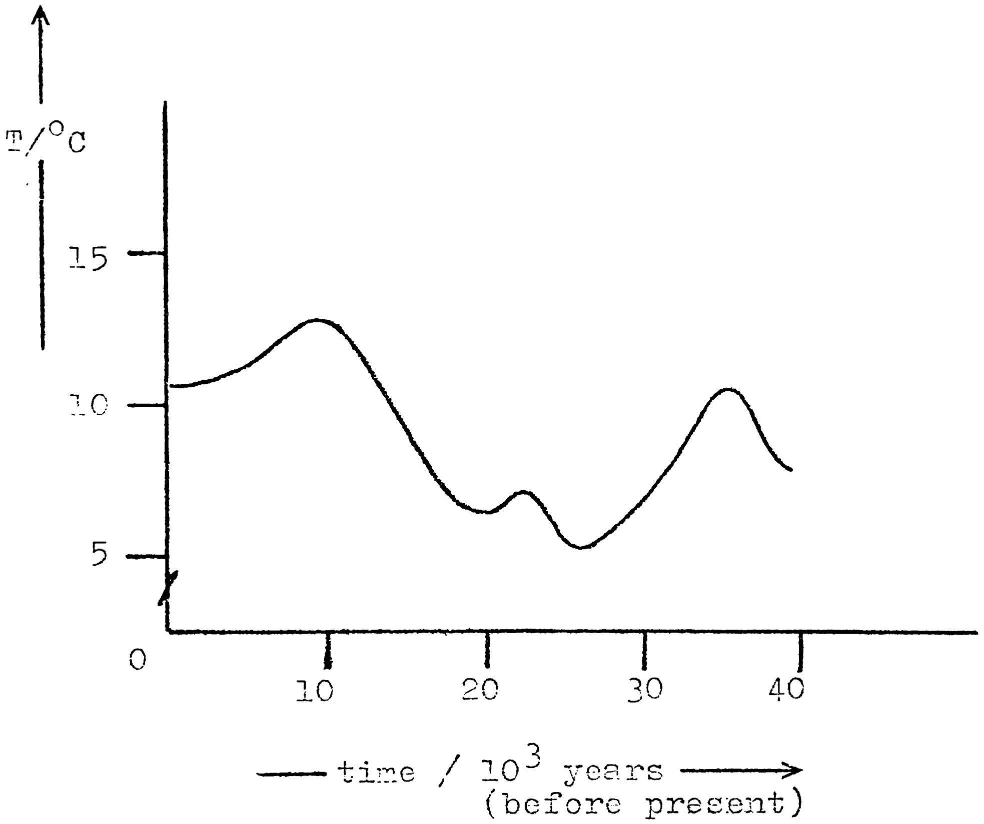
$$x^2 = k_D t$$

and is not the effect on the kinetic expressions of significantly differing temperatures.

FIG. [illegible]

Variation of temperature during the Pleistocene and Holocene in New Zealand, being:

"mean annual temperature for Waitomo, New Zealand, estimated from the oxygen isotopic composition of two speleotherms" - Hendy and Wilson (1968)



S9-13: Conclusion:

The refractive index of a glass shard is an indication of its bulk chemistry, but is certainly affected by hydration after weathering. This effect is greatest over the first ten thousand years, after which time the water content (as determined by an indirect method requiring information on refractive index and ferrous contents of the glass) is essentially constant. Accordingly, for glasses older than this, any significant differences noted between the refractive indices of two glasses probably represents a different eruptive rather than post-eruptive history, provided that the post-eruptive environment is similar. The refractive index bears but a minor relationship to differences in post-eruptive history occasioned by differences in weathering regimes and depths of burial. Such possible relationships, consistent as they are with the raising of the index with great hydration, are complicated by the mean index obtained representing, in some cases, mixtures of rhyolitic glasses.

In general, it is noted that the rhyolitic glasses of the Tirau Ash sequence have higher refractive indices than those associated with the Mairoa Ash sequence. The indices of glasses of the former sequence correspond very nearly to that of other predominantly rhyolitic tephra: Rotoma Ash, Rotorua Ash and Oruanui Formation, for example. That the refractive indices of the glasses of the Mairoa Ash are lower than their Tirau Ash counterparts, in spite of their probable greater age on the estimates of Chapter 6, suggests that this difference is compositional in origin. At the Mairoa Ash type section (at Mairoa itself) the extracted rhyolitic glass was found to be of two distinct refractive indices, a higher valued index of about the value of that associated with Tirau Ash and Oruanui Formation and one of a lower value. This provides confirmatory evidence for the Mairoa Ash deposit being composite, at least in its upper portions. The net decrease in refractive index as the stratigraphic column is descended at the intermediate site (like Parawera) probably further testifies to this composite character. If the lower refractive index is considered to be indicative of differing chemistry, the ashes identified as Rotoehu Ash, below the Oruanui Formation marker bed, appear to have refractive indices atypically low for rhyolitic ashes.

In order to be able to achieve the accuracy needed in these comparisons of refractive index, better determinations of refractive index were needed than is usual to petrological investigations. The technique used of determination by thermal variation is described and is of central importance to a study of this kind wherein the differences in refractive index are so very small. As a result, the pessimism expressed, at least among New Zealand tephrastratigraphers, about the worth of refraction index of glass shards as an identification technique may be dispelled.

CHAPTER 10: CHEMICAL ANALYSIS OF VOLCANIC GLASS.

S10-1: Introduction:

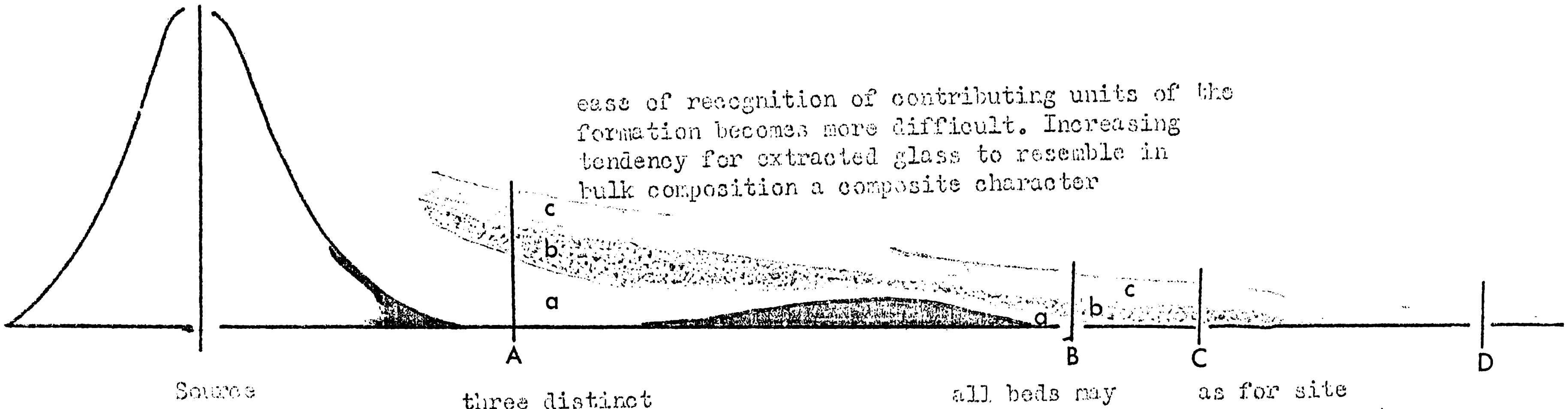
The chemical analysis of glass shards as a tool in the correlation of tephra has been used successfully in the United States and recent work indicates that such analytical methods are likely to be useful in New Zealand tephrostratigraphy. The principal assumption in the method is that the composition of the glass is constant throughout the areal extent of the tephra. For a paroxysmal eruption this is almost certainly justified, but is rather less so where a sequence of eruptive events contributes to the same tephra deposit. As is shown on Fig. 1001, it is possible that some of the tephra units may not reach the distant sources: the telescoped column of tephra units at a distant site may or may not be representative of all the members erupted. This may have a profound effect on the correlative power of glass analyses.

Techniques of analysis fall into the broad categories of bulk and single shard methods. Of modern instrumental methods atomic absorption and x-ray fluorescence are representative of the former with electron probe techniques representative of the latter. The important difference is that bulk methods give an appropriately weighted mean of the chemical composition of the number of shards comprising the specimen whereas the other methods enable the comparison of single shards within and between tephra units. Bulk methods, therefore, are able to correlate analyses of glasses from different distant sites to each other and to correlate glasses whose member status is known. They are usually inept at resolving correlations between shower bedded tephra units close to source with telescoped tephra from distant sites. For this latter problem single shard methods are preferable. Rankin (1973) in a study of trace elements in New Zealand by spark source mass spectrometry noted that:

> "the technique is best applied to the relatively homogeneous or poorly-bedded eruptive tephra."

FIG. 1001

Schematic diagram: lateral variations in shower-bedded tephra



ease of recognition of contributing units of the formation becomes more difficult. Increasing tendency for extracted glass to resemble in bulk composition a composite character

three distinct tephra units, able to be recognised in the field

all beds may be present, but are not readily distinguished. Sample obtained is a weighted average of glasses

as for site B, except that weighted average is different

only one unit present, may resemble unit c if weathering is comparable at sites A andDD

An example of the comparison between bulk and single shard techniques in correlation by chemical analysis of glass is the distinction between the Mazama Ash and Glacier Peak Ash of the United States. Powers and Wilcox (1964) presented data for chemical analyses of glasses of known identification and also for analyses of glasses they considered correlative from sites further from the projected sources. This raw data and some derived parameters are presented in Table 10-1. For effective correlation the difference in proportion of a given element between the known glasses (which are compositionally distinct) should exceed the difference in proportion between the two glasses claimed to be correlative.

Reference to Table 10-1, the results for which were obtained by Powers and Wilcox (1964) by bulk methods, indicates that there appears to be considerable variation in the proportions of certain of the elements, in particular of iron and the alkali metals. In the correlations cited in Table 10-1, the difference in proportion of these elements in glasses claimed to be the same exceeds that difference in proportion in glasses known to be different. This is tantamount to saying that there is a dependence of chemical composition on post-depositional history. However, Smith and Westgate (1969) in analysing glass of the Mazama Ash by electron probe techniques considered that:

> "post-depositional changes in alkali contents are apparently not significant, and these elements are good for distinguishing ashes."

If this statement is taken to be true, then the discrepancies described earlier can only be related to the possibility of different glasses being represented at the near-source and distant sites. However, that there appears to be a dependence of the potassium content of a glass with age (see Sec. 10-3) suggests that there may be a post-depositional change of glass composition.

In that most of the tephostratigraphic problems described in this thesis relate to the correlation between distant sites, bulk methods of analysis are adequate. As will be seen subsequently, however, the information obtained by chemical analysis in no way negates the need for data from other techniques. The remainder of this chapter explores the applicability of chemical analysis of glass in New Zealand tephra studies and examines the inter-relationship of chemical data with physico-chemical parameters.

TABLE 10-1: Comparison of literature data for a single-eruption tephra and a probably episodal tephra - chemical analysis (Composition data from Powers and Wilcox)

	I	II	II-I	III	IV	III-IV	III-I
Oxide	Proportion major oxide (%)						
SiO_2	72.39	72.29	-0.10	73.01	74.67	-0.66	0.62
Al_2O_3	14.79	14.79	0	15.08	14.54	0.54	0.29
TiO_2	0.43	0.46	0.03	0.30	0.23	0.07	-0.13
Fe_2O_3	0.58	0.73	0.15	0.65	0.35	0.30	0.07
FeO	1.27	1.32	0.05	1.14	0.65	0.49	-0.13
MnO	0.06	0.05	-0.01	0.05	0.03	0.02	-0.01
MgO	0.52	0.61	0.09	0.73	0.45	0.28	0.21
CaO	1.58	1.83	0.25	2.30	2.32	-0.02	0.72
Na_2O	5.21	4.90	-0.31	3.72	3.68	0.04	-1.49
K_2O	2.77	2.95	0.18	2.89	3.05	-0.16	0.12
P_2O_5	0.09	0.07	-0.02	0.13	0.03	0.10	0.04

Notes: I : near source; sample from Rogue River, Oregon, U.S., postulated source Crater Lake.

II: sample far from source, Barr Creek, Montana, U.S.

II-I : relatively small differences apart from geochemically mobile elements, consistent with one-event eruption.

Notes: continued:

III : pumice on flanks of Glacier Peak volcano.

IV : sampled in Montana, at considerable distance from source.

III-IV : Note that differences in this column are typically larger than in the II-I column.

III-I : For effective correlation, (II-I) and (III-IV) should be less than (III-I).

S10-2: Analytical Techniques:

There is an extensive literature dealing with analytical techniques for glasses, but for the present purpose, rapid instrumental methods were sought that yielded analyses for a wide range of elements, introducing the possibility of "fingerprinting" the various glasses. Jack, Lajoie and Carmichael (1969) and ANAC (1974) have described the use of x-ray fluorescence in the "fingerprinting" of obsidians, and most of the analytical data referred to in this thesis was obtained using an ORTEC energy dispersive x-ray fluorescence spectrometer. For these determinations the finely divided glass powders were placed in sample containers with a window of "Mylar" film in the base. This method of sample preparation precluded the determination of magnesium and sodium in the glass. Standard glass samples were not available, so concentrations in the glass were determined relative to a calibration curve defined by the analysis of standard rock samples. These latter, being W-1 (a diabase) and AGV-1 (an andesite) were chosen as being compositionally similar to rhyolitic glass, and were finely ground, mixed intimately with powdered cellulose in ratio one part rock to three of cellulose, and pressed in a die at 3.2 tons/cm^2 pressure. To define the zero on the calibration curve a disc of pure cellulose was also pressed. The elemental proportions determined in the glass would be expected to differ from those obtained by other analytical means because of the dilution of the standards relative to the glass and because of possible matrix effects. In Table 10-2 are given the elemental concentrations for glass from

Taupo Pumice after Ewart (1963), and the data obtained by x-ray fluorescence from glass from Taupo Pumice at a different locality. The third column in the Table is the X.R.F. data scaled to comparable silicon contents, the fourth to constant aluminium. The x-ray fluorescence results scaled to constant silicon are in better agreement with the previously published data than are the results scaled to constant aluminium. Accordingly, an adjustment factor of 0.54 may be applied to the concentration values obtained by x-ray fluorescence analysis to render them comparable to those obtained by other methods. On Fig. 1002 the results of analysis of iron and manganese in various samples by x-ray fluorescence and atomic absorption methods are compared, the former being corrected as described above. Good correlation is achieved, suggesting that the analytical data obtained in this thesis may be compared with

TABLE 10-2: Comparison of analyses of glass from Taupo Pumice

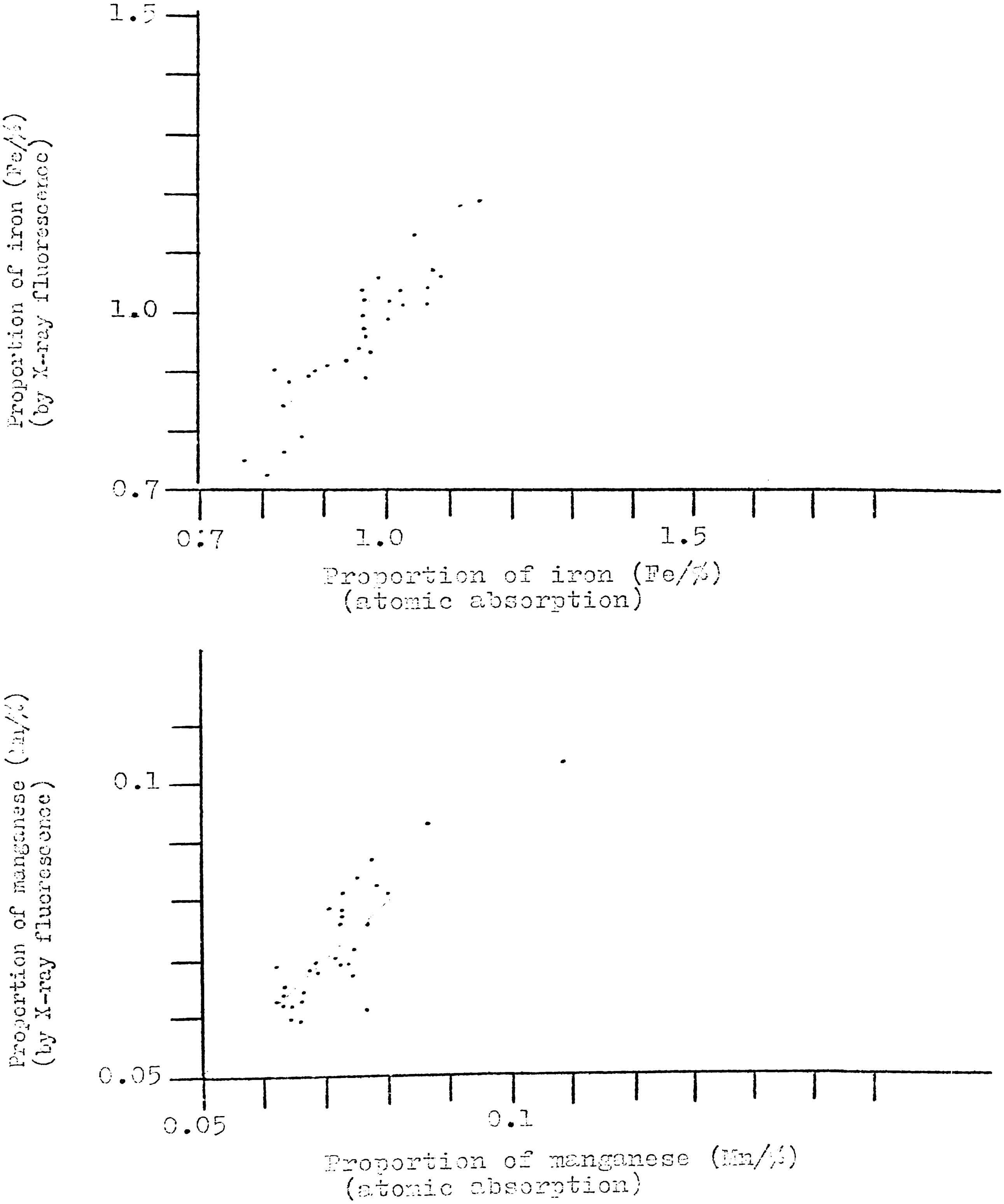
Element E	Proportion (%) after Ewart P_E	Proportion (%) by X.R.F. P'_E	P_E^{Si} $P'_E.(P_{Si}/P'_{Si})$	P_E^{Al} $P'_E.(P_{Al}/P'_{Al})$
Si	33.29	61.43	33.29	36.40
Al	6.99	11.80	6.40	6.99
Fe(II)	1.05) 1.58	3.25	1.76	1.92
Fe(III)	0.53)			
Mg	0.18	---		
Ca	0.97	1.95	1.06	1.16
Na	3.52	3.49	1.90	2.06
K	2.37	4.13	2.23	2.44
Mn	0.077	0.190	0.103	0.112

Instrument: ORTEC, molybdenum target, anode voltage 30kV, anode current 20 microamps, count time 200 secs.

Analysis for sodium probably affected by "Mylar" window.

FIG. 1002

Comparison of concentrations of the elements iron and manganese in rhyolitic glass determined by X-ray fluorescence and atomic absorption analytical methods



analyses obtained by other determinative methods. In that the adjustment factor may vary from element to element the concentration values presented in the tables are not corrected in this way.

S10-3: Major Elements in Glass, and their Relationships with Physico-Chemical Parameters.

In Table 10-3 the major element compositions of various identified glasses are given. It will be noted that even for Oruanui Ash, considered essentially to be a one-event eruption, there are significant compositional differences between glasses from different sites. A plot for example of silicon versus aluminium contents for all glasses gives a scatter diagram of low trend (Fig. 1003). However, when a specific glass (of Oruanui Formation) is considered, the expected inverse relationship between these two elements becomes apparent. Of particular note is that the line defining this relationship passes through or near the plotted points of the rhyolitic glasses associated with the Mairoa Ash sequence at the more westerly sites. As expected there is a decrease in refractive index for rising silicon content; this is shown for Oruanui glasses in Fig. 1004. Again this trend is probably indicative of the contamination of the glass from the Oruanui Formation at the more westerly site with rhyolitic glass associated with the Mairoa Ash sequence. There is no significant correlation between refractive indices and silicon contents for all glasses, since there appear to be important compositional differences in elements other than silicon which preclude such correlation when the refractive index is measured so accurately. This represents an extreme example of the difficulties in refractive index versus silica content plots for glasses of different volcanic suites described by Matthews (1951).

