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A continuous 5300-yr Holocene cryptotephrostratigraphic record from northern New Zealand and implications for tephrochronology and volcanic hazard assessment

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Abstract: A continuous $\sim$5280 calendar (cal.) yr long cryptotephrostratigraphic record of a peat core from northern New Zealand demonstrates that cryptotephra studies can enhance conventional tephra records by extending the known distribution of ash fall and enabling re-assessment of volcanic hazards. A systematic sampling strategy was used to locate peaks in glass-shard concentrations and to determine loci of individual geochemical populations, and a palynological method involving spiking samples with *Lycopodium* spores was adapted to facilitate accurate counting of glass-shard concentrations. Using glass-shard major element compositions, and a core chronology based on eight AMS ^{14}C ages and two visible macroscopic tephra layers, Taupo Tephra (Unit Y) (1688–1748 cal. BP) and Tuhua Tephra (6800–7230 cal. BP) (2σ-age ranges), four cryptotephras were correlated with known eruptions: Whakaipo (Unit V) (2743–2782 cal. BP), Stent (Unit Q) (4240–4510 cal. BP), and Unit K (4970–5290 cal. BP), erupted from Taupo Volcanic Centre, and Whakatane Tephra (5470–5600 cal. BP) erupted from Okataina Volcanic Centre. Mixed glass populations were found in the core, most likely an artefact of post-depositional remobilization of shards vertically (both up and down) in the peat or on its surface by wind, or a result of closely spaced eruption events, or a combination of these. A secondary glass population identified within the macroscopic Taupo Tephra was tentatively attributed to either an earlier phase within that eruption or to mixing with a slightly older Taupo-derived eruptive or (less likely) a currently unknown Okataina-derived eruptive. These results indicate that, in the absence of continuous cryptotephrostratigraphic analysis, a peak in shard concentrations may not in itself be indicative of the 'true' stratigraphic (ie, isochronous) level of a tephra layer. For cryptotephra studies of peat cores, we recommend (1) using a detailed sampling strategy for the analysis of distal tephra-derived glass to detect and account for any mixed populations and possible vertical spread of glass shards through the peat, and (2) analysing more shards from larger samples to help 'capture' sparsely represented cryptic andesitic tephra deposits.

Key words: Cryptotephra, tephra, tephrochronology, glass counts, volcanic hazards, ^{14}C dating, isochrons, peat cores, North Island, Kopouatai bog, Holocene, New Zealand.

Introduction

The development of new methods to detect and characterize low-concentration tephra layers (the unconsolidated, pyroclastic deposits of volcanic eruptions) have greatly enhanced the tools of tephrochronology and tephrostratigraphy (Turney and Lowe, 2001; Hall and Pilcher, 2002; Boygle, 2004; Turney *et al.*,

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2004). In particular, 'cryptic' (from the Greek *kryptein*, to hide; Lowe and Hunt, 2001) tephra layers, henceforth referred to as cryptotephras, provide opportunities to extend the application of this correlation and dating tool well beyond limits of visible layers (Wastegård *et al.*, 2000a, b; Hall and Pilcher, 2002; Davies *et al.*, 2002, 2003, 2005; Turney *et al.*, 2004). Increasingly, distal cryptotephras preserved in peat bogs and lake sediments are shown to provide a more comprehensive record of volcanic events than can be revealed by the more proximal, visible deposits alone (Lowe *et al.*, 1999; Kilian *et al.*, 2003; St Seymour *et al.*, 2004; Shane, 2005). Moreover, tephrochronologists in volcanically active regions are recognizing that distal tephra deposits may provide a more accurate appraisal of the potential aerial impact of future volcanic eruptions (Hunt, 1999; Newnham *et al.*, 1999a; Shane and Hoverd, 2002; Payne and Blackford, 2004; Shane, 2005).

Cryptotephrochronology is now well established in western Europe (eg, van den Bogaard and Schmincke, 2002; Wastegård *et al.*, 2003; Dugmore *et al.*, 2004; Turney *et al.*, 2004) where it relies on the detection of the widespread but diminutive remains of volcanic ash from distal, mainly Icelandic, sources. In contrast, in New Zealand, which has a comprehensive stratigraphic record of macroscopic (visible) tephra layers, cryptotephra deposits have largely been of secondary focus, with the exception of a few studies (eg, Lowe *et al.*, 1981, Eden *et al.*, 1992; Almond, 1996; Eden and Froggatt, 1996). Despite this, recent studies have demonstrated the benefit of examining peat and lake sediment records in more detail to obtain better records of tephra dispersion (Froggatt and Rogers, 1990; Newnham *et al.*, 1995a; Eden and Froggatt, 1996; Shane and Hoverd, 2002).

The North Island of New Zealand contains the world's largest concentration of active rhyolitic centres. These include the Taupo Volcanic Centre (VC) and Okataina VC (Figure 1), which together have erupted 17 tephras during the Holocene alone (Froggatt and Lowe, 1990; Wilson, 1993; Shane, 2000), and the offshore peralkaline Tuhua VC of Mayor Island. These Holocene tephra layers have provided useful correlative and chronological tools for numerous palaeoenvironmental and archaeological studies (eg, Newnham *et al.*, 1998, 1999b; Newnham and Lowe, 1999; Lowe *et al.*, 2000) and a detailed history of volcanic activity (Lowe, 1988b; Froggatt and Lowe, 1990; Wilson, 1993; Lowe *et al.*, 1999; Shane, 2000, 2005). Nonetheless, it is widely acknowledged that the history of volcanic eruptions at any given site in New Zealand, as revealed by macroscopic tephra layers, is not necessarily fully representative of the actual types, frequency and magnitude of past eruptions that have affected the site (Lowe, 1988a; Wilson *et al.*, 1995; Shane, 2000; Carter *et al.*, 2004). Critically, this could imply that predictions of the threat from future eruptions are significantly underestimated. For example, andesitic tephras from the frequently active Tongariro VC and Egmont Volcano (Figure 1) are significantly under-represented in the stratigraphic record but nevertheless pose a significant threat to society as revealed by eruptions of Mt Ruapehu in 1995–1996 (Figure 1; Neall *et al.*, 1995; Cronin *et al.*, 2003).

The increased tephrostratigraphic resolution provided by investigations of thin, distal tephra layers in lakes and peat bogs in New Zealand, and in adjacent marine cores (eg, Newnham *et al.*, 2003; Carter *et al.*, 2004), has been well established (Lowe, 1988b; Alloway *et al.*, 1994; Lowe *et al.*, 1999; Shane and Hoverd, 2002; Shane, 2005). These findings suggest that the detection of cryptotephras could further enhance the tephrostratigraphic framework for the North Island and beyond. On the other hand, it has been argued that cryptotephra layers would be poorly recorded in distal settings because of the frequency and complexity of past volcanic eruptions (Shane, 2000). The remobilization of fine ash and bioturbation would result in diffuse layers of shards with little value in defining isochronous layers for dating (eg, Thompson *et al.*, 1986; Shane, 2000). Furthermore, Hodder *et al.* (1991) demonstrated that glass shards and mineral grains may be vulnerable to alteration or dissolution by acidic interstitial waters in some very acid peat bogs where present in low concentrations.

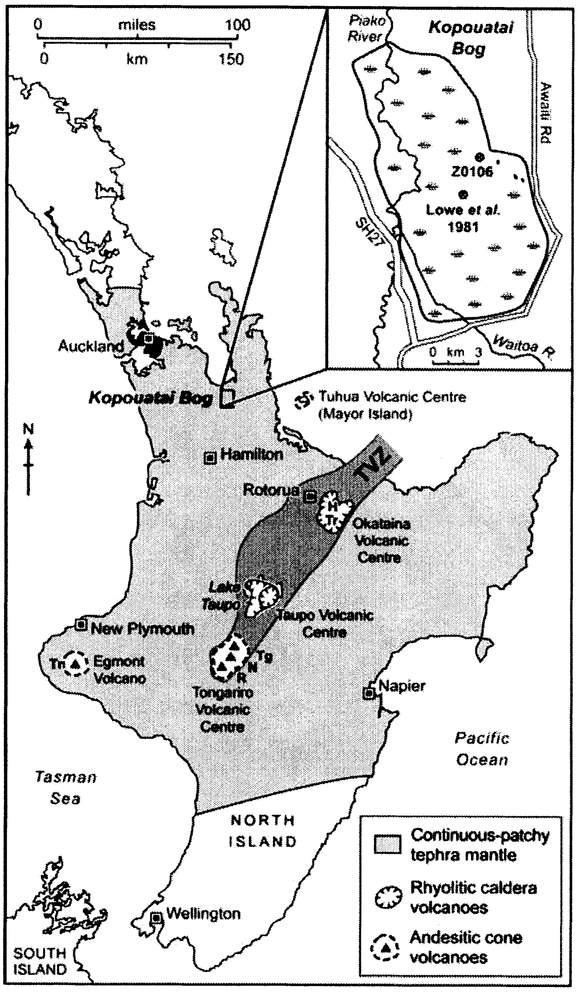

Figure 1 Location of Kopouatai bog in northern North Island and the main tephra-generating volcanoes that have been active in the Holocene. TVZ, Taupo Volcanic Zone; named volcanoes are H, Haroharo; Tr, Tarawera; Tg, Tongariro; N, Ngauruhoe; R, Ruapehu; Tn, Taranaki. After Froggatt and Lowe (1990) and Newnham *et al.* (1995a). The distance from Kopouatai bog to these volcanic centres ranges from ~60 to ~250 km

