
Connecting with tephras: principles, functioning, and applications of tephrochronology in Quaternary science

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1. Introduction: what is tephrochronology?

Tephrochronology is a unique method for linking and dating geological, palaeoecological, palaeoclimatic, or archaeological sequences or events. The method relies firstly on stratigraphy and the law of superposition, which apply in any study that connects or correlates deposits from one place to another. Secondly, it relies on characterising and hence identifying or ‘fingerprinting’ tephra layers using either physical properties evident in the field or those obtained from laboratory analysis, including mineralogical examination by optical microscopy or geochemical analysis of glass shards or crystals (e.g., Fe-Ti oxides, ferromagnesian minerals) using the electron microprobe and other tools. Thirdly, the method is enhanced when a numerical age is obtained for a tephra layer by (1) radiometric methods such as radiocarbon, fission-track, U-series, or Ar/Ar dating, (2) incremental dating methods including dendrochronology or varved sediments or layering in ice cores, or (3) age-equivalent methods such as palaeomagnetism or correlation with marine oxygen isotope stages or palynostratigraphy. Once known, that age can be transferred from one site to the next using stratigraphic methods and by matching compositional characteristics, i.e., comparing ‘fingerprints’ from each layer. Used this way, tephrochronology is an age-equivalent dating method.

Even if a tephra layer is undated, or if it is dated imprecisely, it nevertheless provides an isochron or time-plane that allows the sequence in which it is found to be correlated with other sequences where it occurs. Herein lies the unique power of tephrochronology: deposits and their palaeoarchival evidence are thus able to be connected and synchronized – positioned precisely on a common time scale – using the tephra layer as a stratigraphically fixed tie-point, even where the tephra is poorly or undated. In this situation, the age scale is best envisaged as a length of elastic that can be stretched or contracted when numerical ages are obtained, or age precision is improved, whilst the tephra’s stratigraphic juxtaposition with respect to the enclosing deposits and associated archival data remains fixed on the ‘elastic’. When the tephra age is known, however, that age can be applied directly to the sequence where the tephra has been newly identified. This is because tephra layers are erupted over very short time periods (volcanic eruptions typically last for only hours or days to perhaps weeks or a few months or so at most), and thus each represent an instant in time, geologically speaking (Lowe, 2011).

A tephra layer from a powerful eruption can be spread widely over land, sea and ice, hence forming a thin blanket that has exactly the same age wherever it occurs (unless it has been reworked). For example, the Icelandic Fugloyarbanki tephra, identified in the NGRIP ice core from Greenland, has been dated at $26,740 \pm 390$ (1 σ) calendar (cal.) years before AD 2000 on the basis of multi-parameter counting of annual layers in NGRIP (Davies et al., 2008). It forms a widespread marker horizon or isochron in marine deposits in the North Atlantic and on the distant Faroe Islands between Iceland and Scotland. Thus palaeoarchives at these widely separated localities are now able to be connected precisely. Moreover, the extent of the radiocarbon marine reservoir effect in this region at the time can be examined using the Fugloyarbanki tephra as an independent time-plane.

**Citation for this article is given on p. 28*

In the New Zealand region, the Kawakawa (or Oruanui) tephra, erupted from Taupo caldera c. 25,400 cal. yr BP (Vandergoes et al., 2013), similarly forms an extensive isochron linking numerous terrestrial and marine sequences to the same point in time (Pillans et al., 1993; Carter et al., 1995; Alloway et al., 2007b; Newnham et al., 2007a, 2007b; Holt et al., 2010; Van Eaton and Wilson, 2013) (Fig. 1).

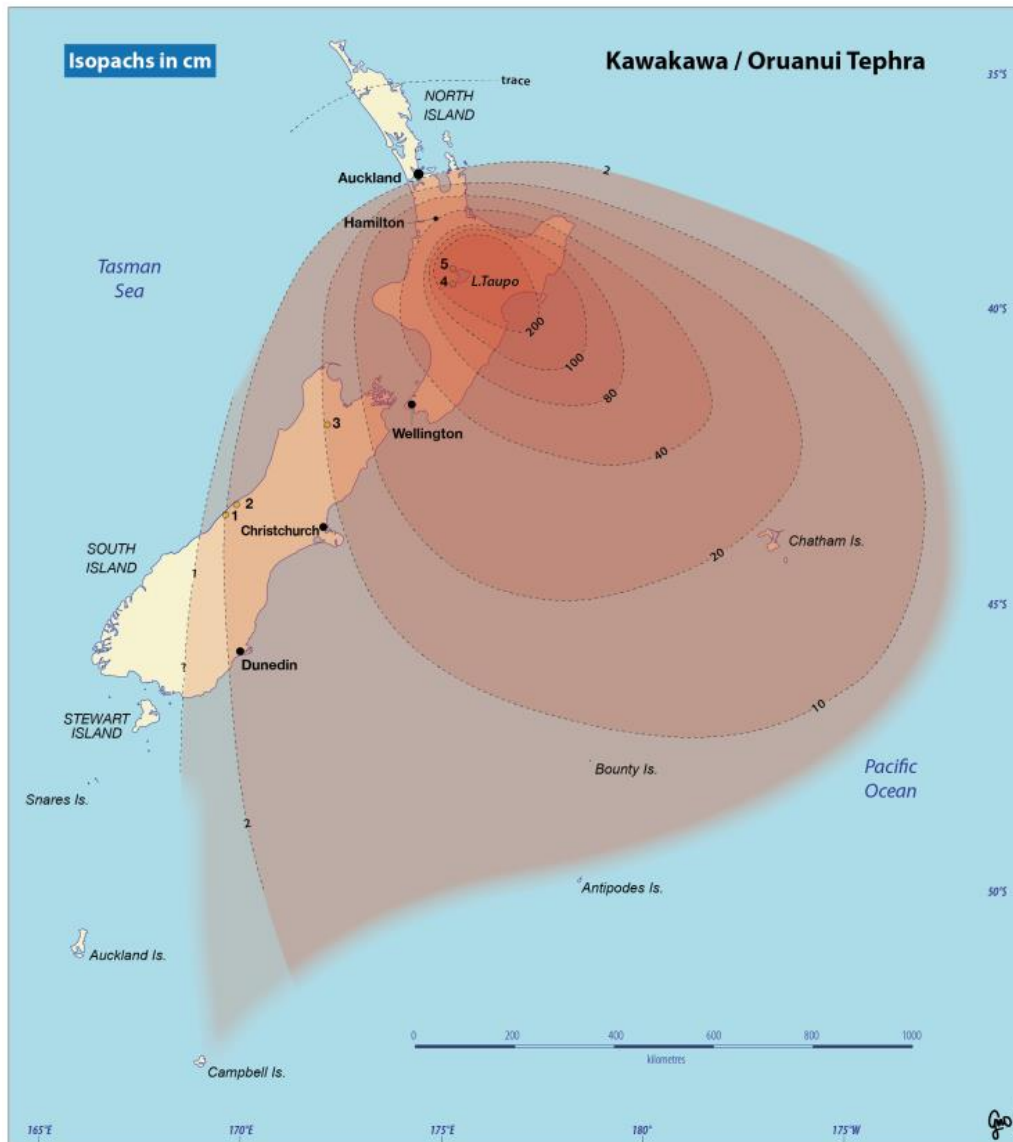


Fig. 1. Isopachs of Kawakawa/Oruanui tephra (in centimetres) showing the tephra's distribution extending >1000 km away from its source at Taupo caldera. Isopachs to the 10 cm mark are from Wilson (2001); beyond 10 cm, the thinner isopachs are based on relatively few sites and are indicative only (from Vandergoes et al., 2013). Trace occurrence in Northland is after Newnham et al. (2004).

Much of this workshop article is based on Lowe (2011), who comprehensively reviewed the basis of the discipline of tephrochronology, documenting recent advances in techniques as well as problems that may be encountered. A short, easy read on tephrochronology was given by Lowe et al. (2008b), and Lowe et al. (2008a) partly updated Froggatt and Lowe (1990). Other reviews pertaining especially to New Zealand include those of Shane (2000) and Alloway et al. (2007a, 2013). Numerous volcanological aspects of tephra studies are covered in detail by Sigurdsson (2000), and Smith et al. (2006) provided an introduction to New Zealand volcanology. Historical aspects of tephra studies in New Zealand were described by Lowe (1990) and Lowe et al. (2008c). A special volume comprising 31 tephra-based papers was published in 2011 (Lowe et al., 2011a).

Undertaking tephrochronology always requires tephrostratigraphy to some degree (Lowe, 2011). Tephrostratigraphy is the study of sequences of tephra and associated deposits, their distribution and stratigraphic relationships (superpositions), and their relative and numerical ages. It involves defining, describing, characterizing, and dating tephra layers using their physical, mineralogical or geochemical properties from field or laboratory-based observations, or both. In the last decade or so, there has been a revolutionary development focussed on detecting diminutive, distal tephra that are invisible in the field and referred to as cryptotephra. From the Greek word *kryptein*, meaning ‘to hide’, cryptotephra usually comprise fine-ash-sized (typically $< \sim 125 \mu\text{m}$) glass shards or crystals, or both, preserved and ‘hidden’ in peats or in lake, marine or aeolian sediments or soils, or in ice cores (Table 1; Lowe, 2011). Cryptotephrostratigraphy refers to the stratigraphic study of tephra-derived glass-shard, or crystal concentrations (e.g., Hogg and McCraw, 1983, p. 182; Matsu’ura et al., 2011, 2012; Wastegård and Boyle, 2012), that are encompassed within sediments or soils but which are not visible in the field as layers. The term ‘cryptotephra’ has replaced an earlier term ‘microtephra’ but the term ‘microshard’, defined as glass shards $< 32 \mu\text{m}$ in diameter, has been proposed by Lowe et al. (in prep).