A plot of ferrous content of the glass (as FeO) as a function of aluminium content is given in Fig. 1005. That the points characterising volcanic glass lie close to a line extrapolated from the corresponding

FIG. 1003

Silicon and aluminium contents of rhyolitic glasses

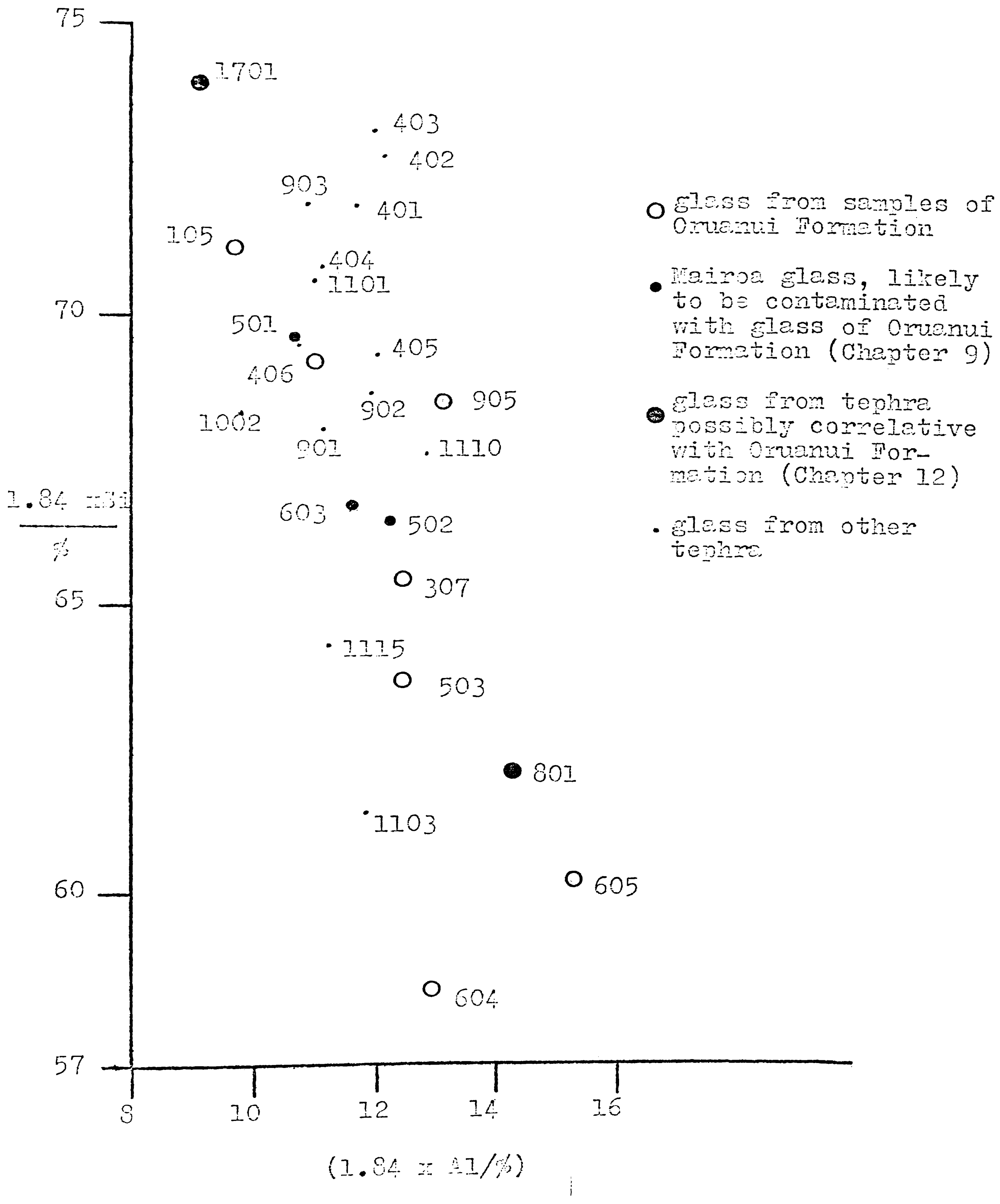
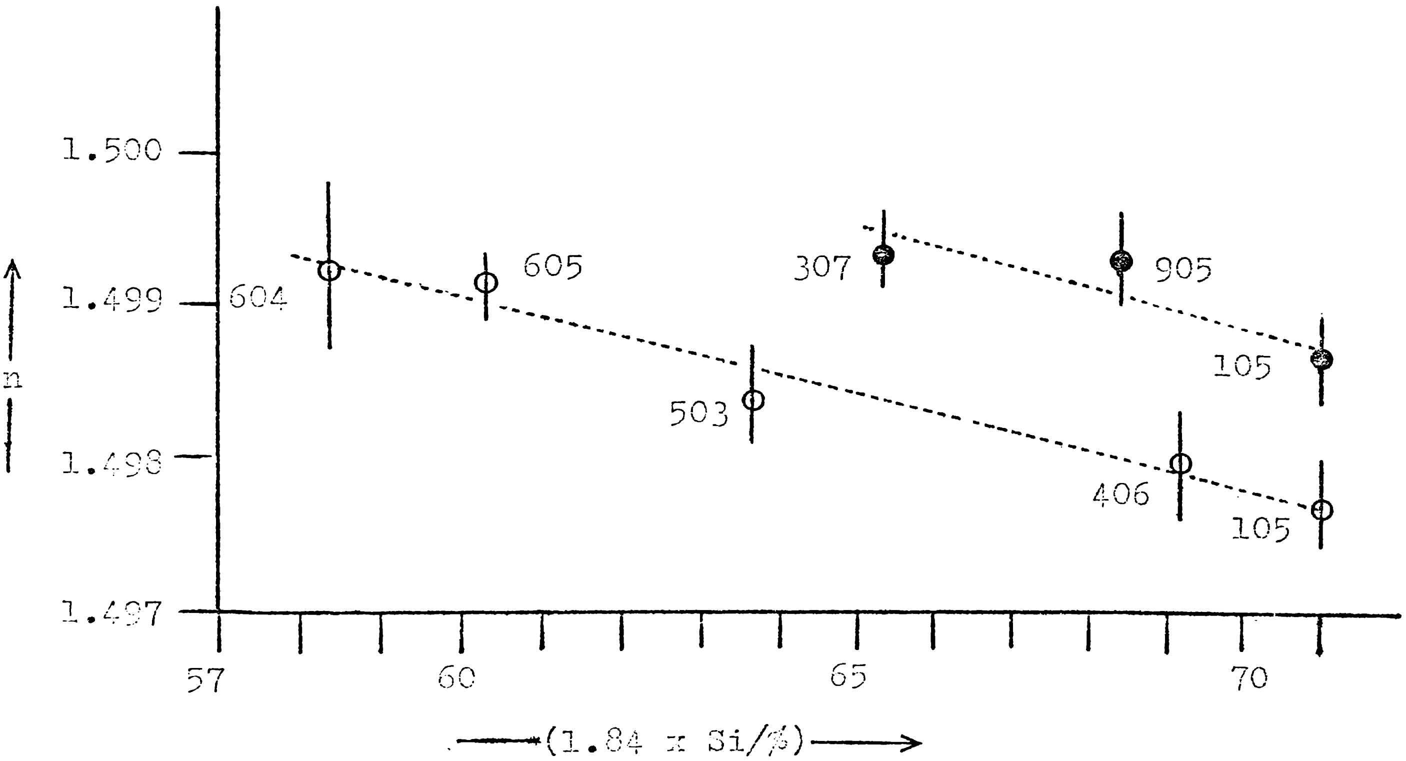


FIG. 1004

Refractive index (n) as a function of silicon content of rhyolitic glasses from samples recognised as Oruanui Formation



There appear to be two curves, suggesting that the Oruanui Formation is composed of two members. On the basis of evidence to be presented in Chapter 12, it would seem that samples indicated as ● are what Vucetich and Pullar (1969) refer to as the Oruanui Breccia Member and those indicated as ○ are the Oruanui Ash Member.

The refractive index data for sample 105 suggested the presence of two glasses when the magnitude of the mean residuals was considered (see Sec. 9-7)

FIG. 10C5

Ferrous content *versus* aluminium content of glass

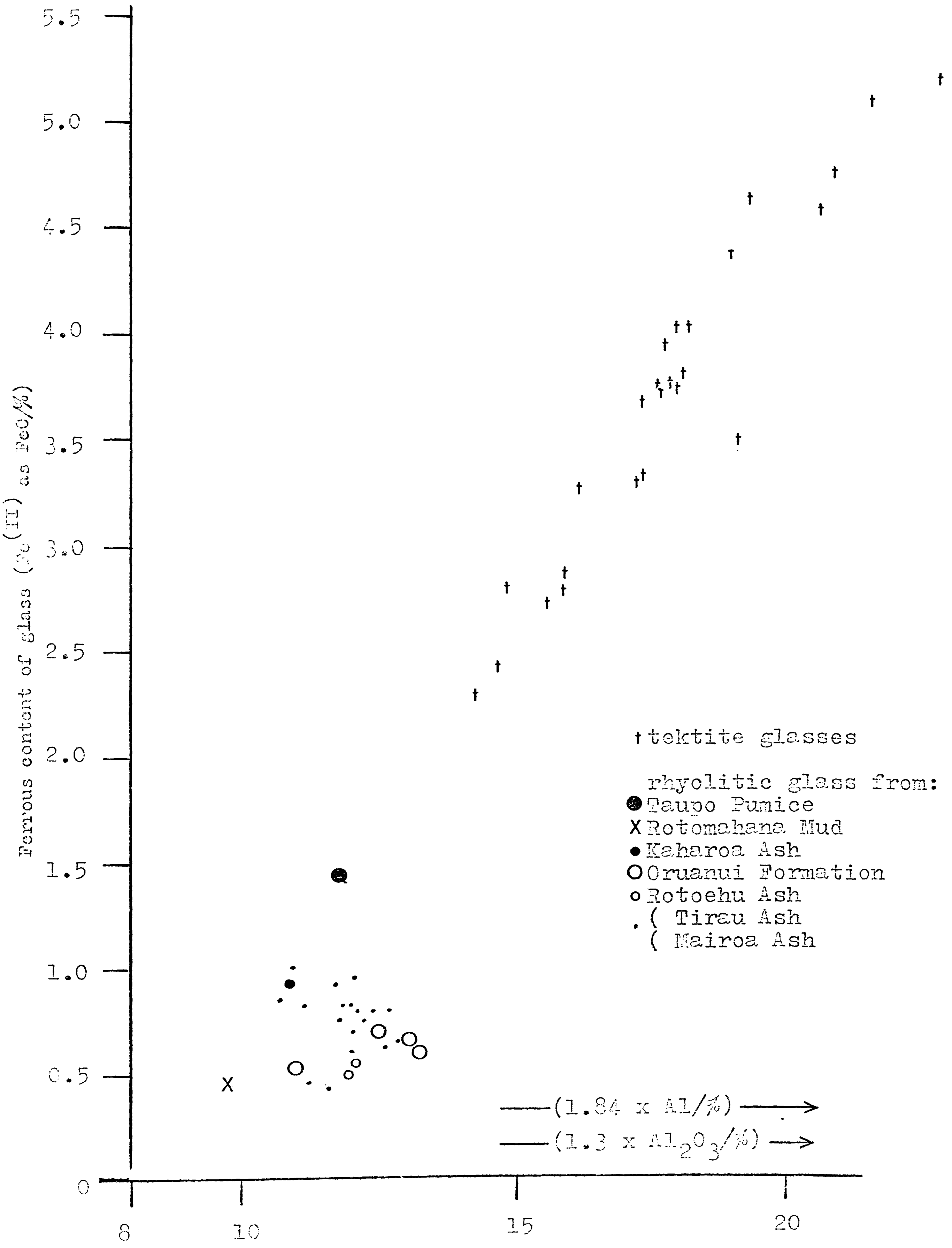


TABLE 10-3: Comparison of Major Element Compositions of Glasses by X-Ray Fluorescence.

Tephra	Sample No.	Element						
		Al	Si	K	Ca	Ti	Mn	Fe
		Proportion/% (XRF)*						
Okareka Ash	101	10.809	72.928	4.769	1.433	0.187	0.117	1.616
Oruanui Ash	105	9.740	71.101	4.794	1.458	0.194	0.136	1.850
	307	12.459	65.351	4.470	1.392	0.194	0.129	1.902
	605	15.299	60.293	4.369	1.415	0.216	0.128	1.975
	406	11.038	69.224	4.383	1.634	0.193	0.119	1.799
Oruanui Breccia	905	13.271	68.419	4.596	1.601	0.220	0.114	2.179
	604	12.956	58.356	4.211	1.360	0.189	0.111	1.902
Rotoehu Ash	109	11.377	73.149	4.788	1.238	0.210	0.153	1.387
	114	12.215	70.280	4.647	1.317	0.200	0.143	1.374
	116	11.104	65.951	4.487	1.351	0.200	0.137	1.319
upper	308	12.014	71.566	4.793	1.374	0.203	0.156	1.407

TABLE 10-3: continued

Tephra	Sample No.	Al	Si	K	Ca	Ti	Mn	Fe
		Proportion/% (XRF)*						
lower	309	12.571	71.571	4.525	1.741	0.203	0.162	1.400
lower	409	12.032	73.971	4.379	2.030	0.196	0.148	1.353
Rotomahana Mud	1101	10.986	70.673	4.618	2.061	0.251	0.109	1.894
Rotoma Ash	1110	12.793	67.604	4.722	1.124	0.192	0.163	1.455
Lapilli bed of Rotoma Ash	1115	11.191	64.349	4.422	1.219	0.217	0.137	1.522
Rotorua Ash	901	11.149	68.069	5.158	1.157	0.192	0.152	1.649
Kaharoa Ash	1002	9.788	68.342	5.694	0.776	0.141	0.135	1.178
Taupo Ash	1103	11.795	61.425	4.134	1.951	0.342	0.190	3.248
Mairoa Ash	603	11.586	66.748	4.700	1.327	0.224	0.109	2.099

* Percentages given are 1.84 times real value, Sec. 10-2.

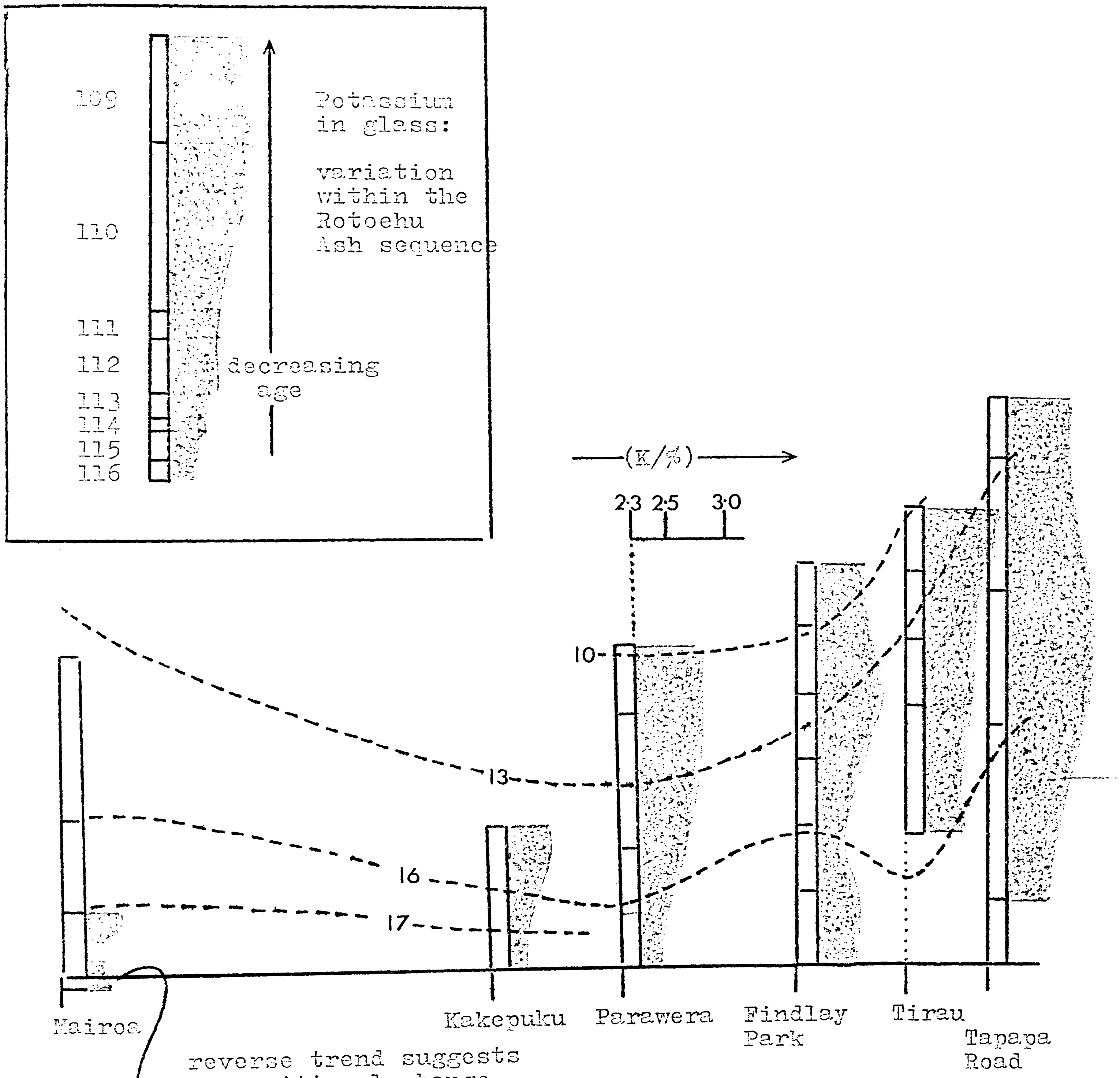
relationship for tektite glasses suggests that aluminium might remain constant during weathering, as was considered by Ruxton (1968) to be the case. Now there is a close relationship between aluminium contents and refractive index in tektites (see Chao, 1963), thereby adding justification to the procedure of establishing dry refractive indices on the basis of ferrous contents as was described in Chapter 9.

A major difficulty in the correlation of glasses by their chemical composition is the geochemical mobility of certain elements. The variation of silicon contents has already been mentioned, and this may partly result from leaching under high-infiltration conditions. Even more striking is the variation of potassium contents. From Fig. 1006, it is clear that the potassium contents are higher in glasses at the top of the stratigraphic sequence and decrease regularly down the sequence. Mason (1958) indicates that the melt is likely to become enriched in potassium as differentiation proceeds, so that glass sampled from higher in an eruptive sequence might be expected to be more potassic than glass lower in the sequence. Such a trend is shown for members of the Rotoehu sequence in the insert to Fig. 1006. Potassium contents of the rhyolitic glasses of the Tirau Ash and Mairoa Ash sequences are shown in Fig. 1006, on which are also given the isochrons based on dating by glass contents of soils. From this there would seem to be a correlation between potassium loss and the age of the tephra. On these grounds the earlier-given statement by Smith and Westgate (1969) on the invariance of the alkalis in glass would appear to be refuted.

It is of note that the titanium content appears remarkably constant for glasses of given parent tephra although there is no great variation in its concentration. The differences in manganese and iron contents is quite striking as is indicated by the Mn/Ti versus Fe/Ti plot of Fig. 1007. From this it may be observed that the rhyolitic glass of the Tirau Ash sequence has a higher manganese and lower iron content than have the rhyolitic glasses of the Mairoa Ash sequence. It is of

FIG. 1006

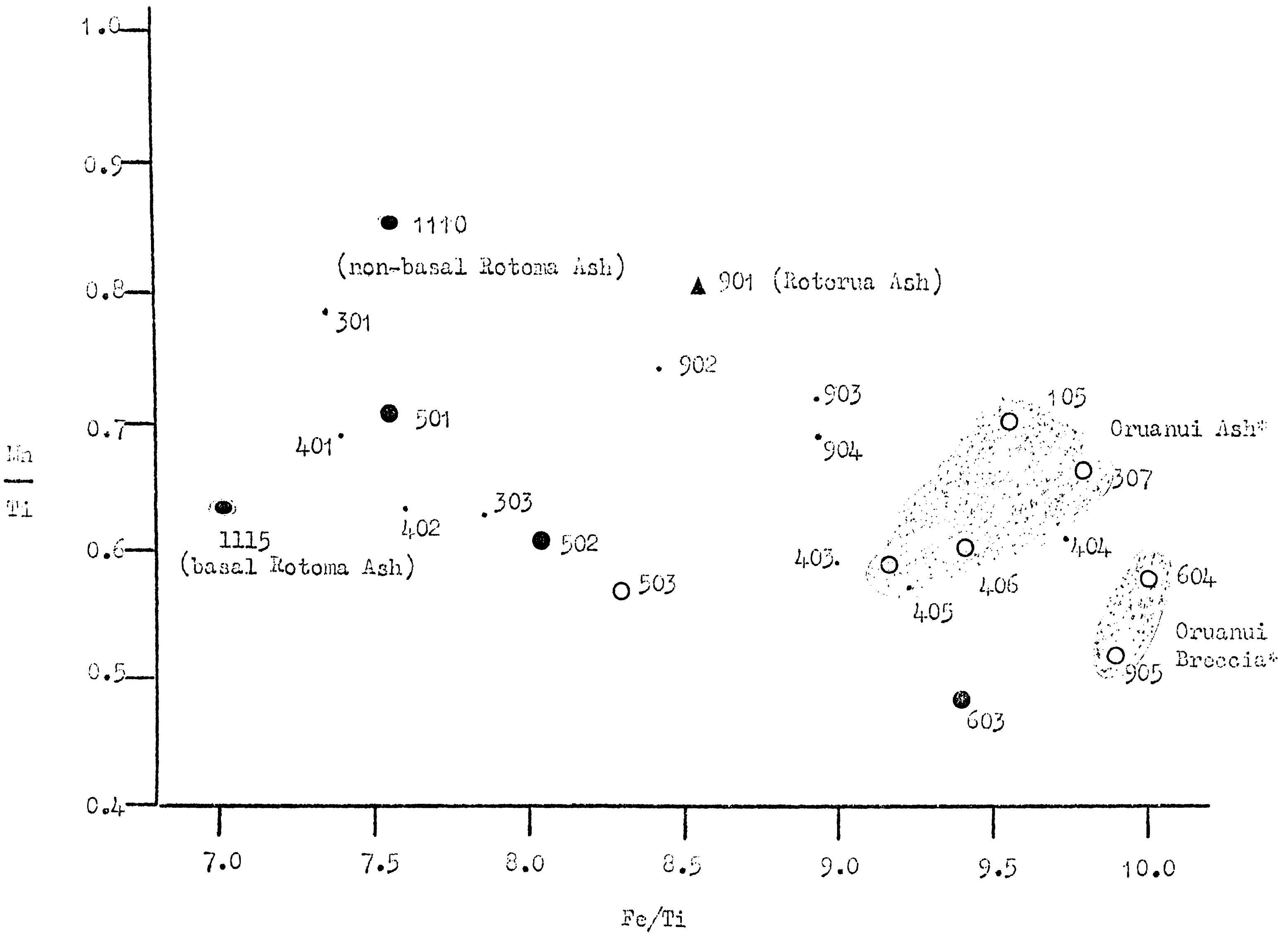
Potassium contents of rhyolitic glasses from sequences of Tirau Ash and Mairoa Ash



Dashed lines are isochrons in thousands of years, based on glass contents of tephras by the method discussed in Chapter 6 and modified in Chapter 9.

FIG. 10.7

Manganese to titanium ratio vs iron to titanium ratio in rhyolitic glasses



(* see Chapter 12)

particular significance that these latter rhyolitic glasses plot in the same area of the diagram as do those of Oruanui Formation: it may be that at least some of the rhyolitic glass accompanying the Mairoa Ash is glass from the Oruanui Formation.

A similar type of field diagram which shows greater separation for different tephras is given in Fig. 1008, where Mn/Fe ratios are plotted as a function of Ca/K ratios. Here it may be seen that there is a satisfactory separation on the diagram of various "pure" glasses. The plotted points of values for the stratigraphic sequences again concur with the correlations previously established. Again, however, the plotted positions for the rhyolitic glasses of the Mairoa Ash and of Oruanui Formation are similar.

From this discussion it may be seen that the major element composition does not make significantly clearer the distinction between the members of the Tirau Ash and Mairoa Ash sequences than has already been achieved, but tends to emphasise further the composite nature of the beds. In that the major elements, being generally geochemically active, are likely to be affected by hydration and leaching properties, any correlation by such elements is likely to be severely hampered. Because of the lower geochemical mobility of certain minor and trace elements, correlation and distinction of glasses may, perhaps, be more readily determined with reference to such elements, and it is to this that attention is now turned.

