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Environmental hazards of fluoride in volcanic ash: a case study from Ruapehu volcano, New Zealand

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Abstract

The vent-hosted hydrothermal system of Ruapehu volcano is normally covered by a c. 10 million m^3 acidic crater lake where volcanic gases accumulate. Through analysis of eruption observations, granulometry, mineralogy and chemistry of volcanic ash from the 1995–1996 Ruapehu eruptions we report on the varying influences on environmental hazards associated with the deposits. All measured parameters are more dependent on the eruptive style than on distance from the vent. Early phreatic and phreatomagmatic eruption phases from crater lakes similar to that on Ruapehu are likely to contain the greatest concentrations of environmentally significant elements, especially sulphur and fluoride. These elements are contained within altered xenolithic material extracted from the hydrothermal system by steam explosions, as well as in residue hydrothermal fluids adsorbed on to particle surfaces. In particular, total F in the ash may be enriched by a factor of 6 relative to original magmatic contents, although immediately soluble F does not show such dramatic increases. Highly soluble NaF and $CaSiF_6$ phases, demonstrated to be the carriers of 'available' F in purely magmatic eruptive systems, are probably not dominant in the products of phreatomagmatic eruptions through hydrothermal systems. Instead, slowly soluble compounds such as CaF_2, AlF_3 and $Ca_5(PO_4)_3F$ dominate. Fluoride in these phases is released over longer periods, where only one third is leached in a single 24-h water extraction. This implies that estimation of soluble F in such ashes based on a single leach leads to underestimation of the F impact, especially of a potential longer-term environmental hazard. In addition, a large proportion of the total F in the ash is apparently soluble in the digestive system of grazing animals. In the Ruapehu case this led to several thousand sheep deaths from fluorosis.
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1. Introduction

Three thin, but widespread tephra deposits were erupted from Ruapehu volcano in 1995–1996. They collectively covered at least 25 000 km^2 of pastoral land with a medium–fine-grade ash layer < 2 mm in thickness. Previously we have documented the beneficial aspects of these deposits, including major additions of soluble sulphur and

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selenium to agricultural soils (Cronin et al., 1997a, 1998). However, in some areas following the 1995 eruptions, volcanic pollution caused the death of several thousand sheep (Shanks, 1997), due in major part to fluorosis. Other isolated fluorosis cases occurred in cattle following both the 1995 and 1996 eruptions. These impacts focussed our attention on the potential health and environmental hazards of fluoride (F^-, hereafter denoted simply as F) in volcanic ash.

Such impacts were not anticipated from the Ruapehu eruptions, since the first measured soluble F concentrations in tephras were mostly < 30 μg g^{-1} (Cronin et al., 1998), which is well below an immediately toxic dietary F intake for grazing animals (> 100 μg g^{-1}; Underwood, 1981). It was also assumed, based on published studies (e.g. Rose et al., 1973; Óskarsson, 1980; Smith et al., 1982), that F within the tephra would be in highly soluble forms, and it would be rapidly leached and adsorbed on to soil particle surfaces (e.g. Bower and Hatcher, 1967; Murray, 1984).

That at least 2000 grazing animals died from fluorosis following the 11 October 1995 Ruapehu eruption, despite heavy rains during the eruption and in the following days, indicated either or both:

(1) there was more soluble F in the tephras than was initially measured, or

(2) there was a less soluble component of F in the tephras that could still be absorbed by (and was toxic to) animals, or be released gradually into the environment.

These properties of andesitic volcanic ash, if true, are important for the assessment and mitigation of environmental hazards associated with tephra falls. This study was carried out in order to elucidate the vent-related and eruption process-related factors controlling the physical, mineralogical and chemical properties of the Ruapehu 1995–1996 tephras. Through this we aimed to understand the form in which F is carried within these types of deposits, explain the grazing animal fluorosis cases and provide information to be used for mitigation of future comparable events.

2. Volcanic gases and fluoride in tephras

Volcanoes emit a variety of gases both between and during eruptions, including H_2O, CO_2, SO_2, HCl, NH_3, H_2S, HF and a few other minor constituents (e.g. Symonds et al., 1994; Giggenbach, 1996). These gases interact rapidly with the ash particles of a volcanic plume and especially atmospheric water to form acidic aerosols (e.g. Rose, 1977; Rampino and Self, 1984). The concentration and type of F-bearing compounds formed in aerosols adhering to tephra particles has been commonly investigated through leaching studies.