Note that the letter ‘o’ rather than ‘a’ is the appropriate connecting letter in all these terms derived from tephra, and that the adjective ‘volcanic’ is redundant when referring to tephra. The term ‘airfall’ is no longer used (tephra-fall or tephra fallout, or ash-fall or ash fallout if appropriate, are used instead). Several other words in useage have *tephra* or *tephrós* (‘ash coloured’) at their root but none normally is relevant to tephrochronological studies. ‘Tephrite’ refers to a typically ash coloured alkalic basaltic volcanic rock erupted effusively as lava, not explosively. ‘Tephroite’ is a mineral, Mn_2SiO_4 , in the olivine group that is commonly ash-grey to olive or bluish green in colour. And ‘tephromancy’ is divination by means of sacrificial (human) ashes, requiring supernatural insight!

Table 1. Tephra-related nomenclature in brief (from Lowe, 2011).

Term	Definition
<i>Tephra</i>	All the explosively-erupted, unconsolidated pyroclastic products of a volcanic eruption (Greek <i>tephra</i> , ‘ashes’).
<i>Cryptotephra</i>	Tephra-derived glass-shard or crystal concentration, or both, preserved in sediment (including ice) or soil and not visible as a layer to the naked eye (Greek <i>kryptein</i> , ‘to hide’).
<i>Tephrostratigraphy</i>	Study of sequences of tephra layers and associated deposits, their distribution and stratigraphic relationships, and their relative and numerical ages. Involves defining, describing, characterizing, and dating tephra layers in the field and laboratory.
<i>Tephrochronology</i> (sensu stricto)	Use of tephra layers as isochrons (time-parallel marker beds) to connect and synchronize sequences and to transfer relative or numerical ages to them using stratigraphy and other tools. An age-equivalent dating method.
<i>Tephrochronology</i> (sensu lato)	All aspects of tephra studies and their application.
<i>Tephrochronometry</i>	Obtaining a numerical age or date for a tephra layer.

3. Mapping tephras: from metre to sub-millimetre scale

Since the mid-late 1920s, tephras have been mapped using field and laboratory based methods in New Zealand. In the field, the most successful approaches have included the so-called ‘hand-over-hand’ method whereby relatively thick sequences of tephras (metre to decimetre scale) are traced from cutting to cutting (Fig. 3) using their stratigraphy and salient physical properties including colour, bedding characteristics, or other features such as pumice density (e.g., hard vs soft) or colour, the presence of accretionary lapilli, or marker mineral grains (crystals) such as biotite visible via a hand lens. Distinctive marker beds provide a useful stratigraphic starting point in unravelling the complexities of a road cutting or other exposure (Fig. 4). The nature of buried soil horizons or loess associated with tephra layers may also provide helpful information in the field. Such methods are ultimately limited as the tephra layers thin away from source and lose diagnostic features in subaerial sequences, or where they become mixed together by soil-forming processes or by cryoturbation in periodically frozen landscapes.

But for several decades now, cores taken from lake sediments and peat bogs in Hawke’s Bay, Waikato, Taranaki, and Auckland have revealed a rich record of visible tephra layers a few centimetres to millimetres in thickness preserved at sites far from source volcanoes (e.g., Lowe, 1988; Molloy et al., 2009; Augustinus et al., 2011) (Fig. 5). Most recently, sub-millimetre-scale cryptotephra studies on such sediments have been initiated in the Waikato and Auckland regions (Table 2). Marine cores have also revealed detailed tephra records – which, together with those from lakes and bogs, provide a record of explosive volcanism that can be more comprehensive than that obtainable near to source because of burial or erosion of eruptives near volcanic centres (Fig. 6). Overseas, new developments in North America have been dramatic and ‘ultra-distal’ cryptotephras have been described by Pyne-O’Donnell et al. (2012).

Recently, Streeter and Dugmore (2013) advocated the development of high-resolution tephrochronology from studies in Iceland where they used digital photography to obtain thousands of stratigraphic measurements of multiple tephra layers intercalated with sediments (at a resolution of ± 1 mm). Further novel applications of tephrochronology to geomorphology were described by Dugmore and Newton (2012).



Fig. 3. Metre-thick, proximal, coarse, partly bedded pumiceous late Holocene rhyolitic tephra beds (mainly blocks/bombs and lapilli) and associated darker buried soil horizons (marking volcanic quiescence) evenly draping an antecedent strongly-rolling landscape near Taupo (from Lowe, 2011).



Fig. 4. Example of a stratigraphic marker bed in a road cutting, Hamilton. The prominent white bed mid-section is Rangitawa tephra (c. 340 ka). Lying at the base of strongly-weathered tephra beds and associated buried soils (Hamilton Ash sequence), rhyolitic Rangitawa tephra contains characteristic coarse-ash-sized golden platy crystals (biotite-kaolinite intergrade) and coarse-ash-sized quartz crystals. This widespread tephra, erupted near the end of MOI stage 10 (Alloway et al., 2007a; Holt et al., 2010), overlies unconformably a dark reddish-brown buried soil $>c.$ 0.78 Ma, about 1 m of volcanogenic alluvium, and (at the base) either the Ongatiti Ignimbrite (c. 1.23 Ma) (Lowe et al., 2001) or the Kidnappers Ignimbrite (c. 1 Ma) (Wilson et al., 1995). Photo: D.J. Lowe.



Fig. 5. Main tephra-producing Quaternary volcanic centres of North Island. The two most frequently active rhyolitic centres are Taupo and Okataina calderas (see Fig. 6). Egmont and Tongariro centres are andesitic, Tuhua (Mayor Island) is peralkaline, and the locally distributed tephras from Auckland Volcanic Field are basaltic. After Wilson and Leonard (2008).