S10-4: Minor and Trace Elements in Glasses:

The characterisation of obsidian artifacts by x-ray fluorescence with respect to minor elements has recently been described (ANAC, 1974). In the case cited, "fingerprints" were obtained, being intensity versus wavelength plots, and compared. Minor elements found to vary in different obsidians included copper, zinc, arsenic, rubidium, strontium and zirconium. In Table 10-4 are given the concentrations of copper,

FIG. 1008

Manganese to iron ratio vs calcium to potassium ratio in rhyolitic glasses

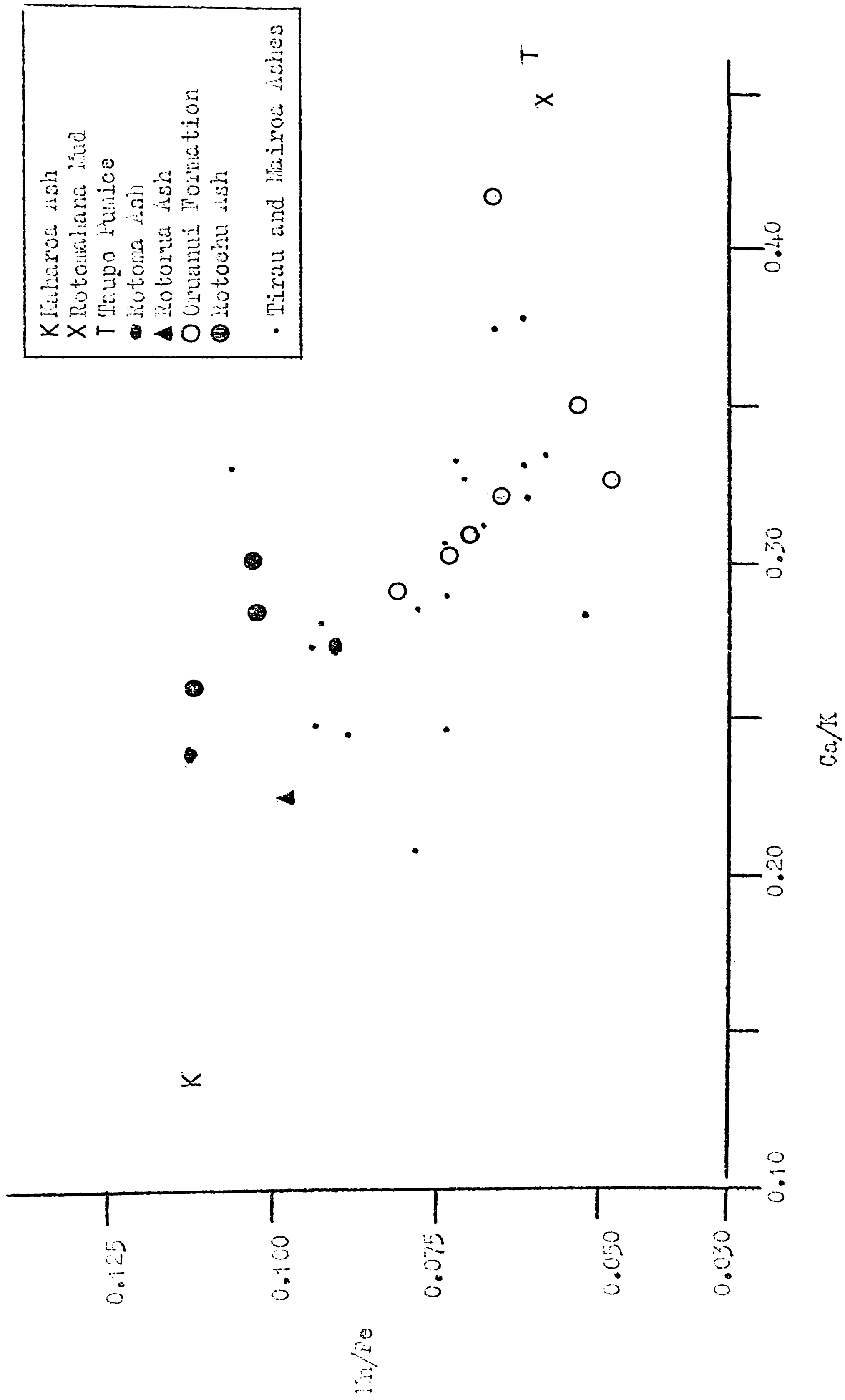


TABLE 10-4: Minor and Trace Elements in Volcanic Glasses.*

Parent Tephra	Sample No.	Element Cu	 Rb	 Sr	 Zr	 Zn	 Cu^+
		Proportion %				Intensity c.p.s.	
Oruanui Ash**	105	0.020	0.025	0.018	0.029	0.1057	9.072
	307	0.022	0.032	0.020	0.036	0	11.8653
	605	0.002	0.018	0.023	0.043	0.350	7.2129
Oruanui Breccia**	905	0.012	0.047	0.023	0.034	1.3432	4.0753
	604	0.007	0.023	0.020	0.030	0	1.3624
Rotoehu Ash	(112	0.025	0.035	0.017	0.020	0	11.297
	(114	0.001	0.034	0.020	0.021	0.1361	0
	(116	0.042	0.066	0.019	0.017	0	15.122
	308	0.214	0.027	0.018	0.021	0	71.0953
	309	0.004	0.030	0.026	0.030	0.3189	3.8012
	409	0.071	0.028	0.028	0.037	0	6.3109
Rotomahana Mud	1101	0.021	0.032	0.025	0.023	0	9.5574
Rotoma Ash	1110	0.009	0.067	0.017	0.026	0.8911	4.1682
Basal Lapilli: Rotoma Ash	1115	0.001	0.043	0.021	0.031	0.5146	0.1224
Rotorua Ash	901	0.001	0.032	0.015	0.030	0.4229	0
Kaharoa Ash	1002	0.019	0.048	0.011	0.012	0	6.6453
Taupo Pumice	1103	0.003	0.047	0.027	0.047	3.0329	0.8600
Mairoa Ash	603	0.053	0.040	0.020	0.023	0	19.2338
Tirau Ash	202	0.090	0.051	0.022	0.033	0	32.5438

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* by wavelength dispersive X.R.F. analysis, concentrations are 1.84 times real values (see Sec. 10-2).

\+ included because negative concentration values sometimes found in analysis for copper.

** These two members make up the Oruanui Formation, see Chapter 12.

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rubidium, strontium, and zirconium, in selected volcanic glasses, together with the intensity of the zinc and copper peaks.

There appears, however, to be a higher content of copper in glasses associated with the Mairoa Ash than is typical for other ashes, although there is considerable variation in copper contents among glasses believed to be correlative. The copper concentrations as the logarithms of peak intensity are plotted on Fig. 1009, and indicates the trend of higher copper for Mairoa glass.

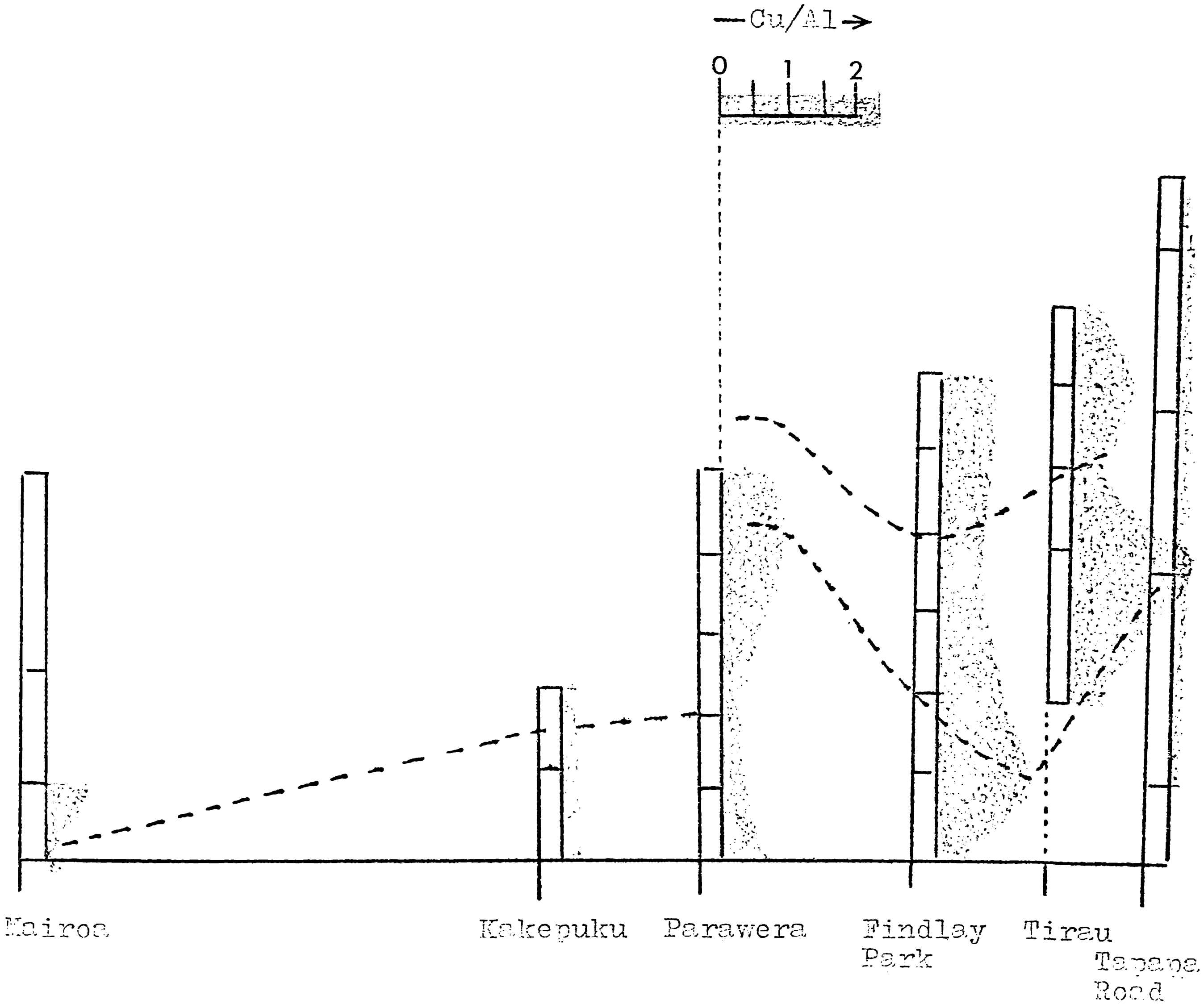
There are minor differences in rubidium and zirconium contents, but no significant variation in strontium levels. A plot of Rb/Sr vs Zr/Sr in glasses of different tephras show some distinction between such tephra (Fig. 1010). Such a plot is less helpful in the case of glasses from the Tirau and Mairoa Ash sequences; for this a plot of Rb/Zr ratio as a function of stratigraphic position is given in Fig. 1011. In Fig. 1011 rubidium to zirconium ratios are plotted as a function of stratigraphic position. As a general rule glasses of the Mairoa Ash sequence are associated with larger values of this ratio than are their Tirau Ash counterparts. Sample 202 of the type Tirau Ash sequence has an anomalously large ratio which is not readily explained.

The plotting of elemental ratios to separate various ash showers on the basis of their trace element composition is not as useful in the problem of the Tirau Ash and Mairoa Ash as might have been hoped on the basis of work on the rare earth components in glass by Rankin (1973) and the elemental composition, particularly of transition metals, in

FIG. 1009

Copper contents of rhyolitic glasses of the Tirau Ash and Mairoa Ash sequences

(Copper contents are expressed as copper to aluminium count ratios determined by X-ray fluorescence techniques)



Tentative correlation on this basis shown as heavy broken lines, viz: - - - -

FIG. 1010

Rubidium to strontium ratio vs zirconium to strontium ratio in rhyolitic glasses

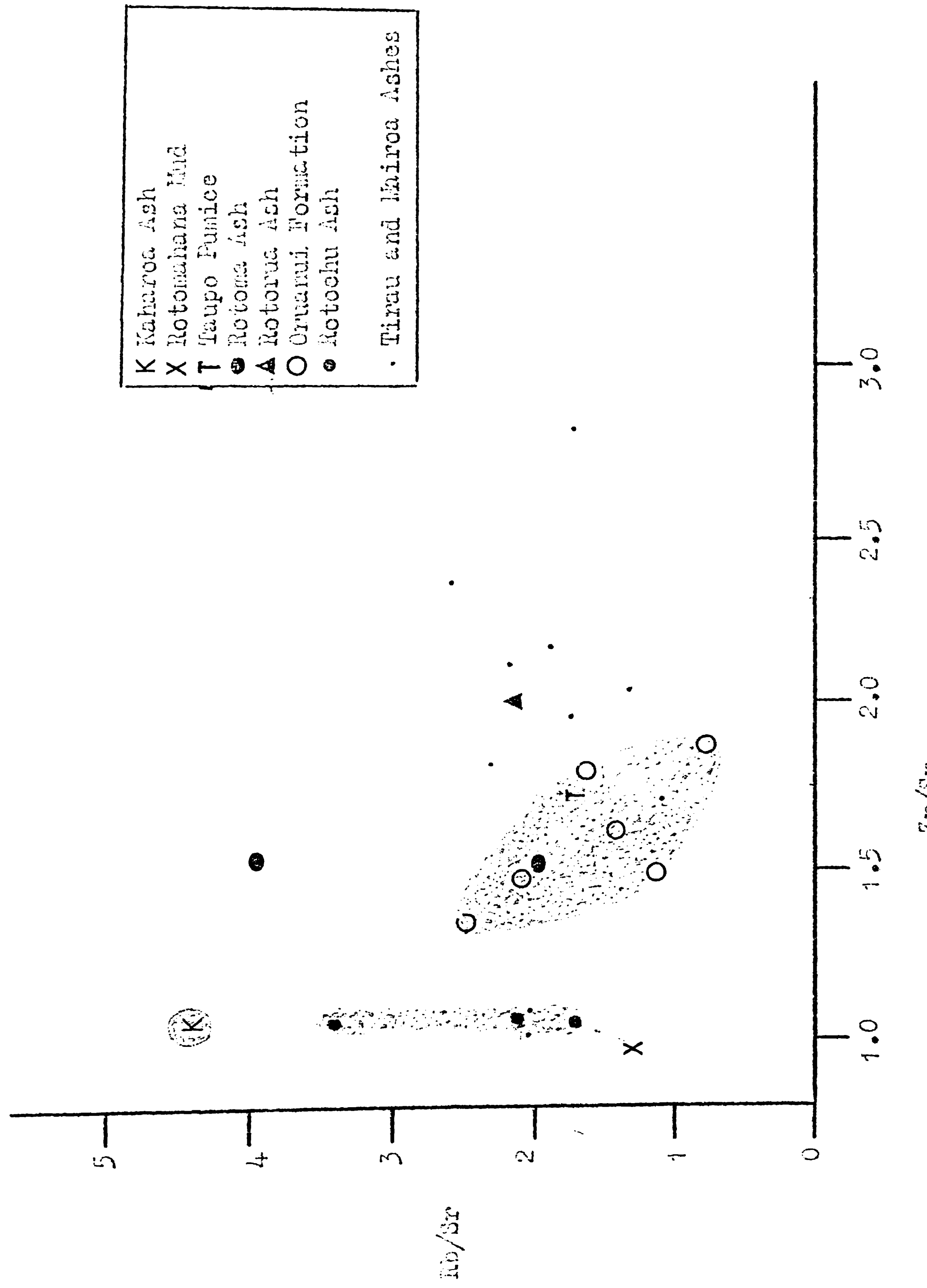
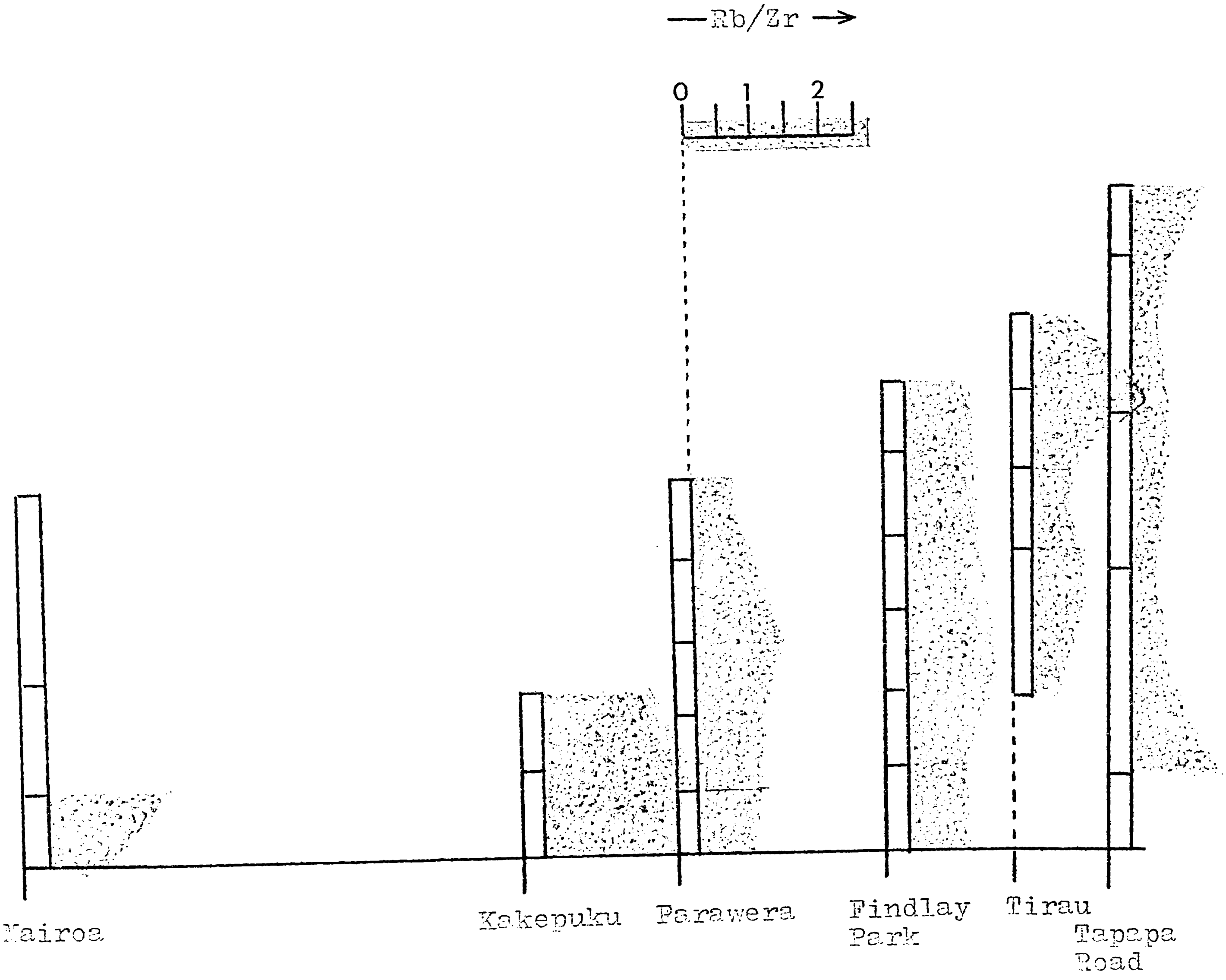


FIG. 10.11

Ratio of rubidium and zirconium contents of rhyolitic glasses from the Tirau Ash and Mairoa Ash sequences



titanomagnetites by Kohn (1970). The difficulty in this probably relates in part to the possibly composite nature of the glasses, their analysis being a bulk one of perhaps vitric components of several eruptive events separated both in place and time, and also to post-depositional effects.

S10-5: The Variation of Chemical Composition within an Eruptive Sequence.

Rankin (1973) has indicated that difficulties may arise in tephra correlation between multi-bedded ashes near the source and singly bedded ashes far from source. Reference to Figs. 1007, 1008 and 1010 indicate that there is, for example, a considerable variation in the ratio for the samples of Rotoehu Ash, which at the site from which samples were taken (Leslie Road) showed a considerable thickness of shower-bedded tephra. Even more noteworthy is the substantial difference in composition between these and the samples recognised as Rotoehu Ash on the basis of their stratigraphy in the Waikato district. It is interesting to compare these results with those for Rb/K and Sr/Ca ratios. These two ratio are expected to vary in the progression of an eruptive sequence. Of rubidium, Mason (1958) writes:

> "The only major element Rb can replace should be K, and this is found to be true. Rubidium forms no minerals of its own, being always incorporated in potassium minerals. Since Rb^+ is considerably larger than K^+, rubidium is admitted into potassium minerals, and accordingly the Rb:K ratio increases with increasing differentiation....."

Rb/K ratios for selected samples from the sequence of Rotoehu Ash sampled at Leslie Road (Hauraki district) are given in Table 10-5, wherein it may be seen that the ratio increases down the sequence. If a gradient exists in the magma chamber such that Rb/K ratios are as Mason (1958) suggests higher at the top than lower down, then if this is ejected from the vent the first deposited material would be expected to have the highest ratio and subsequent deposits to be of lower ratios, and this is the trend observed. Comparison of the ratio with those obtained in the Waikato district suggests that these latter are associated with the later phases of the eruptive sequences, suggesting that the ejectamenta was more widely dispersed for later members of the sequence.

Mason (1958) notes that strontium tends to be admitted in place of calcium, and that its concentration is expected to rise as crystallisation of the magma proceeds. There is also the possibility of strontium being captured by potassium minerals and for this reason the Sr/K ratios are also given in Table 10-5.

TABLE 10-5: Variation of Elemental Concentration Ratios within the Rotoehu Eruptive Sequence.

Sample No.		Rb/K	Sr/Ca	Sr/K
(Leslie Road sequence)	109	0.0052	0.0132	0.0034
	112	0.0074	0.0138	0.0035
	114	0.0074	0.0153	0.0043
	116	0.0147	0.0141	0.0042
(Waikato district)	308	0.0056	0.0131	0.0038
	309	0.0066	0.0149	0.0058
	409	0.0064	0.0137	

The Sr/K ratios vary in similar manner to the Rb/K ratio, although the Sr/Ca ratios differ from the trend expected on the basis of Mason's statement. The identification and correlation of glasses on the basis of strontium contents and ratios between far from source tephras and multi-bedded ashes is not as clear as was the case for rubidium contents and ratios. However, the correlation is undoubtedly assisted by the age trend with potassium contents already noted.

Similar studies on the Oruanui Formation might be expected to give rather less variation in ratios, but the problem here is complicated by there being two members of this formation, whose glass may be intermixed. This problem will be specifically described in Chapter 12.

It appears then that the correlative ability of glass compositions, particularly between glasses observed in singly-bedded deposits and multi-bed deposits, is to some extent dependent on the element or ratios considered. This seems less a problem in comparison between tephra units.

S10-6: Conclusion:

While the value of composition data in the solution of problems in tephrostratigraphy should not be overlooked, neither should the chemical analysis of glass be seen as the solution to all correlation and identification problems. As has been suggested previously correlation appears to be more readily attained between single beds far from source and single beds near to source than of the former with multiple ash beds near to source. This is well-evidenced in the case of Rotoehu Ash, whose composition as a single bed in the Waikato bears a complex relationship to the multi-bedded deposit sampled on the Mamaku Range (Hauraki district). As with other techniques described, the Oruanui Formation marker bed is particularly amenable to correlation, particularly once the two member status of this bed is allowed for.

The chemistry of the glass does not in general offer a satisfactory distinction between the Mairoa Ash and Tirau Ash sequences, the greatest distinction occurring on a plot where the amounts of iron and manganese relative to titanium are compared. Such a plot might suggest that the glasses from Tirau Ash contain more manganese and less iron than do their Mairoa Ash counterparts. It is interesting that there is some suggestion on the basis of chemical data, that the glass of the Mairoa Ash is compositionally similar to that of Oruanui Formation; refractive index data has previously suggested contamination of this kind. For ultimate resolution of this possibility recourse would need to be made to electron microprobe analysis of individual shards. With regard to trace elements there does seem to be a trend for the glasses from Mairoa Ash to have a higher content of copper and rubidium than their Tirau Ash counterparts, which may be due to either a difference in eruption type (primarily andesitic rather then rhyolitic) or to a different stage in magmatic differentiation having been reached at the time of eruption.

