Cover sheet

TEPHROCHRONOLOGY

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TEPHROCHRONOLOGY

Synonyms

Tephrostratigraphy; chronostratigraphy; stratigraphic correlation using tephra

Definitions

Tephra. All the explosively erupted, unconsolidated pyroclastic products of a volcanic eruption.

Cryptotephra. Tephra-derived glass shard and/or crystal concentration preserved in sediments or soils/paleosols but not visible as a layer to the naked eye.

Tephrostratigraphy. Study of sequences of tephra layers or cryptotephras (and associated deposits) and their lithologies, spatial distribution, stratigraphic relationships, and relative and numerical ages. Involves defining, describing, characterizing, and dating tephra layers or cryptotephra deposits in the field and laboratory as a basis for their correlation.

Tephrochronometry. Obtaining a numerical age or calendrical date for a tephra or cryptotephra deposit.

Tephrochronology sensu stricto. Use of primary tephra layers or cryptotephras as isochrons to connect and synchronize depositional sequences, or soils, and to transfer relative or numerical ages to the sequences or soils using lithostratigraphic, compositional, and other data pertaining to the tephras/cryptotephras.

Tephrochronology sensu lato. All aspects of tephra/cryptotephra studies and their application.

Extract [not part of published article – for internet/library purposes only]

Tephrochronology is the use of primary, characterized tephras or cryptotephras as chronostratigraphic marker beds to connect and synchronize geological, paleoenvironmental, or archaeological sequences or events, or soils/paleosols, and, uniquely, to transfer relative or numerical ages or dates to them using stratigraphic and age information together with mineralogical and geochemical compositional data, especially from individual glass-shard analyses, obtained for the tephra/cryptotephra deposits. To function as an age-equivalent correlation and chronostratigraphic dating tool, tephrochronology may be undertaken in three steps: (i) mapping and describing tephras and determining their stratigraphic relationships, (ii) characterizing tephras or cryptotephras in the laboratory, and (iii) dating them using a wide range of geochronological methods. Tephrochronology is also an important tool in volcanology, informing studies on volcanic petrology, volcano eruption histories and hazards, and volcano-climate forcing. Although limitations and challenges remain, multidisciplinary applications of tephrochronology continue to grow markedly.

Introduction and definitions

Tephras are the explosively-erupted, unconsolidated pyroclastic (fragmental) products of a volcanic eruption (Greek *tephra*, "ashes") (Lowe, 2011). Typically they comprise volcanic glass (including shards, pumice, and scoriae or cinders), rock (lithic) fragments, and crystals (mineral grains), which are erupted through the atmosphere and deposited on the land, the sea-floor, or ice caps relatively quickly – usually in a matter of hours or days according to eruption duration (Lowe, 2011; Stevenson et al., 2012). A tephra layer deposited from a powerful eruption, and not reworked, consequently forms a widespread, thin blanket on the surface of the Earth that has effectively the same age – an isochron – wherever it occurs. The term "tephra" encompasses all grain sizes: ash (grains <2 mm in diameter), lapilli (64–2 mm), or blocks (angular) or bombs (rounded) (>64 mm) (White and Houghton, 2006). Diminutive, distal tephras that are not visible as layers in the field are called cryptotephras (Greek *kryptein*, "to hide"). Cryptotephras comprise concentrations of ash-sized glass shards or crystals, or both, usually <150 μm in diameter, preserved in sediments (including ice), in cave deposits, or in soils or paleosols (Lowe, 2011; Lane et al., 2014).

Tephrochronology may be defined as the use of primary tephra layers or cryptotephra deposits as isochronous beds to connect and synchronize depositional sequences, and to transfer relative or numerical ages (or dates) to such sequences using stratigraphic information together with lithological, compositional, and geochronological data obtained for the tephras or cryptotephras. Tephrochronology is thus a method for correlating and dating geological, palaeoecological, palaeoclimatic, or archaeological sequences or events, or soils, using characterized tephras or cryptotephras as chronostratigraphic marker beds (Alloway et al., 2013).

Tephrochronology is undertaken typically in three steps. Firstly, tephra deposits are correlated from place to place in the field using their lithostratigraphic and relative age relationships along with intrinsic physical properties, associations with other deposits, and spatial distribution, i.e., tephrostratigraphy **(Fig. 1).** Field-work is carried out at a range of scales because tephra deposits become thinner, and constituent components become smaller, from proximal to distal locations. A potential complication is tephra remobilisation, which is discussed later. Secondly, the components of the deposits are characterized or "fingerprinted" using mineralogical or geochemical analytical methods, often both, in the laboratory to aid their correlation. Such laboratory characterization is essential in cryptotephra studies. Thirdly, when a numerical age or date for a tephra or cryptotephra deposit is obtained, i.e., tephrochronometry, that age or date can be transferred from one site to the next by comparing the compositional characteristics or "fingerprints" of its components with those of equivalent deposits elsewhere. These three steps – (*i*) mapping tephras and determining their lithostratigraphic relationships, (*ii*) characterizing tephras/cryptotephras in the laboratory, and (*iii*) dating them – enable tephrochronology to function as a unique stratigraphic and geoscientific dating tool, and are described below in detail after a subsection on volcanological applications.

Fig. 1. Stratigraphic sequence of four Holocene tephra deposits of ash- and lapilli-grade, and buried soil horizons, near Mt Tarawera, New Zealand. Exposure is ~2 m high. From top, Tarawera tephra (mainly Rotomahana Mud member) (erupted 10 June 1886); shower-bedded Kaharoa tephra (AD 1314 ± 12), characterised by abundant biotite; Taupo tephra (AD 232 ± 10) (note that the grey and very dark-brown soil horizons evident in the upper part of the nonwelded Taupo deposit, Taupo ignimbrite, are the result of podzolization, an acidic soil-leaching process that occurred here prior to the soil's burial by the Kaharoa eruptives); Whakatane tephra (5526 ± 145 cal. yr BP) (ages from Lowe et al., 2013). Photo: Megan Balks.

Volcanological applications of tephrochronology

As well as providing isochrons for geological, archaeological, and palaeoenvironmental applications, tephrochronological studies involving mapping, characterization, and dating are critical for developing a comprehensive record of past explosive eruptions and recurrence rates from which time-space relationships of volcanism can be established, and volcanic hazards evaluated (e.g., Óladóttir et al., 2008; Kuehn and Negrini, 2010). Knowledge of the distribution and thickness relationships of tephra or cryptotephra deposits enables magma volumes to be calculated (Wilson et al., 2009; Ponomoreva et al., 2013a). Near to volcanic centres, deposits may include lavas as well as an array of different types of pyroclastic deposits (fall, surge, flow and density current, and explosion breccias; **Fig. 2**), and detailed studies of their stratigraphic intercalation and physical, mineralogical, and geochemical properties provide insight into volcanic history and petrogenesis (e.g., Ponomareva et al., 2004; Smith et al., 2005; Turner et al., 2011a; Cioni et al., 2014). Information about the release of volatiles into the atmosphere and associated climatic impacts can also be gleaned from studies on tephras (e.g., Zdanowicz et al., 1999; Alloway et al., 2013; Sigl et al., 2013).