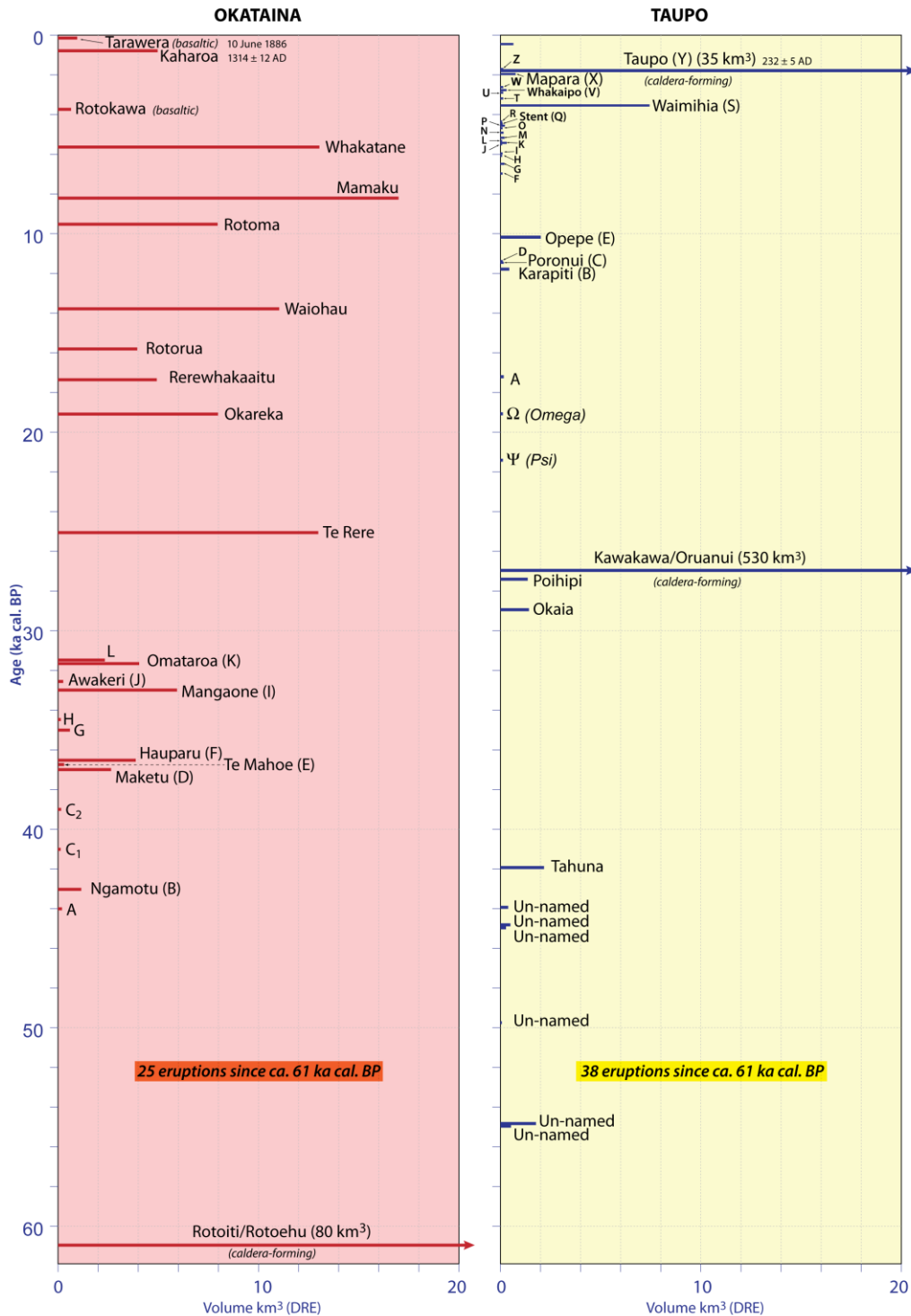


Fig. 6. Interfingering stratigraphic relationships, ages, and volumes (as non-vesiculated, void-free magma, i.e., dense-rock equivalent, DRE) of tephras erupted from Okataina and Taupo caldera volcanoes in North Island, New Zealand, since ca. 60 ka cal. BP (based on Wilson et al., 2009). Another significant unit (not depicted) in this period is the rhyolitic Earthquake Flat tephra (7 km³ DRE), which was erupted from the Kapenga caldera volcano (adjacent to Okataina) immediately after the Rototiti/Rotoehu eruption (Wilson et al., 2007). Note that since this diagram was published by Lowe (2011), Danišik et al. (2012) re-dated the Rotoiti/Rotoehu and EFT eruptives using (U-Th)/He and high-resolution ¹⁴C dating to attain ages of c. 45-50 cal ka; Vandergoes et al. (2013) re-dated the Kawakawa/Oruanui eruptives using high-resolution ¹⁴C dating on new, optimal sample materials to derive an age 25,358 ± 162 cal yr BP (2σ); and ages on around 20 other widespread tephras erupted since 30,000 cal yr BP were recently revised by Lowe et al. (2013).

4. Fingerprinting

Tephra fingerprinting in New Zealand has been undertaken using a range of analytical methods, almost always in conjunction with stratigraphic and chronological criteria where available (Table 3). Accurate fingerprinting is an essential element (!) in developing any age models for tephra, and the level of probability that can be applied to their identification and correlation is an important consideration in quantitative tephrochronology. Ideally, multiple criteria (more than one thread of evidence) should be used to secure the correlation: for example, stratigraphic position together with mineralogical assemblage and glass major element composition. Numerical age data are also useful.

Table 2. Special techniques used to identify and map thin distal tephra, or detect cryptotephra in cores or sections, in New Zealand (after Lowe et al., 2008a) (see also Gehrels et al., 2008).

Application	Method
<i>Field</i>	Ground radar
	Magnetic susceptibility
<i>Laboratory</i>	X-radiography
	Magnetic susceptibility
	Dry bulk density
	Rapid X-ray fluorescence
	Spectrophotometry (reflectance and luminescence)
	Refractive indices of glass
	Glass counts (cryptotephra)
	Total organic carbon, loss on ignition

Table 3. Summary of main analytical methods (excluding geochronology) used in New Zealand over past few decades to characterize and correlate tephra erupted since c. 30,000 cal. yr BP (after Lowe, 2011).

Tephra component/properties	Methods of analysis	Example
<i>Ferromagnesian minerals</i>		
Assemblages	Petrographic microscope	Table 4
Pyroxenes, amphiboles, olivine, biotite crystals	Electron microprobe	Fig. 9
<i>Fe-Ti oxides</i>		
Major and minor elements in crystals	Electron microprobe	Fig. 8
Eruption temperatures and oxygen fugacities	Electron microprobe	Table 4
<i>Glass shards or selvages</i>		
Major elements	Electron microprobe	Figs. 10, 11
Rare-earth and trace elements	LA- or SN-ICPMS, INAA, SIMS ^a	
Shard morphology	Optical microscope, SEM	
<i>Feldspars</i>		
Anorthite (An) content of plagioclase crystals	Electron microprobe	

^aLA- or SN-ICPMS, laser ablation or solution nebulisation inductively coupled plasma mass spectrometry; INAA, instrumental neutron activation analysis; SIMS, secondary ionisation mass spectrometry (ion microprobe); SEM, scanning electron microscope.

Mineralogy

One of the most common methods has been to use optical microscopy (using a petrological or polarizing microscope) to identify ferromagnesian mineralogical assemblages where such minerals are abundant. These minerals can be extracted using magnetic separators (e.g., Frantz) together with non-toxic heavy liquids (e.g., sodium polytungstate). With stratigraphic constraints, the relative abundances of ferromagnesian minerals typically allow a source volcano to be identified. For eruptives <30,000 cal. yr BP, orthopyroxene is always dominant in Taupo Volcanic Centre (TP)-derived tephtras whereas biotite, hornblende, cummingtonite, or orthopyroxene predominate in Okataina Volcanic Centre (OK)-derived tephtras (Table 4). Sometimes a mineral assemblage is sufficiently distinctive for an individual tephtra – for example, Tuhua Tephtra (from Mayor Island), which contains sodic phases such as aegirine – to be readily identified by only a few grains. However, the absence of diagnostic minerals does not necessarily negate an identification because minerals such as olivine are readily depleted by weathering, and biotite and orthopyroxene may be rapidly dissolved in some acid peat bogs (e.g., Hodder et al., 1991). Ferromagnesian minerals also tend to be sparse or absent at distal localities, having dropped out from proximal ash clouds earlier because of their high density. Recent studies of the OK-derived tephtras (erupted since 30,000 cal. yr BP) have shown that all but two comprise multiple magma types (Table 4), adding complexity to the use of ferromagnesian minerals for correlation purposes but increasing in some the potential for fingerprinting by chemical analysis of constituent minerals and glass (see below). Andesitic eruptives are usually distinguishable from rhyolitic tephtras because of their high pyroxene, or hornblende plus clinopyroxene, contents.

Microprobe analysis

In undertaking electron microprobe analysis (EMPA), sample preparation (Fig. 7) and probe operating conditions are critically important in deriving accurate and robust data, especially for glass which normally requires a defocussed beam to minimise volatilisation of Na and K (Froggatt 1992; Hunt and Hill, 1996, 2001; Turney et al., 2004; Lowe, 2011). Appropriate standards must be checked (analysed) frequently and there is now a general requirement for analyses of such standards to be published alongside new EMPA data (e.g., Westgate et al., 2008). A revised set of protocols for microprobing glass (and reporting such analyses) was published by Kuehn et al. (2011) following an intensive interlaboratory comparison exercise in 2010-2011. Glass EMPA analyses are usually normalized (summed to 100%, most of the deficit being attributable to water) to enable valid comparisons of analyses. Some consider that such normalization can ‘cover up’ poor data (low totals), and should therefore not be undertaken (e.g., Pollard et al., 2006). Recently, Hayward (2012) has developed robust protocols that enable the routine use of narrow beam diameters of 5 μm , and as low as 3 μm , without loss of Na. Such a development is extremely important because it enables many fine-grained samples to be analysed from wider, more distal geographic locations than previously, it reduces or prevents bias in data collection because most or all shards in a sample can be analysed, it enables more shards that are vesicular or microlite-rich (such as occur frequently in andesitic or basaltic tephtras) to be analysed than previously possible, and EPMA data acquisition is more easily automated and hence potentially more cost-effective (Hayward, 2012).

Analyses of Fe-Ti oxides, titanomagnetites and ilmenites, by EMPA have been useful for tephtra fingerprinting (Table 4). An example of the use of minor elements (Mn, Mg) to distinguish five TP-derived tephtras is given in Fig. 8. Egmont (EG) or Tongariro Volcanic Centre (TG) sources are usually determinable. The eruption temperature and oxygen fugacity (oxidation state of magma) of rhyolitic tephtras – estimated using single-grain EMPA of Fe-Ti oxide pairs of titanomagnetite and ilmenite – have provided a relatively new way to distinguish and match tephtras and, in some cases, magma batches within an eruptive sequence (Table 4).

The compositions of pyroxene, amphibole and olivine, obtained by EMPA, generally allow few individual tephra eruptive events to be identified but source volcanoes may be readily distinguished. For example, clinopyroxene and hornblende in EG-derived tephtras are typically more calcic than those from TG, hornblende from these two andesitic sources is more pargasitic than that from the rhyolitic centres, and olivine in TG-derived tephtras is forsteritic (Mg-rich) compared with that from Mayor Island which is fayalitic (Fe-rich). More recently, however, it has been demonstrated that the FeO and MgO contents of biotite derived from Kaharoa (two eruptive phases), Rotorua, Rerewhakaaitu, and Okareka tephtras were different, thus enabling them to be distinguished from other OK-derived eruptives (Fig. 9).