Finally, it is to be noted that the idea of the "frozen" nature of glass, as being indicative now of original composition, is probably not justified. There is good evidence for post-depositional loss of potassium by leaching from the glass, and this effect is probably not confined to this element: the variation of silicon content under differing weathering conditions and water contents with age may also be indicative of this. This, combined with the already mentioned difficulties of correlating far from source to near source beds necessitates considerable care being taken in the correlation of tephras by this method. Rather than being seen as a cure-all for all tephrostratigraphic problems, chemical analysis should be seen as one further tool in a series of possibly useful techniques to be applied to a given problem.

PART THREE

APPLICATION OF TECHNIQUES

CHAPTER 11: THE TIRAU AND MAIROA ASHES.

S11-1: Introduction:

Throughout the second part of this thesis, the applicability of the various techniques described have been assessed with particular reference to resolving the problem of whether the Tirau and Mairoa Ash beds are of intrinsically different origin, or whether they merely represent differently weathered products of the same parent material. In this chapter all the information derived about this problem as a result of the investigations of the various techniques will be reviewed in order that the solution to this problem of tephrostratigraphy may be appreciated.

S11-2: Mineralogical Investigations:

The members of these two sequences are allophanic tephra-derived soils at depths of some 30 to 120 cm below the present ground surface. The samples taken of these sequences from various localities were first ultrasonically cleaned to separate the clay minerals from the primary mineral grains. The yield of mineral grains was higher for samples believed to be representative of the Mairoa Ash sequence than those of Tirau Ash; this being surprising in view of the fact that the Mairoa Ash occurs typically in regions of higher rainfall (being at higher altitude) than does Tirau Ash. This observation, although of itself possibly specious, was, however, suggestive that the weathering of different ash types might be involved.

The material recovered from the ultrasonic cleaning, effectively a "sand fraction," was examined, particular attention being paid to the vitreous components. This, together with consideration of the relative proportions of quartz and feldspar, suggested that the Mairoa Ash sequence might have an appreciable andesitic component while the Tirau Ash sequence was primarily rhyolitic. Quantitative infra-red studies established both the presence and proportion of andesitic glass, and enabled the assignment of "rhyolitic parameter" having its basis in the ratio of rhyolitic to andesitic glass. The overall effect (shown in Figs. 506 and 1101) was that samples recognised in the field as Mairoa Ash had low values of the rhyolitic parameter (α) whereas those recognised as Tirau Ash are characterised by higher values.

From this information, estimates of the initial amounts of glass in ashes for various values of the rhyolitic parameter, and some indication as to the probable variation of weathering rate with time the tephra residua may be dated. In so doing, the implicit assumption is made that the weathering rates of andesitic and rhyolitic glasses are comparable. On this basis, the deposition of Tirau Ash would appear to cover the period from about 10 - 15 thousand years ago, being underlain by Mairoa Ash which has Oruanui Formation as its lower bound. At Mairoa itself the dates indicated for the Mairoa Ash, appeared older than for this tephra dated at other sites. While this could be attributed to the erosion of the upper members, the thickness of ash deposited at Mairoa is actually greater than that which might be expected on the basis of the extrapolation of isopach data. Studies of the refractive index of the rhyolitic glass indicate that a significant proportion is the same as the Oruanui glass. Corrections for this accretion reduces the ages of the top and base of the Mairoa Ash to 14 and 17 thousand years respectively.

By comparing these tentatively assigned dates of the sequences, with the known dates of tephras originating from the Egmont and Okataina volcanic centres, the principal component of the Tirau Ash sequence would seem to be the Rotorua and Rerewhakaiitu Ash, and possibly Rotoma Ash, and for the Mairoa Ash, at least a portion of the Egmont-derived Oakura and Okato tephras.

FIG. 1101

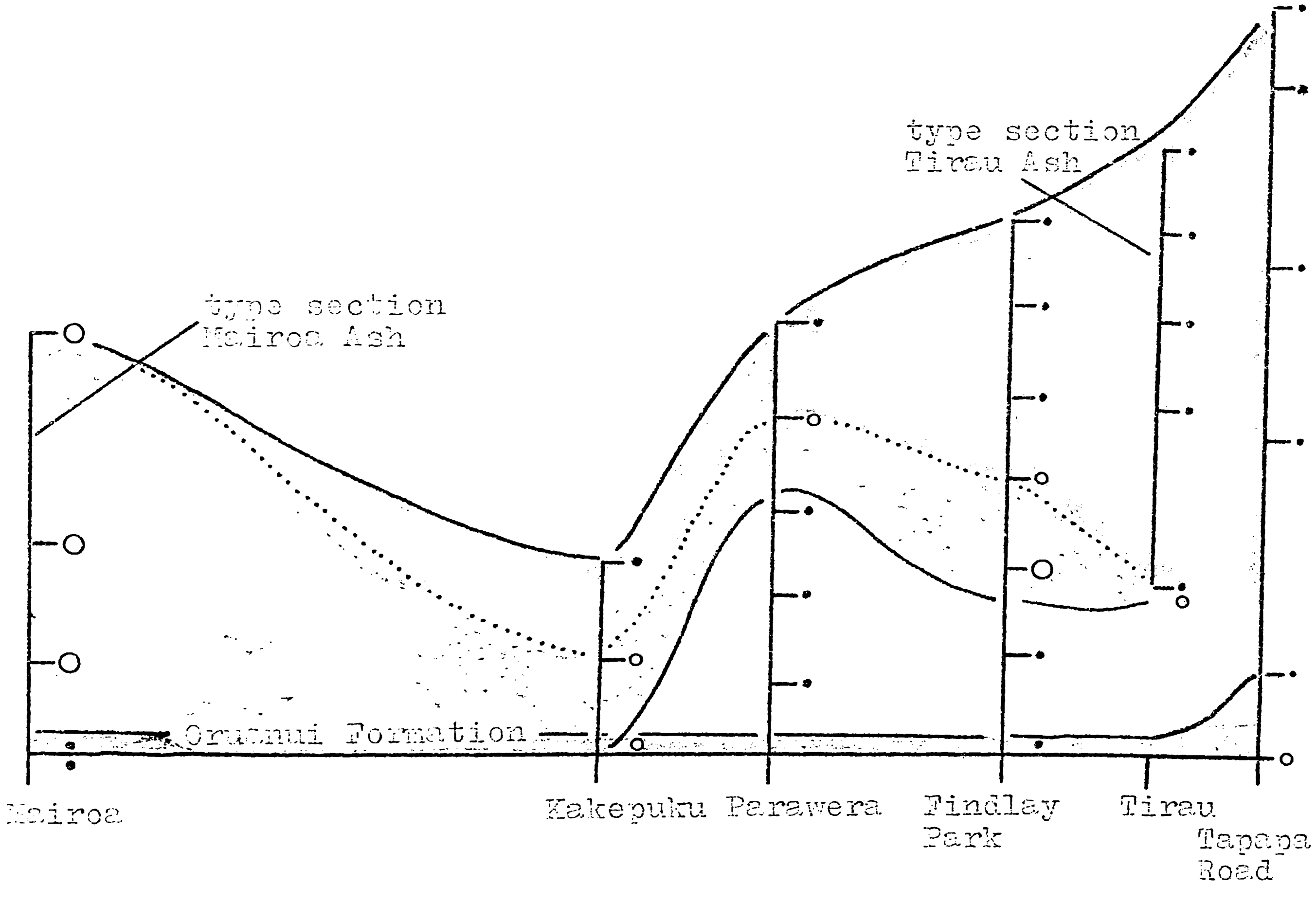
Distribution of Tirau and Mairoa Ashes on the basis of the rhyolitic character of the tephra

Rhyolitic character

0 - 0.25 andesitic
◯ 0.25 - 0.50
○ 0.50 - 0.75
• 0.75 - 1 rhyolitic

Tephra identified, on basis of character, as:

░ Tirau Ash
▒ Mairoa Ash
☐ late Pleistocene tephras (Te Rere Ash, Okaroka Ash)



S11-3: Results from Physico-Chemical Parameters and Chemical Analysis:

Mention has already been made of the difficulties encountered by dating techniques because of the differing effects of weathering of different samples at various sites. This has some effect on the chemical composition of the glass associated with the ash, and has, therefore, also affected the attendant properties of refractive index, density, and magnetic susceptibility. As far as the density of glass was concerned, the natural variation in the glass (as evidenced by the width of the bands in the density gradient columns) exceeded the differences between samples. However the densities of glasses from both sequences were slightly higher than that of the glass from the underlying Oruanui Formation, suggestive of a difference in composition.

For refractive index, the natural variation was less than the difference between the various samples: the rhyolitic glasses associated with Mairoa Ash generally had lower refractive indices than did the glass of Tirau Ash. In that the water contents, evaluated indirectly from the difference between the "wet" refractive index measured and a "dry" value obtained from the ferrous contents of the glass (itself determined from magnetic susceptibility measurements) are very similar, this difference in refractive index presumably represents a difference in chemical composition. The glasses of the Tirau Ash sequence have similar refractive indices to the glasses of Rotoma and Rotorua Ashes and of Oruanui Formation, so that, although the refractive index techniques are able to distinguish the Mairoa Ash and Tirau Ash glasses, there are difficulties in relating these glasses to possible parent materials on this basis. One further point of interest in refractive index measurements is the observation of there being two rhyolitic glasses associated with the Mairoa Ash at Mairoa itself, one of low refractive index, and the other of refractive index more typical of Oruanui Formation and other rhyolitic tephras. This is clear evidence of the contemporaneous incorporation of ejectamenta from at least two eruptive events or sources, of which Oruanui Formation would appear to be one and Mairoa Ash the other, or alternatively of re-working of the material to include previously deposited material. Trends in elemental ratios and concentrations are also suggestive of these possibilities.

The inter-relationships on the basis of magnetic susceptibilities (to give ferrous contents) and ferrous to ferric ratios are difficult to evaluate. In general terms, the ferrous to ferric ratio is lower in Mairoa Ash's rhyolitic glass than in that of Tirau Ash, although the total iron content of Mairoa glasses is greater. The position is complicated by the geochemical mobility of iron. Geochemical mobility is a problem that besets the use of chemical analysis in tephrostratigraphy: the chemical composition data clearly shows that in tephra exposed to and incorporated in the soil-forming process, the volcanic glass that remains may be significantly different in composition from what it was originally. For this reason, chemical data may be no more useful in tephrostratigraphic correlation than mineral assemblages and physico-chemical parameters. In the case of the Tirau and Mairoa Ashes such data plays a confirmatory rather than an initiating role in their identification and correlation.

S11-4: Distribution of the Tirau and Mairoa Ashes:

Having demonstrated clear differences between the two tephra sequences and attributed them to different sources, it is of interest to ascertain their distribution across the Waikato region. In Fig. 1101 is shown a distribution plot based on the rhyolitic parameter. As has been mentioned, low values of this parameter indicate andesitic accretion, high values indicate an ash of rhyolitic character. The plot clearly shows that the andesitic Mairoa Ash underlies the more rhyolitic Tirau Ash at least as far east as Findlay Park and possibly is represented at Tirau itself. At these more eastern sites the marker bed (Oruanui Formation) is separated from the Mairoa Ash by primarily rhyolitic material that probably is representative of the Okareka Ash and Te Rere Ash. The trends in refractive index lead to similar stratigraphic assignments as is shown in Fig. 1102. Low refractive indices are considered indicative of Mairoa Ash. Not unexpectedly the refractive index is higher in the eastern sites; it may be inferred that there is some mixing of the glass of the thinly bedded Mairoa Ash with glass of the Pleistocene beds referred to above.

This problem of the intermingling of glasses causes uncertainties in correlation by chemical composition. However it is possible to gain some information about the tephra distribution on the basis of element concentration profiles. Glass extracted from the middle of the Mairoa Ash sequence seems to be rather lower in manganese than the upper and lower members and this minimum in the profile can be traced throughout the distribution of the tephra, as is shown in Fig. 1103. The distribution of the two tephras can thus be traced by a number of methods, but it would seem that the most consistent are those that rely on the variation of tephra type, as evidenced by the rhyolitic parameter and the refractive index, rather than by the small variations in chemical composition.

Electron microprobe studies on individual glass shards, rather than bulk analysis would enable an assessment of the amount of intermixing of glasses derived from the various tephra, and thus perhaps permit a more accurate distribution to be compiled. In addition, for reasons outlined earlier, such a method might enable better correlation of the glasses with proposed parent materials. There is reason for optimism in this regard, in that refractive index studies were capable of resolving two glasses in a mixture in the Mairoa Ash after determining the indices on a mere ten shards (see Sec. 9-7).

S11-5: Conclusion:

The problem of the identity of Tirau and Mairoa Ashes which has

FIG. 1102

Distribution of Tirau and Mairoa Ashes on the basis of refractive index of rhyolitic glass

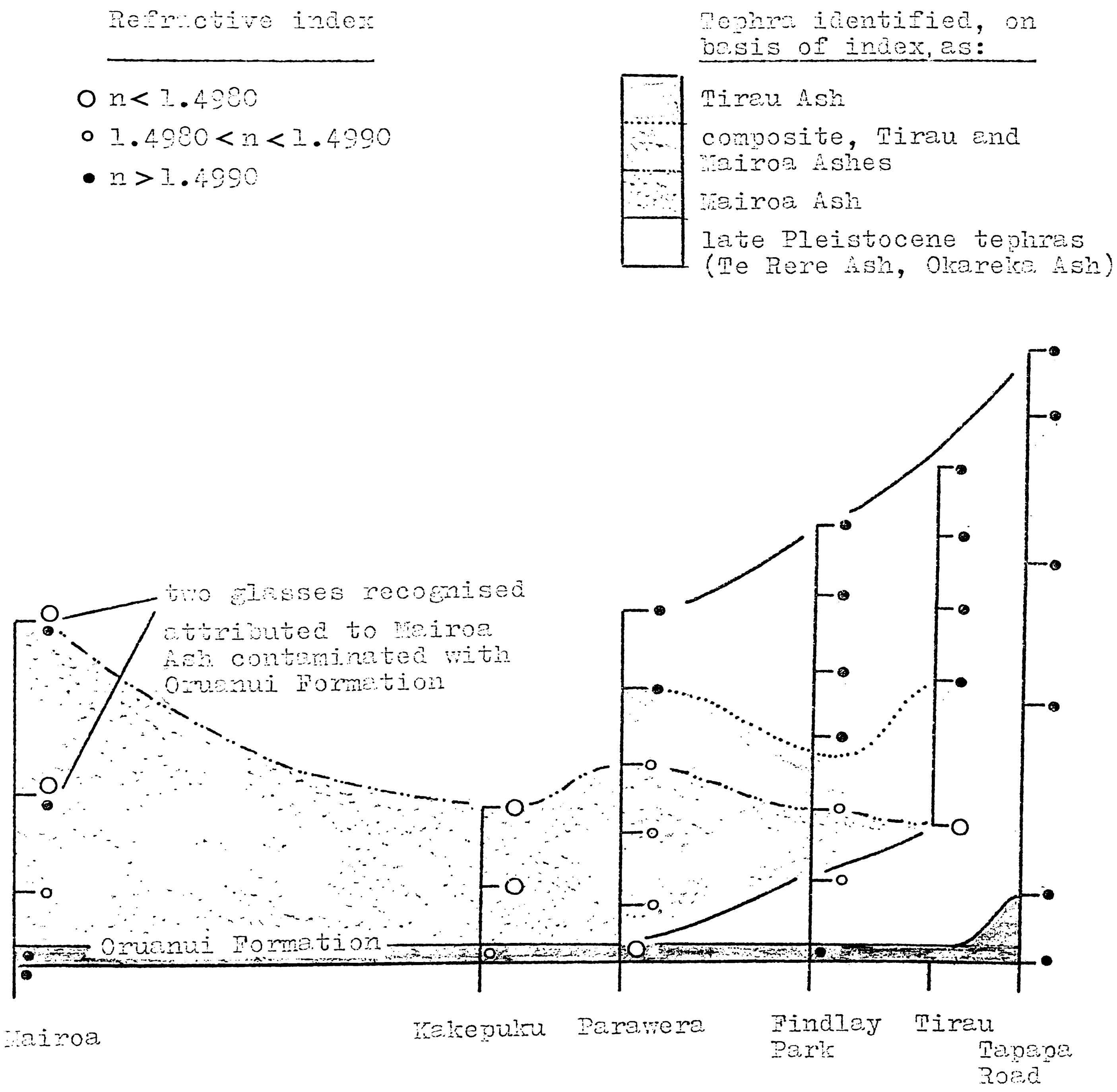
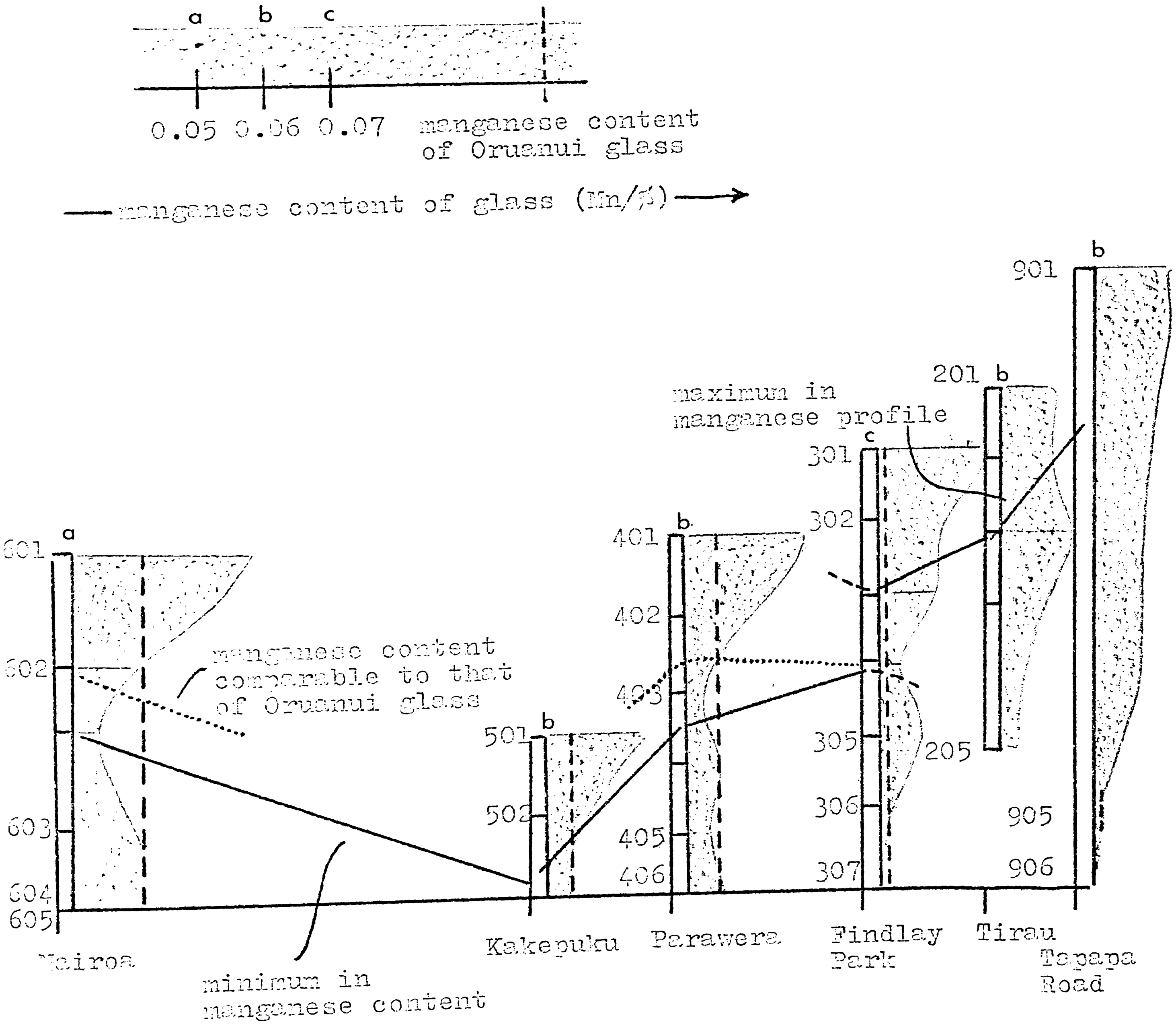


FIG. 110B

Stratigraphic variation of manganese contents of rhyolitic glasses in sequences of Tirau and Mairoa Ashes



been debated by New Zealand tephrostratigraphers for many years would appear to be resolved by the application of chemical and particularly physico-chemical techniques. Laboratory studies indicate mineralogical differences, and differences in the vitreous components that suggest that the Mairoa Ash is of primarily andesitic origin whereas the Tirau Ash is primarily rhyolitic. The rhyolitic glasses associated with the deposits were examined, and there were found to be differences in refractive index and chemical composition, although the usefulness of these techniques was hampered by the possible influence on bulk properties of there being more than one glass present. These differences were consistent with different glasses being primarily responsible for the two sequences. Crude methods of dating by glass contents suggested that the Mairoa Ash sequence was older than Tirau Ash. In that the former sequence appears to be contaminated with Oruanui Formation, which underlies the sequences, the ages of the Mairoa Ash sequence, particularly at Mairoa itself may be over-estimated. If this is not the case, then the upper members of the Mairoa Ash are not represented at Mairoa. This is unlikely if Egmont is considered to be a significant source of this material, and this provides indirect evidence for the inclusion of glass within the Mairoa deposit that was not deposited contemporaneously.

The probable parent materials have been proposed on the basis of these derived dates. Because the Tirau and Mairoa Ashes appear to represent the margins of several shower-bedded tephras, accurate correlation with parent materials would need to be effected by the use of electron microprobe studies on individual shards.

CHAPTER 12: THE DISTRIBUTION OF ORUANUI FORMATION:

S12-1: Introduction:

The Oruanui Formation, as has been earlier mentioned, is rhyolitic tephra units, characteristically little weathered, that is recognisable over a large portion of the northern half of the North Island. Attributed to a source near Taupo, the deposit has been dated by radiocarbon methods at twenty thousand years, and forms a convenient marker bed beneath the Tirau and Mairoa Ashes in the Waikato-Hauraki region. Two members are frequently recognised: a lapilli breccia (Oruanui Breccia Member) and an underlying chalazoidite-bearing (Oruanui Ash)unit. There appears, on the basis of radiometric dates, to be little time interval between the deposition of these members and it would seem that the deposition of the formation occurred in two principal events. Beds of similar appearance to the lower of these units have been described in the Manawatu district, and as far south as North Canterbury. This chapter explores the possibility of these latter occurrences being Oruanui Ash. The techniques described in this thesis have so far been used in the solution of a problem where the beds were at considerable distance from source and the stratigraphic relationships were uncertain. In the present case, the tephrostratigraphy is clear, in that the bed to be examined is clearly different from surrounding material, but the distance over which correlation is to be attempted is considerably greater, and spans widely differing climatic and weathering regimes. It has already been noted that the glass of the Oruanui Formation is chemically distinctive, but nevertheless the problems of correlation with parameters that vary with the geochemical mobility of elements in response to weathering may be expected to be the principal difficulty in such long-range stratigraphy.