Fig. 2. (A) Road section in the vicinity of Lago Blanco, Chaitén sector (42° S), southern Chile. The stratigraphy at this section reveals (from top) a prominent rhyolitic (c. 76 % SiO_2) pumiceous lapilli deposit (Cha-1 correlative) dated at c. 8700 ^{14}C yr BP and sourced from an ancestral Chaitén volcano, closely overlying a rhyolitic (c. 71% SiO_2) surge and fall couplet informally named Lepué tephra. This lower rhyolitic eruptive couplet, dated at c. 9800 ^{14}C yr BP, is sourced from the nearby Michinmahuida Volcanic Complex (MVC). The buried soil horizon ("Andic paleosol") marks the hiatus between the Lepué and Cha-1 eruptions. (B) Low-angle cross-bedding and cross-cutting relationship of the surge deposit across its co-eruptive fall deposit, Lepué tephra. (C) The Michinmahuida-sourced eruptive couplet is closely underlain by a widespread and distinctive layer of banded high-Si rhyolite breccia (indicated by arrows) that likely represents the products of an explosion of a pre-Cha-1 lava dome (ancestral Chaitén volcano). Such sections are particularly important in terms of recognising eruptives with different field expression and composition, as well as for unravelling the complex and variable histories of closely situated (adjacent) eruptive centres. Photos: Brent Alloway.

Mapping and correlating tephras

The most successful approaches in the field include the so-called hand-over-hand method whereby relatively thick sequences of tephras, typically metre to decimetre scale, at proximal or medial locations, are documented and traced from one outcrop or section to the next using distinctive physical properties in combination with their stratigraphic associations (**Fig. 3**). Physical properties include colour, bedding characteristics, or particle-specific features such as pumice/scoria, lithic, and crystal componentry, the presence of accretionary lapilli, or marker mineral grains (crystals) such as biotite identifiable via a hand lens. Distinctive marker beds provide a useful stratigraphic starting point in unravelling the complexities of geological sequences seen in road cuttings or natural exposures, and detailed lithostratigraphic columns are constructed to provide the basis essential for correlating from one site to the next (Fig. 3). The nature of buried soil horizons, or loess or other deposits associated with tephra layers, including (for example) fossils or other attendant palaeoecological information such as pollen assemblages (e.g., Newnham and Lowe, 1999; Housley et al., 2013; Westgate et al., 2013a), or archaeological relationships (Feibel, 1999; Mullen, 2012; Riede and Thastrup, 2013), may provide additional contextual information helpful for affecting correlation (**Fig. 4**). High-resolution tephrostratigraphic records in Iceland were constructed by Streeter and Dugmore (2013) using digital photography to obtain thousands of stratigraphic measurements of multiple tephra layers intercalated with sediments at a resolution of one millimetre.

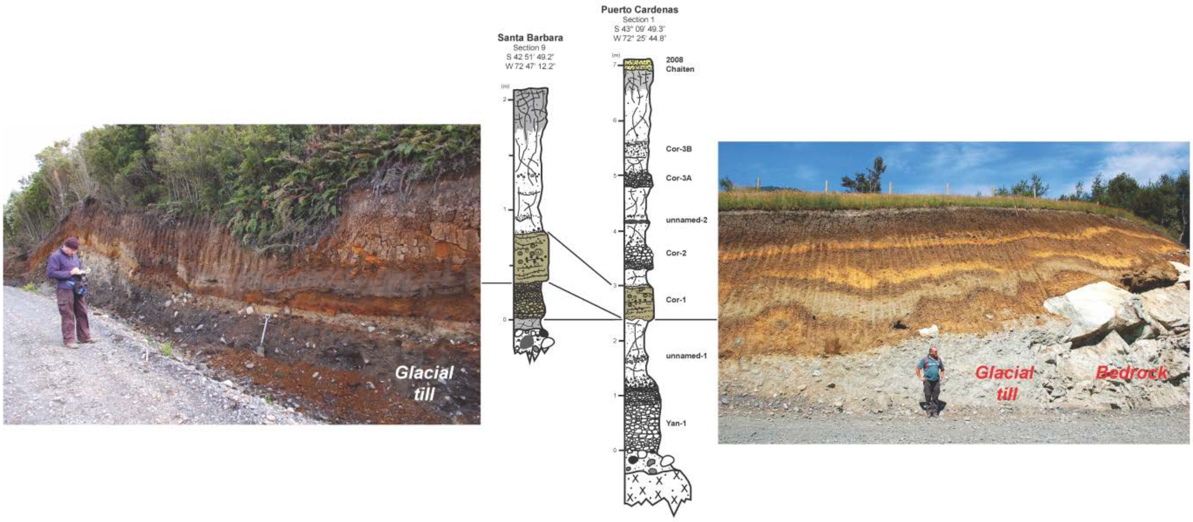

Fig. 3. Stratigraphic columns and corresponding section photos detailing the tephrostratigraphy of deposits at two sites, Santa Barbara and Puerto Cardenas, in the Chaitén sector (42° S) of southern Chile. The tephra notation is from Naranjo and Stern (2004). A key tephra of interest is the prominent decimetre-thick grey tephra layer (Cor-1; now more recently and informally referred to as Lepué tephra) that contains conspicuous accretionary lapilli throughout. This tephra is the product of a large-scale phreatomagmatic eruption sourced from the glaciated Michinmahuida Volcanic Complex (MVC) dated at c. 9800 ^{14}C yr BP. Tephra from the 2008 eruption of Chaitén volcano occurs on the present-day ground surface. Other strongly pedogenically weathered tephra beds represented within these sections have yet to be geochemically characterized and are probably variably sourced from other near-by volcanoes (Puyuhuapi, Melimoyu, Yanteles, and Corcovado). The tephra sequences at both localities rest on glacial till with a minimum age of c. 14,000 ^{14}C yr BP. Photos: Brent Alloway.