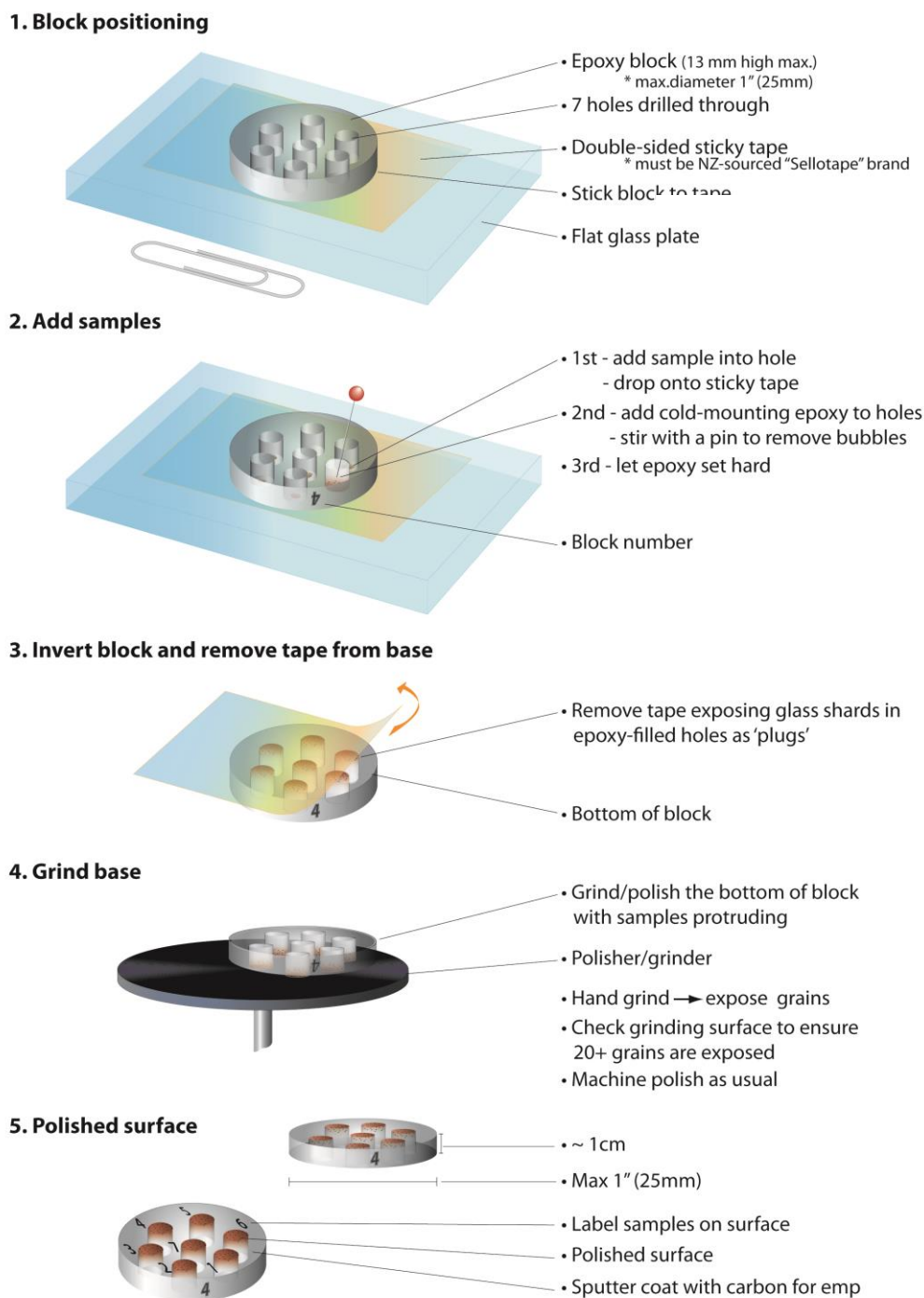


Fig. 7. Preparation of crystals or glass shards in 'blocks' for analysis by electron microprobe. Grains must be polished flat before analysis (from Lowe, 2011).

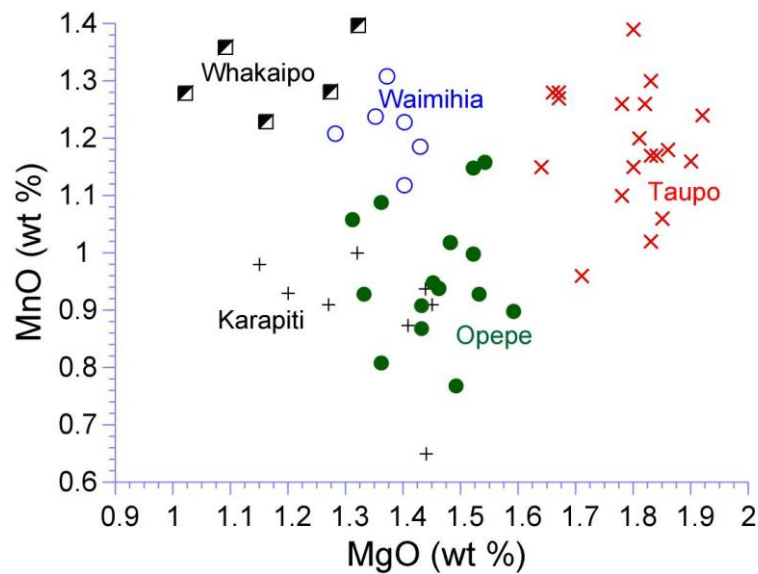


Fig. 8. Biplot of MnO vs MgO (wt%) analyses for ilmenites obtained using EMPA from five TP-derived tephra showing that Taupo (Unit Y), Whakaipo (V), and Waimihia (S) and are distinguishable from one another and from Karapiti (B) and Opepe (E) (from Lowe et al., 2008a).

The most commonly used tephra fingerprinting technique in New Zealand involves major-element analysis of volcanic glass shards using EMPA (Shane, 2000; Shane et al., 2006; Lowe et al., 2008a). Established initially in New Zealand in the early 1980s by Paul Froggatt (Froggatt and Gosson, 1982; Froggatt, 1983), EMPA of glass enabled volcanic sources to be readily identified for almost all eruptives <30,000 cal. yr BP in age. Although analyses of individual rhyolitic tephra of this age-range from Taupo or Okataina centres show many to be compositionally similar, some are distinguishable using bi-plots such as FeO or K₂O vs CaO content (Fig. 10), or using canonical discriminant function analysis (DFA) that incorporates eight or nine elements (oxides).

Detailed studies by EMPA, however, of thick sequences of proximal tephra erupted from Okataina have revealed much more compositional diversity and heterogeneity within individual lapilli-sized clasts and at different azimuths around the volcanic centre than previously recognised (Shane et al., 2008a). This heterogeneity is a consequence of the mingling of separate batches of magma that were tapped simultaneously or sequentially, accompanied by changes in wind direction, as eruptions proceeded. The recognition of more than one magma type in most of the OK-derived tephra has in some circumstances increased their potential for precise correlation in that some tephra beds might be identified uniquely, even where stratigraphic control is uncertain, because they were derived from two or three magma batches and so have multiple fingerprints or ‘handprints’ (Lowe et al., 2008a). For example, Kaharoa and Rotorua tephra are each the product of two magmas that can be distinguished on the basis of glass chemistry, one high (>4 wt%) and the other low (<4 wt%) in K₂O. Similarly, Rerewhakaaitu, Okareka, and Te Rere tephra are characterised by three magma types, the high K₂O-types (T2) containing distinctive biotite as well. However, it is also evident that the newly-recognised heterogeneity has increased complexity and potentially ambiguity, and glass compositions of some eruptive phases may overlap those for other tephra. An implication is that some tephra may have been misidentified (miscorrelated) in the past. The heterogeneity warns of the difficulty of characterising (thus fingerprinting) tephra beds using a limited set of distal samples from restricted dispersal sectors (Shane et al., 2008a).

Table 4. Ferromagnesian mineralogical assemblages and magma temperatures and oxygen fugacities of 22 marker tephra erupted since c. 30,000 cal. yr BP in New Zealand (from Lowe et al., 2008a)

Tephra name	Relative abundances of ferromagnesian minerals ^a	Eruption temperature ^b (° C)	Oxygen fugacity fO_2 (NNO) ^c
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Taupo Volcanic Centre (rhyolitic)(see Fig. 5)

Taupo (Unit Y)	Opx >> Cpx	862 ± 17	-0.17 ± 0.11
Whakaipo (Unit V)	Opx	785 ± 10	-1.06 ± 0.12
Waimihia (Unit S)	Opx >> Hbe	816 ± 10	-0.72 ± 0.08
Unit K	Opx	822 ± 16	-0.59 ± 0.11
Opepe (Unit E)	Opx >> Cpx	812 ± 18	-0.54 ± 0.17
Poronui (Unit C)	Opx >> Cpx		
Karapiti (Unit B)	Opx >> Cpx + Hbe	788 ± 33	-0.75 ± 0.24
Kawakawa/Oruanui	Opx > Hbe	774 ± 12	-0.14 ± 0.10
Poihipi	Opx > Hbe > Bio	771 ± 6	0.07 ± 0.10
Okaia	Opx > Hbe	789 ± 17	0.21 ± 0.09

Okataina Volcanic Centre (rhyolitic)