S12-2: Correlation of Oruanui Ash - Previous Work:

Mention has been made in an early chapter of the white or pale yellow lapilli beds of Oruanui Ash which are found in the northern half of the North Island. Because of its use as a marker bed, it has been dated at many localities and found to be of age 20,000 years, and this, together with its remarkable appearance and the frequent occurrence of chalazoidites virtually confirms its identification. In the Manawatu district (Fig. 1201) a similar ash interbedded with loess has been described by Cowie (1964) and Rhea (1968) pointed to the Taupo volcanic centre as the source, although there was no real evidence for his proposal:

> "The Taupo-Rotorua volcanic district 100 miles to the north, is the most probable source of the ash, but the erratic thicknesses and the indefinite upper boundary of the ash preclude a determination of origin from the direction of thickening."

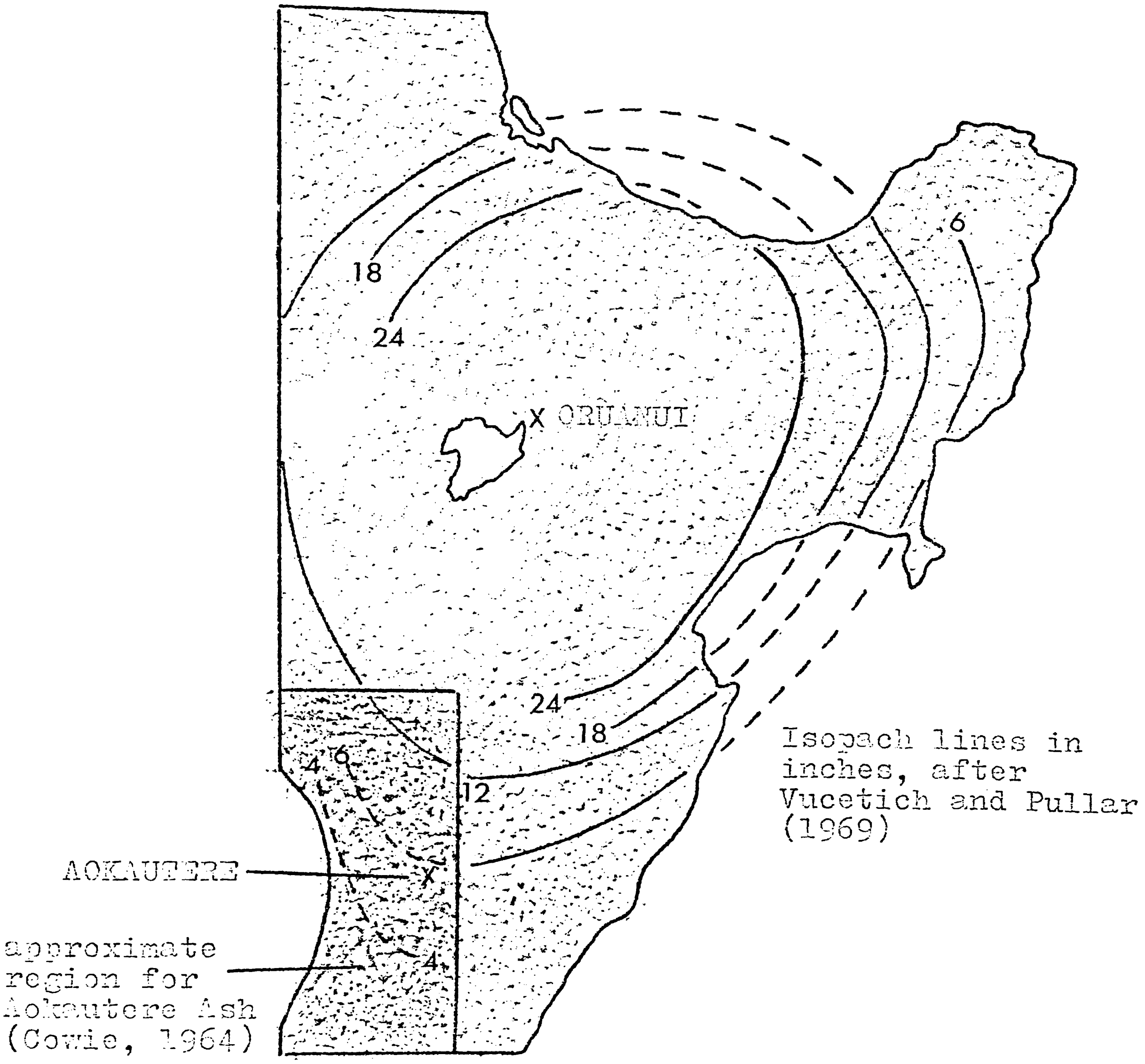
Nevertheless, Vucetich and Pullar (1969) proposed a correlation with Oruanui Ash:

> "The lowest shower-bedded ash and ash-lapilli of the Oruanui Ash, totalling 60 in. (150 cm) in thickness at the type section (of Oruanui Formation) are provisionally correlated with Aokautere Ash in the Manawatu district. If this correlation is sustained the Oruanui Ash Member will be redefined: the name Aokautere Ash to apply to the basal shower beds and Oruanui Ash to comprise the chalazoidite ash bed."

Recently Rankin (1973) has studied the trace element composition of selected glasses, of which glasses from Oruanui Ash and Aokautere Ash were two, and concluded that these two were in fact identical. However the Oruanui Formation is composed of two members which Rankin assumed had the same chemical properties. From data already presented (in Table 10-3 for example) there are differences here that may be helpful in determining the distribution and perhaps giving some insight into the eruptive history of this deposit, and thus a further examination of the Oruanui Formation and Aokautere Ash may be useful.

FIG. 1201

Distribution of Aokautere Ash and its relationship to the Oruanui Formation



In addition to this, some anomalously thick deposits of material near Mairoa have been tentatively suggested to be Oruanui Ash (Gibbs, pers. comm.). The deposit here is rather thicker than might be expected at this distance from the source, and is a massive bed, and differs in appearance from the Oruanui Ash, identified at Mairoa as underlying the Mairoa Ash. As an ultimate test to any correlating technique, Vucetich (pers. comm.) has suggested that Teviotdale Ash, found in North Canterbury in the South Island of New Zealand might also be correlative with Oruanui Ash. The field and site data for these samples are given in Table 12-1.

TABLE 12-1: Field and Site Data for Tephra Deposits possibly Correlative with Oruanui Formation.

		Sample			
		Aokautere Ash	Teviotdale Ash	Oruanui Ash	Oruanui Formation(1)
Sample No.		1701	1801	801(2)	905, 906
Site	Locality	Aokautere	Amberley	Hauturu Road	Tapapa Road
	District	Manawatu	North Canterbury	King Country	Hauraki
CLIMATIC DATA:				(3)	(4)
Nearest climate station		Palmerston North	Ashley Forest		
Rainfall		92 cm	88 cm		
Potential evapotrans-piration		68 cm	65 cm		
Infiltration		24 cm	23 cm		
Rate Constant(5)		0.02	0.02	0.12	0.13

(1) included for comparison.
(2) Plate 121
(3) Rate constant taken as that at Mairoa, see Table 6-7.
(4) See Table 6-7.
(5) Evaluated from infiltration vs rate constant data of Ruxton (1968) Fig. 606.

PLATE 121

Oruanui Ash in the King Country

Site 8: Hauturu Road

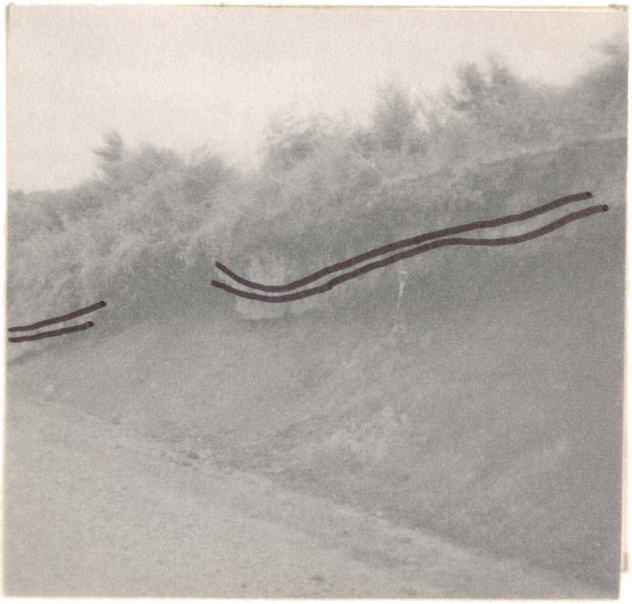


PLATE 121

Oruanui Ash in the King Country

Site 8: Hauturu Road

The next sections seek to ascertain whether the tephra are correlative, firstly on the basis of glass contents, then on the basis of the physico-chemical parameters described earlier, and finally on the basis of composition data.

S12-3: The Glass Contents of the Members of Oruanui Formation and Postulated Correlative Tephras.

It has been previously noted that the glass contents of the members of the Oruanui Formation are higher than would be expected from the deposit's age. The glass contents of the whole member, and of the "sand fraction" resulting from ultrasonic cleaning are given in Table 12-2. On this table it may be seen, not only that the glass contents are high but that those of the upper members are higher than those lower in the sequence in the eastern Waikato district (samples 905, 906). Vucetich and Pullar (1969) have suggested that the upper member (Oruanui Breccia Member), having a similar distribution to the Taupo Pumice Formation, might have resulted from a "nuee ardente" type of eruption. The rapid burial of the underlying Oruanui Ash Member by this means could well account for the Ash Member itself having a higher glass content than would be expected for a rhyolitic tephra on the criterion of age. In other localities the Oruanui Ash has been suggested as being protected from weathering by previous and subsequent accumulations of loess.

The Taupo Pumice Formation contains presently about 80% rhyolitic glass in sections protected from rigorous weathering (Ewart, 1963). If plots of the proportion of glass remaining versus the proportion of clay for the samples are considered, using the Taupo Pumice Formation as indicative of an ignimbrite ("nuee ardente" eruption type) as is shown in Fig. 1202, it may be observed that some of the identified exposures of Oruanui Formation are more akin to ignimbrites than to rhyolitic tephra. The diagram also indicates that certain exposures of Oruanui Ash are contaminated by andesitic accretions, since they lie rather closer to the field for andesitic tephra than might be expected. It

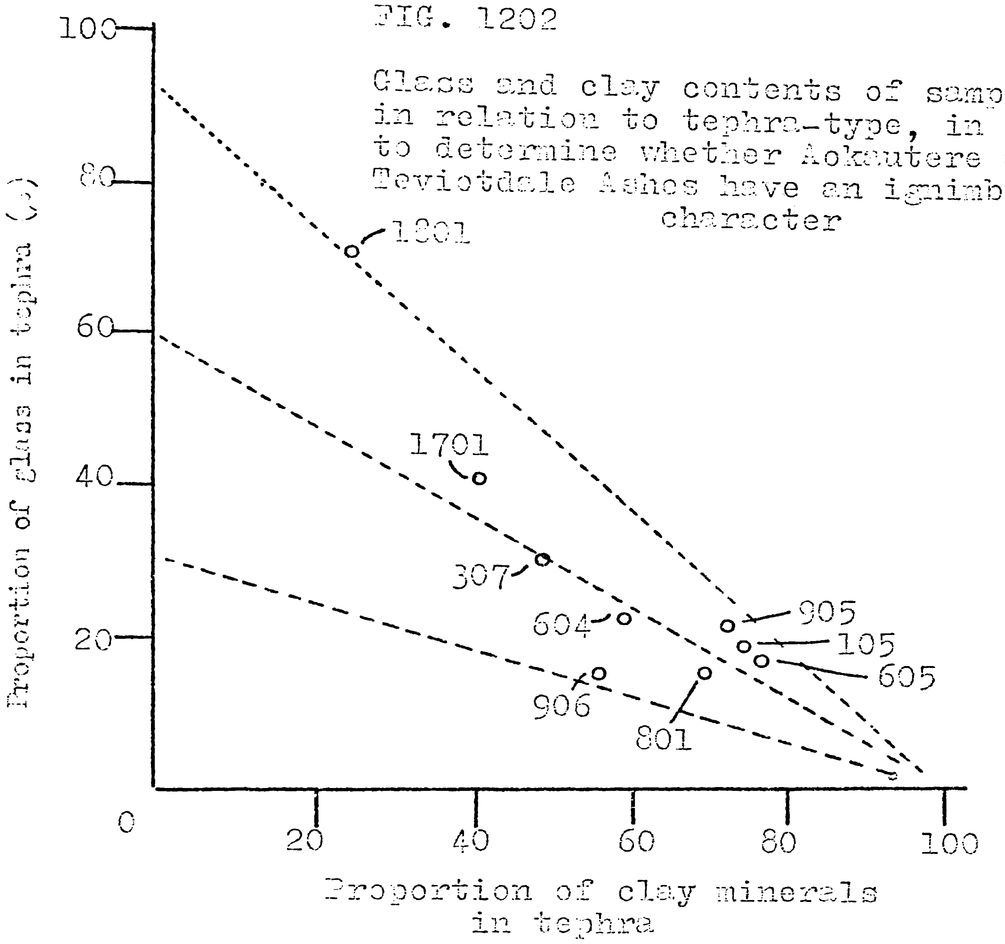
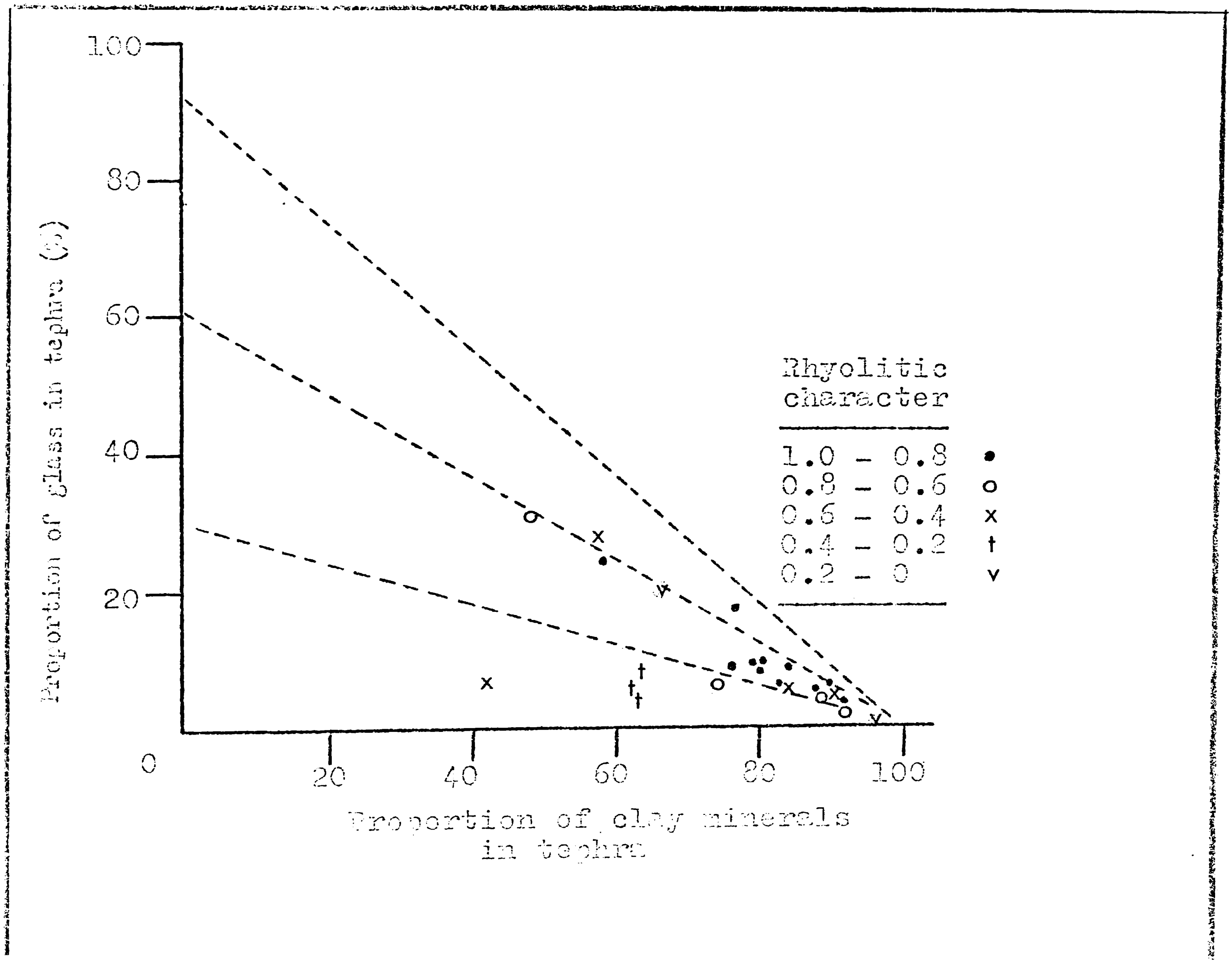


FIG. 1202

Glass and clay contents of samples in relation to tephra-type, in order to determine whether Aokautere and Teviotdale Ashes have an ignimbritic character



is also noteworthy that the Aokautere Ash and even more markedly, the Teviotdale Ash plot in the ignimbrite field of Fig. 1202.

TABLE 12-2: Glass and Clay Contents for Tephra Deposits possibly Correlative with Oruanui Formation.

Tephra (Locality)	Sample No.	Clay Content (1) (%)	Glass Content of sand (2) (%)	Glass Content of Whole Sample (%)
Oruanui Formation	105	74	72.5	19
Mamaku Plateau (Hauraki district)	905	72	78	22
	906	55	32.8	15
Oruanui Formation	307	48	45.8	24
(King Country and Waikato districts)	604	58	56.5	23.6
	605	76	70	15.7
Oruanui Ash (King Country)	801	69	48	15
Aokautere Ash (Manawatu)	1701	40	68	41
Teviotdale Ash (Canterbury)	1801	24	94	71

(1) being the proportion weight loss on ultrasonic cleaning.

(2) The "sand" taken to be the material recovered after ultrasonic cleaning.

The precision of assignments of tephra character from a diagram such as Fig. 1202 is no greater than the worth of the assumption that the clay content of the sample is the weight loss on ultrasonic cleaning. The empirical justification of the diagram is shown in the inset of Fig. 1202: samples of α-values corresponding to rhyolitic and andesitic tephra plotting into the appropriate fields of Fig. 1202. This diagram makes the implicit assumption of a similar mode of soil formation: for all samples except Aokautere and Teviotdale Ashes the resulting soils are yellow brown earths and yellow brown pumice soils, and this may affect the validity of Fig. 1202 for these latter Ashes. Further, such a plot makes the implicit assumption that the clay content is derived solely from the glass, which although substantially true for samples of rhyolitic origin, is not quite as valid for those of andesitic origin, and certainly questionable for mixtures of volcanic ejectamenta and other sedimentary material as may be the case for the samples of Aokautere and Teviotdale Ashes.

An alternative method of establishing the nature of the eruptive deposit is by the kinetic interpretation of glass contents as described in Chapter 6. For the present purpose, however, an age of 20,000 years may be assumed, and the mean rate constant over the period established. When, for example, sample 905 is considered to be ignimbritic and sample 906 is considered to be a rhyolitic tephra, the same rate constant is obtained, thereby attesting to the worth of the identification of the former as the Oruanui Breccia Member and the latter as the Oruanui Ash Member. Since sample 105 is from a nearby locality a similar rate constant would be expected, and is indeed obtained if the sample is considered to be a rhyolitic tephra. By determining the ratio of the rate constant over the past twenty thousand years to the present-day rate constant, a parameter is obtained that is site-independent, provided that the post-Oruanui Formation history is similar at the sites under consideration, and enables the rate constant data to be compared for different sites. This data is given in Table 12-3.

The results from this table suggest that the Oruanui Breccia Member may overlie the Oruanui Ash Member at least as far west as Mairoa, although its distribution here is indistinct, since the sample 801 from a nearby locality appears to be the ash-member, if the climatic regimes at Mairoa and Hauturu Road are similar. Typically the ratio of the

TABLE 12-3: Evaluation of Mean Rate Constants since Deposition of Oruanui Formation from Glass Contents in Whole Member and Relationship with Present-Day Constants based on Estimates of Infiltration.

Sample No.	Member Status[(a)]		Glass Content		Rate Constants		Ratio of rate[(e)] constants k_{20}/k_c	
	Assigned in field	Assigned for calculation	$C_o^{(b)}$ %	C %	$k_{20}^{(c)}$	$k_c^{(d)}$	B	A
Eastern Hauraki District -								
105	A	B (f) A	90 60	19	0.079 0.058	0.18	0.44	0.33
905	B	B A (f)	90 60	22	0.072 0.050	0.18	0.36	0.28
906	A	B (f) A	90 60	15	0.091 0.069	0.18	0.51	0.39
Mairoa District (King Country)-								
604	A?	B A	90 60	23.6	0.068 0.047	0.16	0.42	0.29
605	A	A	60	15.7	0.067	0.16		0.42

TABLE 12-3: continued

Sample No.	Member Status[(a)]		Glass Content		Rate Constants		Ratio of rate constants k_{20}/k_c[(e)]	
	Assigned in field	Assigned for calculation	C_o[(b)] %	C %	k_{20}[(c)]	k_c[(d)]	B	A
801	(F)	B	90	15	0.091	0.13	0.69	0.53
		A	60		0.069			
Waikato District - 307		B	90	24	0.067	0.06		0.75
		A	60		0.045			

At this locality the Oruanui Formation has a significant andesitic component in that [illegible] = 0.77.

This affects the estimated value of C_o, and hence:-

Sample No.	Assigned in field	Assigned for calculation	C_o %	C %	k_{20}	k_c	B	A
307		B	71	24	0.054	0.06		0.56
		A	46		0.033			
Long range tephrostratigraphy - 1701 (Aokautere Ash)	(F)	B	90	41	0.040	0.02	0.50	*ca* 1.0
		A	60		0.019			

TABLE 12-3: continued:

Sample No.	Member Status(a)		Glass Content		Rate Constants		Ratio of rate constants k_{20}/k_c (e)	
	Assigned in field	Assigned for calculation	C_o (b) %	C %	k_{20} (c)	k_c (d)	B	A
1801 (Teviotdale Ash)	(F)	B A	90 60	71	0.013 -	0.02	0.65	-

(a) A represents Oruanui Ash Member, B the Oruanui Breccia Member, (F) indicates that correlation with Oruanui Formation in doubt as well as member status.

(b) for rhyolitic tephra C_o = 60% after Fieldes and Weatherhead (1968), for rhyolitic breccia, C_o = 90% after Ewart (1963) for Taupō Pumice.

(c) mean rate constant over last 20,000 years.

(d) rate constant based on infiltration estimates (see Chapter 6).