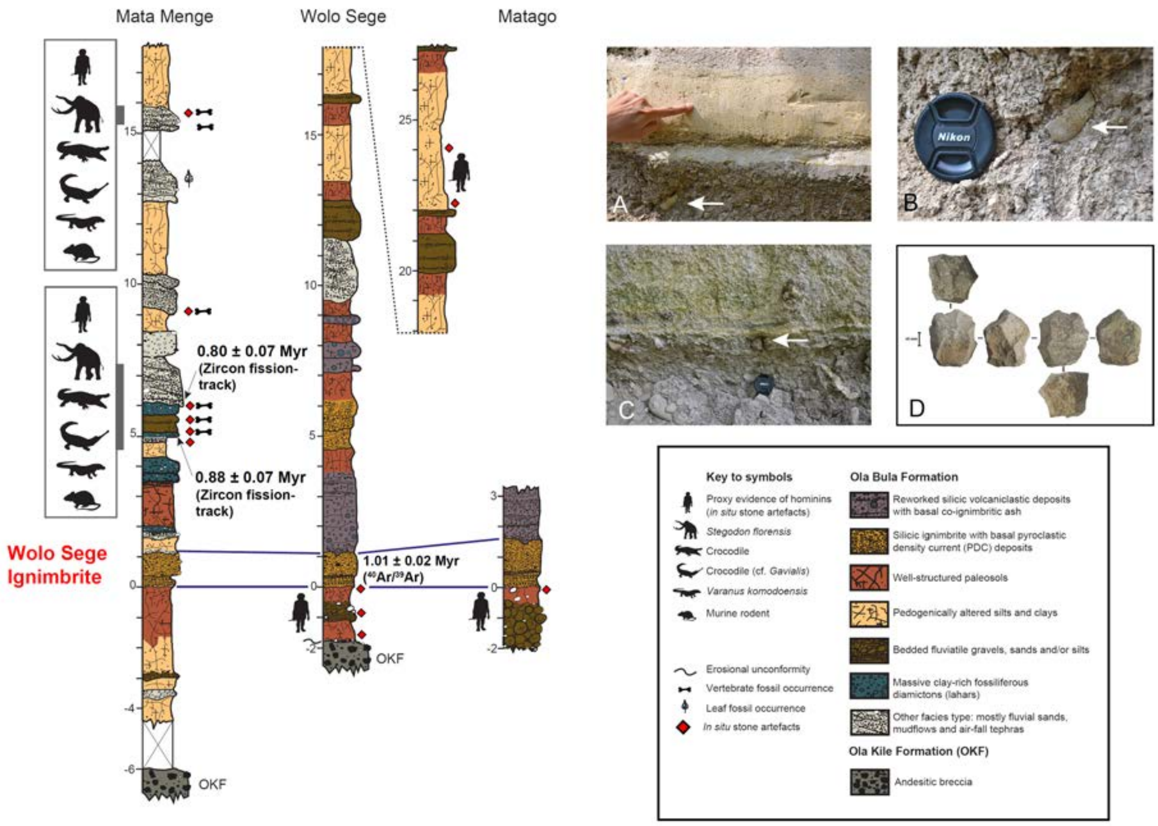

Fig. 4. Stratigraphy associated with hominin stone artefacts and vertebrate fossil remains from the So’a Basin, central Flores, Indonesia (unpublished data of B. V. Alloway, A. Brumm, G. van den Bergh, and R. Setiawan; after O’Sullivan et al., 2001, and Brumm et al., 2010). The in situ stone artefacts occur immediately beneath a nonwelded (unconsolidated) ignimbrite deposit (Wolo Sege ignimbrite, WSI) that can readily be correlated and distinguished from other enveloping silicic tephra inter-beds across the So’a Basin on the basis of its unique depositional architecture as well as its major element glass-shard composition. The WSI, dated at 1.02 ± 0.02 Ma by $^{40}Ar/^{39}Ar$ (Brumm et al., 2010), provides important evidence for the presence of hominins on Flores for over 1 million years. (A) The base of WSI at the Wolo Sege section showing distinctive surge-like sub-units containing accretionary lapilli and bedding consistent with density segregation of entrained particles. Note the in situ bifacial flake in the paleosol immediately beneath the base of the WSI (indicated by arrow). (B) Close-up photo of the in situ bifacial flake identified at Wolo Sege. (C) In situ flaked core stone identified at the Matago section on the palaeo-ground surface buried by the WSI. (D) Close-up photo showing the detail of the flaked core stone from the Matago section. Photos A-C: Brent Alloway; Photo D: Adam Brumm.

One potential difficulty in tephrostratigraphy arises where tephra remobilisation has occurred or where glass shards or crystals have been disseminated or dispersed in sediments or soils, and hence primary isochron positions are not clear (Alloway et al., 2004a; Pyne-O’Donnell, 2011; Housley et al., 2012). Remobilisation of tephra resulting from widespread landscape instability in combination with climatic factors (e.g., Manville and Wilson, 2004) can remobilise large volumes of tephra for decades in the aftermath of a paroxysmal eruption (e.g., following the 1991 Pinatubo eruption: Torres et al., 2004). Remobilisation of tephra can also be triggered by human activities (Swindles et al., 2013). Such reworked or disseminated tephra-derived constituents, including glass shards, form diachronous rather than isochronous surfaces and hence their use as stratigraphic tie points is compromised unless remobilisation is very localised or near-contemporaneous with the primary depositional event. The non-reworked part of a tephra deposit provides an isochron of maximum age (the date of the tephra eruption and primary deposition) but any reworked components are younger (Lowe, 2011).

Field correlation methods are increasingly limited as the tephra layers become thinner and finer with increasing distance away from source (e.g., **Fig. 5),** and the tephras may become more irregularly distributed (e.g., Turney and Lowe, 2001; Lawson et al., 2012). The tephras typically lose diagnostic physical features (such as internal bedding) in subaerial sequences, and thin, separate beds can become mixed together by soil-forming processes including bioturbation, or by cryoturbation in periodically or perennially frozen landscapes (Sanborne et al., 2006; Lowe and Tonkin, 2010; Dugmore and Newton, 2012). Cores taken from lake sediments and peat bogs potentially provide a reliable means to record thin and/or fine-grained distal tephra layers, or at proximal or medial locations where tephras tend to be thicker and may have more restricted dispersal patterns around source vents – for example, in basaltic volcanic fields (Shane and Hoverd, 2002). These lake or bog depositional environments allow thin tephras or glass-shard concentrations (cryptotephras) to be preserved amidst organic-bearing sediments (**Fig. 6**) (de Fontaine et al., 2007; Smith et al., 2013), notwithstanding potential taphonomic difficulties posed by tephra reworking or dispersion (Lowe, 2011; Liu et al. 2014). Marine cores, especially from locations downwind of eruption centres, may also contain detailed records of tephra layers or cryptotephras intercalated with sediments (e.g., Gudmundsdóttir et al., 2012; Abbott et al., 2013; Ponomareva et al., 2013b;

Austin et al., 2014). Possible reworking of tephras (by currents, ice-rafting, bioturbation) adds complexity in some cases (Brendryen et al., 2010; Larsen et al., 2014; Todd et al., 2014).

Fig. 5. A distal occurrence of fine-grained Mazama tephra, 1–2 cm in thickness and composed mainly of glass shards, shows up as the pale "break" (where the person is touching) in an alluvium-soil sequence on the lowermost terrace alongside the North Saskatchewan River in Edmonton, Alberta, Canada. Multiple buried soils formed on intermittent flood deposits are evident in the section, with the high sedimentation (up-building) rate contributing to the rapid burial and preservation of the thin, fine-grained Mazama tephra as an inconspicuous layer. The Mazama tephra, dated at 7627 ± 150 cal. yr BP (Zdanowicz et al., 1999), provides a key isochronous time-plane (chronostratigraphic marker bed) for Holocene archaeological and palaeoenvironmental studies in the United States and southwestern Canada. Located ~1450 km northeast of its source (Crater Lake, Oregon), the tephra was first identified here by Westgate et al. (1969). Photo: Maria Lowe.