We suggest that the potential for cryptotephras to improve the tephrostratigraphic record for New Zealand needs further exploration. In addition to enhancing the power of tephrochronology as a tool for correlating and dating, cryptotephra layers could be used to re-appraise the volcanic hazards' assessment in populous regions of the North Island by considerably extending the ash-fall isopachs, which are currently based mainly on macroscopic (non-cryptic) deposits, thereby enabling ash-fall hazards to be modelled with higher reliability (eg, Hurst and Smith, 2004). It is possible also that cryptic tephra layers could record eruptions previously unrecognized because of burial by subsequent eruptives at proximal sites or because of erosion or weathering (Lowe, 1988a; Alloway *et al.*, 1994), thus improving the known frequency of past eruptions (Shane, 2005).

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The primary aim of this research was to detect and identify cryptotephra in a peat core from the North Island of New Zealand to enhance the chronology of the core. Using major element compositions of glass shards and a chronology based on radiocarbon dating and two well-dated macroscopic tephra marker beds, it was anticipated that cryptotephra could be linked to known tephra-producing eruptions. As a second aim, we evaluated the potential of cryptotephra deposits to provide definitive tephrostratigraphic markers in peat by appraising both chemical uniformity and stratigraphic integrity of the glass-shard populations used to match cryptotephras with known tephra-producing events.

The core used (Z0106) was one of several taken for palaeohydrological studies of ombrogenous bogs in the Waikato region of the North Island (Hazell, 2004). The stratigraphic interval of interest in the core was constrained by two macroscopic tephra layers, Taupo Tephra (*c.* 1718 calendar (cal.) BP, *c.* AD 232 ± 15; Sparks *et al.*, 1995; Lowe and de Lange, 2000) and Tuhua Tephra (*c.* 7000 cal. BP; Lowe *et al.*, 1999), which had been identified in previous studies (Newnham *et al.*, 1995a). Within this time interval from *c.* 7000 to *c.* 1718 cal. BP, spanning ~5280 calendar years, eight radiocarbon dates were obtained from the core to provide additional chronological control (Hazell, 2004).

Study site

Core Z0106 was taken from Kopouatai bog, an ombrogenous restiad bog in the Hauraki Lowlands (Figure 1). The term restiad refers to bogs dominated by members of the Southern Hemisphere family of jointed rushes, Restionaceae, the main species of which are *Empodisma minus* and *Sporadanthus ferrugineus* (de Lange *et al.*, 1999; Clarkson *et al.*, 2004). As the dominant peat formers (especially *E. minus*), these species have unique hydrological and peat-forming characteristics (Campbell and Williamson, 1997; Campbell and Jackson, 2004; Clarkson *et al.*, 2004). The bog began forming around 13 600 cal. BP (calibrated age estimates are based on Stuiver *et al.*, 1998) within a fault-bound depression floored with volcaniclastic alluvium (Hinuera Formation; Manville and Wilson, 2004) deposited by an ancestral Waikato river system (Newnham *et al.*, 1995a). The bog expanded to form a single, mesic low-moor bog by *c.* 12 000 cal. BP and subsequently developed into a large, raised restiad bog up to 14 m deep (Newnham *et al.*, 1995a). Covering an area of 10 500 ha and only *c.* 4 m above sea level at its highest point, Kopouatai bog is the largest remaining raised restiad bog in New Zealand. The fast rates of peat formation in this temperate, lowland region of North Island mean that sedimentation rates are comparatively high and thus useful for high-resolution palaeoenvironmental studies based on pollen, plant macrofossil and charcoal remains (Newnham *et al.*, 1995a; Shearer, 1997; Kuder *et al.*, 1998; Hazell, 2004).

Kopouatai bog is an effective archive of medial-distal tephra layers. At least 17 macroscopic tephra layers have been detected in previous studies and many have been identified and correlated using a combination of stratigraphic position, field properties, ^{14}C ages and ferromagnesian mineral assemblages (de Lange and Lowe, 1990; Newnham *et al.*, 1995a; Newnham and Lowe, 1999). Despite this, glass shards from only one of the 17 tephra layers (Kaharoa Tephra) had previously been analysed by electron microprobe (Hodder *et al.*, 1991) and so the remaining tephra identifications remained tentative. Six tephras were provisionally identified between Taupo and Tuhua tephras, namely Mapara (Unit X), Whaikapo (Unit V), Egmont-2, Egmont-4, Hinemaiaia (Unit K) and Whakatane (de Lange and Lowe, 1990; Newnham *et al.*, 1995a; alternative eruptive names in parentheses are from Wilson, 1993). None of these tephra layers was actually visible in core Z0106 – only Taupo and Tuhua tephras were observed as macroscopic layers (Hazell, 2004).

Methods

Coring

Z0106 was retrieved near the eastern margin of central Kopouatai bog (Figure 1). This site, at grid reference T13/377194 (of 1:50 000 New Zealand Map Series 260) (37° 24′ S, 175° 35′ E), was selected to ensure the core extended beyond the most southerly extent of marine deposits arising from the *c.* 7000 cal. BP mid-Holocene sea-level transgression (Newnham *et al.*, 1995a) and was sufficiently distant from marginal drainage canals to minimize their possible effects on peat hydrology. A 'wide' Russian corer with a 30-cm long and 10-cm diameter barrel recovered a total of 5.62 m of peat. This comprised mainly restiad root matter interspersed with occasional woody fragments, and with a substantial clay layer at depth 6.89–7.41 m that was interpreted to represent freshwater ponding at the time of the mid-Holocene marine transgression (Hazell, 2004). The Taupo Tephra (2 cm thick) at 1.79–2.81 m depth, and Tuhua Tephra (11 cm thick) at 7.73–7.84 m depth, were readily identified in the field from their physical properties and stratigraphic positions (confirmed below using glass compositions).

Sample treatment and microscopy

A 2-cm-thick contiguous sampling strategy was adopted for determining continuous concentrations of tephra-derived glass shards between 2.50 m and 7.96 m depth in the core (ie, including both Taupo and Tuhua tephras). For each sample, approximately 1 g of wet peat was extracted from a cleaned surface. This moderate sample size, in comparison with European cryptotephra studies, reflects the higher tephra concentrations resulting from closer proximity to volcanic sources (Figure 1).

The method for isolating glass shards from the organic matrix of the peat followed the ashing method described by Pilcher and Hall (1992) and TEFRATRACE (2002). Each sample was ashed at 550°C for 3 hours and washed in warm 10% HCl to remove sesquioxides and (burnt) ash particulates. The residue was spiked with one tablet of *Lycopodium* spores (to facilitate measurement of glass-shard concentrations) and centrifuged to remove HCl and excess water. Using a micropipette, 500 μl of the sample suspension was dispensed onto cover slips, which were air dried and mounted on micro-slides using the synthetic mounting medium Hystomount.