(e) member correlation on basis of similarity of ratio indicated by shading thus: ▨

(f) included for comparison, although member status certain.

derived rate constant to the present-day (climate-derived) rate constant is about 0.4 for the sites at higher altitude and a little higher for the lowland sample. This suggests a basically similar post-depositional history at all Waikato sites.*

If the Aokautere ash is correlated with Oruanui Breccia, then the ratio would appear to agree well with the Oruanui Breccia and Oruanui Ash sampled in the Waikato. However the tentative correlation on field evidence is of Aokautere Ash with Oruanui Ash (Vucetich and Pullar 1969). Under these conditions the ratio value obtained for sample 1701 is lower than expected, but this may reflect a protected weathering environment since in many localities Aokautere Ash is underlain and overlain by and interbedded with loess (Cowie, 1964).

From these results it appears that Aokautere Ash has been better preserved than Oruanui Ash, as indicated by the glass contents and derived rate constants. It is interesting to compare this result with the conclusion reached by Birrell and Pullar (1973) using Tamm's reagent as an indicator of weathering extent:

> "Few sites have been found where Oruanui Ash appears to have been exposed to weathering for a long period of time, as it was generally covered with loess before Holocene tephras fell on the surface. However, the very low Tamm-extractable aluminium and iron values for (a) sample ..... from a site where no loess cover is apparent and the similarly low levels of the values at all other sites, suggest that both Oruanui and Aokautere tephras are indeed only very weakly weathered."

---

* It will be recalled from Chapter 1 that the lowest of the Tirau and Mairoa sequence that mantle Oruanui Formation in the Waikato are considered to have been deposited nearly contemporaneously.

S12-4: Chemistry of Glass of Oruanui Formation and Proposed Correlative Tephra.

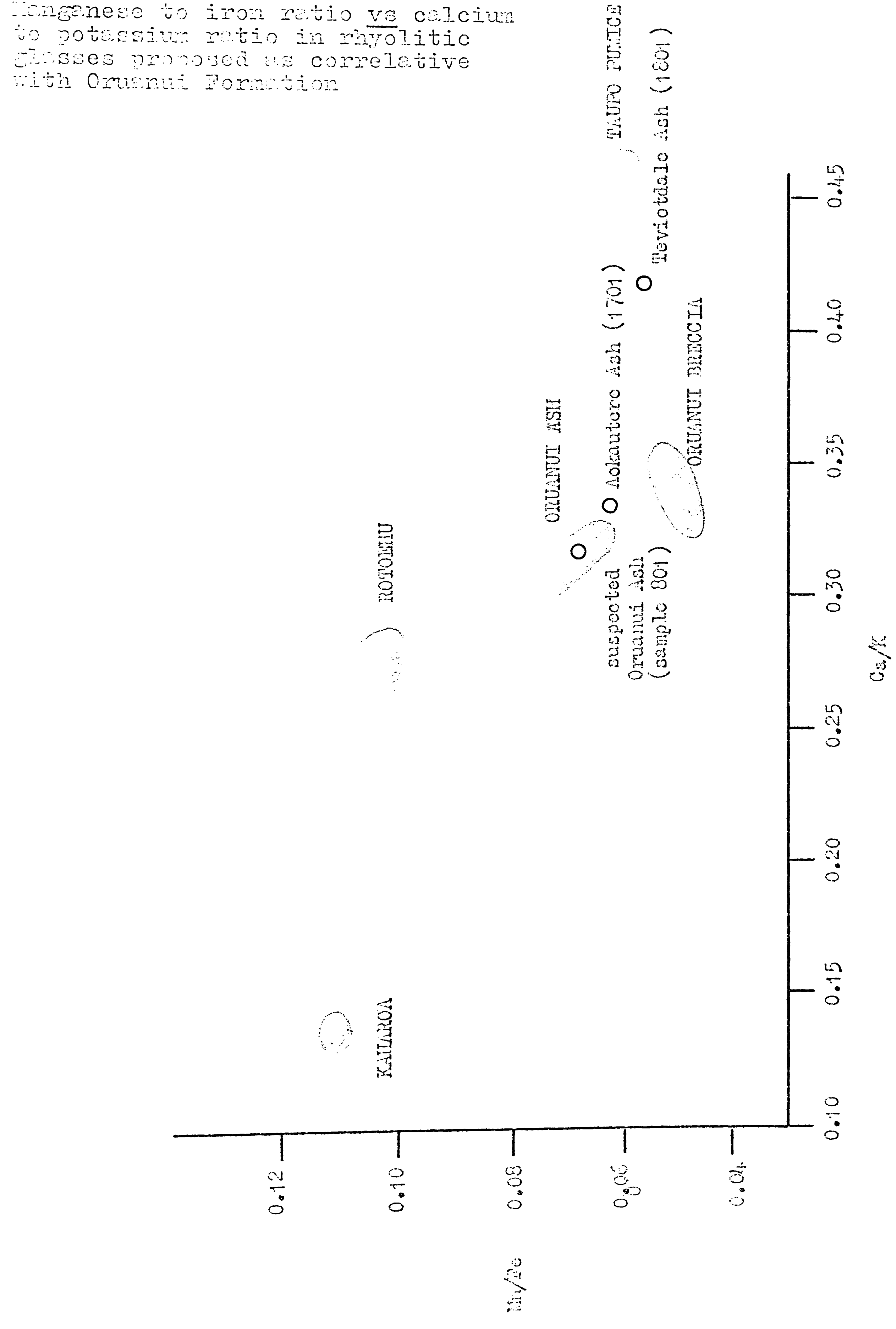
The major and trace element compositions of the recognised Oruanui glasses have already been given (Tables 10-3 and 10-4) and these may be compared with corresponding data for the Oruanui Ash from Hauturu Road, the Aokautere Ash and the Teviotdale Ash given in Table 12-4.

All of the samples have high levels of calcium and levels of potassium similar to that of known Oruanui glasses. The Teviotdale Ash has a rather higher iron content than the other samples, but apart from this there are no significant differences in major and trace element composition. As in Chapter 10 the samples are plotted on a Mn/Fe versus Ca/K plot (Fig. 1203) whereon it is seen that the data for glass from the Oruanui Ash from Hauturu Road plots without question in the zone for other glasses from known exposures of Oruanui Ash, Aokautere Ash glass plots near this zone, between the zone for Ash and Breccia Members, and the Teviotdale Ash is significantly different. A plot of Zr/Ti versus Rb/Sr for glasses extracted from known tephras is given in Fig. 1204, from which the same conclusions emerge. Thus on the basis of the chemical compositions, the correlation of Aokautere and Oruanui Ashes is sustained, but the proposed correlation with the Teviotdale Ash is untenable.

It is interesting that the glasses are not significantly distinguished by refractive index and derived parameters, as is shown in Table 12-5. Nevertheless those glasses considered to be of ignimbritic (breccia) origin do have higher refractive indices than do the glasses of the ash-bed which they overlie. Glasses from ignimbrites might be expected to have a higher refractive index, perhaps because of the greater surface area available for hydration and possibly because of higher initial water contents resulting from a high vapour pressure in the magma prior to its explosive release (Kennedy, 1955). While it must be conceded that the same result would be observed if the hydration

FIG 1203

Manganese to iron ratio vs calcium to potassium ratio in rhyolitic glasses proposed as correlative with Oruanui Formation



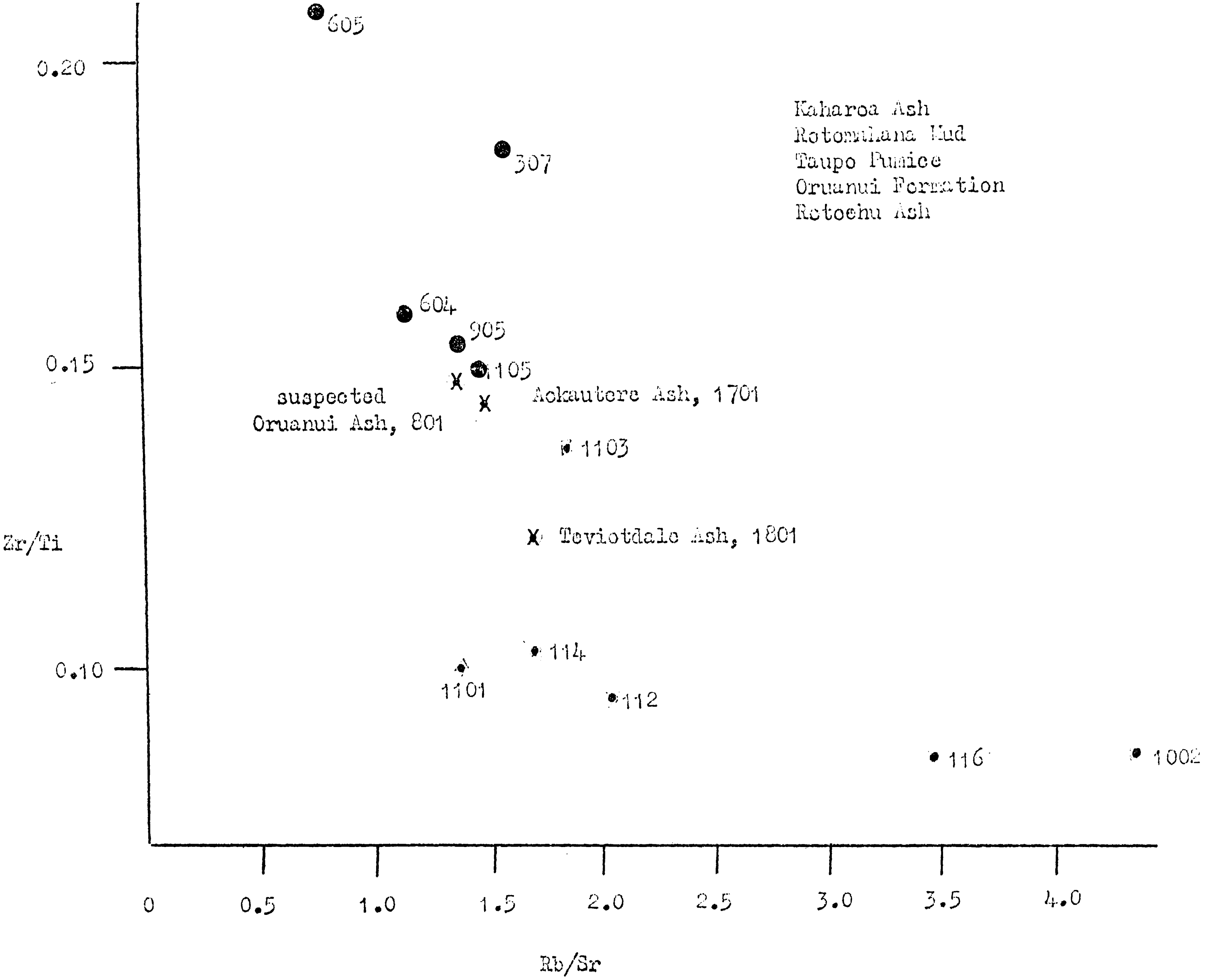


FIG 12.4

Zirconium to titanium ratio vs rubidium to strontium ratio in rhyolitic glasses proposed as correlative with Oruanui Formation

TABLE 12-4: Chemical Composition of Glass from Tephras possibly Correlative with Oruanui Formation.

	Element										
Sample	Al	Si	K	Ca	Ti	Mn	Fe	Cu	Rb	Sr	Zr
	Concentration/%*										
Oruanui Ash (801)	14.32	62.18	4.41	1.40	0.20	0.13	1.92	0.01	0.026	0.19	0.029
Aokautere Ash (1701)	10.29	73.95	4.72	1.68	0.23	0.11	1.88	0.032	0.039	0.026	0.033
Tevictdale Ash (1801)	10.15	72.43	4.68	1.95	0.25	0.13	2.32	0.011	0.038	0.024	0.031

* Concentration values by X.R.D., values are 1.84 times real concentration, see Sec. 10-2.

of the lower glass is inhibited by the presence of the overlying breccia layer, the similarity of water contents for samples 105 and 906,(only the latter of which is overlain by the breccia, but which apart from this have undergone similar post-depositional history) attests to the correctness of the former statements.

The Teviotdale glass has an anomalously high magnetic susceptibility, and by the method of Chapter 8 yields a higher ferrous content than the total iron content determined by x-ray fluorescence. Clearly, this anomalous magnetic susceptibility is related to factors other than the ferrous content, and serves to again dispute the correlation of this bed with Oruanui Formation generally and with the Oruanui Ash Member and Aokautere Ash specifically.

TABLE 12-5: Refractive indices, iron contents and derived water contents of glasses from tephra possibly correlative with Oruanui Formation.

Sample	Refractive Index$^{(1)}$	FeO$^{(2)}$ (%)	$n_o^{(3)}$	$\Delta n^{(4)}$	$W^{(5)}$ (%)
105 (A)	(1,4977$^{(6)}$)	0.98	1.4813	0.0164	4.1
	(1.4987)			0.0174	4.4
905 (B)	1.4994	0.53	1.4789	0.0205	5.4
906 (A)	1.4977$^{(6)}$	0.85	1.4806	0.0171	4.3
604 (B)	1.4993	0.65	1.4794	0.0199	5.2
605 (A)	1.4992	0.70	1.4797	0.0195	5.0
307 (Oruanui Ash)	1.4994	0.70	1.4797	0.0197	5.1
406 (Oruanui Ash)	1.4980$^{(6)}$	0.53	1.4787	0.0193	5.0
503 (Oruanui Ash)	1.4984	0.90	1.4808	0.0176	4 5
1701 (Aokautere Ash)	1.4989	0.53	1.4789	0.200	5.2

TABLE 12-5: continued

Sample	Refractive Index(1)	FeO(2) (%)	n_o(3)	n(4)	W(5) (%)
1801 (Teviotdale Ash)	1.4993	5.2(7)	1.5053	not determined	
801 (Oruanui Ash)	1.4993	0.60	1.4791	0.0202	5.3

Some of this data previously presented as Table 9-6, included here for comparison.

(1) as measured, attendant error of ±0.0003

(2) from magnetic susceptibility measurements.

(3) from relation: $n_o = 0.0057\ (FeO) + 1.4767$.

(4) being the difference $n - n_o$.

(5) from Fig. 907.

(6) on average larger shards than is usual; this probably accounts for the lower refractive index.

(7) this derived value exceeds that obtained for total Fe by X.R.F. determination.

(A) on the basis of glass proportions taken to be the Oruanui Ash Member.

(B) on the basis of glass proportions taken to be the Oruanui Breccia Member.

S12-5: Mechanistic Implications:

As has been previously indicated (S10-5) the rubidium to potassium ratio is an indicator of the extent of magmatic differentiation. This ratio and the member status of the sample on the basis of glass contents is given in Table 12-6.

TABLE 12-6: Rb/K Ratios for Glasses of possible Correlatives of Members of Oruanui Formation.

Sample	Member Status	Rb/K
105	Ash	0.0052
307	Ash	0.0071
605	Ash	0.0041
905	Breccia	0.0102
604	Breccia	0.0055
1701 (Aokautere Ash)	Ash	0.0082
801 (Oruanui Ash - Hauturu Road)	Ash	0.0059
1801 (Teviotdale Ash)	Uncertain	0.0081

Sample 905, which is certainly Oruanui Breccia, has a higher Rb/K ratio than the underlying ash. If this is compared with data from the Rotoehu Ash sequence, it would seem that magmatic differentiation is a part of the eruptive process since the Rb/K ratio may be inferred to increase both up the stratigraphic column, and up the magma chamber. Deposits of mixed glasses would be expected to show ratios between the value for the Ash-member and the Breccia, and suggests that the Aokautere Ash, sample 801, and Oruanui Ash, as recognised in the Waikato, may be composite. It is of interest that the ratio for Teviotdale Ash is virtually identical to that of Aokautere Ash, and is the only evidence suggestive of a correlation between these two ashes.

S12-6: Conclusion:

There is always the desire to extend the use of analytical techniques to areas that may approach the limits of the applicability. The challenge of correlation of ashes over many hundreds of miles is indeed drawing, and a tentative correlation of Aokautere, Oruanui and

Teviotdale Ashes is such a challenge. On the basis of techniques described in this thesis, the correlation of Aokautere Ash with Oruanui Formation can be positively sustained. Evidence suggests that Aokautere Ash, although primarily composed of the material recognised north of the proposed source as Oruanui Ash may be contaminated with glass from the overlying breccia member. On the basis of Rb/K ratios, this contamination may be estimated as some 40%. Teviotdale Ash differs markedly from the Aokautere and Oruanui Ashes in its high magnetic susceptibility of the glass. Compositionally its glass does appear different from the others but it has been remarkably well preserved, as is evident from the high glass content of the deposit. Although elemental ratio plots that give good separation of various tephra suggest that the Teviotdale Ash is not correlative with Oruanui Formation, it has a similar Rb/K ratio to Aokautere Ash, which provides some evidence for a correlation. The weathering and post-depositional history at the site of Teviotdale Ash is so different from those at which Oruanui Ash, and to a lesser extent, Aokautere Ash, are recognised, that the limits of applicability of these physico-chemical techniques may be being realised.

CHAPTER 13: AGRICULTURAL IMPLICATIONS OF CHEMICAL ANALYSIS OF RHYOLITIC GLASS

S13-1: Introduction:

It was mentioned in Chapter 6 that volcanic glass weathers rapidly. If volcanic glass constitutes a large proportion of the original tephra, then much of the resulting soil chemistry must originate from the glass. Where the vitric component is exceptionally high, as in ignimbrites, the glass may be the only source of chemical elements; as the rhyolitic character decreases the effect of other minerals becomes more apparent. Thus the soil chemistry will bear less relationship to the glass chemistry, the more andesitic the tephra. In addition, the older the soil, the more likely it is that significant contributions may have been realised from the more slowly weathering minerals. Accordingly, in this chapter attention will largely be focussed on soils developed on relatively young tephras, in particular those derived from the Taupo eruptions (1.8 thousand years ago), the Kaharoa Ash (930 years ago), and the Tirau Ash.

On the basis that soil chemistry is related to the chemical composition of the parent glass, the availability of a given element for agriculture may depend on:

(i) the amount of the element initially within the glass,

(ii) the rate of decomposition of the glass to free the element to the soil,

(iii) the "fixing" of the freed element by soil processes, so that it is unavailable for plants,

(iv) the leaching of the element from that part of the soil profile accessible to plants.

It may be readily appreciated that if the amount of a given element in the glass is lower than is required for agriculture, then the soil is inherently deficient. If, however, the reserves of the element in the glass are high, then any elemental deficiency in the soil is acquired, being caused by either some "fixing" process, or by leaching from the soil or by a lack of time for sufficient glass to have weathered to meet the agricultural requirements. Gibbs (1961) refers to the problem of agriculture in the pumice country in:

> "The volcanic ashes of the Bay of Plenty are higher in silica and lower in metallic elements such as Co, Ni, Cu, Fe, V, Ca and Mg than average sedimentary rocks. Moreover, and especially in the pumice soils weathering is at an early stage and supplies of elements to plant roots are derived mainly from the least stable minerals. Available Al and Fe are generally high whereas available Co, Ni, V or B may be low, due either to slow decomposition of a mineral or by partial fixation by free Al or Fe. Hence pumice soils and yellow brown loams may be unable to meet demands for all nutrients required by rapidly growing plants."

Gibbs (1961) does not discount the possibility of the original material being inherently unable to meet the agricultural requirements. Analysis of glass enables this very important aspect to be determined. In New Zealand agriculture the trace elements cobalt and selenium are of considerable economic significance and the element supply, soil availability, and agricultural demand will be considered for these elements.

S13-2: Selenium and Cobalt in Magmas and Glasses:

Of the distribution of cobalt in relation to magmatic differentiation, Mason (1958) writes:

> "The bivalent cobalt ion is practically the same size as the ferrous ion, and cobalt should thus be camouflaged in ferrous compounds. It is found however that the Co:Fe ratio is greatest in early-formed minerals and decreases steadily with increasing fractionation. The effective radius of cobalt is, therefore, somewhat less than the radius given above and is apparently almost identical with that of Mg, ... the Co:Mg ratio (is) almost

constant throughout a rock series. The major part of the cobalt in a magma is removed in the early formed magnesian minerals, especially alinine."

Since volcanic glass, and particularly rhyolitic glass, is probably representative of an advanced stage of magmatic differentiation, the amount of cobalt in glass is expected to be very small. By comparison "the relative concentration of sulfur and chalcophile elements (like selenium) probably increases in the late liquid fraction of a crystallising magma as a result of the removal of the lithophile elements in the silicate minerals" (Mason, 1958). On Fig. 1301 are given the relative concentrations of copper and gallium (as representative of chalcophile elements) and of cobalt as a function of magmatic differentiation of an intrusive pluton. The indication of relative enrichment of chalcophile elements and depletion of cobalt for later differentiation is clear. Wells (1967a) indicated that the amount of selenium tends to follow that of copper, particularly in volcanic rocks, which further suggests from Fig. 1301 that selenium will be relatively enriched in later differentiates. However, Wells (1967a) stated too that there are lower (usually 10-fold) amounts in rhyolites and rhyolitic pumices than there are in andesites, particularly andesitic tephras: this might suggest a maximum in the relative concentration versus differentiation profile.

From these considerations it would appear that the significant source of selenium is likely to be the vitric component. By comparison cobalt needs would appear to be best supplied by the weathering of mafic minerals; only in their absence would such needs be supplied from the glass.