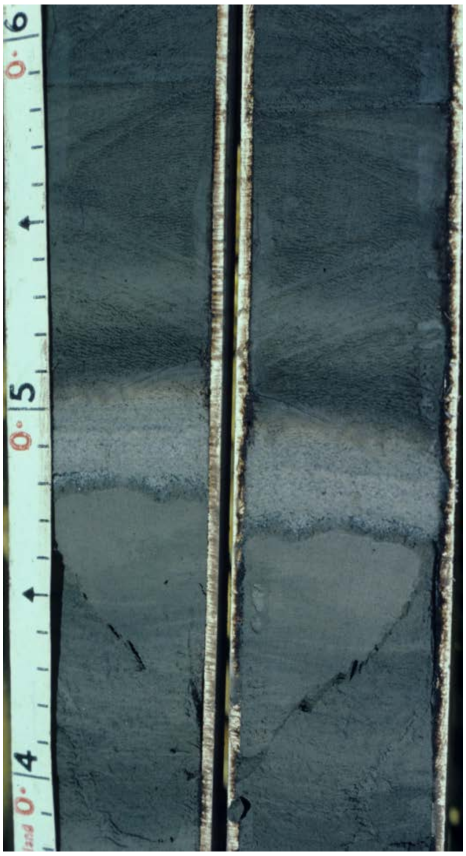

Fig. 6. Close-up of a near-basal part of a lake sediment core from Lake Okoroire, New Zealand, showing (in middle of photo) 3-cm-thick Rerewhakaaitu tephra, erupted 17,496 ±462 cal. yr BP from Mt Tarawera in the Okataina Volcanic Centre (Lowe et al., 2013; see Fig. 8 below). Many tiny black specks in the pale layer represent free biotite crystals diagnostic of this (and some other) tephras derived from Mt Tarawera. Different sediment colours above and below the tephra reflect a climatically-driven change from shrubland/grassland to forest in the region soon after the eruption (Newnham et al., 2003; Alloway et al., 2007). An indistinct uncorrelated tephra lies ~2 cm above the Rerewhakaaitu tephra. Scale marks in centimetres. Photo: David Lowe

Together with those from lakes and bogs, many of the records of marine tephra deposits can thus document patterns of explosive explosive volcanism in time and space, and integrate the stratigraphic interfingering of eruptives from multiple volcanic sources (Shane et al., 2006; Swindles et al., 2011; Ponomareva et al., 2013a, 2013b). Such compilations are often more comprehensive than those obtainable near volcanic centres because of burial or erosion of eruptives at such proximal locations, but an important caveat is that proximal deposits are typically more compositionally variable than distal deposits (e.g., Smith et al., 2005; Shane et al., 2008a). On this basis, distal deposits usually have a more restricted compositional range than otherwise might be generated during a particular eruptive episode.

Distal tephras and cryptotephra deposits

Sub-millimetre-scale studies have involved the development of new approaches to enable cryptotephras, and very thin distal tephras, to be mapped, albeit discontinuously, across landscapes using a range of methods firstly to *detect* and *isolate* glass shard or crystal concentrations (e.g., Hall and Pilcher, 2002; Gehrels et al., 2006; Swindles et al., 2010; Lane et al., 2014), and secondly to *correlate* them with known (previously characterized) deposits using geochemical analyses of glass shards, melt inclusions (glass) within crystals, or crystals (Matsu'ura et al., 2011; Swindles et al., 2013) as described below. Cryptotephras have been discovered in peat, lake, marine, aeolian, or frozen sediments or ice, in deposits in caves or rock shelters, and in soils or paleosols. They (and thin visible tephras) have been detected using ground-penetrating radar, magnetic susceptibility and remanent magnetisation, X-radiography, X-ray fluorescence (including use of scanners), spectrophotometry, micro-petrography, enumeration of glass shards, and measurements of total organic carbon and loss-on-ignition (Turney and Lowe, 2001; Gehrels et al., 2008; Lawson et al., 2012). These novel cryptotephra studies, although not without problems and limitations (e.g., Davies et al., 2007; Payne and Gehrels, 2010; Swindles et al., 2011), have documented tephra-fall occurrences at sub-millimetre scales at distances of hundreds to some thousands of kilometres from source, greatly extending known geographical limits (e.g., Payne et al., 2008; Davies et al., 2010, 2012; Balascio et al., 2011; Cullen et al., 2014). Pyne-O'Donnell et al. (2012) showed that "ultra-distal" cryptotephras derived from Holocene eruptions in Alaska and the Pacific Northwest occur up to ~7000 km from source in easternmost North America, and one tephra, the Alaskan White River ash (eastern lobe, erupted around AD 860), occurs over ~7,000 km away in Ireland (Jensen et al., 2014). Lane et al. (2013) identified the c. 75,000-year-old Youngest Toba Tuff tephra as a cryptotephra deposit in Lake Malawi sediments in east Africa, >7000 km west of the source volcano in Sumatra. Cryptotephra associated with the eruption of the Campanian Ignimbrite in Italy c. 40,000 calendar (cal.) yr BP was identified across much of central Europe and the Mediterranean area by Lowe et al. (2012). As noted earlier with regard to visible tephra deposits, cryptotephra studies can help also in elucidating the eruptive history of volcanoes (e.g., Shane et al., 2013).

Ice cores provide detailed and valuable records of volcanism (Davies et al., 2010; Dunbar and Kurbatov, 2011; Abbott and Davies, 2012; Coulter et al., 2012). Until recently, analytical limitations of geochemical techniques have hindered adequate characterisation of ultra-fine glass particles (<5 μm) and identification of their eruptive source. Similarly, sulphate records in ice cores may not always act as suitable proxies for the occurrence of tephra or cryptotephra deposits composed of (typically sparse) glass shards in the cores (Davies et al., 2010; Abbott and Davies, 2012).

Characterizing tephras and cryptotephras in the laboratory

The characterization, or "fingerprinting", of mineral and glass components of tephras or cryptotephras can be undertaken using a range of analytical methods (**Table 1**). Such characterization is almost always carried out in conjunction with lithostratigraphic and chronological criteria to obtain cogent correlations (Alloway et al., 2013).

Table 1. Analytical methods (excluding geochronology) used to characterize glass or minerals in tephras to facilitate their correlation (after Lowe, 2011).