Kaharoa	T1 ^d	Bio >> Hbe >> Cgt ± Opx	731 ± 10	0.09 ± 0.14
	T2	Bio >> Cgt > Hbe ± Opx		
Whakatane	T1	Hbe > Cgt > Opx	746 ± 13	0.33 ± 0.09
	T2	Hbe > Cgt > Opx	737 ± 9	0.29 ± 0.11
	T3	Opx > Hbe > Cgt	770 ± 5	0.52 ± 0.05
Mamaku		Hbe > Opx >> ± Cgt	735 ± 19	0.18 ± 0.13
Rotoma	T1	Cgt > Hbe > Opx	752 ± 19	0.47 ± 0.12
	T2	Hbe > Opx > Cgt	752 ± 19	0.47 ± 0.12
	T3	Opx > Hbe > Cgt	752 ± 19	0.47 ± 0.12
Waiohau		Opx > Hbe	762 ± 23	0.36 ± 0.22
Rotorua	T1	Opx > Hbe >> Cpx	871 ± 10	1.11 ± 0.13
	T2	Bio > Hbe >> Opx	745 ± 30	0.17 ± 0.20
Rerewhakaaitu	T1	Opx > Hbe	721	-0.31
	T2	Hbe + Bio >> Opx	750 ± 18	0.43 ± 0.14
	T3	Opx > Hbe		
Okareka	T1	Opx + Hbe >> Cgt	759 ± 20	0.30 ± 0.20
	T2	Hbe + Bio >> Opx	724 ± 14	0.05 ± 0.15
	T3	Opx > Hbe	794 ± 12	0.82 ± 0.08
Te Rere	T1	Opx + Hbe	801 ± 24	1.43 ± 0.16
	T2	Opx + Hbe + Bio > Cpx	708 ± 3	-0.07 ± 0.01
	T3	Opx + Hbe		

Tuhua Volcanic Centre (peralkaline rhyolitic)

Tuhua	Aeg > Cpx > Opx ± Aen ± Rie ± Hbe ± Olv(fa) ± Tuh		
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Tongariro Volcanic Centre (andesitic)

Okupata	Opx > Cpx >> ± Olv(fo) ± Hbe	~900-1100	
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Egmont Volcanic Centre (andesitic)

Konini	Hbe > Cpx >> ± Opx	~950	
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(footnotes contd below)

Table 4 (contd)

^aOpx, orthopyroxene (mainly hypersthene); Cpx, clinopyroxene (mainly augite); Hbe, hornblende; Cgt, cummingtonite; Bio, biotite; Aeg, aegirine; Aen, aenigmatite; Rie, riebeckite; Olv, olivine (fa, fayalite; fo, forsterite); Tuh, tuhualite.

^bPre-eruption temperature data (mean \pm 1 standard deviation).

^cOxygen fugacity data reported in NNO units relative to the NiNiO buffer.

^dT1–T3 represent separate magma types (early to late eruptive phases, respectively) identified by Smith et al. (2005) for some Okataina eruptive episodes.

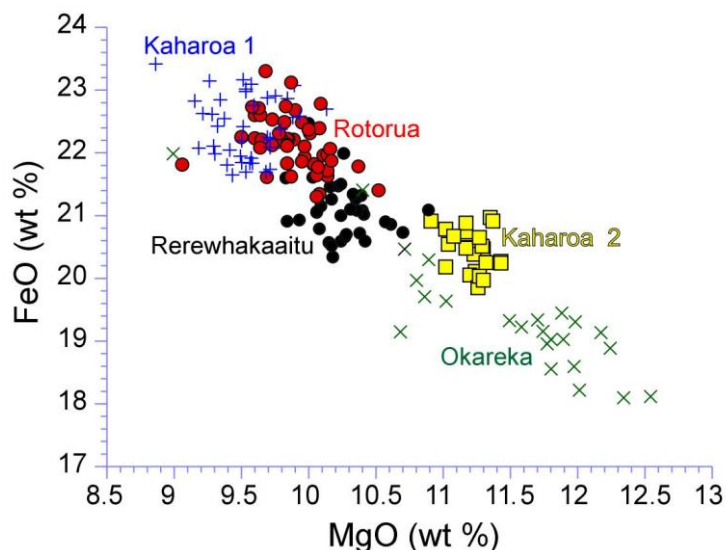


Fig. 9. Biplot of FeO vs MgO (wt%) analyses for biotite obtained using EMPA from four OK-derived tephras showing that Okareka (magma type T2), Rerewhakaaitu (magma type T2), and Rotorua (magma type T2) are distinguishable from one another, and that Kaharoa Tephra comprises two populations relating to early (Kaharoa 1, magma type T1) and late (Kaharoa 2, magma type T2) phases of the eruption that correspond to high K_2O and low K_2O glass compositions, respectively (from Lowe et al., 2008a).

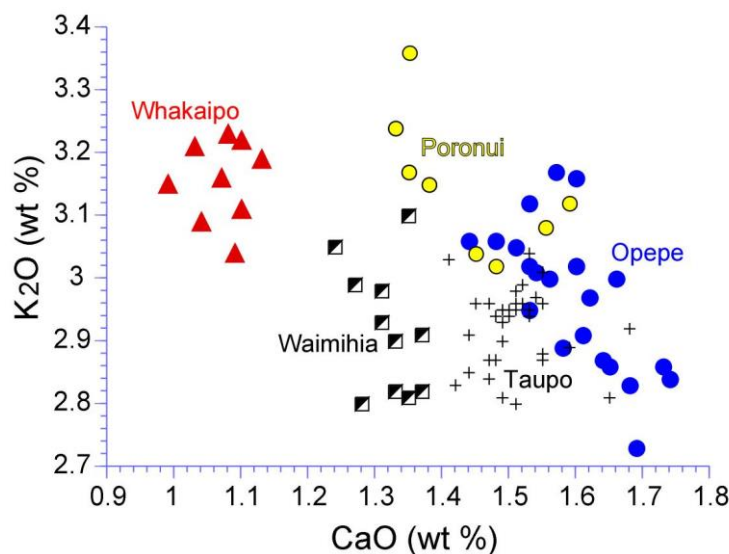


Fig. 10. Biplot of K_2O vs CaO (wt%) analyses for glass obtained using EMPA from five TP-derived tephras illustrating that Taupo (Unit Y), Whakaipo (V) and Waimihia (S) generally are able to be distinguished from one another but Poronui (C), Opepe (E), and Taupo (Y) partly overlap (from Lowe et al., 2008a).

The correlation of andesitic tephra using glass chemistry generally has not been straightforward for various reasons including the multiplicity of units, the paucity of suitable glass for probing (few shards are free of microlite inclusions, and shards may be highly vesicular) and its vulnerability to weathering, and wide compositional ranges ($\text{SiO}_2 = \sim 58\text{--}75$ wt %) and heterogeneity arising from multiple magma-mixing events (e.g., Shane et al., 2008b; Turner et al., 2008, 2011). Moreover, there are no comprehensive databases for tephra from EG and TG and hence direct correlation is uncertain without precise radiometric age or stratigraphic control (Shane, 2000; Lowe, 2011). However, analyses of glass from >40 EG-derived tephra by Shane (2005) showed them to be enriched in K_2O (>4 wt %) and depleted in CaO , TiO_2 and FeO in comparison with andesitic tephra erupted from TG, and hence easily distinguished (see also Donoghue et al., 2007; Lowe et al., 2008a). Further, the compositional variation (heterogeneity) in glasses from some individual andesitic tephra allows their identification within short stratigraphic intervals of c. 5,000–10,000 cal. years (Shane, 2005). Platz et al. (2007) proposed an evaluation procedure using mixing calculations to reduce microprobe-determined glass heterogeneity arising from plagioclase microlites, and this method is proving useful in emerging cryptotephra studies (e.g., Gehrels et al., 2010). Most recently, Moebis et al. (2011) demonstrated that tephra from the three main centres of the Tongariro Volcanic Centre (Ruapehu; Ngauruhoe; Red Crater, Tongariro) could be distinguished by major elements, specifically via K_2O and FeO (Fig. 11).

Basaltic tephra in New Zealand, of restricted distribution, have been analysed by Shane and Smith (2000) and Shane and Zawalna-Geer (2011) and others.