Slides were examined at 400× magnification with a polarizing microscope to distinguish and count glass shards ~ > 40 μm across. Recognition of isotropic glass shards was straightforward because little other inorganic material was encountered on the slides (cf. Turney *et al.*, 2004). The tephric material was composed of mainly glass shards and particles of micro-pumice, which were recognized from distinct morphological characteristics including shape, vesicularity, stretching, colour, fracture and weathering characteristics (Figure 2) (eg, Nelson *et al.*, 1986; Lowe, 1988b). Glass shards were recorded and counted alongside *Lycopodium* spores, a quantification method adapted from palynology. Replicate counts of selected slides indicated that the number of shards counted for 100 *Lycopodium* spores was adequately representative of the

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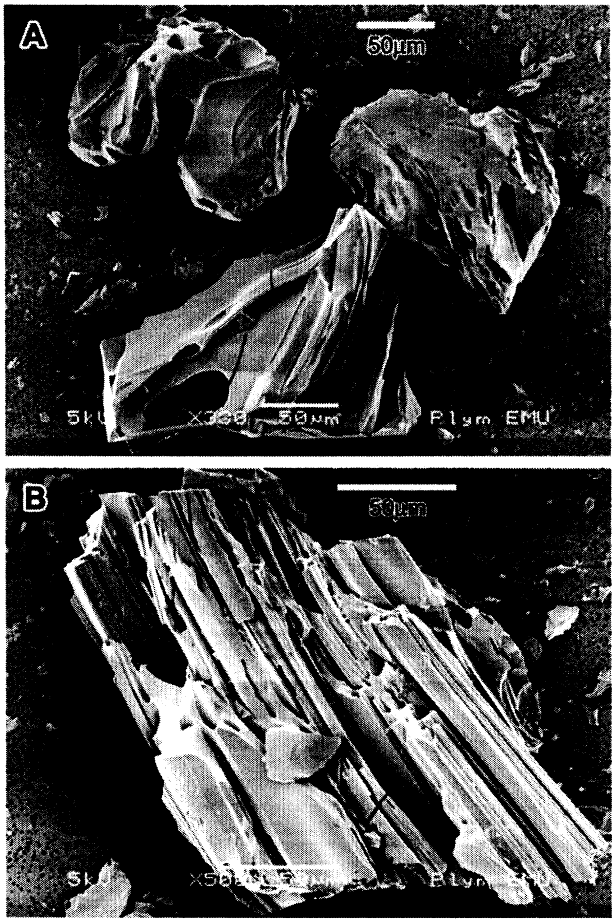

Figure 2 SEM images of rhyolitic glass shards from depth 5.78–5.80 m in core Z0106 (probably representative of Unit K or Whakatane Tephra, or both)

sample. Glass shard concentrations are reported as shards per milligram dry weight calculated using the formula:

$$c = l \times \frac{a}{bd}$$

where a is shard count; b is *Lycopodium* spore count; d is sample dry weight in milligrams; and l is the number of *Lycopodium* spores in the tablet added to sample.

Glass attenuation study

Peat-accumulating environments have long been established as effective repositories for low concentrations of tephra-fall-derived glass shards in regions far from source volcanoes (eg, Pilcher and Hall, 1996; Kilian *et al.*, 2003; Payne and Blackford, 2004; Bergman *et al.*, 2004). Cryptotephra layers detected in distal depositional environments typically form distinct and isolated markers in the enclosing sediments and have been used as precise chronozone markers for dating such sediments. Conversely, in New Zealand the peat bogs are more medially positioned in relation to eruption sources and the eruption frequency of large silicic eruptions, during the Holocene at least, far exceeded that of many other regions of the world. For this reason alone it was important to appraise the effectiveness of the peat to archive cryptotephras as discrete units. To assess the extent of attenuation of glass shards from tephra deposits in core Z0106, we completed a microscopic examination of shard concentrations and their particle size through the full distribution of the Taupo Tephra layer to include any cryptic components above and below it. Contiguous, 1- to 2-cm-thick samples were taken through the peat extending from 10 cm above the visible component of the Taupo Tephra to 18 cm below it. Samples were prepared for microscopy as described above.

The point-count method described by Clarke (1982) was used to determine the different size fractions of glass shards throughout zones of concentration. Point-counting followed a representative transect of contiguous fields of view across the slide. In each field of view, only the shards covered by, or in contact with, the visible scale bar were counted. The counts were grouped into three different size ranges: 10–25 µm, 25–75 µm and > 75 µm. Size fractions of shards were represented as a percentage of total shards.

Total organic carbon (TOC)

Samples taken at 4-cm intervals were analysed for TOC using a Schmaszu TOC-5000 analyser from CO_2 release following combustion at 900°C (Hazell, 2004).

^{14}C dating

Eight peat samples were taken at regular *c.* 50-cm intervals between Taupo and Tuhua tephra layers for AMS radiocarbon processing and dating at the NERC Radiocarbon Laboratory, East Kilbride, UK. Samples were pretreated with 1M HCl (at 80°C for 8 h) and then washed with distilled water. Where sample weight was low, samples were burnt on their glass filter papers to minimize loss (Hazell, 2004).

Electron microprobe (EMP) analysis

Samples (numbered 1–6) from six depths were selected for EMP analysis from zones containing the maximum concentrations of glass shards (Figure 3). Two of these zones included Taupo Tephra (Sample 1) and Tuhua Tephra (Sample 6). The other samples were taken from concentrations at 3.75 m (Sample 2), 5.37 m (Sample 3), 5.46 m (Sample 4) and 5.63 m (Sample 5) (Figure 3).

Samples were prepared for microprobe analysis using acid digestion to remove organic matter and to concentrate glass shards, and then dried (Dugmore, 1989; TEFRATRACE, 2002). The glass separates were then mounted in pre-drilled araldite blocks with araldite epoxy resin, ground and polished, carbon coated and analysed for major elements using a wavelength-dispersive Jeol-633 'Superprobe' at the Analytical Facility, Victoria University of Wellington, with standards and analytical conditions as described by Froggatt (1983), Lowe (1988b) and Lowe *et al.* (1999): 20 µm defocused beam, 8 nA current, 15 kV accelerating voltage. Analyses were calculated from 11 × 2 s counts across the peak, curve integrated.

Results

Glass-shard distribution

Total down-core glass-shard counts are shown in Figure 3 alongside TOC values, which provided an effective reconnaissance measure for assessing potential concentrations of cryptotephras through an inverse relationship. The glass-shard content of core Z0106 was based on 290 contiguous samples of 2-cm thickness between 2.50 m and 8.30 m depth in the core (Figure 3). Of 290 samples, 62 had negligible or zero glass shard counts. In addition to the two visible tephra layers, there were two significant zones of cryptotephra shard

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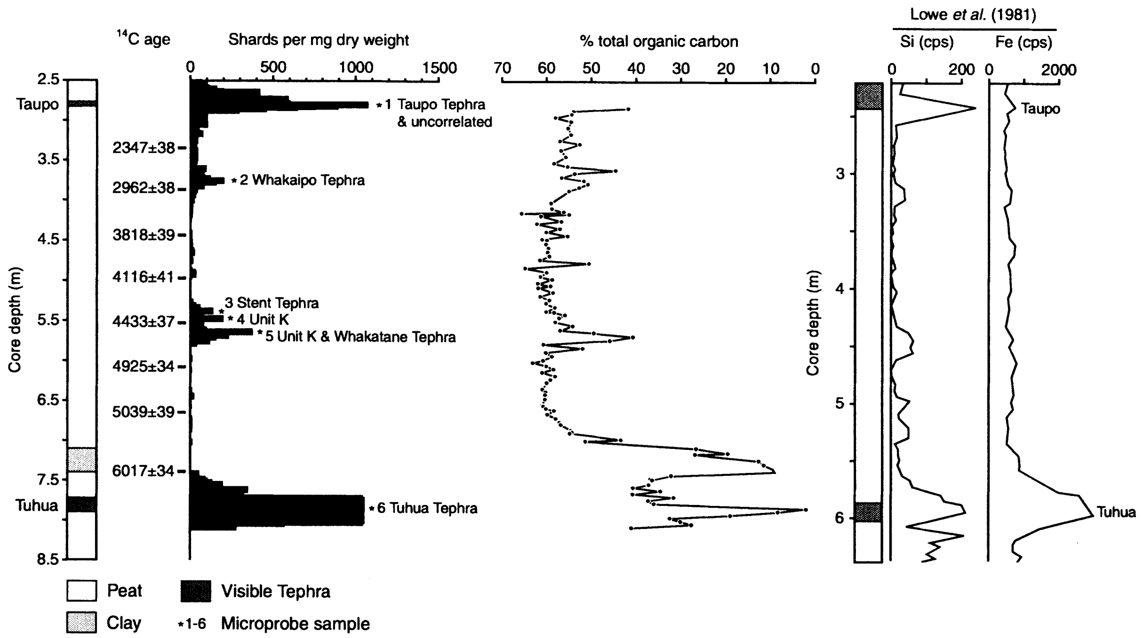

Figure 3 Stratigraphy of core Z0106 with ^{14}C sampling positions, glass-shard counts and electron microprobe analysis sampling positions, and total organic carbon (note scale is reversed). Plot on right shows Si and Fe values (as counts per second) obtained by rapid XRF analysis of samples of dried slices of peat from a core from Kopouatai bog (Figure 1, inset)

concentrations and at least eight other isolated levels with minor concentrations of shards.