S13-3: Selenium in Soils and Plants:

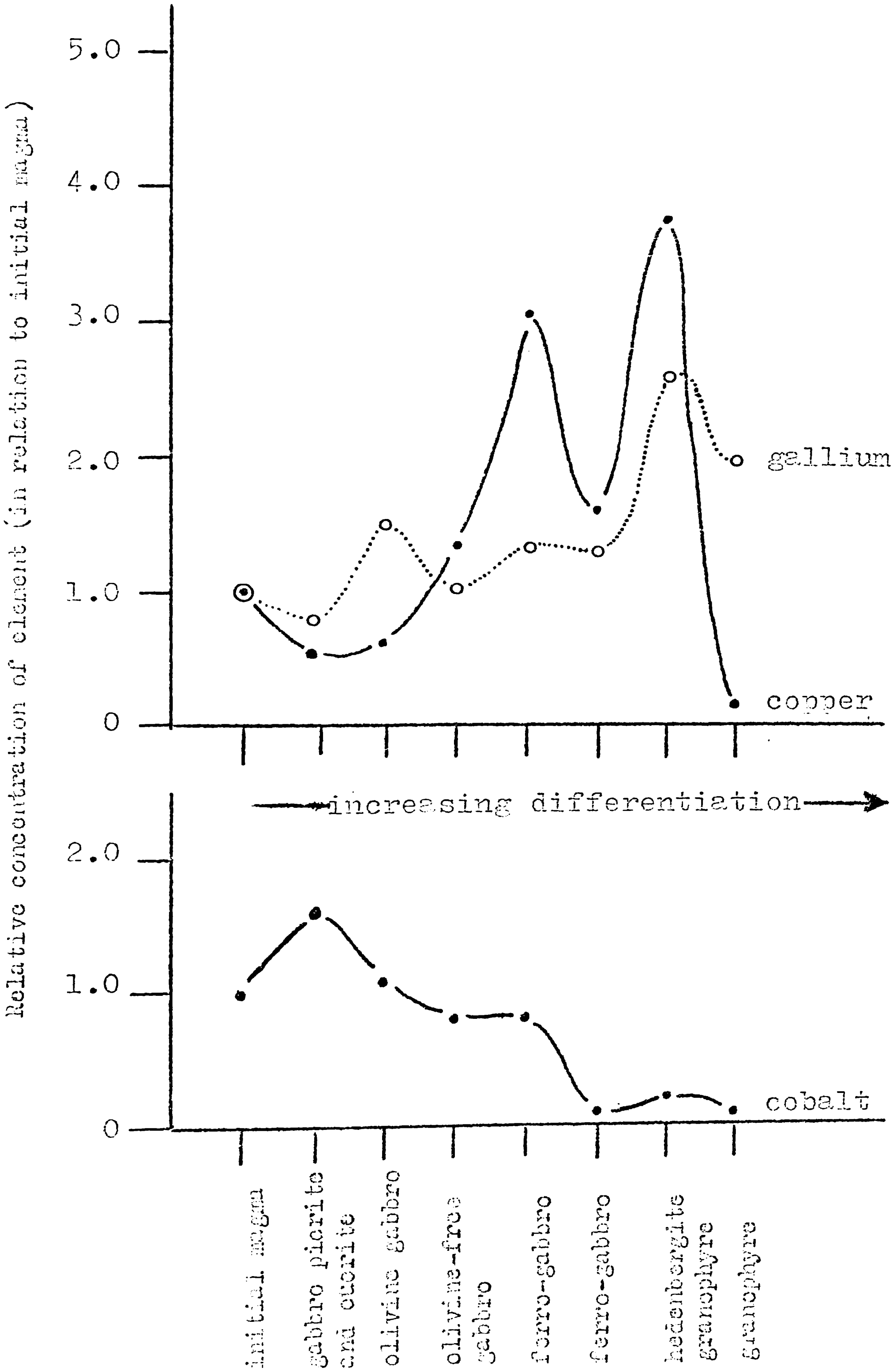
Wells (1967b) indicates that the average selenium contents in topsoils exceeds that of parent rocks and consequently that selenium

FIG. 1301

Relative concentration of chemical elements as a function of the extent of magmatic differentiation.

Upper plot: copper and gallium (representative of chalcophile elements)

Lower plot: cobalt



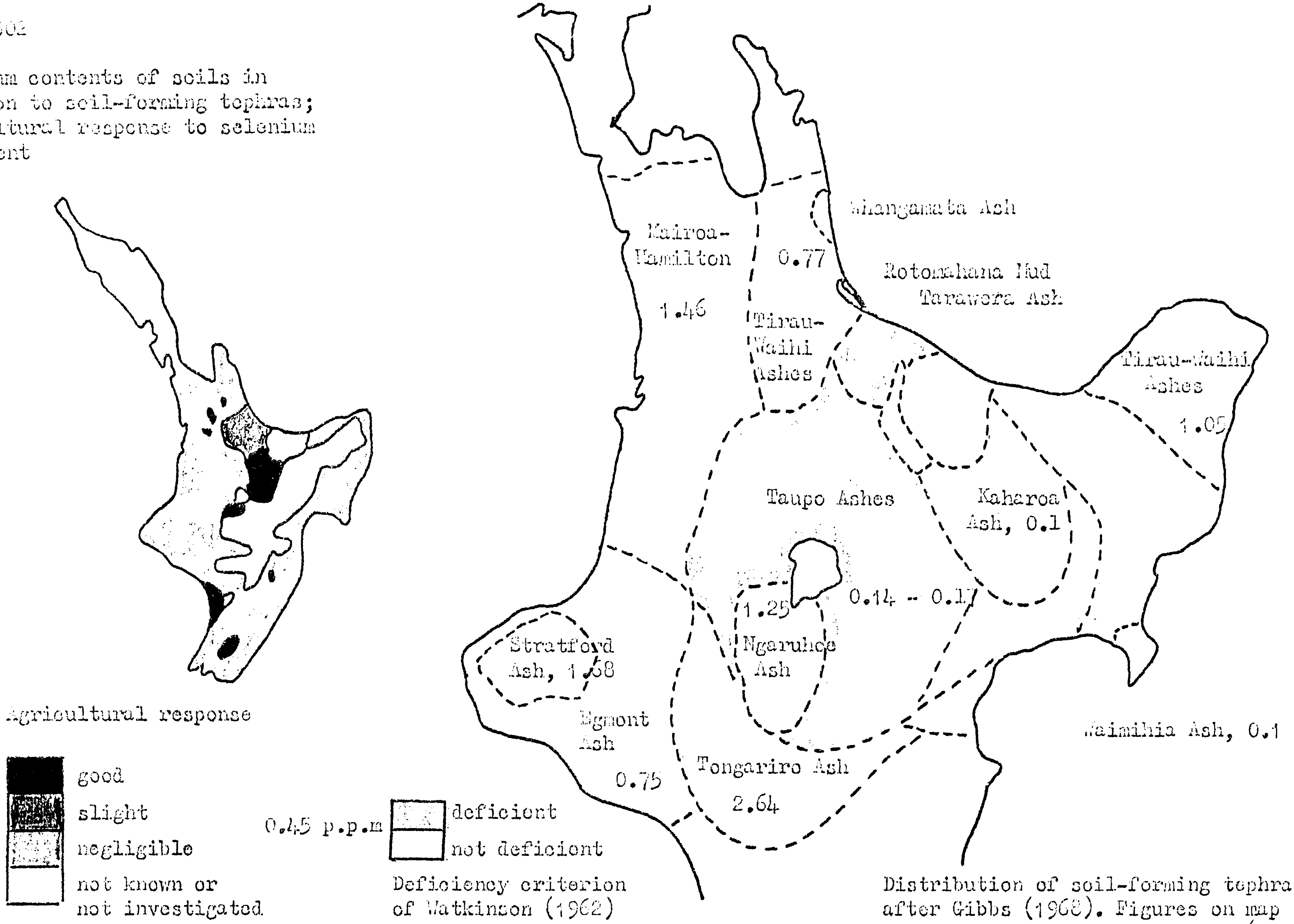
accumulates during soil formation, being most likely retained on clay-sized particles, of kaolin, gibbsite, and particularly ferric oxide. Because of this, the selenium contents of young soils would be expected to be low, partly because only small amounts of selenium will have been gained by the soil as a result of the weathering of glass, and partly because the selenium may not be retained by the small amounts of hydrous oxide. Thus a deficiency in selenium in a soil of young age, may simply represent an inadequate time interval for weathering rather than an inherent deficiency. There is, too, a further problem in that sufficient concentration of an element in a soil does not necessarily mean that sufficient is available for plant growth. Bisbjerg and Nielson (1969) indicate that the selenium concentration in plants decreased as the clay content of the soil increased. Thus it would appear that selenium deficiencies are possible too, on heavily weathered soils where the high clay content results in excessive retention of selenium rendering it unavailable to plants and thus to animals.

Andrews et.al. (1968) describes the physiological effects of selenium deficiency in animals. These include congenital and delayed white muscle disease of lambs and calves, selenium responsive infertility in ewes, and "selenium responsive unthriftiness of sheep and cattle, which is widespread, not always recognised or correctly identified and therefore economically the most important."

A map showing the distribution of areas that have shown agricultural responses to additional applied selenium is given in Fig. 1302. Associated with this figure is a map showing the distribution of the principal soil-forming tephra, after Gibbs (1968) on which are superimposed the selenium contents of the tephra residua given by Wells (1967a). From these diagrams it appears that the selenium deficiencies are primarily associated with the younger tephra. This would imply that the deficiencies are unlikely to be the result of the retention of the element on pedogenetic products, but are more likely to be the

FIG. 1302

Selenium contents of soils in relation to soil-forming tephras; agricultural response to selenium treatment



Distribution of soil-forming tephras after Gibbs (1968). Figures on map are selenium contents of soils (Wells, 1967a) consequence of either an inherent deficiency or of a lack of time of soil formation. These last two possibilities are examined in the next section.

S13-4: Selenium Deficiency: Inherent or Pedogenetic?

In order to ascertain the relationship between selenium contents of parent glasses and derived soils, the selenium contents of glass representative of the soil-forming tephra were determined and compared with selenium contents of the tephra residua (the latter after Wells, 1967a). The glasses were extracted from the soils by the methods previously described and the samples dissolved in hydrofluoric and perchloric acids. The selenium levels in these prepared solutions were determined by Dr J.H. Watkinson. The determination of selenium is by a fluorometric method whereby the selenite is complexed with 2,3 diaminonapthalene solution and extracted into cyclopropane with the masking of potential interferences with di-amminium E.D.T.A. (Watkinson, 1966).

The selenium contents of glasses and their derived soils are given in Table 13-1 in order of increasing age. From this table it is clear that the selenium content of the parent glass is above that of the average crustal abundance of some 0.5 ppm, and is essentially independent of the age of the parent tephra. This constancy suggests that the selenium in soils is the result of mineral structural breakdowns rather than leaching of the element from the glass. It is readily seen too that the selenium content, although small in the younger soils, becomes appreciable in the soils derived from Tirau Ash and Mairoa Ash (see Fig. 1303). Watkinson (1962) indicates that selenium levels greater than 0.45 ppm should be adequate for agricultural requirements, indicating therefore that soils derived from Tirau and Mairoa Ashes should be free of selenium deficiency. Further, it is clear that the low selenium state of the soils derived from young tephra is a consequence of the time available for weathering, and thus of the extent and rate of the breakdown of the glass to liberate selenium. The selenium status of tephra-derived soils, therefore, is pedogenetic in origin rather than being dependent on the selenium content of the parent glass. It is of interest that the Tirau and Mairoa Ashes may in time give rise to an acquired selenium deficiency when the hydrous oxide contents of the resulting soils become sufficiently high to retain the selenium derived from the weathering of glass and render it unavailable to plants. The problem, if in fact it arises, will be compounded by the low amounts of selenium remaining in the rhyolitic glass at that time.

TABLE 13-1: Selenium in Glasses and Derived Soils.

	Selenium in parent materials (p.p.m.)	Selenium in derived soils (p.p.m.)
Average abundance:(1) p.p.m.	0.5	0.5 - 0.9
Minimum Se level(2) for no agricultural deficiencies p.p.m.	-	0.45
	Selenium in rhyolitic(3) glass (p.p.m.)	Selenium in tephra(4) residuum (p.p.m.)
Kaharoa Ash	0.614	0.11
Taupo Ash	0.838	0.14 - 0.17
Tirau Ash	0.590	1.05
Mairoa Ash	0.842	1.46
Hamilton Ash(5)	10.7	
	Selenium in andesitic(6) glass (p.p.m.)	
Mairoa Ash	0.714	
Hamilton Ash	1.96	

Notes: (1) after Day (1963).

(2) after Watkinson (1962).

(3) glass extracted as previously described, and dissolved in HF, $HClO_4$; Se analysis of this solution by J.H. Watkinson.

(4) after Wells (1967a).

(5) Hamilton Ash : a multi-bedded tephra series of widespread distribution and of undetermined source and extent; considerably older than any other tephra examined in this thesis. Sample, from the principal soil-forming bed, supplied by A.G. Hogg.

(6) probably contaminated with quartz (see Chapter 5).

S13-5: Selenium Contents of Andesitic Tephras and Derived Soils.

Andesitic tephra, containing as they do, appreciable amounts of andesitic glass, might be expected to contribute to the selenium contents of their derived soils, selenium from this source. Reference to Table 13-1 indicates that while the selenium contents of the rhyolitic and andesitic glasses are comparable for Mairoa Ash, there is a ten-fold compositional difference between the rhyolitic and andesitic glasses of the Hamilton Ash. It is also of interest that the selenium content of the rhyolitic glass associated with the andesitic Mairoa Ash is higher than that of Tirau Ash, in spite of the former's greater age. This is suggestive that rhyolitic glasses associated with andesitic tephra are inherently higher in selenium than are their counterparts from rhyolitic tephra.

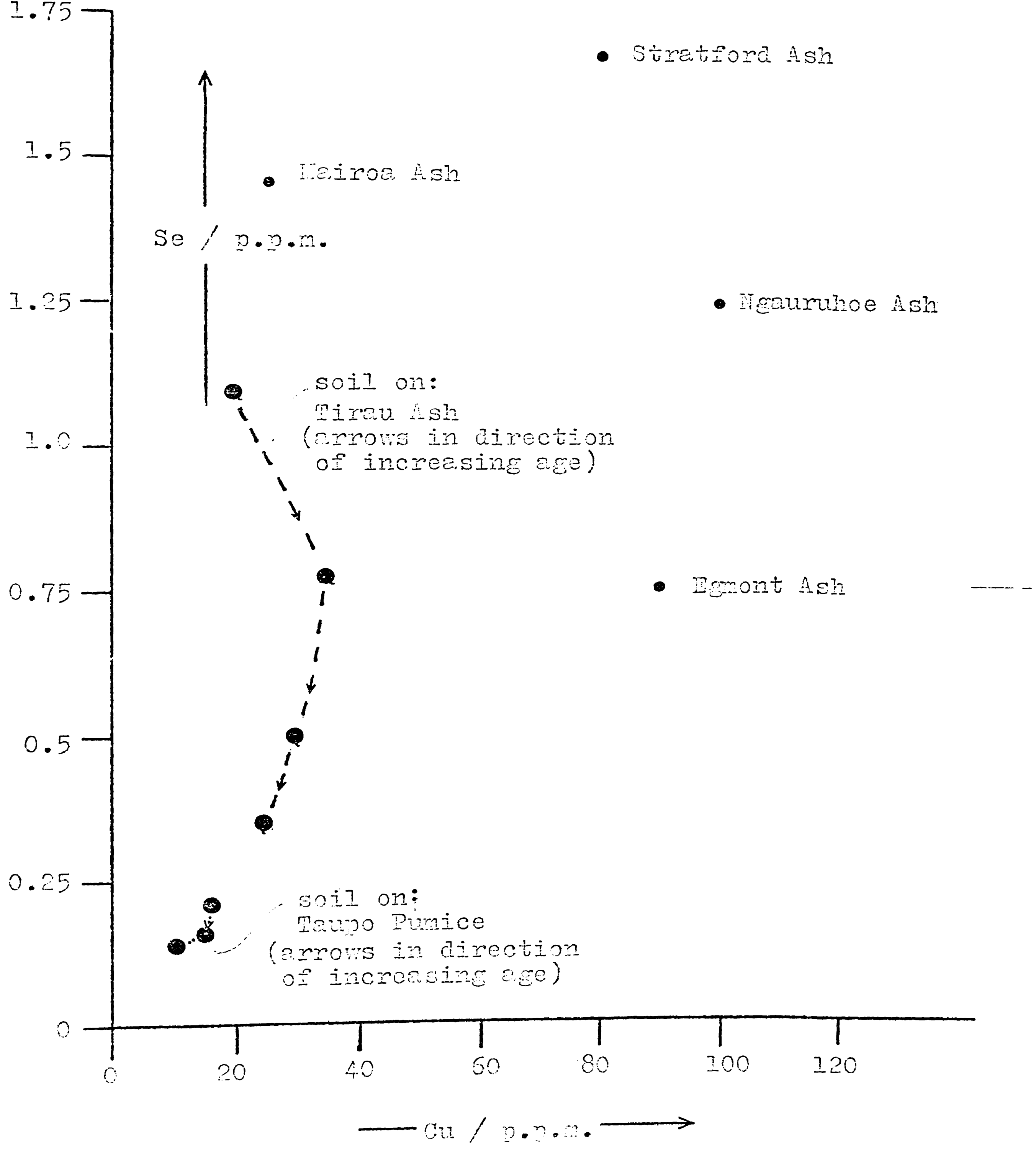
Wells indicated that there was a relationship between selenium and copper contents in soils. This relationship is shown in Fig. 1303, where it may be seen that relative to the selenium axis, the function shows a maximum, being presumably related to the retention of selenium but the loss of copper from the clay mineral particles. In the parent glasses there is also a tendency for high selenium contents to be

FIG. 1303

Selenium contents versus copper contents of tephra units and derived soils

● Copper and selenium contents for Tirau Ash and Taupo Pumice derived soils for various horizons from the soil profile; copper contents after Wells and Young (1968), selenium after Wells (1967b)

• For tephra units for which the selenium contents are given by Wells (1967a), the copper content is taken as that of the lowest soil horizon (Wells and Young, 1968)



associated with high copper contents, particularly is this the case with the glasses associated with the older tephra (see Fig. 1303). Also, there tends to be an inverse relationship between copper (and therefore probably selenium) contents and the rhyolitic parameter of the whole tephra(as is shown on Fig. 1304). On such a basis, it might be suggested that selenium levels in rhyolitic glass might be a useful tool in tephra correlation. In particular, such a chemical technique may be worthy of consideration in identification and distribution studies of the Hamilton Ash sequence.

S13-6: Cobalt Deficiency on New Zealand Pumice Soils:

As the lands of the central North Island were brought into agricultural production, unthriftiness and anaemic conditions became apparent in sheep, and to a lesser extent, in cattle. Initially the symptoms were attributed to an iron deficiency and was corrected by the use of limonite stock licks. Subsequently, it was found that cobalt was responsible, the low levels inhibiting the formation of vitamin B.12 (Underwood and Filmer (1935) and Marston and Lines (1935)).

Generally, it was the soils derived from rhyolitic tephra of recent age that showed the symptoms most severely, although soils derived from the weathering of granite and other siliceous rocks also showed deficiency symptoms (see Fig. 1305). Sutherland (1966) picturesquely described the "bush-sick" soils derived from volcanic tephra:

> "In the agricultural sense these (soil-forming ash) showers ranged between 'hospitable' and 'inhospitable.' The hospitable showers brought among other elements, a cobalt content adequate for subsequent farming, while the latter deficient in cobalt, laid the foundations for what in centuries to come was to become known as bush-sick soil.
>
> "Thus it is true to say of some farming areas of the ash showered

FIG. 1304

Relationship between copper content of rhyolitic glass and rhyolitic character of the associated tephra.

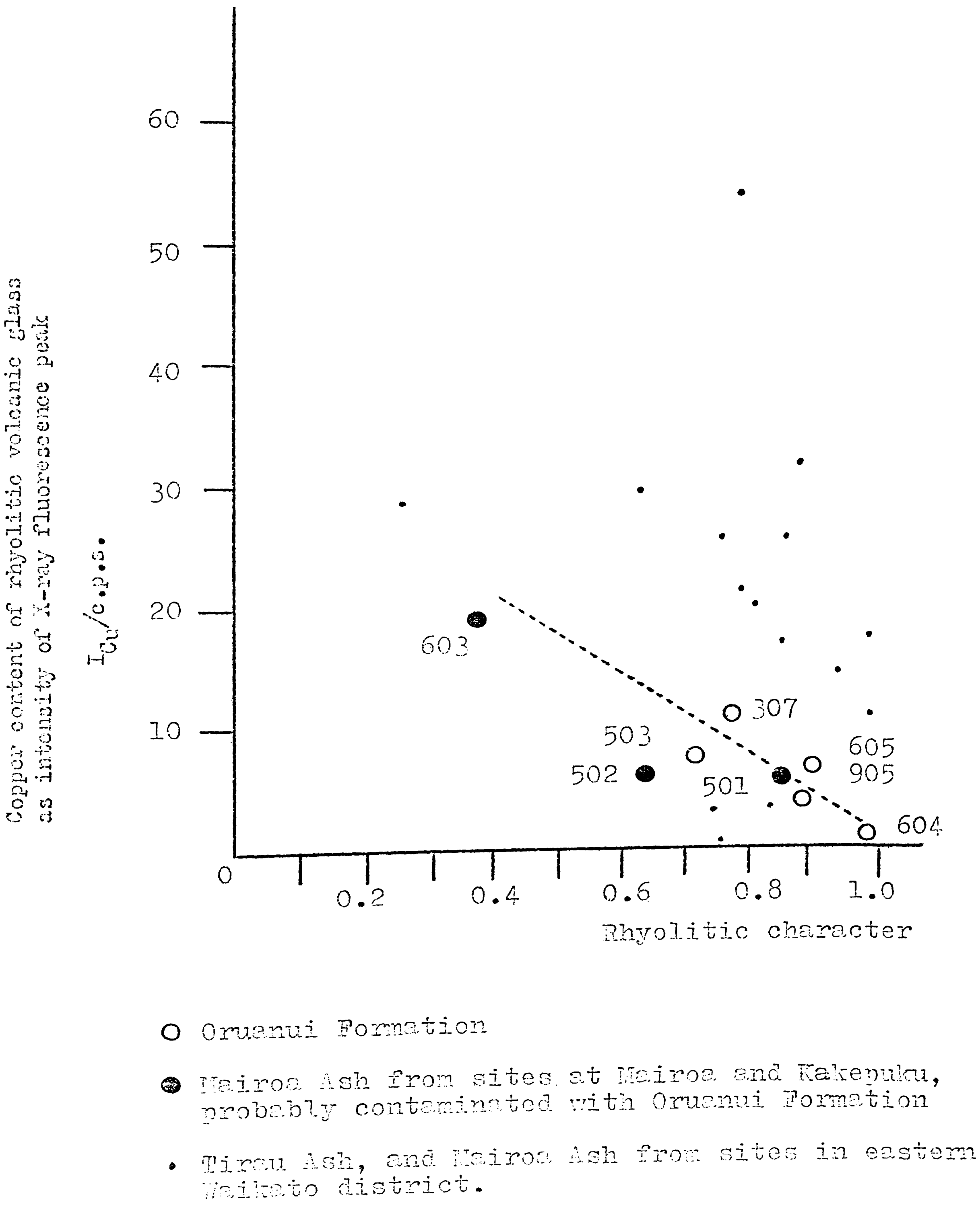


FIG 1305

Geographical distribution of cobalt-deficient
soils in New Zealand.

country that whether a farm was good or poor may have been determined by the direction the wind happened to be blowing when the last volcano blew its top. Kaharoa and Taupo volcanoes, for instance, emitted stingy showers for farming on, their cobalt content slightly over or under one part per million. Tongariro and Ngauruhoe were more liberal with their cobalt and Tarawera, with six to seven parts per million, relatively generous, though not comparable with many soils of other origin."

From what has been said earlier in this chapter, only small amounts of cobalt would be expected to be contributed to the soil by the weathering of volcanic glass. Indeed, analyses for cobalt of the rhyolitic glasses associated with the Kaharoa, Taupo and Tirau Ashes show negligible differences. Since, therefore, the weathering of mafic minerals renders the principal contribution to cobalt contents of soils, some relationship might be expected between the rhyolitic parameter and cobalt deficiency, or more specifically, between the proportion of mafic minerals and cobalt deficiency. Such a relationship is demonstrated in Table 13-2. On this basis it would appear that cobalt deficiencies in soils derived from tephra of low mafic mineral content may be inherent, but may simply be caused by a lack of time for weathering the cobalt from the abundant glass and the scant mafic minerals. The addition of an andesitic component, as occurs in the Tirau and Mairoa Ashes, increases the potentially available cobalt, and in addition these tephra have had sufficient time to weather to establish cobalt reserves in the soil. During (1966) indicates that while "soils derived from Tirau Ash are not known to be deficient in cobalt, deficiencies are reported from high rainfall areas in which Mairoa Ash is the soil-former.*" Since Mairoa Ash is appreciably andesitic, such deficiency is likely to

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* This deficiency is referred to in early work by Grange (1931) and was originally attributed to calcium deficiency, Aston (1928).

result either from leaching of the cobalt reserves or the fixing of cobalt, perhaps on the clay, or the particularly abundant ferric oxide. It will be recalled from Chapter 10 that the glass associated with Mairoa Ash, particularly in the hill-country, as at Mairoa itself, contains abundant iron and the derived soil may be expected to be likewise.