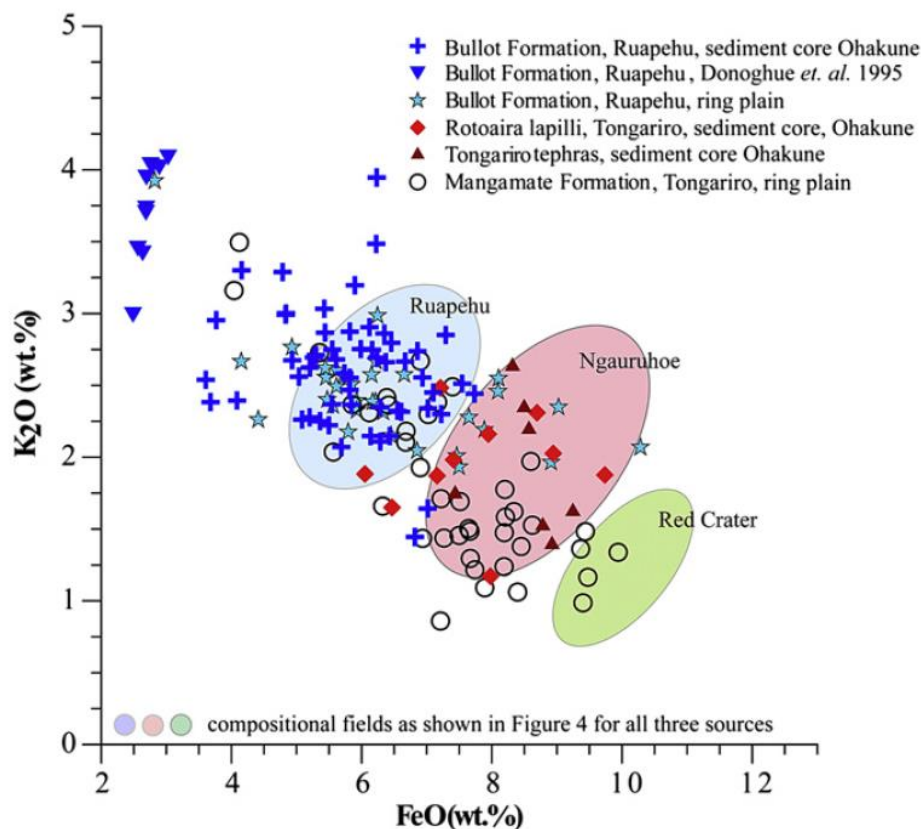


Fig. 11. Biplot of K_2O and FeO (total Fe expressed as FeO) derived by electron microprobe analyses of glass from tephra erupted from Ruapehu and Tongariro volcanoes younger than c. 12,000 cal. years, showing separation according to three sources (from Moebis et al., 2011, p. 359).

Trace- and rare-earth element (REE) data have not been widely employed in New Zealand tephrostratigraphy, although comprehensive studies have now been undertaken of Pleistocene tephros in the Auckland region (Pearce et al., 2008a) and in a core from ODP Site 1123 in the Pacific Ocean east of New Zealand (Allan et al., 2008). Earlier, various REEs and trace elements, based on analyses of small, bulk-glass samples, enabled some tephros from TP and OK within the <30,000 cal. yr BP time-frame to be distinguished. TP-derived tephros tend to show greater abundances of Sm, Eu, Tb, Lu, Hf, and Sc (Shane, 2000). Tuhua Tephra is distinguishable from both TP and OK-derived tephros because it has greater abundances of all REEs and other elements including U, Th, and Hf.

Because glasses from many OK-derived tephros are now known to be compositionally heterogeneous, the trace-element and REE analyses need to be re-examined and revised, probably using inductively coupled plasma mass spectrometry methods (LA-ICPMS). Advances in this method now enable it to obtain detailed major- and trace-element compositions from individual glass shards and for fingerprinting individual tephra beds or tephra successions of similar mineralogy or provenance, i.e., it is probably most useful to separate beds that are compositionally similar and not distinguishable using major element chemistry (Pearce et al., 1999, 2004, 2007, 2011; Allan et al., 2008; Westgate et al., 2008; Kuehn et al., 2009). The main advantage of a single-grain technique is that it allows mixed populations to be identified (such mixing arising from magmatic or volcanic eruption processes, or from post-depositional blending of thin tephros in soil-forming environments or the dissemination of glass shards in peat or in lake sediments, e.g., Gehrels et al., 2006).

Analyses by ion microprobe (secondary ionisation mass spectrometry, SIMS) of tephra components are also now being undertaken (e.g., Denton and Pearce, 2008) and look set to expand as the technique becomes more readily available (Lowe, 2011).

5. Statistical techniques to aid correlation

Statistical techniques in New Zealand have been limited mainly to DFA. Whilst not without potential flaws (see below), DFA has several advantages, the most important being that all or most elements in the analyses are taken into account non-subjectively, samples are able to be classified (matched) with known probability, and their degree of similarity is reflected in the Mahalanobis multidimensional distance statistic, D^2 , which is preferable to the frequently used numerical 'similarity coefficients' measure. The efficacy of the technique can be tested using an iterative process to measure classification efficiency. DFA has been applied reasonably successfully to studies involving major-element analyses of glass, Fe-Ti oxides or hornblende for both rhyolitic and andesitic tephros including composite (mixed) tephra deposits. In all these studies, many individual tephra layers or groups of tephros were able to be discriminated with a high-degree of probability (up to 100% classification efficiency) using either glass or titanomagnetite compositions, but some tephros, very similar compositionally, were less-well discriminated or unidentifiable using major elements alone.

The successful use of DFA is directly reliant upon the quality and comprehensiveness of the reference datasets against which unknowns are compared (e.g., Lowe, J.J. et al., 2007; Lowe, 2008a; Bourne et al., 2010). The generally poor analytical precision of some elements obtained by EMPA may limit the effectiveness of some DFA models, and the somewhat piecemeal glass compositional datasets for New Zealand tephros, acquired over several decades at a number of EMPA facilities, are of variable quality for several reasons, including changes in microprobe analytical procedures in the mid-1990s. Although further advances using DFA to identify and correlate rhyolitic tephros in New Zealand may now be feasible with the acquisition of the new glass major-element data (summarised in Smith et al., 2005; Lowe et al. 2008a), the approach must be cautionary. Elsewhere, the statistical (or Euclidian) distance function (which is a variation of the similarity coefficient method), cluster analysis, or the Student's *t*-test have been used (e.g., Pollard et al., 2006; Pearce et al., 2008b; Preece et al., 2011). A review paper on

statistical correlation methods is being prepared (Lowe et al., in prep), but ultimately such statistical techniques will rely on the development of more comprehensive, regional tephrostratigraphic and geochemical databases of uniformly high quality (Lowe, 2011).

6. Developments in dating methods and age modelling

Dating methods relevant to tephra studies have described by Lowe (2011). A key advance has been the development of the isothermal-plateau fission-track dating method (ITPFT) for glass (Alloway et al., 2007a). It has enabled ages to be obtained on many distal tephras that previously were unable to be dated because their main component, glass, was unreliable because of annealing (e.g., Westgate et al., 2007). Examples of such applications are the dating of initial loess deposition in Alaska at about 3 million years ago (Westgate et al., 1990), dating Quaternary glacioeustatic sedimentary cycles in the Wanganui Basin (Pillans et al., 2005), and dating marine tephra sequences from ODP sites east of New Zealand, thus testing chronologies based on alternative methods (Carter et al., 2004; Alloway et al., 2005; Allan et al., 2008). Another promising method for more proximal deposits, until recently used mainly for pre-Quaternary petrological or provenance studies, is the use of U-Pb analyses to date zircons using SIMS techniques (e.g., SHRIMP: Brown and Fletcher, 1999; Wilson et al., 2008; ID-TIMS: Crowley et al., 2007) or LA-ICPMS (e.g., Chang et al., 2006) (see also Dickinson et al., 2010).

For tephras erupted within the past c. 50,000–60,000 cal. years, the radiocarbon (^{14}C) technique remains by far the most important method for developing age models (other methods are documented by Alloway et al., 2007a; Westgate et al., 2007; Lowe et al., 2008a) (Table 5). Calendar dates on two late Holocene tephras, Kaharoa and Taupo, have been obtained by wiggle-matching log-derived tree-ring sequences dated by ^{14}C . The date obtained for Kaharoa (1314 ± 12 AD) (95% probability) by Hogg et al. (2003) was supported by Bayesian statistical analysis of an independent ^{14}C -age dataset (Buck et al., 2003). The main plinian phases of the Kaharoa eruption took place during the austral winter (on the basis of tree-ring data). The date for Taupo tephra is now established as 232 ± 10 AD (Hogg et al., 2012; 95% probability). This date contrasts with several other calendar dates suggested for this eruption and indicates that the Greenland ice-core date of 181 ± 2 AD, and the Roman and Chinese sunset date of c. 186 AD, are no longer viable. Tree-ring data and preserved plant macrofossils have shown that the Taupo eruption took place during the austral late summer–early autumn period, i.e. probably late March–early April.

Bayesian age modelling

Together with wiggle-matching methods, Bayesian age modelling, derived ultimately from the theorem of 18th Century Englishman, Thomas Bayes, is adding another revolutionary aspect to the construction of enhanced and more precise chronologies in tephrochronology (e.g., Blockley et al., 2007b, 2008, 2012; Lowe, J.J. et al., 2007; Lowe, 2011). For example, 14 Holocene and late Pleistocene tephras comprising a sequence from Waimihia Tephra (3370–3450 cal. yr BP) to Rerewhakaaitu Tephra (17,200–18,050 cal. yr BP), preserved in peat at montane Kaipo bog in eastern North Island, were dated by using flexible depositional age-modelling (similar to wiggle-matching) their stratigraphic order and 51 associated ^{14}C -age points simultaneously against the IntCal04 calibration curve (Hajdas et al., 2006). The flexible depositional age-modelling of the Kaipo sequence was undertaken using the programme OxCal3, developed by Chris Bronk Ramsey, which utilises a Bayesian statistical framework (successor OxCal4: Bronk Ramsey, 2008, 2009). Subsequently, Lowe et al. (2008a) analysed the same age data independently using an alternative Bayesian age-depth modelling programme, Bpeat (Blaauw and Christen, 2005; Wolfarth et al., 2006; Blaauw et al., 2007). The 2σ -age ranges for the tephras derived from both OxCal3 and Bpeat were listed in Lowe et al. (2008a), and are closely aligned.