The first zone of cryptotephra was in the upper part of the core section where there was a continuum of shards below the visible Taupo Tephra layer (2.79–2.81 m) down to 4.08 m. Peaks in shard concentration (> 150 shards/mg dry weight, shards/mg-dw) occurred at 3.29 m and 3.60 m with a maximum shard concentration of ~220 shards/mg-dw at 3.74 m. The second concentration of shards was located between 5.30 and 5.78 m. In this zone there were three significant peaks at 5.37, 5.46 and 5.63 m with shard concentrations > 200 shards/mg-dw. The isolated peaks of shards were at 4.62 m, 4.90 m, 5.89 m, 6.03 m, 6.58 m, 6.68–6.78 m and 6.96 m depth with concentrations < 50 shards/mg-dw. Shard counts from the Taupo and Tuhua tephra layers were in excess of 1000 shards/mg-dw. These distributions of the siliceous glass (see Table 1) are generally mimicked by the silicon concentration plot derived from earlier studies on Kopouatai bog (Figure 3) obtained by a simple X-ray fluorescence (XRF) whole-peat analytical method (Lowe *et al.*, 1981; Hogg and McCraw, 1983).

Numerous other samples contained sufficient shards (< 20 shards/mg-dw) to ensure an almost continuous 'background' concentration throughout the core (Figure 3). These broad 'background' zones attenuated above and below a level of maximum concentration. The pattern of shard concentration around the 2-cm-thick Taupo Tephra showed significant components extending at least 13 cm above and 18 cm below the visible layer (Figure 4). Maximum shard concentration and shard size occurred in the visible layer with clear attenuations in concentration and size both above and below it (Figure 4). Shard size fractions < 25 μm and > 75 μm showed distinct changes away from the visible layer, but the 25–75 μm-fraction showed less variation across the visible layer. Below the visible Taupo Tephra layer the concentration and size of shards diminished. Above it there was greater variability in shard size.

A complication in interpreting these findings is the occurrence of a secondary population of glass shards within the Taupo Tephra sample that may derive from intermixing with an earlier eruptive (see below). It is possible therefore that the dissemination of glass shown in Figure 4 may not relate entirely to components of Taupo Tephra.

Major element analyses of glass

The major element compositions of glass populations from the six samples (Figure 3) are given in Table 1, which includes their most likely correlatives based on the EMP analyses and new chronological data together with stratigraphy. Suffixes a and b denote different geochemical populations.

The EMP analyses are typical of those obtained previously on glass from proximal and distal rhyolitic tephras in New Zealand (eg, Shane, 2000), the raw analytical totals averaging between 94.5% and 98.8%. The analyses of Na_2O and K_2O especially are in accord with values obtained previously and with standards used for EMP analyses, and thus indicate that alteration of glass from chemical etching or from sample processing has not been significant despite the low concentrations of shards in most samples (cf. Hodder *et al.*, 1991).

A plot of FeO versus CaO content for individual shard analyses of samples 1–5 illustrates major trends in the data (Figure 5) but we note that all elements were considered together for identifying likely correlatives.

Tephra correlations using glass analyses

Sample 1 (2.79 m): Taupo Tephra (one or more of subunits Y5-Y7) with uncorrelated tephra

This sample comprised two distinct geochemical populations dominated by population (pop.) 1a, glass which closely matched analyses of Taupo Tephra (Unit Y of Wilson, 1993) as published in numerous previous studies (eg, Lowe, 1988b; Lowe *et al.*, 1999). The analyses are very similar to those representative of later phases of the Taupo eruption sequence (Froggatt, 1983; Stokes *et al.*, 1992), namely Taupo Plinian/Lapilli and Taupo Ignimbrite members (and presumably co-ignimbrite ash/lapilli fallout deposits), or subunits Y5–Y7

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Table 1 Electron microprobe analyses[a] of glass from six sample depths in core Z0106, Kopouatai bog

Anal no.: Tephra name(s) (source)	1a Taupo Tephra Subunit(s) Y5–Y7 (Taupo)	1b Uncorrelated (Taupo or Okataina?)[b]	2 Whakaipo Unit V (Taupo)	3a Stent Unit Q (Taupo)	3b Whakatane? (Okataina)	4 Unit K (Taupo)	5a Unit K (or H/G?) (Taupo)	5b Whakatane (Okataina)	6 Tuhua Tephra (Tuhua)
SiO_2	75.00 (0.35)	77.18 (0.28)	76.64 (0.25)	75.81 (0.57)	77.50	74.89 (0.76)	75.86 (0.20)	77.52 (0.73)	74.04 (0.59)
Al_2O_3	13.45 (0.20)	12.74 (0.13)	12.77 (0.25)	13.33 (0.20)	12.68	13.01 (0.22)	13.32 (0.10)	12.57 (0.35)	9.53 (0.20)
TiO_2	0.29 (0.06)	0.12 (0.04)	0.16 (0.03)	0.19 (0.03)	0.14	0.21 (0.05)	0.24 (0.05)	0.11 (0.030	0.30 (0.06)
FeO[c]	2.02 (0.28)	1.14 (0.12)	1.59 (0.20)	1.79 (0.14)	0.79	1.64 (0.24)	1.66 (0.15)	0.90 (0.07)	5.68 (0.38)
MnO	0.12 (0.05)	0.07 (0.05)	0.13 (0.02)	0.09 (0.08)	0.04	0.09 (0.06)	0.10 (0.10)	0.05 (0.04)	0.15 (0.06)
MgO	0.28 (0.04)	0.13 (0.02)	0.13 (0.02)	0.18 (0.03)	0.08	0.19 (0.03)	0.19 (0.02)	0.10 (0.02)	0.01 (0.02)
CaO	1.49 (0.11)	1.09 (0.08)	1.02 (0.04)	1.30 (0.10)	0.67	1.29 (0.11)	1.25 (0.08)	0.69 (0.06)	0.24 (0.04)
Na_2O	4.37 (0.20)	3.92 (0.19)	4.28 (0.14)	4.08 (0.43)	4.04	4.20 (0.13)	4.25 (0.15)	3.90 (0.15)	5.61 (0.27)
K_2O	2.79 (0.13)	3.44 (0.15)	3.17 (0.14)	3.08 (0.20)	3.83	3.12 (0.21)	2.98 (0.11)	3.98 (0.14)	4.22 (0.12)
Cl	0.18 (0.05)	0.18 (0.27)	0.16 (0.06)	0.13 (0.03)	0.23	0.12 (0.03)	0.16 (0.04)	0.19 (0.05)	0.21 (0.02)
H_2O[d]	2.95 (1.00)	5.52 (1.49)	3.10 (1.82)	2.07 (1.43)	4.61	1.25 (0.89)	1.97 (0.16)	3.60 (0.98)	1.35 (1.22)
n	16	4	12	13	1	12	10	8	12

[a] Means and standard deviations (in parentheses) of *n* analyses (individual glass shards) normalized to 100%-loss-free (wt.%). Analyses undertaken by K. Wilson at Victoria University of Wellington (see text). Sample depths in core were as follows: 1, 2.79 m; 2, 3.75 m; 3, 5.37 m; 4, 5.46 m; 5, 5.63 m; 6, 7.84 m (analytical subpopulations for each sample are denoted with suffixes a or b). Individual grain analyses are given in the Appendix.

[b] See text.

[c] Total iron reported as FeO.

[d] Water by difference between original analytical total and 100.