TABLE 13-2: Cobalt Deficiency in Agricultural Soils in Relation to Mineralogy of Parent Tephra.

Tephra from which soil is derived	Cobalt status of soils	Rhyolitic parameter (α)	Proportion of mafic minerals (%)	(Representative sample no.)
Rotomahana*	not-deficient	0.22	0.66	(1101)
Kaharoa	deficient	0.63	0.11	(1002)
Taupo	deficient	0.82	0.54	(1104)
Tirau	not-deficient	1.0	1.12	(201)
Mairoa	not-deficient+	0.36	4.1	(601)

* The agricultural soil is usually developed on the Tarawera ash of basaltic composition, rather than the hydrothermally deposited Rotomahana Mud which is associated with the same historic eruption. The mud probably contains a lower proportion of mafic minerals than the ash, although the value of α is probably similar.

\+ Deficiencies are known in high-rainfall areas, "Mairoa disease" and are presumably related to leaching or cobalt retention on clay particles.

S13-7: Conclusion:

Rhyolitic glass, the principal parent material in soil formation from tephra, may be viewed as the principal provider of chalcophilic elements to the soil and hence to agriculture. In particular it may be considered to be the source of the microelement selenium. Comparison of the levels of selenium in glasses and soils suggest that deficiencies in the latter have their origins in pedogenetic factors rather than in any initial inherent deficiency in the glass. In that the selenium status of soils eventually increases with time, the soils developed on the young rhyolitic tephra, Kaharoa and Taupo Ashes in particular, will in time cease to be selenium deficient. However in that some of the selenium in soils is retained on hydrous oxides and clay particles, and that there is some evidence that soils of a high clay content have a reduced amount of selenium available to plants, it may be tentatively suggested that soils like those developed on Tirau and Mairoa Ashes may eventually become deficient after prolonged weathering.

Cobalt levels in glass differ little, the significant source of cobalt is probably the more mafic minerals. The recent rhyolitic tephras that are the parent materials for many of the agricultural soils are low in mafic minerals and the reserves in the parent material are probably low. This, coupled with the comparatively small degree of soil development, almost certainly accounts for the observed cobalt deficiencies. Older rhyolitic soils and soils of andesitic origin, which typically contain a higher proportion of cobalt-bearing mafic minerals, are not deficient in cobalt except under conditions of high rainfall, wherein the deficiency is probably the result of the leaching of available cobalt from the soil.

Thus, it would appear that pedogenetic factors are of paramount importance in the agricultural status of soils as regards the availability of microelements. Such factors include the time interval available for soil development, the rate of leaching of the element from the parent material, and the possible retention of the element leached from those materials by the product of pedogenesis. In general there would appear to be adequate reserves in the parent material to meet agricultural demands were pedogenesis more favourable.

CHAPTER 14: CONCLUSION

The purpose of the research for this thesis was to investigate the worth of various physical and chemical properties of tephra and their constituents, particularly as they apply to the vitreous components. Analytical methods are reviewed and developed, some to the point at which the precision in determination exceeds the natural variation of the parameter within the material. The worth of these techniques is considered with reference to selected problems in tephrostratigraphy.

Mineral assemblages, particularly mafic ones, have long been used to characterise tephra, although doubts have been expressed about the universality of such methods. In that there might be less lateral variation in the lighter density felsic minerals, rather more emphasis has been placed on such assemblages. Rhyolitic glass, of characteristically low density (some 2.4 $gm.cm^{-3}$) was separated by heavy liquid centrifugal techniques. The remaining felsic minerals, predominantly quartz, feldspar, and andesitic glass, were similarly separated from the mafic minerals of yet greater density. The densities of the components of the felsic fractions are sufficiently similar as to render physical separation difficult. The respective proportions were, therefore, estimated indirectly by infra-red spectroscopy. Although probably of lower precision than quantitative x-ray diffraction, the quantitative infra-red analytical procedure developed enabled the proportion of vitreous component to be determined. From such data the relative proportions of rhyolitic and andesitic glasses could be established, and from this the rhyolitic character of the deposit. Such a parameter is useful in that it assists in defining the source of the tephra: material erupted from the Okataina and Taupo volcanic centres is primarily rhyolitic, whereas that from the Egmont and Tongariro centres is primarily andesitic. The value of the rhyolitic parameter is indicative of the extent of mixing of tephras of differing initial composition. This comparatively simple technique has been used to clearly demonstrate the andesitic character of the Mairoa Ash sequence, and its distribution into the Waikato region as underlying and probably interdigitating with the more rhyolitic Tirau Ash sequence.

If the weathering of volcanic glass to allophane is considered to be represented kinetically as a first order reaction, and the andesitic and rhyolitic glasses are assumed to be lost at comparable rates, approximate ages of the tephra can be assigned. In so doing, it is necessary to make estimates as to the initial glass contents of tephra of various rhyolitic parameter, and some knowledge is needed of the climatic variation (particularly the variation of rainfall and infiltration, rather than temperature) over the period of deposition and weathering. The implicit assumption is made that there is minimal re-working of the deposit, that is to say that all the glass is of contemporaneous deposition. On such a basis, the Mairoa Ash sequence at Mairoa may be assigned a minimum age of seventeen thousand years, while the Tirau Ash sequence is rather younger, spanning the interval from some ten to fifteen thousand years. Studies of the rhyolitic glass of the Mairoa Ash sequence from the more westerly sites indicated some contamination from the glass of the underlying Oruanui Formation. The effect of this contamination can be quantified on consideration of the observed refractive index as a weighted mean of two constituent glasses. When this is done, the glass contents can be corrected, and this has the effect of lowering somewhat the age of the Mairoa Ash; it may be suggested, as a result, that this tephra spans the interval of some 15 to 17 thousand years.

The nature of the volcanic glass has often been thought to be representative of the magma at the time of eruption. On this basis, the chemical similarity of glasses from widespread localities of differing climatic regime has been used, particularly in the United States, as clear evidence of the same tephra being involved. In New Zealand the widely differing weathering environments and the comparatively small compositional differences between obviously distinct glasses has made such correlations difficult. Some success has been achieved by some workers using trace elements of low geochemical mobility. In fact the data obtained by chemical analysis seems no better able, of itself, to resolve tephrostratigraphic problems than any other single method. It is, however, of value when employed in conjunction with other techniques. As an example, the similarity of the composition of rhyolitic glass extracted from the Mairoa Ash to that extracted from the Oruanui Formation suggest a correlation, but refractive index techniques indicated that two glasses were involved, and that one of these resembled that of the Oruanui Formation very closely.

Physico-chemical methods (such as refractive index) are indicative of the bulk chemistry of the glass and have been found to be effective and useful in tephra identification and correlation. Of particular value in this regard is the refractive index of the rhyolitic glass. Claims of the insensitiveness of refractive index may be refuted by the work of this thesis which uses the use of a thermal variation method of index determination. This method has as its basis the variation of refractive index with temperature of certain optically suitable organic liquids. With such liquids, a hot-stage microscope, and the usual optical techniques determinations can be made to an accuracy of ±0.0003 units of refractive index, thereby adding a decimal place to the values obtainable with typical sets of refractive index oils. By such a method, small differences in refractive index are noted between the rhyolitic glasses associated with the Mairoa Ash from those with the Tirau Ash. The determination of refractive index is complicated by hydration effects. This is particularly marked for glasses of young tephras, and for such tephras increases the error attendant on the refractive index. Empirical estimates of the water content of rhyolitic volcanic glasses, being a function of the difference between the measured refractive index and a "dry" value, itself related to the magnetic susceptibility of the glass, suggests that glasses older than about ten thousand years are uniformly hydrated. Under these conditions the differences in indices of the Mairoa and Tirau Ash glasses probably reflect an initial compositional difference. Refractive index techniques are, however, less suitable for distinguishing glasses of similar origin; for example, the Tirau Ash glasses differ but little from the Oruanui Formation glass. It is particularly noteworthy that the determination of refractive index is a technique applied to single shards. In this it differs from all other techniques used, which are effectively bulk methods. The importance of this distinction are taken up in the closing paragraphs.

The principal use of magnetic susceptibilities seems to be in the empirical assignment of the refractive indices of the dehydrated glasses. This is achieved by analogy with the relationship that exists between the refractive index and ferrous content of the essentially anhydrous tektite glasses, in which the ferrous content and magnetic susceptibility are linearly related. Ferrous to ferric ratios, the ferrous content being determined by susceptibility and the ferric content as the difference between this and total iron determined by chemical analysis, are effectively constant for all glasses.

The densities of various glasses were determined by density gradient techniques, these gradients being established over the range 2.0 to 2.5 gm/ml by "pile-on" techniques. Unfortunately, the band width of the material added to the column, usually meant that the natural variation in density, presumably due to variations in chemical composition, exceeded the differences that there might be between the glasses. In one case two bands were seen, indicating two glass types in the one tephra unit. The differences between Mairoa and Oruanui glasses that were resolved by refractive index techniques were not so resolved by density methods.

In essence then the broad conclusion to be reached from this work is that a given problem in stratigraphy may be amenable to solution by the use of a combination of analytical techniques. Some of these, like refractive index, are capable and worthy of exploitation beyond the precision usual to petrology, others like magnetic measurements and densities tend to be rather more limited in their application, but may be useful when coupled with other methods. Of particular importance is the need to recognise that the vitreous components, although a sensitive indicator of the magmatic composition at the time of eruption, may be modified according to post-depositional history. In addition, the difficulties of correlation of beds distant from the source with those, and particularly multi-bedded tephras, nearer the source, needs to be recognised, since this may have marked effects on the bulk chemistry and the attendant physico-chemical properties of the glass.

By the application of these techniques, it has been possible to resolve the long-standing debate on the identity of the Tirau and Mairoa Ash beds. There is a significant andesitic component of the Mairoa Ash, as is evidenced by the existence and proportion of andesitic volcanic glass, the low refractive index of the associated rhyolitic glass, and aspects of its chemistry. This sequence of ashes underlies and probably interdigitates the lower members of the Tirau Ash sequence recognised as thinning westward across the Waikato district. This latter sequence is rhyolitic in character, and appears of younger age. In addition to the resolution of whether these ashes are the same or different, the same techniques have been used to provide further evidence to sustain a correlation between Oruanui Ash, as recognised in the Waikato, with the Aokautere Ash of the Manawatu.

Since the weathering of volcanic tephra, in particular the weathering of the glass, gives rise to the agricultural soils of the central North Island of New Zealand, it was considered worthwhile to investigate whether deficiencies of chemical elements in the soils were consequential on inherent deficiencies in the parent glass, or whether such imbalances result from weathering or a lack thereof. By analysis of the glass, it would seem that such problems are pedogenetic in nature, usually resulting from an insufficient time having elapsed for sufficient of the element to be made available to the soil by the breakdown of the glass structure with weathering. In particular, selenium deficiency in soils developed on young tephra would seem to be in this category. Cobalt deficiencies which occur on the same soils may be similarly caused. However, the most significant source of cobalt, the mafic minerals, are poorly represented in the parent tephra, and the deficiency may well be inherent.

It is of interest to speculate on further work that the course of this investigation has revealed. Selenium levels in old andesitic tephra, in of what little glass remains, could be revealing, particularly in work on the Hamilton Ash beds. Positive identification of the Mairoa Ash with the proposed eruptives from Egmont would also be worthy of study, and may be possible using the correlation of refractive index. Other tephrostratigraphic problems, such as correlations of the multi-bedded Rotoehu Ash, and of Teviotdale Ash may also warrant study by such methods, although the indications are that such problems may need to await the general use of single shard methods such as electron microprobe techniques. Complex problems involving mixtures of tephras and correlation of thin beds with multi-bedded parent tephra tax fully the resources of bulk methods. The use of refractive index, effectively a single shard technique, in the resolution of such problems is indicative of the power of such techniques.

This thesis thus represents a transition between the traditional methods of tephrostratigraphy based largely on field evidence and that which, at this stage, appears the ultimate, is based on single grain methods. Doubtless even these refinements will have their limitations as has now been shown to be the case for bulk chemical analyses, and similar parameters dependent on many glass shards or mineral grains. Even so, for many problems, for reasons of cost or by the nature of the problem the rather simpler techniques described and applied in this thesis are likely to be of use in tephrostratigraphy at least in the immediate future.

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SAMPLE CONCORDANCE

This sample concordance provides a guide as to the identity and stratigraphic relationships of the various samples, the numbers for which are used extensively in the discussions in this thesis. The assignment of sample numbers is such that the numbers increase down the stratigraphic sequence, the first digit representing the site. The site numbers and their geographic localities are given in Fig. S.C.1: for further details the reader is referred to Chapter 1 for a full description of the geographic setting, and to Chapter 2 wherein the field descriptions of the samples' occurence is given. Omissions in the numerical sequence of samples given in the concordance only indicates that data from such samples have been incorporated in this work.

The concordance is set out in tabular form, giving sample number, identification based on field evidence, the problem or application within the thesis in which the sample is used, its rhyolitic character and derived age where appropriate, and, where applicable, the assignment of identity on the basis of laboratory investigations. Characters and ages underlined are those assumed from previous work. Identifications underlined are those used as standards in the correlation of tephra and the comparison of glass, and the reliability of the identification of these particular samples is tacitly assumed.

The abbreviations used in the concordance are set out below:

Rhyolitic character:	I	ignimbritic
	R	rhyolitic
	D	dacitic
	A	andesitic
Sample applied to:	T-M	Tirau Ash - Mairoa Ash tephrostratigraphic relationships
	O-A	Oruanui Ash - Aokautere Ash correlation

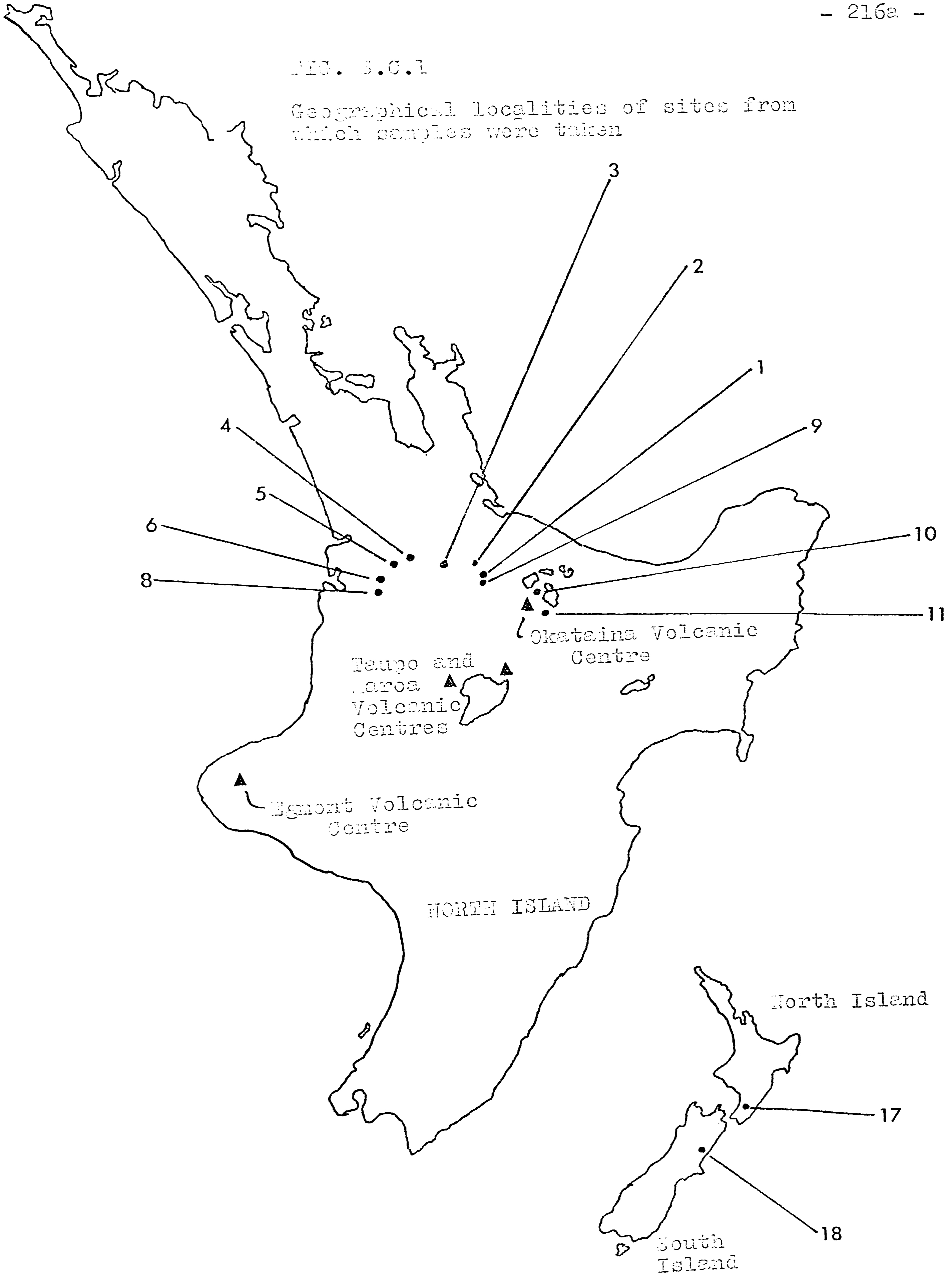
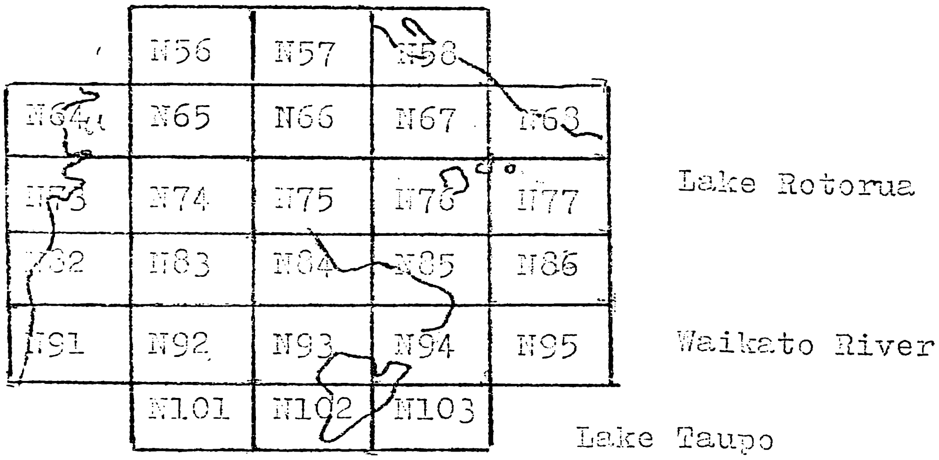


FIG. 8.C.1

Geographical localities of sites from which samples were taken

FIG. 5.6.1 (continued)

Map below shows the arrangement of NZMS1 (New Zealand Map Series: 1 mile to 1 inch) maps in the geographical region of interest for the distribution of Tirau and Mairoa Ashes.



Grid references from these maps for the sites on p.216a are given below:

Site No.	Locality	Map No.	Grid reference
1	Leslie Road	N75	381157
2	Tirau	N66	272250
3	Findlay Park	N66	135224
4	Parawera	N74	950117
5	Kakepuku	N74	790135
6	Mairoa	N82	505748
8	Hauturu Road	N82	525810
9	Tapapa Road	N66	360215
11	Waimungu Road	N85	825870

The sample of Aokautere Ash was obtained from the type locality
Aokautere of grid reference N149 132313 (site no. 17)

For the sample of Teviotdale Ash, the grid reference is
S68-69 158033 (site no. 18)

Sample applied to:
AGR Agricultural implications
COR distant and near-source correlations
VAR variation in eruptive sequences
STD used as standard in correlation

Sample No.	Field Id.	Applied to	Character	Age	Lab. Assign.
101	Okareka	STD	R	20	
105	Oruanui	O-A	R	20	
		STD			
109	Rotoehu	COR	D	47	
		VAR			
112	Rotoehu	COR	D	47	
		VAR			
114	Rotoehu	COR	D	47	
		VAR			
116	Rotoehu	COR	D	47	
		VAR			
201	Tirau	AGR			Tirau
		T-M	R	11	
202	Tirau	T-M	R	13	Tirau-Rotorua
203	Tirau	T-M	R	13	Tirau- Rotorua
204	Tirau	T-M	R	13	Tirau-Rotorua
205	Tirau	T-M	R	14	Tirau
206	under Tirau	T-M	A	14	
301	Tirau	T-M	R	9	Tirau-Rotoma
302	Tirau	T-M	R	9	Tirau-Rotoma
303	Mairoa	T-M	R	11	Tirau-Rotorua
304	Mairoa	T-M	A	15	Mairoa
305		T-M	A	16	Mairoa
306	Te Rere	T-M	R	20	

Sample No.	Field Id.	Applied to	Character	Age	Lab. Assign.
307	Oruanui	T-M	R (I)	20	
308	Rotoehu	COR	R	47	
309	Rotoehu	COR	R	47	
401	Mairoa	T-M	R	10	Tirau
402	Mairoa	T-M	A,R	12	Tirau-Mairoa
403		T-M	R	14	Mairoa
404		T-M	R	15	Mairoa
405		T-M	R	17	Mairoa
406	Oruanui	T-M	R	20	
		O-A			
407	Oruanui ?	O-A	A ?		
409	Rotoehu	COR	R	47	
501	Mairoa	T-M	R	?	Mairoa+Oruanui
502	Mairoa	T-M	A,R	?	Mairoa+Oruanui
503	Oruanui	T-M	R	20	Oruanui+Mairoa
601	Mairoa	AGR			
		T-M	A	15	Mairoa+Oruanui
602	Mairoa	T-M	A	16	Mairoa+Oruanui
603	Mairoa	T-M	A	17	Mairoa+Oruanui
604	Oruanui	T-M	(I) R	20	
		O-A			
605	Oruanui	T-M	R	20	
		O-A			
801	Oruanui	O-A	R		Oruanui
901	Rotorua	T-M	R		
902	Tirau	T-M	R		
903	Tirau	T-M	R		

Sample No.	Field Id.	Applied to	Character	Age	Lab. Assign.
904	Tirau	T-M	R		
905	Oruanui	T-M O-A	I		
906	Oruanui	T-M O-A	R	20	
1002	Kaharoa	AGR STD	R	0.9	
1101	Rotomahana	AGR STD	R	0.1	
1104	Taupo	AGR STD	R	1.8	
1110	Rotoma	AGR STD	R	8	
1115	Rotoma (basal lapilli)	AGR STD	R	8	
1201	Hamilton	AGR			
1701	Aokautere	O-A	R (I)	20	Oruanui
1801	Teviotdale	O-A	R (I)		

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A.P.W. Hodder

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