Tephra components and properties	Main methods of analysis[a]
Glass shards[b]	
Major and minor elements[c]	Electron microprobe
Trace elements[c] including rare earths	LA- or SN-ICPMS, INAA, SIMS
Sr, Nd, and Pb isotopes	LA-ICPMS, multi-collector NMS
Shard morphology	Optical microscope, SEM
Melt inclusions (glass)	
Major and minor elements	Electron microprobe
Trace elements	SIMS, LA-ICPMS
Ferromagnesian silicate minerals	
Assemblages or marker minerals	Petrographic microscope, XRD
Pyroxenes, amphiboles, olivine, or biotite crystals/phenocrysts	Electron microprobe
Crystal geometry	Optical microscope, SEM
Apatite, zircon	
Apatite or zircon[d] crystals/phenocrysts	Electron microprobe, TIMS-TEA
Crystal geometry	Optical microscope, SEM
Fe-Ti oxides	
Major and minor elements	Electron microprobe
Eruption temperatures and oxygen fugacities	Electron microprobe
Feldspars[d]	
Plagioclase, anorthoclase, or sanidine crystals/phenocrysts	Electron microprobe

[a]LA- or SN-ICPMS, laser ablation or solution nebulisation inductively coupled plasma mass spectrometry; INAA, instrumental neutron activation analysis; SIMS, secondary ionization mass spectrometry (ion probe); NMS, nuclide mass spectrometry; SEM, scanning electron microscopy; XRD, X-ray diffraction; TIMS-TEA, thermal ionization mass spectrometry-trace element analysis.
[b]May also include glass coats (selvedges) or matrix glass in pumice clasts.
[c]Major elements expressed as oxides usually are defined as >1 wt%, minor element oxides as 0.1 to 1 wt%, and trace elements as <0.1 wt% or <1000 parts per million (ppm) of the element (not oxides).
[d]Analyses of these minerals generally are less useful for correlating individual tephras.

Ferromagnesian silicate mineral assemblages

A common method is to use a petrographic microscope to identify ferromagnesian or mafic mineralogical assemblages where such minerals are abundant, usually at proximal or medial sites. These minerals can be extracted using a magnetic separator together with non-toxic heavy liquids such as sodium polytungstate. With stratigraphic and age constraints, the relative abundances of ferromagnesian minerals may allow a source volcano to be identified. For example, in the Yukon Territory of Canada, Preece et al. (2000, 2011a) showed that tephras erupted from the Aleutian arc-Alaska Peninsula, so-called Type I beds, had low crystal contents comprising mainly pyroxene (and mainly bubble-wall shards), whereas tephras derived from the Wrangell volcanic field and Hayes volcano, Type II beds, generally had high crystal contents comprising mainly hornblende (and mostly pumiceous shards). In New Zealand, orthopyroxene (mainly hypersthene) is dominant in tephras erupted from the Taupo Volcanic Centre since c. 30,000 cal. yr BP whereas biotite, hornblende, cummingtonite, or orthopyroxene predominate in tephras erupted from the Okataina Volcanic Centre over the same period (Lowe et al., 2008).

In some cases an individual tephra can be identified using distinctive, diagnostic marker minerals, such as aegirine and aenigmatite in the Tuhua Tephra that were erupted from peralkaline Mayor Island volcano c. 7000 cal. yr BP in New Zealand. However, the absence of diagnostic minerals does not necessarily negate correlation because minerals such as olivine, biotite, and hypersthene can be dissolved comparatively quickly in some very acid peat bogs (within 700 years: Hodder et al., 1991) or in soil-forming environments (Lowe, 1986; Churchman and Lowe, 2012). Ferromagnesian minerals and Fe-Ti oxides also tend to be sparse or absent at distal localities, dropping out from proximal or medial ash clouds earlier because of their high density (Juvigné and Porter, 1985).

Although of limited application, the crystal geometry (crystal width) of apatite (a phosphate-group mineral) was shown to be useful, along with apatite trace element data, for differentiating beds in a study of Late Ordovician K-bentonites in USA by Sell and Samson (2011). Similarly, Donoghue et al. (1991) showed that two distinct crystal geometries of olivine (skeletal, non-skeletal) were useful in correlating some andesitic tephras in New Zealand.

Major-element analysis of glass shards, melt inclusions, and minerals

The electron microprobe enables a range of tephra components to be analysed for major elements on a grain-by-grain basis: individual glass shards, glassy coatings on crystals, melt inclusions (glass preserved within crystals including quartz, pyroxenes, amphiboles), pumice fragments, and loose crystals or phenocrysts including various ferromagnesian silicate minerals, apatite, zircon, and Fe-Ti oxides such as titanomagnetite (Table 1). The main advantage of the microprobe and other single-grain techniques is that they allow mixed or heterogeneous populations to be identified. Because volcanic glass is amorphous, its analysis by microprobe needs especially careful sample preparation and mounting, use of appropriate standards, and optimum probe-operating conditions to derive accurate and robust data (Kuehn et al., 2011; Hall and Hayward, 2014; Pearce et al., 2014; Suzuki et al., 2014).

Usually a defocused (e.g., 10–20 µm) or rastered beam is deployed to minimise mobilisation of Na, although protocols that use narrower beam diameters (3−5 µm) without loss of Na have been recently developed for analysing fine-grained glass shards, as occur in distal or ultra-distal tephras or cryptotephras, or glasses with microlites (Hayward, 2012; Pyne-O'Donnell et al., 2012; Hall and Hayward, 2014). Glass microprobe analyses are usually normalized (summed to 100%, most, but not all, of the deficit being attributable to water) to enable useful comparisons of analyses (Shane, 2000; Lowe, 2011; Westgate et al., 2013a). Using stratigraphic or age constraints, and usually also a knowledge of geochemical affinities of potential source rocks/deposits and spatial distribution patterns, the microprobe analysis of glass may allow tephra source volcanoes to be identified, and individual eruptives may also be correlated in some cases where compositions through time have changed from one eruptive event to the next. Complexities arise where glass analyses show heterogeneity, a consequence potentially of (*i*) mingling or mixing of separate batches of magma that were tapped simultaneously or sequentially as eruptions proceeded (e.g., Tryon et al., 2010; Turner et al., 2011b), (*ii*) major element evolution by fractional crystallisation or crustal assimilation (Bogaard and Schminke, 1985; Ukstins Peate et al., 2008; Óladóttir et al., 2012), (*iii*) blending of thin tephras in soil-forming or cryogenic environments (Lowe, 1986; Eden et al., 2001; Dugmore and Newton, 2012), or (*iv*) from post-depositional dissemination of glass shards in peat, lake, or marine sediments (Gehrels et al., 2006; Allan et al., 2008; Abbott et al., 2013). Heterogeneity arising from magmatic or volcanic eruption processes accompanied by changes in wind direction 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). Another problem can arise with analyses of melt inclusions where these do not reflect the full compositional range of glass shards or matrix glass (e.g., Shane et al., 2008b; Chesner and Luhr, 2010; Allan et al., 2013), or they show a pattern different from that associated with matrix glass analyses (e.g., Kilgour et al., 2013). Once recognized, such compositional variability can enhance correlation by providing additional fingerprinting criteria, but sampling from the full spatial and temporal range of deposits of an eruptive sequence is required (Alloway et al. 2013).

The correlation of andesitic or basaltic tephras using glass chemistry generally can be complicated for various reasons including the multiplicity of units, the paucity of suitable glass for microprobing (shards may contain micro-inclusions, and can be highly vesicular), susceptibility of glass to weathering, and wide compositional ranges and potential heterogeneity as noted previously (Moebis et al., 2011; Shane and Zawalna-Geer, 2011; Óladóttir et al., 2012). Platz et al. (2007) provided a procedure to evaluate glass compositional variability arising from the inadvertent microanalysis of plagioclase microlites in shards using a wide beam, but the recent use of narrower beam diameters is helping to obviate this problem (Hayward, 2012; Pearce et al., 2014).