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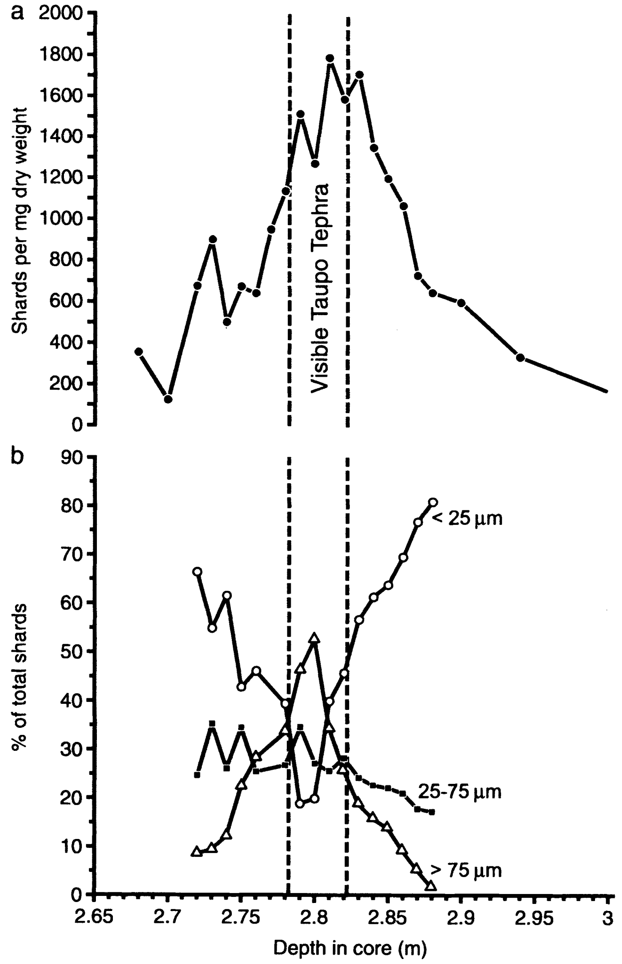

Figure 4 (a) Attenuation of cryptic glass shards above and below the visible layer of Taupo Tephra in core Z0106. Concentrations of shards for cryptic component of Taupo Tephra (only) include counts of shards < 25 µm in length (hence the apparent peak in shards slightly outside visible unit). (b) Grain-size distributions of shards counted in (a)

(Wilson, 1993). Notable features are very high FeO, TiO_2, and Na_2O, relatively high CaO and relatively low K_2O contents. We thus correlate pop. 1a glass with one or more subunits of Y5 to Y7 (Taupo) sequence that was erupted *c.* 1718 cal. BP (ages are from Table 3, reported below).

Pop. 1b glass analyses, with moderate FeO, TiO_2, and CaO, are currently not able to be correlated with certainty. Assuming that they are not simply outliers (cf. Shane, 2000) or a function of previously unrecorded geochemical heterogeneity (eg, Shane *et al.*, 2005), and that there has been no sample contamination in the laboratory, possible correlatives for pop. 1b include the following.

(1) Earlier phases of the Taupo eruption sequence such as Hatepe Plinian/Lapilli and Hatepe Ash (subunits Y2–Y3) erupted *c.* 1718 cal. BP. Stokes *et al.* (1992) demonstrated that these were clearly distinguishable from the later phases (subunits Y5–Y7) on the basis of discriminant function analysis of glass major-element compositions (Mahalanobis $D^2 = 3.02$). However, both TiO_2 and FeO, and possibly CaO, seem lower than might be expected.

(2) Mapara Tephra (Unit X), which was erupted from Taupo VC *c.* 2150 cal. BP (Wilson, 1993), only ~300 years before Taupo Tephra. The analyses are similar to those published previously for this tephra (Stokes *et al.*, 1992; Eden *et al.*, 1993), apart from FeO which is much lower than expected.

(3) An unknown late Holocene eruptive from Okataina VC. Okataina-derived Holocene eruptives tend to have moderate FeO and CaO values (typically $\leq \sim 1.0$ wt.%), commensurate with those recorded for pop. 1b (eg, see Lowe, 1988a; Stokes *et al.*, 1992; Shane, 2000). No rhyolitic eruptions, however, are known from Okataina VC between the Whakatane (*c.* 5500 cal. BP) and Kaharoa (*c.* AD 1314) events, and so this possibility is unlikely.

Sample 2 (3.75 m): Whakaipo Tephra (Unit V)

This sample comprised a homogenous set of glass analyses that are similar to those of Whakaipo Tephra (Unit V) erupted 2743–2782 cal. BP (2σ age range) from Taupo VC. This tephra is distinctive geochemically in comparison with other Holocene eruptives from this volcano (Lowe, 1988a; Stokes *et al.*, 1992; Newnham *et al.*, 1995b).

Sample 3 (5.37 m): Stent tephra (Unit Q) with 1 grain Whakatane Tephra

This sample comprised two populations, the glasses from pop. 3a predominant and matching best those of the Taupo VC-derived Stent tephra (Unit Q), which is previously unrecorded in the north Waikato region (Alloway *et al.*, 1994). Stent (Unit Q) was erupted 4240–4510 cal. BP. In contrast, 'population' 3b (1 grain), if not an analytical outlier, is from the Okataina VC and probably represents the Whakatane Tephra (Lowe *et al.*, 1999) (cf. Sample 5), which was erupted ~1000 years before

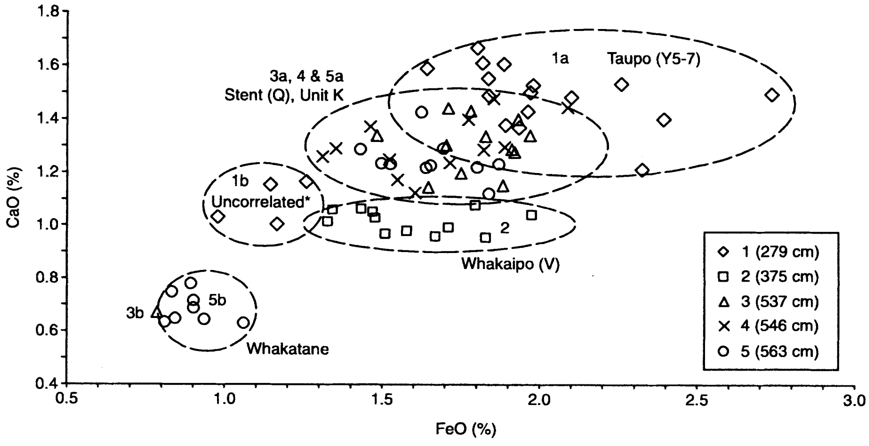

Figure 5 Plot of CaO versus FeO_{total} (wt.%) of glass obtained from samples 1–5 using electron microprobe analysis. Tuhua Tephra analyses omitted for clarity (FeO% is much greater, Table 1). Stratigraphic positions of samples are shown in Figure 3. * See text

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Stent tephra. This grain therefore is probably the result of reworking (or possibly laboratory contamination).

Sample 4 (5.46 m): Unit K

Sample 4 comprised an homogenous set of glass analyses typical of widespread Unit K from Taupo VC (Alloway *et al.*, 1994; Lowe *et al.*, 1999). Unit K, aged 4970–5290 cal. BP, is one of ten closely spaced, mid-Holocene, Taupo-derived eruptives that previously were undifferentiated (unrecognized) components within the 'Hinemaiaia Tephra' (eg, Lowe, 1986; Froggatt and Lowe, 1990), a name abandoned after Wilson (1993) published his revised stratigraphy for Taupo VC.

Sample 5 (5.63 m): Unit K with Whakatane Tephra

This sample consisted of two distinctive populations, pop. 5a being most like glass from Unit K (ie, matching Sample 4). If so, Unit K (4970–5290 cal. BP) has been dispersed at least 17 cm in the core (ie, below Sample 4) through attenuation. (Another interpretation is that Sample 4 is reworked Unit K tephra, but the purity of Sample 4 suggests to us that it probably marks the primary layer of Unit K.) Population 5a may possibly represent units H or G (previously known as Motutere Tephra; Froggatt and Lowe, 1990) from Taupo VC, which were erupted *c.* 6650 to 6050 cal. BP (estimated ages only; Wilson, 1993), and for which there are no definitive EMP analyses available (Froggatt and Rogers, 1990; Eden and Froggatt, 1996). These units seem less widely dispersed than Unit K (Wilson, 1993) and hence (reworked) Unit K is our preferred correlative. Pop. 5b is similar to analyses of glass from Whakatane Tephra (Stokes *et al.*, 1992; Lowe *et al.*, 1999), erupted 5470–5600 cal. BP.

Sample 6 (7.84 m): Tuhua Tephra

This sample consisted of a homogenous set of glass analyses (Table 1) with distinctive peralkaline features typical of Tuhua Tephra (*c.* 7000 cal. BP), namely very high Na_2O and K_2O values and low Al_2O_3 values (Lowe, 1988a,b; Stokes and Lowe, 1988; Lowe *et al.*, 1999; Manighetti *et al.*, 2003). Its very high FeO content shows up clearly on the XRF-derived Fe plot obtained from earlier studies at Kopouatai bog (Figure 3, right-hand side).