A revised age model for the Kaipo tephra sequence has been developed for the NZ-INTIMATE project using another Bayesian programme, *Bacon* (Blaauw and Christen, 2011), in conjunction with OxCal4 and the associated *P_Sequence* function (Bronk Ramsey, 2009), and was published earlier this year (Lowe et al., 2013). Older tephras (those erupted earlier than c. 18,000 cal. yr BP) were also re-dated using OxCal4 and the associated *Tau_Boundary* function (Lowe et al., 2013) (Fig. 12).

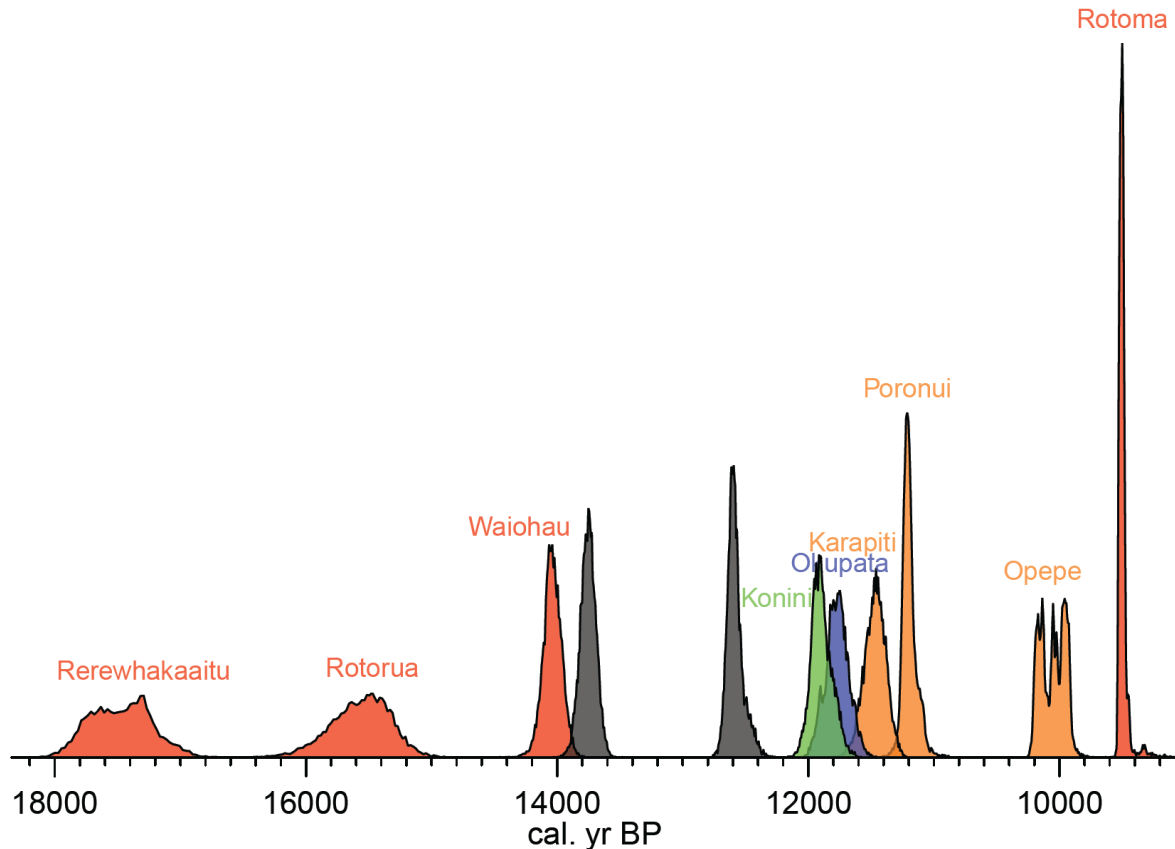


Fig. 12. Bayesian-derived age models for nine Lateglacial to Holocene tephras. Ages derived from modelling for part of a peat sequence at Kaipo bog in eastern North Island using *Bacon* (from Lowe et al., 2013). Probability plots (all are equal in area) are coloured according to tephra source volcanoes: red, Okataina; orange, Taupo; green, Egmont/Taranaki; blue, Tongariro. Grey plots show the *Bacon*-derived start and end ages of the Lateglacial cool episode (i.e., New Zealand climate event NZce-3 of Barrell et al., 2013) between the Waiohau and Konini tephras.

The new age modelling has shown Waiohau tephra to have been erupted around 14,000 cal. yr BP (*cf.* c. 13,700 cal. yr BP in Lowe et al., 2008a). Regarding the very widespread Kawakawa/Oruanui tephra, its age has been problematic (Lowe et al. 2008a, 2010). Wilson et al. (1988) published a ^{14}C age of c. 22,590 ^{14}C yr BP, equivalent to about 27,000 cal. yr BP, but recent dating of optimal material using the *Tau_Boundary* function of OxCal4 showed this tephra is now dated firmly at $25,358 \pm 162$ cal yr BP (95% probability) (Vandergoes et al., 2013).

7. Tephrochronology as a high-precision synchronization or correlation tool

A critical recent development has been the enhanced use of tephrochronology to affect more precise correlations between marine, ice-core, and terrestrial records. This application holds the key to testing the reliability of high-precision correlations between sequences and current theories about the degree of synchronicity of climate change at regional to global scales – provided the tephra correlation is certain (e.g., see Denton and Pearce, 2008). Numerous studies have utilised this unique chronostratigraphic capability (e.g. Lowe, 2008a; Zanchetta et al., 2011).

In Europe, Blockley et al. (2007a) for example showed that there is now potential to independently test climate synchronicity between Greenland and Europe as far south as the Alps via the Vedde ash. Similarly, Rasmussen et al. (2008) correlated the NGRIP, GRIP, and GISP2 ice core records across marine oxygen isotope stage 2 using mainly tephras as a means of applying the recent NGRIP-based Greenland ice-core chronology to the GRIP and GISP2 ice cores, thus facilitating the synchronizing of palaeoclimate profiles of the cores in detail. Remarkably, Lane et al. (2011, 2012) have now linked northern, central, and southern European climate records in part using cryptotephrochronology.

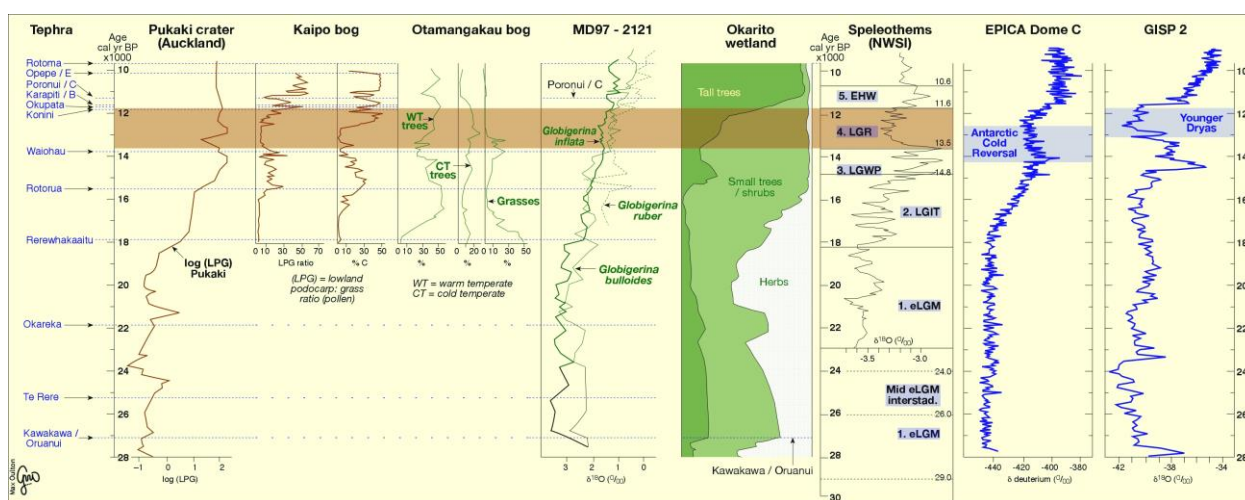


Fig. 13. Compilation of partial high-resolution palaeoenvironmental records spanning the interval c. 28,000 to 9500 cal. yr BP and showing how sites are linked by one or more tephra isochrons (NZ-INTIMATE project). Antarctic (EPICA Dome C) and Greenland (GISP2) records shown for comparison. The climatic events 1–5 are based on the speleothem record obtained from northwest South Island (NWSI) (Williams et al., 2005, 2010). (1) eLGM, ‘extended’ Last Glacial Maximum (Newnham et al., 2007a); (2) LGIT, last glacial–interglacial transition; (3) LGWP, late-glacial warm period; (4) LGR, late-glacial reversal; (5) EHW, early-Holocene warming. The boundary between events 1 and 2 is marked by Rerewhakaaitu Tephra (Newnham et al., 2003); the boundary between events 3 and 4 is marked approximately by Waiohau Tephra (Newnham and Lowe, 2000); the end of event 4 is marked by the closely spaced couplet of Konini and Okupata tephras, the former tephra essentially marking the start of the Holocene at c. 11,700 cal. yr BP in northern New Zealand (Walker et al., 2009). Evidence for event 4 (late-glacial reversal) (brown shading) is recorded at Kaipo, Otamangakau, MD97-2121 and to a lesser degree at Pukaki crater (see also Putnam et al., 2010; Newnham et al., 2012; Barrell et al., 2013; Sikes et al., 2013).