Analyses by microprobe of ferromagnesian silicate minerals, such as biotite (Shane et al., 2003; Smith et al., 2011) and cummingtonite (Matsu'ura et al., 2012), apatite (a phosphate-group mineral) (Sell and Samson, 2011), and Fe-Ti oxides such as titanomagnetite and ilmenite (Shane, 1998; Preece et al., 2011b; Marcaida et al., 2014), have also been used for tephra fingerprinting. In some cases, and after taking into account compositional zoning within crystals, trace elements such as Mg, Cl, Mn, Fe, Ce, and Y identified in apatite crystals and phenocrysts provide a means of distinguishing or matching tephras (Sell and Samson, 2011). The eruption temperature and oxygen fugacity (oxidation state of magma) of rhyolitic tephras – estimated using single-grain EMPA of Fe-Ti oxide pairs of titanomagnetite and ilmenite – provide another way to correlate tephras and, in some cases, magma batches within an eruptive sequence (Smith et al., 2005; Preece et al., 2011b; Marcaida et al., 2014).

Trace-element and isotope analysis of glass

Although the microprobe is now the key analytical tool for undertaking major-element analyses of glass, tephras or cryptotephras cannot always be distinguishable uniquely by major-element data alone. In these cases, other analytical methods are needed (Westgate et al., 2013c). Trace-element analyses of glass separates from tephra or cryptotephra deposits offer a greater range of elements for use in correlation/provenance studies, and may also provide additional information on volcanic petrogenesis. In the last decade, trace-element techniques have become more common, the most widely available being laser ablation inductively coupled plasma mass spectrometry (LA-ICPMS) (e.g., Albert et al., 2012; Ponomareva et al., 2013a; Sulpizio et al., 2013) (Table 1). Pearce (2014) provides protocols for the application of LA-ICPMS to glass shards. Around 150 individual glass shards can be analyzed for about 30 trace elements in one day using LA-ICPMS (Pearce et al., 2011). Comprehensive studies using this method were undertaken on Pleistocene tephras in northern New Zealand (Pearce et al., 2008b) and in marine cores from Ocean Drilling Project (ODP) Site 1123 (Allan et al., 2008). The most useful elements for correlating and distinguishing between the ODP Site 1123 tephras were found to be the abundances of Rb, Ba, Sr, Y, Zr, Hf, Mg, Mn, and Ti and trace element ratios including Rb/Sr, Ba/Sr, Zr/Y, Y/Th, Ba/Th and Rb/Sm. Using trace element data for glass shards, Allan et al. (2008) demonstrated that (*i*) tephras with similar major element compositions (e.g., Kawakawa tephra vs. Omataroa tephra) were easily distinguishable (**Fig. 7**), and (*ii*) two previously unidentified repeated sections of ODP cores 1123A (~4.5 m thick) and 1123C (~7.9 m thick) were recognised (Allan et al., 2008). As with the microprobe, there is a possibility of microlites affecting trace element characterizations of individual shards via LA-ICPMS and so anomalous assays need to be evaluated carefully (Abbott et al., 2013).

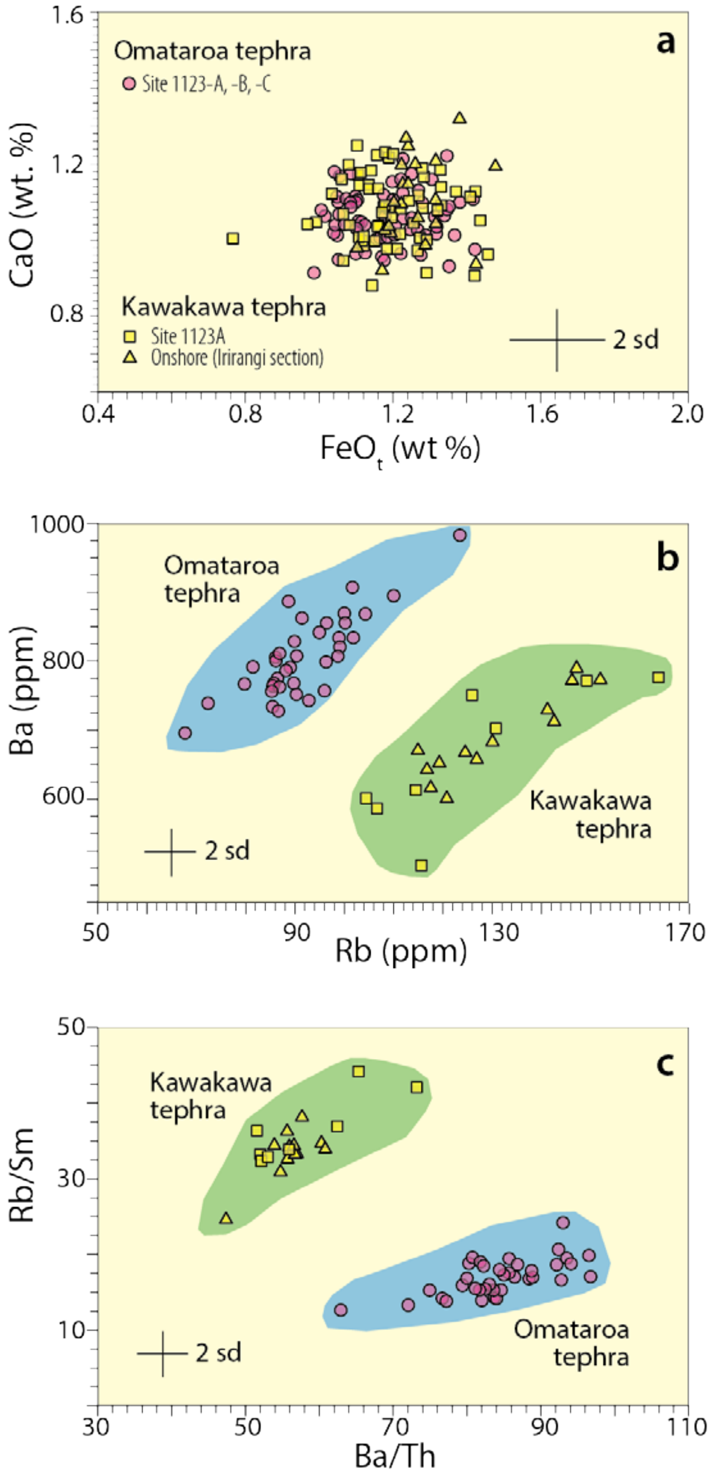

Fig. 7. Bivariate plots for some major and trace elements derived from analyses of individual glass shards from two New Zealand tephras, Omataroa (c. 31,600 cal. yr BP, erupted from Okataina Volcanic Centre) and Kawakawa (c. 25,400 cal. yr BP, erupted from Taupo Volcanic Centre), identified in marine cores A, B, and C from ODP Site 1123 about 1200 km east of New Zealand (modified after Allan et al., 2008, p. 2351, with permission of Elsevier). **(a)** CaO versus FeO_t (total iron expressed as FeO) derived by electron microprobe. Glass analyses from an on-shore occurrence of Kawakawa tephra (at Irirangi) are also shown for comparison. The plot shows that the analyses of marine and on-shore samples of Kawakawa tephra are identical, and that Kawakawa and Omataroa tephras cannot be distinguished using these two oxides alone. In contrast, trace element concentrations (in ppm), derived by LA-ICPMS, in **(b)** and **(c),** show that the tephras are distinctly different with respect to their elements/element ratios and hence can be readily distinguished.