Age–depth model

Hazell (2004) developed a detailed age–depth model for the core using the eight AMS ages (Table 2) together with tephrochronological ages for Taupo and Tuhua tephras. The calibrated AMS ages were plotted using the median value of the age ranges against the midpoint depth, as recommended by Telford *et al.* (2004). Several alternative age models were compared to assess their suitability. Linear interpolation, between age points – whilst acknowledged to have its disadvantages, in particular that it assumes constant accumulation rates between age points, and that sedimentation rates change precisely at these points – was used (Figure 6). The alternative methods investigated were rejected on the grounds that they had relatively poor fit and performance: (1) a quadratic relationship showed a systematic distribution of ages around the line; (2) fitting two linear relationships by eye showed a mid-core change in accumulation rates that could not be supported by plant macrofossil analysis (Hazell, 2004); and (3) fitting a single linear relationship through the AMS ages and then joining this to the tephra ages at either end of the model suggested sudden and unrealistic changes in peat accumulation rates. In comparing age models, it was also noted that the maximum difference between them was only approximately 200 years, and that there were substantial intervals when the age models were effectively identical (Hazell, 2004).

Discussion

The EMP data reported here not only confirm the rhyolitic tephrostratigraphy reported previously for Kopouatai bog but also allow us to identify a rhyolitic tephra (Stent/Unit Q) not previously recorded (Table 3). We show that glass geochemistry and ^{14}C dating provide a reasonable fit between the newly identified cryptotephra layers and the original tephrochronostratigraphic framework. In some cases minor age discrepancies are evident. Possible explanations for such discrepancies include: (1) inaccuracy in established age of tephra; (2) inaccuracy in our age model; (3) the eruption history is more complex than previously envisaged or the established record may be missing some events; (4) post-depositional processes may have caused glass shards to move to new stratigraphic levels in the peat; (5) the level of maximum shard concentration from which the sample was selected for microprobe analysis is an artefact of overlapping or mixed tephra populations and does not therefore represent the true stratigraphic position of the tephra isochron.

From the contiguous analysis of shard concentrations through the peat it is evident that the cryptotephra concentrations have not formed discrete layers but widely diffuse zones of shards forming a parabolic pattern with a single peak in concentrations flanked with 'tails' of declining shard concentrations above and below (Figure 3). This pattern is evident where glass-shard concentrations are quantified through and beyond the 2-cm-thick visible Taupo Tephra layer where the

Table 2 Radiocarbon ages and calibrated ages on samples obtained from core Z0106, Kopouatai bog. Sampling positions are shown in Figure 3

Laboratory sample no.	Depth in core (m)	Radiocarbon age ^{14}C yr BP	Calibrated age range (2σ) cal. yr BP	Median calibrated age cal. yr BP
AA-54136	3.41–3.42	2347±38	2154–2426	2290
AA-54137	3.90–3.91	2962±38	2947–3209	3078
AA-54138	4.44–4.46	3618±39	3721–3981	3851
AA-54139	4.98–4.99	4116±41	4422–4809	4616
SUERC-1481	5.55–5.57	4433±37	4851–5255	5053
SUERC-1482	6.09–6.10	4925±34	5492–5708	5600
SUERC-1483	6.63–6.65	5039±39	5613–5889	5751
SUERC-1517	7.36–7.37	6017±34	6682–6890	6786

Calibrations are based on CALIBv.4.4.2 (Stuiver and Reimer, 1993) and INTCAL98 (Stuiver *et al.*, 1998) with correction for Southern Hemisphere offset based on Hogg *et al.* (2002).

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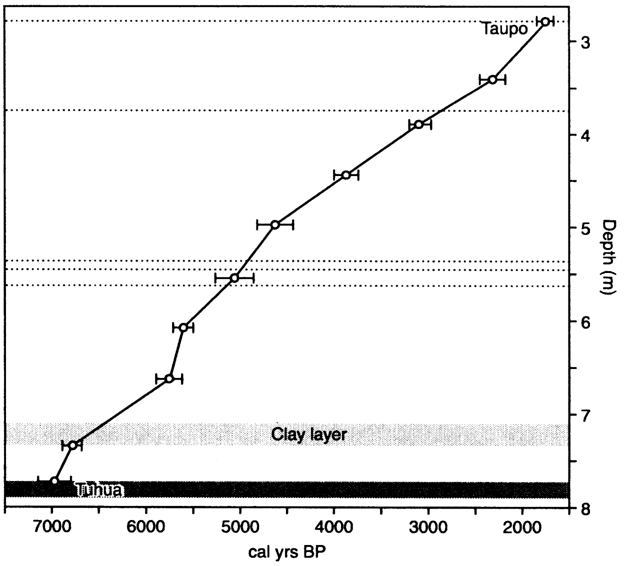

Figure 6 Linear interpolation age–depth model for core Z0106 including AMS dates (Table 2) and tephrochronological dates on Taupo and Tuhua tephras (see text). Horizontal lines mark points sampled for EMP analyses of glass

cryptic 'tails' appear to extend at least 30 cm through the core (Figure 4). The occurrence of a secondary population (1b) within the Taupo Tephra layer, of uncertain origin and age (Table 1), may have contributed towards this tail of shards. If pop. 1b simply derives from an earlier phase of the Taupo eruption then the entire suite of glass in Sample 1 has effectively the same age and so our interpretation from concentration and particle-size data for this layer remains largely unqualified. Alternatively, if pop. 1b is a correlative of Mapara Tephra (Unit X), or another pre-Taupo Tephra eruptive, then our interpretation regarding shard remobilization needs to be reconsidered. Either model could be tested by EMP analysis of glass components sampled throughout the shard concentration zones. In addition, a detailed compositional study of the individual subunits of the Unit Y (Taupo) eruption sequence, extending the findings of Stokes *et al.* (1992) that showed earlier and later phases were significantly different, would provide a better understanding of the degree of heterogeneity within this sequence. Such studies are the focus of ongoing work.

Glass analyses of the Unit K tephra similarly reveal that shards had been disseminated for at least 17 cm through the peat. The presence of two peaks in shard concentrations suggests that reworking has taken place but the continuum of shards both above and below these peaks equally demonstrates that shard attenuation or *in situ* remobilization can be associated with cryptotephras as well as with macroscopic tephras. This recurrent pattern suggests that either the eruption history of New Zealand is more complex than previously thought or that post-depositional processes are causing substantial vertical redistribution of the tephra-derived glass and presumably other components. A similar pattern of shard distribution was described from a study of cryptotephra in lake sediments in The Netherlands: shards beneath the prominent peak in glass-shard concentrations were attributed to downward relocation via plant root channels, and shards above to secondary deposition, probably by wind transport following the primary deposition of the tephra (Davies *et al.*, 2005). We are investigating possible tephra redistribution processes in further work on North Island peat bogs and lakes.

Although this pattern in shard concentrations is clear for individual tephra units, closely spaced and mixed tephra populations may result in a more complex pattern of shard distribution. For example, the 'true' stratigraphic (isochronous) position of individual tephra layers may be difficult to interpret from shard concentrations alone, as shown for samples 3, 4 and 5 (Figure 3), and may pose problems when selecting samples for geochemical analysis or when applying tephrochronology to high-resolution palaeoenvironmental studies. In addition, the cryptic component of visible tephra layers could potentially mask the presence of adjacent cryptotephra. The presence of an additional eruptive phase, or possibly separate cryptotephra, within the visible component of the Taupo Tephra, for example, was revealed only through EMP analysis. Such an occurrence was not evident from the determination of shard concentrations by optical microscopy.

Notwithstanding the implications of possible shard attenuation for the interpretation and identification of individual cryptotephras in volcanic regions, we have obtained important results. Our findings raise issues regarding all analyses of tephras in peat cores and in particular the use of cryptotephras as precise chronostratigraphic markers or isochrons. Where mixing and attenuation of shards are likely to be problematic we recommend a thorough sampling strategy that includes both contiguous sampling to determine shard concentrations and regularly spaced sampling for microprobe analysis throughout the range of the shard concentrations (including those of visible tephra layers).

The number of shards analysed for major or other elements should also be increased to try to include sufficiently large data sets so that each subpopulation (if present) is able to be identified. That andesitic glass shards were not found in any of our samples was possibly the result of insufficient numbers of shards being analysed or because our sample sizes (1 g) were too small, or both. Andesitic tephras had been recorded in the Waikato region by Lowe (1988a,b) mainly using EMP analyses of glass from lake cores. Andesitic glass, though, was always sparse and in many cases difficult to probe because of its greater vesicularity and its microlite-rich character compared with rhyolitic glass. Andesitic glass has a much greater Parker weathering index (Lowe, 1988b) and is more susceptible to weathering or biochemical attack than rhyolitic glass (Lowe, 1988b; Hodder *et al.*, 1990), and so would tend to be underrepresented, suggesting further that much greater numbers of shards should be analysed. Lowe (1988b) additionally noted that samples from lake cores he prepared for EMP analysis typically showed a 'background' component of rhyolitic glass, even in andesitic tephra layers, and our findings from Kopouatai bog suggest that this 'background' represents attenuation or reworking of the dominant tephra-derived glasses throughout the sediments.