Óskarsson (1980) demonstrated that F within tephra from the 1970 eruption of Hekla (Iceland) was highly soluble. In leaching studies on the Hekla ash (2 g tephra to 100 ml water), after 15 min of shaking, 1000 μg F was released per g of tephra; after 300 min, this had only increased to 1100 μg g^{-1}. Óskarsson also found, using scanning electron microscope techniques, that the soluble F was bound to the tephra particle surfaces, and further showed that leachable concentrations increased with decreasing particle size (hence increasing total surface area) of the tephra.

A three-zone model was proposed (Óskarsson, 1980) for adsorption of magmatic gases on to tephra (Fig. 1A).

(1) At magmatic or near magmatic temperatures (> 700°C) tiny (aerosol) salt particles crystallise, probably including NaF and CaF_2. Such sublimates are confirmed by direct sampling from Hawaiian lava fountains (Naughton et al., 1974).

(2) Between 700 and c. 340°C the halogen gases are adsorbed directly on to the silicate glass surfaces of tephra particles. In the Hekla tephra, F seems to have been adsorbed at the highest rate in this zone, with experimental studies showing adsorption increasing dramatically once temperatures dropped below 600°C.

(3) Below 340°C, sulphuric acid aerosols begin to condense, and below 120°C halogen acids condense.

The F compound Óskarsson found at temperatures above 700°C was CaF_2, and below 600°C, where far more adsorption occurs, it was $CaSiF_6$. Leaching studies also suggested $CaSiF_6$ was the
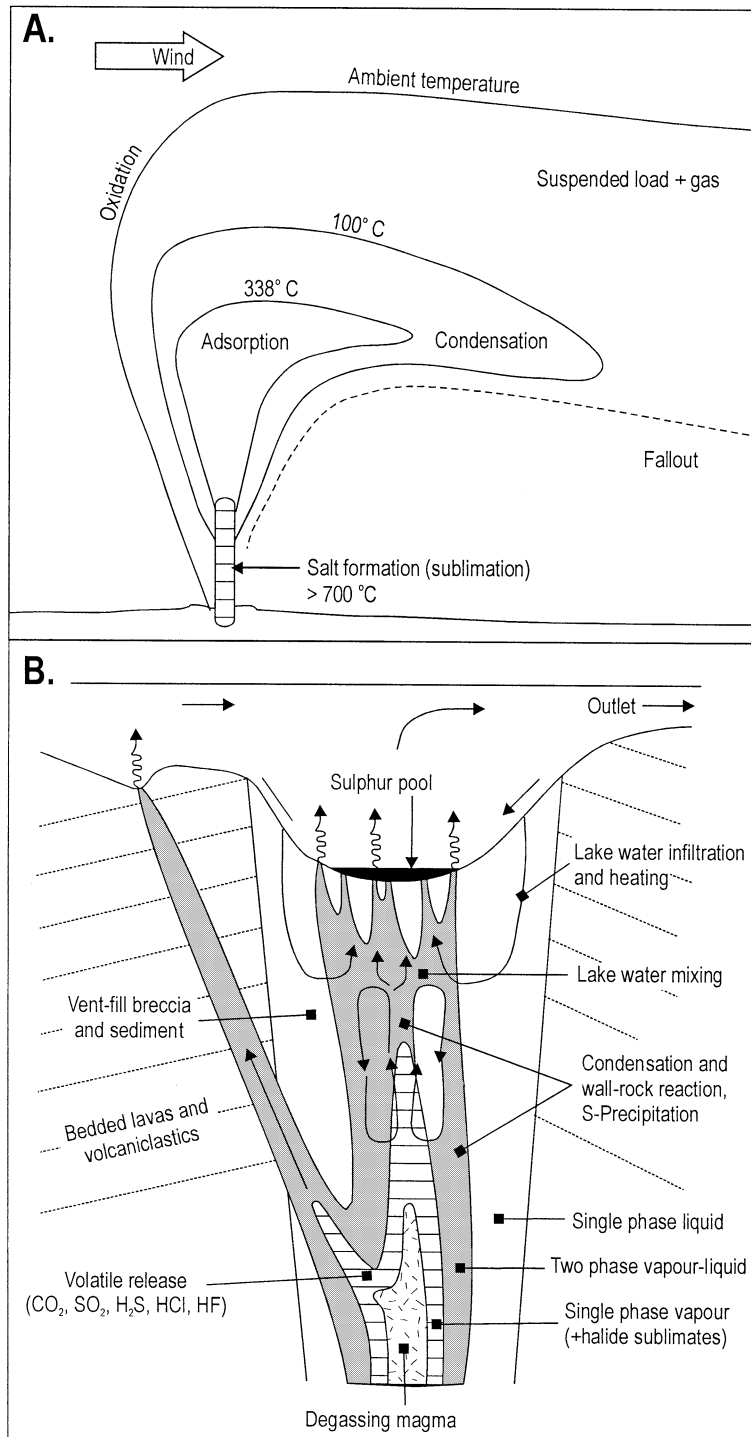
Fig. 1. (A) Model of adsorption of magmatic gases on to tephra particles in an eruption plume, adapted from Óskarsson (1980). (B) Model of the vent–hydrothermal system on Ruapehu prior to the 1995 eruptions, adapted from Christenson and Wood (1993).

most important F-bearing compound, along with lesser NaF and minor AlF_3.