Analyses of isotopes of Sr, Nd, and Pb in glass (or pumices) have been utilised in several studies to help determine tephra source volcanoes (e.g., Roulleau et al., 2009; Westgate et al., 2008, 2011; Giaccio et al., 2013).

Comparing compositional data using graphical, numerical, and statistical methods

Major- or trace-element datasets obtained from analyses of glass or minerals may be displayed and compared, and hence compositional variability evaluated, using various methods: graphical (e.g., bivariate or trivariate plots), numerical (e.g., similarity coefficients), or statistical (e.g., statistical distance measure, dendrograms, discriminant function analysis, principal components analysis) (Pearce et al., 2008a; Bourne et al., 2010; Lowe, 2011; Sell and Samson, 2011). In many cases, the bivariate plots alone can provide sufficient guidance to enable anomalous data points to be identified (and possibly explained using compositional databases for comparison), and potential correlations or otherwise established with reasonable likelihood, especially where multiple criteria provide independent support, such as concordance of glass major- and trace-element data together with Fe-Ti oxide data (e.g., see Preece et al., 1999, 2011b). In other situations, however, statistical methods such as principal components analysis can allow units to be distinguished objectively on the basis of multiple oxides or elements (not just two or three) analysed from glass shards or crystals (e.g., Tryon et al., 2010; Chiasera and Cortés, 2011; Sell and Samson, 2011).

Dating tephras (tephrochronometry)

Tephras may be dated directly using primary minerals (e.g., zircon, hornblende, K-feldspars, biotite, quartz) or glass from within the tephra layer, or indirectly on either enclosing or encapsulated material, using a range of methods including radiometric, incremental (e.g., varves, layering in ice), and age-equivalency (**Table 2**) (Svensson et al., 2008; Alloway et al., 2013; Zalasiewicz et al., 2013). These ages can then be transferred from one site to others where the tephra is recognised using the lithostratigraphic and compositional-based methods described above. Only the main radiometric methods, and age modelling, are touched on here.

Table 2. Methods used for dating tephras directly or indirectly (after Lowe, 2011).

Main method	Applications
Radiometric	Radiocarbon dating (radiometric/beta counting, AMS)[a] Fission-track dating of zircon or glass-ITPFT or glass-DCFT dating Argon isotopes (K/Ar, Ar/Ar including SCLP/F, LIH) Luminescence dating (TL, OSL, IRSL, pIR-IRSL) U-series including (U-Th)/He, U-Pb, and ^{238}U/^{230}Th zircon dating (SIMS/TIMS, SHRIMP, LA-ICPMS) Electron spin resonance ^{210}Pb, ^{137}Cs, ^{3}He and ^{21}Ne surface exposure dating
Incremental	Dendrochronology, varve chronology, layering in ice cores (ice sheets/ caps, glaciers)
Age equivalence	Magnetopolarity, paleomagnetic secular variation, astronomical (orbital) tuning, correlation with marine oxygen isotope stages, climatostratigraphy, biostratigraphy, palynostratigraphy, palaeopedology
Age modelling	Various age-depth methods including Bayesian flexible depositional modeling and wiggle matching, spline-fit modelling
Relative	Obsidian hydration dating, amino acid racemisation
Historical	Eyewitness accounts or observations (e.g., via remote sensing)

[a]AMS, accelerator mass spectrometry; ITPFT, isothermal-plateau fission track; DCFT, diameter-corrected fission track; SCLP/F, single-crystal laser probe or fusion; LIH, laser incremental heating; TL, thermoluminescence; OSL, optically stimulated luminescence; IRSL, infra-red stimulated luminescence; pIR-IRSL, post infrared-infrared stimulated luminescence; SIMS, secondary ionization mass spectrometry; TIMS, thermal ionization mass spectrometry; SHRIMP, sensitive high resolution ion microprobe; LA-ICPMS, laser ablation inductively coupled plasma mass spectrometry.

For tephras erupted within the past c. 60,000 calendar years, the radiocarbon (^{14}C) technique (e.g., Hogg et al. 2007) remains the most important method for developing calibrated age models. In recent years, the advantages of using pollen concentrates and terrestrial plant macrofossils (e.g., leaves, twigs), rather than bulk organic samples, as reliable dating materials via AMS have been demonstrated (Newnham et al., 2007; Staff et al., 2011). Together with dendrochronological wiggle-matching methods (Hogg et al., 2012; Yin et al., 2012), Bayesian flexible depositional age modelling has added a revolutionary aspect to the construction of enhanced and more precise chronologies in tephrochronology involving ^{14}C and other dating methods (Blockley et al., 2008; Smith et al., 2013). Lowe et al. (2013) dated late Quaternary tephras in New Zealand by modelling ^{14}C age data using two Bayesian-based programs, *Bacon* (Blaauw and Christen, 2011) and OxCal's *P_Sequence* function (Bronk Ramsey, 2009), and the IntCal09 dataset (**Fig. 8**). Lohne et al. (2013) also used *P_Sequence* and IntCal09 to obtain high precision ages of 12,066 ± 42 and 10,210 ± 35 cal. yr BP (± 1σ) for the Vedde and Saksunarvatn tephras, respectively, from sediments in Kråkenes Lake, Norway. Similarly, the AT tephra of Japan was dated to 30,009 ± 189 cal. yr BP (95% probability) using *P_Sequence* modelling of ^{14}C data and varves (Smith et al., 2013). Vandergoes et al. (2013) used OxCal's *Tau_Boundary* function, also Bayesian, to precisely date the Kawakawa/Oruanui tephra of New Zealand to 25,358 ± 162 cal. yr BP (95% probability).