Conclusions

Our study has demonstrated that in addition to visible tephra layers in peat cores there is an extensive suite of cryptotephras, manifest as glass concentrations, that can be successfully correlated with known eruptions using major element analyses of glass shards by electron microprobe. In addition to the two visible (macroscopic) tephra layers, Taupo Tephra (Unit Y) (*c.* 1718 cal. BP) and Tuhua Tephra (*c.* 7000 cal. BP), we detected and identified four additional rhyolitic cryptotephras (Table 3, 2σ age ranges): Whaikapo (Unit V) (2743–2782 cal. BP), Stent (Unit Q) (4240–4510 cal. BP) and Unit K (4970–5290 cal. BP), all erupted from Taupo VC, and Whakatane Tephra

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Table 3 Summary of visible and cryptic tephras identified in core Z0106 and their ages

Sample no.	Depth in core (m)	No. of shards in population (pop. a, b)	Eruptive source	Interpolated age in cal. yr BP, 2σ range (from Figure 6)	Identification of tephra[a]	Calibrated ages[b] of tephras in cal. yr BP, 2σ range (original ^{14}C ages)	Primary reference(s) for original ^{14}C ages on tephras	Primary reference(s) for glass major element chemistry
1	2.79	(a) 16	Taupo	*	Taupo Tephra (Subunit(s) Y5-Y7)	1688–17483[c] (1850±10)	Froggatt and Lowe (1990)	Lowe *et al.* (1999)
		(b) 4	Taupo or Okataina?	*	Uncorrelated (see text)			
2	3.75	12	Taupo	2765–3150	Whakaipo (Unit V)	2743–2782 (2685±20)	Wilson (1993)	Newnham *et al.* (1995b)
3	5.37	(a) 12	Taupo	4738–5134	Stent (Unit Q)	4240–4510 (3970±31)	Alloway *et al.* (1994)	Alloway *et al.* (1994)
		(b) 1	Okataina	*	Uncorrelated (see text)			
4	5.46	12	Taupo	4806–5208	Unit K	4970–5290 (4510±20)	Alloway *et al.* (1994); Lowe *et al.* (1999)	Alloway *et al.* (1994); Lowe *et al.* (1999)
5	5.63	(a) 10	Taupo	4984–5347	Unit K	4970–5290 (4510±20)	As for sample 4	As for sample 4
					Unit H? Unit G?	6050 (*c.* 5300)[d] 6650 (*c.* 5800)[d]	Wilson (1993)	Eden and Froggatt (1996); Froggatt and Rogers (1990)
		(b) 8	Okataina	4984–5347	Whakatane	5470–5600 (4830±20)	Froggatt and Lowe (1990); Lowe *et al.* (1999)	Lowe *et al.* (1999)
6	7.84	12	Tuhua	*	Tuhua	6800–7230 (6130±30)	Froggatt and Lowe (1990); Lowe *et al.* (1999)	Lowe *et al.* (1999); Manighetti *et al.* (2003)

[a] Nomenclature follows Froggatt and Lowe (1990) and Alloway *et al.* (1994); alternative tephra names as units/subunits are from Wilson (1993).

[b] Calendar ages obtained by calibrating error-weighted mean ages of named tephras using CALIB and INTCAL98 data set after applying a correction of −41 ± 14 years for Southern Hemisphere offset.

[c] Date range based on dendrochronological estimate by Sparks *et al.* (1995) of AD 232±30 (we doubled the published 1σ error of 15 years) (see also ages reported in Lowe and de Lange, 2000).

[d] Ages estimated only (Wilson, 1993).

*Unable to interpolate from age–depth model.

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(5470–5600 cal. BP) eruptive from Okataina VC. A secondary glass population identified within the Taupo Tephra layer was attributed to either an earlier phase within that eruption or to mixing with a slightly older Taupo-derived eruptive such as Mapara (Unit X, *c.* 2150 cal. BP) or (less likely) a currently unknown Okataina-derived eruption. The discovery of the Stent tephra/Unit Q in the core, a tephra not previously detected this far north of its source, confirmed that cryptotephra analysis may be used to extend ash-fall isopachs for the region which can be used in turn to improve volcanic hazard appraisal and modelling (Hurst and Smith, 2004; Magill and Blong, 2005).

Mixed glass populations identified in the core may be the result of reworked tephra blown (or washed) in to the site, post-depositional remobilization of shards vertically in the peat (possibly by as much as 30 cm in one case), or a result of the closely spaced eruption events, or all three. Because maximum shard concentrations may arise spuriously from overlapping or mixing of glass populations, such peaks do not necessarily indicate the true isochronous stratigraphic position of a tephra. From our analysis of shard concentrations continuously through the core section it is evident that cryptotephra concentrations form widely diffuse zones of shards in a parabolic pattern with a single peak in shard concentrations flanked with tails of shards declining in concentration (Figure 3). The same pattern is evident in **Figure** 4 with the cryptic components extending several decimetres through the core. Numerous lesser concentrations of cryptotephras are likely to represent additional tephra-depositing eruptions (including andesitic events), disseminated glass derived from the tephras identified here or reworked tephra. This recurrent pattern suggests that either the eruption history of New Zealand is more complex than previously thought or that post-depositional processes and reworking are significant factors in causing the vertical redistribution of components of the tephra. In either case, the results reinforce the value of cryptotephra analysis even where the visible tephra record is well established.

For cryptotephra studies of peat cores we recommend using a detailed sampling strategy for the analysis of glass, and other components if present, to account for mixed populations and for the attenuation of glass shards through the peat. In addition, we recommend that more shards from larger samples should be analysed to help 'capture' sparsely represented or poorly preserved glass from cryptic andesitic tephra deposits.

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Appendix

Electron microprobe analyses of individual glass shards (raw data, not normalized) from samples 1–6 in core Z0106, Kopouatai bog (see text for analytical conditions)

Sample no. [population] no. of analysis (see Table 3)	Depth in core (m)	Order analysed	SiO_2	Al_2O_3	TiO_2	FeO^a	MnO	MgO	CaO	Na_2O	K_2O	Cl	Total
1 [a] *n* = *16*	2.79	2	72.12	12.87	0.33	1.88	0.13	0.22	1.37	3.92	2.86	0.14	95.84
		3	71.37	12.90	0.28	1.75	0.12	0.25	1.48	4.22	2.73	0.22	95.32
		4	72.19	12.89	0.19	1.85	0.07	0.17	1.31	3.94	2.89	0.13	95.63
		5	71.95	13.22	0.30	1.58	0.15	0.28	1.53	4.40	2.64	0.21	96.26
		6	72.40	13.28	0.24	2.04	0.09	0.29	1.44	4.43	2.77	0.18	97.16
		7	71.79	13.18	0.32	1.73	0.11	0.30	1.60	4.16	2.66	0.15	96.00
		9	73.56	12.96	0.23	2.69	0.13	0.32	1.47	4.24	2.58	0.09	98.27
		10	72.23	13.07	0.22	2.18	0.02	0.28	1.48	4.10	2.73	0.22	96.53
		11	74.04	13.25	0.26	2.28	0.11	0.28	1.19	3.88	2.65	0.15	98.09
		12	72.96	12.99	0.26	2.34	0.14	0.32	1.37	4.31	2.83	0.26	97.78
		13	75.58	13.23	0.31	1.90	0.20	0.29	1.62	4.74	2.72	0.19	100.78
		14	73.35	12.87	0.43	1.93	0.06	0.23	1.49	4.50	2.54	0.13	97.53
		15	73.05	13.18	0.30	1.79	0.18	0.33	1.45	4.26	2.66	0.22	97.42
		18	73.79	13.16	0.20	1.93	0.06	0.21	1.47	4.20	2.74	0.18	97.94
		19	75.10	13.14	0.32	1.88	0.11	0.24	1.37	4.39	2.63	0.20	99.38
		20	72.14	13.24	0.25	1.76	0.15	0.28	1.56	4.41	2.86	0.17	96.82
1[b] *n* = *4*	2.79	1	71.84	11.97	0.08	1.08	0.04	0.13	0.93	3.40	3.04	0.13	92.64
		8	73.24	12.05	0.11	1.09	0.13	0.13	1.10	3.82	3.36	0.19	95.22
		16	72.60	11.99	0.16	0.92	0.03	0.10	0.97	3.87	3.15	0.21	94.00
		17	73.97	12.13	0.10	1.21	0.07	0.13	1.12	3.74	3.45	0.14	96.06

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Appendix (*continued*)