The Australasian INTIMATE project, built along similar lines to the very successful INTIMATE project (integration of ice-core, marine and terrestrial records) of the North Atlantic (Lowe, J.J. et al., 2008; Davies et al., 2012), has developed a climate event stratigraphy for the region for the past 30,000 years (Alloway et al., 2007b; Barrell et al., 2013). The role of tephrochronology in linking all of the selected palaeoenvironmental records (apart from those based on speleothems) has been highlighted (Fig. 12; Lowe et al., 2008a, 2013). The advantage provided by key marker tephras in the NZ-INTIMATE project led to the development of new age models based on Bayesian probability methods noted above

Tephras also provide the means to help quantify the marine reservoir effect for correcting the marine-based radiocarbon time-scale, as shown by studies in the Mediterranean Sea, the Adriatic Sea, the North Atlantic, and the South Pacific Ocean (e.g., Sikes et al., 2000; Lowe, J.J. et al., 2007; Carter et al., 2008; Lowe et al., 2013). Further, they enable AMS-based radiocarbon dating of pollen concentrates or biological remains to be evaluated, and for demonstrating and hence correcting for the ‘hard water’ effect in dating lake sediments (Lowe, 2008a).

Tephrochronology, long used to provide ages on early hominins, is being increasingly applied to archaeology and studies of humans in antiquity (e.g., Tryon et al., 2008, 2009, 2010), including determining the timing and extent of initial human impacts on landscapes and ecosystems such as those of Great Britain, Ireland, Iceland, and New Zealand (e.g., Dugmore et al., 2000, 2007; Lowe et al., 2000; Hogg et al., 2003; Wastegård et al., 2003; Edwards et al., 2004; Lowe and Newnham, 2004; Lowe, 2008b; Streeter et al., 2012). The potential key role of cryptotephrochronology in underpinning the study of the adaptation of humans to climatic change in Europe since about 20,000 years ago was highlighted by Blockley et al. (2006), and most recently further findings from the RESET project were published in a remarkable paper by Lowe et al. (2012). Noteworthy tephrochronological studies with a disease and medical focus have also been undertaken recently (D'Costa et al., 2011; Streeter et al., 2012).

8. Summary and conclusions

Tephrochronology, the characterisation and use of volcanic-ash layers as a unique chronostratigraphic linking, synchronizing, and dating tool, has become a globally-practised discipline of immense practical value in a wide range of subjects including Quaternary stratigraphy, palaeoclimatology, palaeoecology, palaeolimnology, physical geography, geomorphology, volcanology, geochronology, archaeology, human evolution, anthropology, and human disease and medicine. The advent of systematic studies of cryptotephra – the identification, correlation, and dating of sparse, fine-grained glass-shard concentrations ‘hidden’ within sediments or soils – over the past 10–15 years has been revolutionary (Table 5). New cryptotephra techniques developed in northwestern Europe and Scandinavia in particular, adapted or improved to help solve problems as they arose, have now been applied to sedimentary sequences (including ice) on all the continents of the world. The result has been the extension of tephra isochrons over wide areas hundreds to several thousands of kilometres from source volcanoes. Taphonomic and other issues, such as understanding and quantifying uncertainties in correlation, provide plenty of scope for future work (Lowe, 2011).

Developments in dating and analytical methods have led to important advances in the application of tephrochronology in recent times. In particular, the ITPFT (glass fission-track) method has enabled landscapes and sequences to be dated where previously no dates were obtainable or where dating was problematic; the LA-ICPMS method for trace element analysis of individual shards $\sim 10\ \mu\text{m}$ in diameter or smaller is generating more detailed and more robust ‘fingerprints’ for enhancing tephra-correlation efficacy (Pearce et al., 2011); and the revolutionary rise of Bayesian probability age modelling has helped to improve age frameworks for tephra of the late-glacial to Holocene period especially.

Developments in the understanding of magmatic heterogeneity at some volcanoes have shown that multiple fingerprints may arise according to tephra-dispersal direction during a ‘single’ eruption episode, adding complexity and the need for a careful approach in making long-range correlations. New debates on how various statistical methods should be used to aid correlation have emerged recently. The applications of tephrochronology and cryptotephrochronology are now seen as key correlation or ‘synchronization’ tools in high-resolution palaeoclimatic projects such as INTIMATE (Integration of ice-core, marine and terrestrial records since 30,000 years ago) and in dating, integrating and interpreting human-environmental interactions in antiquity. New INQUA-based projects SHAPE (Southern Hemisphere assessment of palaeoenvironments) and CELL50K (Calibrating environmental leads and lags over the last 50 ka) will utilise tephrochronology and cryptotephrochronology as well as other dating methods to meet their objectives.

INTAV, the leading INQUA-based global group of >100 tephrochronologists (Table 6), remarkably, now contains many geoscientists working in non-volcanic countries. These ‘neo-tephrochronologists’ have added new enthusiasm and skills to those of the geoscientists working on the typically thick, complex, multi-sourced tephrostratigraphic sequences in ‘traditional’ volcanic regions – Japan, New Zealand and western USA, for example – in an excellent example of intra-disciplinary mutualism (Froese et al., 2008; Lowe, 2008a).

An INTAV-led project INTREPID (Enhancing tephrochronology as a global research tool through improved fingerprinting and correlation techniques and uncertainty modelling) was initiated in 2009 and will continue to 2015. Some results were presented at the Inter-INQUA INTAV conference “Active Tephra” held in Kirishima, Kyushu Island, southern Japan, in May 2010. Papers from that meeting were published by *Quaternary International* (Lowe et al., 2011a). An INTREPID-led Bayesian age-modelling course was held in San Miguel de Allende, Mexico, in August 2010. In May, 2011, a workshop on the Eyjafjallajökull eruptions of 2010, and their implications for tephrochronology, volcanology, and Quaternary studies, was held in Edinburgh, U.K., by the ‘Tephra in Quaternary Science’ (TIQS) group (e.g., see Stevenson et al., 2012). This meeting was also sponsored in part by the INTREPID project.

Table 5. Some recent advances in methodology and applications in global tephra studies (after Lowe, 2008a) (*table contd on next page*).

Advance/method	Application
1. Cryptotephra studies: identifying, correlating, and dating ash-sized glass-shard and/or crystal concentrations (not visible as layers) ‘hidden’ within sediments (including ice) or soil	Extending isochrons over wider areas, some >1000 km from volcano source including ‘ultra-distal’ (hence see 4), and improving records of volcano eruption history and thus developing better models of volcanic hazards and their mitigation
2. Isothermal-plateau fission-track dating of glass (ITPFT)	Dating tephtras (especially those comprising only glass shards), hence dating landscapes or palaeoenvironmental or geoaerchaeological sequences not previously datable at distal and other locations
3. Laser-ablation inductively-coupled plasma mass spectrometry (LA-ICP-MS) and ion microprobe (SIMS) analysis of single grains	Correlation of tephtras using trace elements and REEs of glass shards (especially of tephtras with similar major-element compositions as determined by electron microprobe), with enhanced reliability obtained using single-grain analysis that can reveal magma mingling or contamination
4. Connecting and dating palaeoenvironmental sequences and geoaerchaeological deposits with high precision using tephtras or cryptotephtras as isochrons	Classical tephrochronology applied in high-resolution palaeoclimatic projects such as INTIMATE to test synchronization of various stratigraphic records, correcting for marine reservoir or hard-water effects, and dating, integrating and interpreting human-environmental interactions in antiquity
5. Bayesian probability analysis of age sequences involving tephtras	Bayesian methods are providing enhanced and more precise chronologies for tephrostratigraphic sequences via OxCal, BCal, Bacon (etc)

6. Recognition of heterogeneity in the composition of some tephtras, especially high vs low K ₂ O contents; mainly by analysis of glass components but also of some minerals (e.g., biotite)	Petrological insight into magma processes such as mingling and volcano eruptive histories, including the finding that multiple fingerprints of some tephtras differ according to direction of dispersal
7. Improving the reliability of electron microprobe-derived analyses of andesitic glass using geochemical models	Novel procedure to evaluate and correct for common microlite contamination in andesitic glass shards, thereby increasing the potential of andesitic tephtras as marker beds
8. 'Neof ormation' of International Focus group on Tephrochronology and Volcanism (INTAV) in 2007 (previously known as SCOTAV and COT: see Lowe et al., 2011b)	INQUA*-based global group of tephrochronologists with interests in developing and improving analytical techniques of known reliability to characterize tephtras, to map their distributions and improve volcano eruptive histories, to develop high-precision age models for tephtras, and to apply tephrochronology to numerous disciplines as a precise correlation and dating tool

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