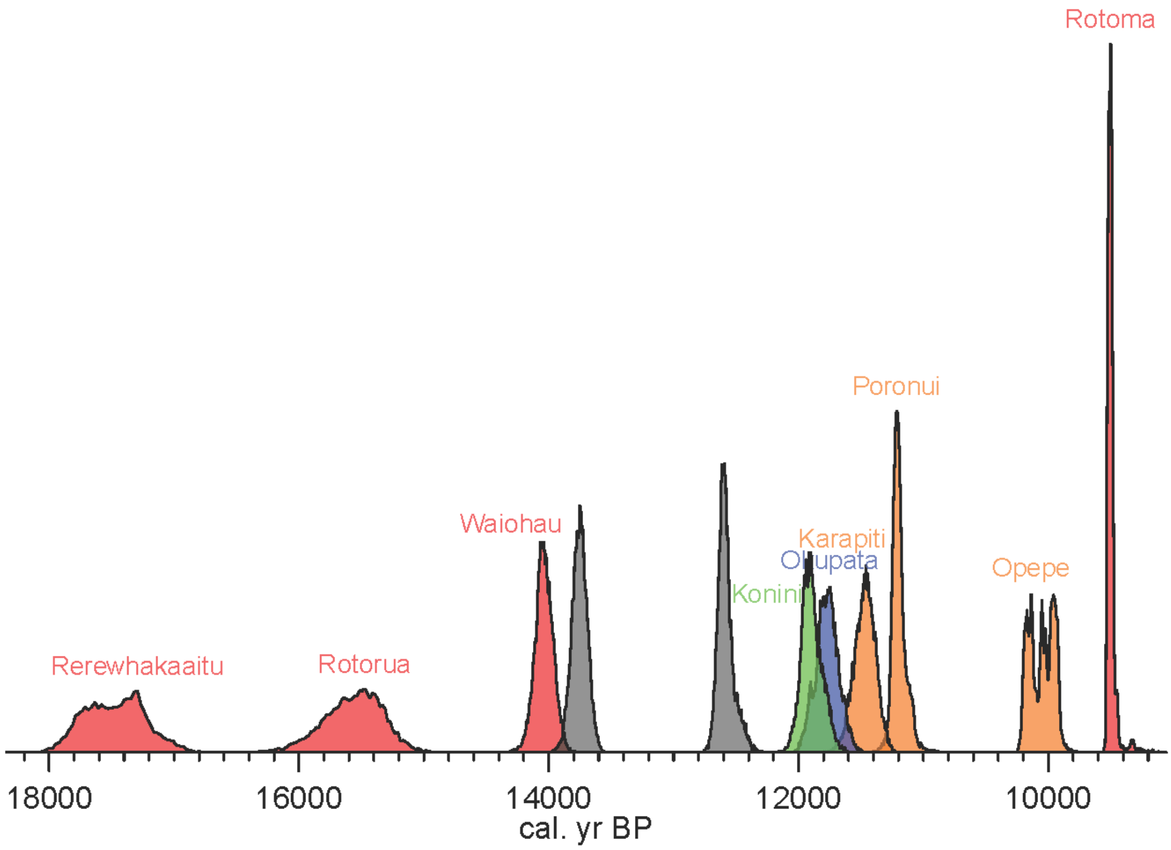

Fig. 8. Bayesian-derived age models (95% probability) for nine late Quaternary tephras in New Zealand (from Lowe et al., 2013, p. 179, with permission of Elsevier). Probability plots are coloured according to tephra source volcanoes: red, Okataina; orange, Taupo; green, Taranaki; blue, Tongariro. Grey plots show the start and end ages of the lateglacial cool episode, designated climate event NZce-3 by Barrell et al. (2013), in part constrained chronologically by the ages on the adjacent tephras.

Another key advance in tephrochronology has been the development of the isothermal-plateau fission-track dating method (ITPFT) for glass (Westgate, 1989; Alloway et al., 2004b, 2013; Westgate et al., 2013b). ITPFT and the diameter-corrected fission track method (Sandhu and Westgate, 1995) have enabled ages to be obtained on many distal vitric-rich tephras that previously were unable to be dated because of low abundance of dateable mineral constituents, fine grain size, and presence of detrital grains. Examples of such applications include dating Quaternary glacioeustatic sedimentary cycles in the Wanganui Basin (Alloway et al., 1993; Pillans et al., 2005) and dating initial loess deposition in Alaska at ~3 million years ago (Westgate et al., 1990). The glass-FT techniques have been used, for example, also to test chronologies based on alternative methods (such as magnetic polarity and astronomical tuning) for marine tephra sequences (Alloway et al., 2005; Allan et al., 2008) and for fossiliferous alluvial and lacustrine sediments in Beringia (Preece et al., 2011b; Westgate et al., 2013a).

Where suitable minerals are available (e.g., sanidine, biotite, leucite, anorthoclase), the $^{40}Ar/^{39}Ar$ method has been useful, such as dating the Laacher See tephra in Germany (Bogaard, 1995), ultra-distal to distal deposits of the Youngest Toba Tuff tephra of Indonesia (Westgate et al., 1998; Storey et al., 2012), a widespread Holocene tephra erupted from Ulleungdo stratovolcano in South Korea (Smith et al., 2013), a 400,000-year-old sequence of eruptives from Nemrut volcano preserved in Lake Van, eastern Anatolia in Turkey (Sumita and Schminke, 2013), and distal tephras preserved in lacustrine and fluvial sediments of intermontane basins of central Italy (Giaccio et al., 2013). A relatively new method for dating proximal pyroclastic deposits, previously applied to petrological studies, is the use of U-Pb analyses to date zircons (Schmitt, 2006; Dickinson et al., 2010; Wilson et al., 2010). Luminescence and (U-Th)/He dating methods are also being applied systematically to tephra deposits (Danišík et al., 2012; Biswas et al., 2013).

A trend in dating lake sediment sequences containing tephras or cryptotephras is to apply multiple methods, as exemplified by Staff et al. (2013) and Sirocko et al. (2013).

Conclusions

Tephrochronology is the use of primary tephras or cryptotephras as isochrons to link and synchronize geological, palaeoenvironmental, or archaeological sequences or events, or soils, and, uniquely, to transfer relative or numerical ages to them using stratigraphic information and mineralogical and geochemical compositional data, especially from individual glass-shard analyses, obtained for the tephras/cryptoephras. To function therefore as an age-equivalent correlation and chronostratigraphic dating tool, tephrochronology can be undertaken in three steps: (*i*) mapping and describing tephras and determining their stratigraphic relationships, (*ii*) characterizing tephras or cryptotephras in the laboratory, and (*iii*) dating them using a wide range of geochronological methods. Tephrochronology is also an important tool in volcanology, informing studies on volcanic petrology, volcano eruption histories and hazards, and volcano-climate forcing. Although limitations and problems remain, multidisciplinary applications of tephrochronology continue to grow markedly (e.g., Alloway et al., 2013; Lane et al., 2014).

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Cross references

^{14}C Dating
^{210}Pb Dating
Accelerator mass spectrometry
Ar-Ar and K-Ar dating
Biostratigraphy
Dendrochronology, volcanic eruptions
Fission track dating
Geochronology
Ice cores
Laser ablation inductively coupled mass spectrometer (LA ICP-MS)
Lacustrine environments (^{14}C)
Luminescence dating
Magnetostratigraphic dating
Marine isotope stratigraphy
Paleosol
Peat (^{14}C)

Plant materials (^{14}C)
Principle of cross-cutting relationship
Principle of superposition
Relative dating methods
Single crystal laser fusion
Uranium-lead, zircon
U-Th: He dating
Varve chronology
Volcanic glass (fission track)
Zircon