Sample no. [population] no. of analysis (see Table 3)	Depth in core (m)	Order analysed	SiO_2	Al_2O_3	TiO_2	FeO^a	MnO	MgO	CaO	Na_2O	K_2O	Cl	Total
2 *n* = *12*	3.75	1	76.62	12.28	0.17	1.97	0.08	0.13	1.04	4.20	3.18	0.14	99.81
		2	75.67	12.13	0.19	1.80	0.04	0.08	0.94	4.41	3.05	0.14	98.45
		3	73.52	12.51	0.19	1.29	0.07	0.11	1.02	4.20	3.03	0.15	96.09
		4	75.26	12.56	0.16	1.48	0.08	0.15	0.95	4.21	3.04	0.17	98.06
		5	73.40	12.47	0.11	1.60	0.07	0.11	0.92	4.09	3.01	0.08	95.86
		6	74.15	12.35	0.16	1.53	0.05	0.13	0.95	4.09	3.37	0.19	96.97
		7	72.53	12.36	0.12	1.36	0.12	0.16	1.01	4.16	2.85	0.23	94.90
		8	73.67	12.17	0.14	1.42	0.21	0.09	0.99	4.18	3.17	0.10	96.14
		9	75.20	12.35	0.21	1.67	0.03	0.13	0.97	3.83	3.19	0.09	97.67
		10	73.76	12.29	0.19	1.41	0.05	0.13	1.01	4.09	2.86	0.17	95.96
		11	74.13	12.39	0.14	1.28	0.18	0.13	0.98	4.19	2.99	0.11	96.52
		12	73.32	12.56	0.14	1.73	0.03	0.12	1.04	4.06	3.15	0.25	96.40
3 [a] *n* = *12*	5.37	1	73.31	12.79	0.16	1.84	0.01	0.15	1.24	3.94	2.66	0.17	96.27
		2	73.70	13.11	0.18	1.44	0.25	0.15	1.30	3.91	2.93	0.11	97.08
		3	76.59	13.17	0.20	1.82	0.12	0.21	1.33	2.78	3.16	0.14	99.52
		5	74.99	13.21	0.22	1.93	0.13	0.20	1.40	4.51	3.22	0.13	99.94
		6	72.86	13.06	0.14	1.91	0.01	0.16	1.30	3.98	3.41	0.18	97.01
		7	73.61	13.02	0.17	1.73	0.05	0.16	1.39	4.09	2.81	0.11	97.14
		8	74.28	13.12	0.16	1.61	0.16	0.16	1.12	4.13	2.94	0.10	97.78
		9	73.79	13.17	0.26	1.66	0.03	0.11	1.27	4.04	3.03	0.11	97.47
		10	72.86	13.20	0.18	1.66	0.16	0.20	1.40	4.21	3.17	0.10	97.14
		11	74.09	13.09	0.18	1.71	0.10	0.19	1.17	4.12	2.89	0.15	97.69
		12	76.75	13.15	0.24	1.94	0.00	0.18	1.29	4.18	3.15	0.12	101.00
		13	74.15	12.58	0.18	1.83	0.07	0.19	1.12	4.08	2.84	0.13	97.17
3 [b] *n* = *1*		4	73.93	12.10	0.13	0.75	0.04	0.08	0.64	3.85	3.65	0.22	95.39
4 *n* = 12	5.46	1	75.12	13.03	0.25	1.29	0.05	0.17	1.24	4.06	3.09	0.12	98.42
		2	74.70	13.13	0.22	1.50	0.16	0.19	1.23	4.03	3.19	0.12	98.47
		3	74.27	12.85	0.29	1.57	0.12	0.19	1.10	4.28	3.10	0.07	97.84
		4	74.10	12.80	0.22	1.32	0.07	0.14	1.26	3.96	3.66	0.09	97.62
		5	74.51	13.01	0.16	1.80	0.03	0.20	1.27	4.27	3.30	0.20	98.75
		6	73.67	13.51	0.17	1.82	0.14	0.16	1.45	4.28	2.88	0.11	98.19
		7	75.46	12.69	0.23	1.53	0.08	0.25	1.16	4.24	3.12	0.07	98.83
		8	75.59	13.17	0.27	1.88	0.00	0.16	1.29	4.05	2.97	0.12	99.50
		9	74.90	12.94	0.15	1.69	0.07	0.18	1.22	4.23	3.07	0.12	98.57
		10	76.41	12.95	0.22	2.11	0.20	0.16	1.46	4.32	3.08	0.14	101.05
		11	75.48	12.90	0.16	1.45	0.09	0.19	1.36	4.30	3.06	0.12	99.11
		12	74.49	13.18	0.18	1.75	0.11	0.23	1.38	4.34	2.89	0.12	98.67
5 [a] *n* = *10*	5.63	1	74.65	13.24	0.24	1.63	0.09	0.18	1.21	4.13	2.99	0.21	98.57
		4	72.89	12.90	0.25	1.77	0.09	0.21	1.08	4.14	2.77	0.16	96.26
		6	75.19	13.15	0.24	1.68	0.37	0.16	1.28	3.96	3.01	0.11	99.15
		9	76.24	13.28	0.20	1.64	0.10	0.16	1.22	4.20	2.89	0.13	100.06
		10	73.36	12.97	0.13	1.57	0.01	0.19	1.38	4.03	2.89	0.16	96.69
		12	75.32	13.13	0.29	1.51	0.06	0.22	1.22	4.19	2.80	0.20	98.94
		13	73.06	12.77	0.21	1.74	0.15	0.17	1.18	4.41	2.75	0.17	96.61
		14	75.09	13.03	0.28	1.48	0.05	0.17	1.22	4.27	3.04	0.19	98.82
		16	74.28	12.96	0.25	1.40	0.07	0.20	1.26	4.27	3.06	0.10	97.85
		18	73.55	13.09	0.22	1.82	0.04	0.21	1.20	4.07	2.98	0.12	97.30
5[b] *n* = *8*	5.63	2	75.26	12.23	0.10	0.87	0.02	0.11	0.76	3.98	4.02	0.11	97.46
		3	73.91	12.77	0.05	0.87	0.05	0.09	0.69	3.89	3.89	0.25	96.46
		5	75.86	12.05	0.15	0.88	0.10	0.08	0.67	3.76	3.82	0.15	97.52
		7	75.46	12.18	0.11	0.82	0.07	0.08	0.63	3.62	4.04	0.18	97.19
		8	74.44	12.19	0.13	0.90	0.00	0.14	0.62	3.91	3.75	0.14	96.22
		11	74.73	12.09	0.11	0.78	0.05	0.09	0.61	3.67	3.80	0.27	96.20
		15	74.12	11.92	0.10	1.01	0.01	0.09	0.60	3.61	3.63	0.16	95.25
		17	74.00	11.52	0.10	0.79	0.09	0.10	0.71	3.61	3.76	0.19	94.87
6 *n* = *12*	7.84	1	70.98	9.29	0.26	5.61	0.18	0.01	0.21	5.18	3.97	0.21	95.90
		2	73.13	9.56	0.39	5.32	0.21	0.03	0.20	5.26	4.04	0.21	98.35
		3	73.44	9.44	0.39	5.19	0.12	0.01	0.31	5.78	4.31	0.21	99.20
		4	73.13	9.34	0.27	5.28	0.15	0.01	0.23	5.65	4.10	0.23	98.39
		5	74.08	9.25	0.23	4.88	0.12	0.00	0.24	5.19	3.99	0.21	98.19
		6	73.69	9.37	0.27	6.03	0.26	0.00	0.20	5.55	4.25	0.18	99.80
		7	73.41	9.38	0.30	6.11	0.13	0.06	0.23	6.09	4.13	0.20	100.04
		8	73.23	9.23	0.25	5.41	0.20	0.00	0.29	5.46	4.33	0.22	98.62

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Appendix (*continued*)

Sample no. [population] no. of analysis (see Table 3)	Depth in core (m)	Order analysed	SiO_2	Al_2O_3	TiO_2	FeO^a	MnO	MgO	CaO	Na_2O	K_2O	Cl	Total
		9	71.77	9.35	0.28	5.81	0.10	0.04	0.27	5.20	4.30	0.22	97.34
		10	72.80	9.33	0.30	5.76	0.05	0.00	0.18	5.51	4.20	0.21	98.34
		11	74.22	9.34	0.26	6.14	0.16	0.00	0.25	5.51	4.14	0.24	100.26
		12	72.56	9.97	0.38	5.71	0.13	0.01	0.25	6.02	4.19	0.18	99.40
		13	75.45	10.15	0.20	5.84	0.12	0.00	0.18	5.46	3.85	0.22	101.47

*Total Fe expressed as FeO.

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