Smith et al. (1982) used a three-step successive leaching method, with firstly water (5 g tephra to 20 ml), secondly a weak acid at the same volume ratio (HCl, pH 3.5–4), and thirdly a 0.05 M $Na_2CO_3+NaHCO_3$ buffered solution at pH 9.9, shaken at 80°C for 1 week. For the first two leaches the tephra samples were shaken for 1 h and left to sit overnight. For fresh tephras of three Guatemalan volcanoes (an andestic–dacitic and two basaltic volcanoes), an average of 21–29 µg F g^{-1} (tephra) was released in the basalts and 14 µg F g^{-1} from the andesite. The following acid leach released an additional amount, around 50% of the initial value. The third treatment, which was intended to simulate longer-term diagenesis, released a further 12–32 µg F g^{-1} from the tephras.

Smith et al. (1983) repeated the above three-stage leaching process on tephra from the 18 May 1980 eruption of Mt St. Helens, a dacitic tephra. Similar results were found, with 7–12 µg F released per g of ash in the water leachates, around 50% of these values in the following acid leachates, and an additional 2.5–14 µg F g^{-1} released in the carbonate–bicarbonate diagenesis simulation.

Smith et al. (1982, 1983) considered that the water and acid washes attacked water-soluble salts adsorbed on to particle surfaces, while the carbonate–bicarbonate treatment caused incipient and incongruent dissolution of volcanic glass. Intrasite variability in soluble measurements for individual tephra layers were thought to arise from combinations of sampling error, particle fractionation during transport and time–temperature history of individual particles in the three-zone ash plume model of Óskarsson (1980).

In evaluating a suspected fluorosis hazard after the 1991 eruption of Mt Hudson (Chile), Rubin et al. (1994) used a similar carbonate–bicarbonate leaching (although cold), as well as a parallel extraction using acetic acid (to simulate in vivo extraction). For fresh tephra samples, carbonate–bicarbonate leached 11–25 µg F per g of ash, and the acetic acid method approximately doubled these values.

3. Volcanic fluorosis

The first recorded cases of acute animal fluorosis were from volcanic ashfalls and gases in Iceland (Roholm, 1937). Tens of thousands of sheep, cattle and horses died mostly from acute fluorosis during the 1783 eruption of Lakagigar (Sigurdsson and Pálsson, 1957; Thorarinsson, 1979). Following the 1970 Hekla eruption, F concentrations of ash-covered pastures exceeded 4000 µg g^{-1} and 7500 animal deaths ensued (Óskarsson, 1980).

Acutely lethal doses of F for most mammals are >100 µg g^{-1} of body weight (NRC, 1974), and grazing animals show immediate toxic impacts with >100 µg g^{-1} of dietary F (Underwood, 1981). Impacts of lower doses depend on the duration of exposure and chemical form of dietary F. In the form of CaF_2, fluoride bioavailability is estimated to be around 50% of that in the highly soluble NaF (Clay and Suttie, 1985). Sheep can generally tolerate dietary intakes of up to 60 µg F g^{-1} (dry diet), but cattle generally only around 40 µg F g^{-1} (Thompson, 1978; NRC, 1980).

A chronic form of fluorosis in cattle (Underwood, 1981) occurred during and following the 1988–1989 eruption of Lonquimay in southern Chile (Araya et al., 1990, 1993). Here, the pastures contained 240–315 µg F g^{-1} and the animals did not show signs of fluorosis until about 10 weeks after the eruption began. In the 2 years following the eruption, pasture F concentrations ranged between 7 and 34 µg g^{-1}, which was enough to maintain fluorosis symptoms in cattle that lived during the eruption.

4. Ruapehu case study

4.1. Ruapehu vent-hosted hydrothermal system

Ruapehu (2797 m) is the highest and largest (110 km^3) andesitic stratovolcano in the central North Island of New Zealand, located at the southern end of the Taupo Volcanic Zone (Hackett and Houghton, 1989). A crater lake periodically covering the active vent is suspected since
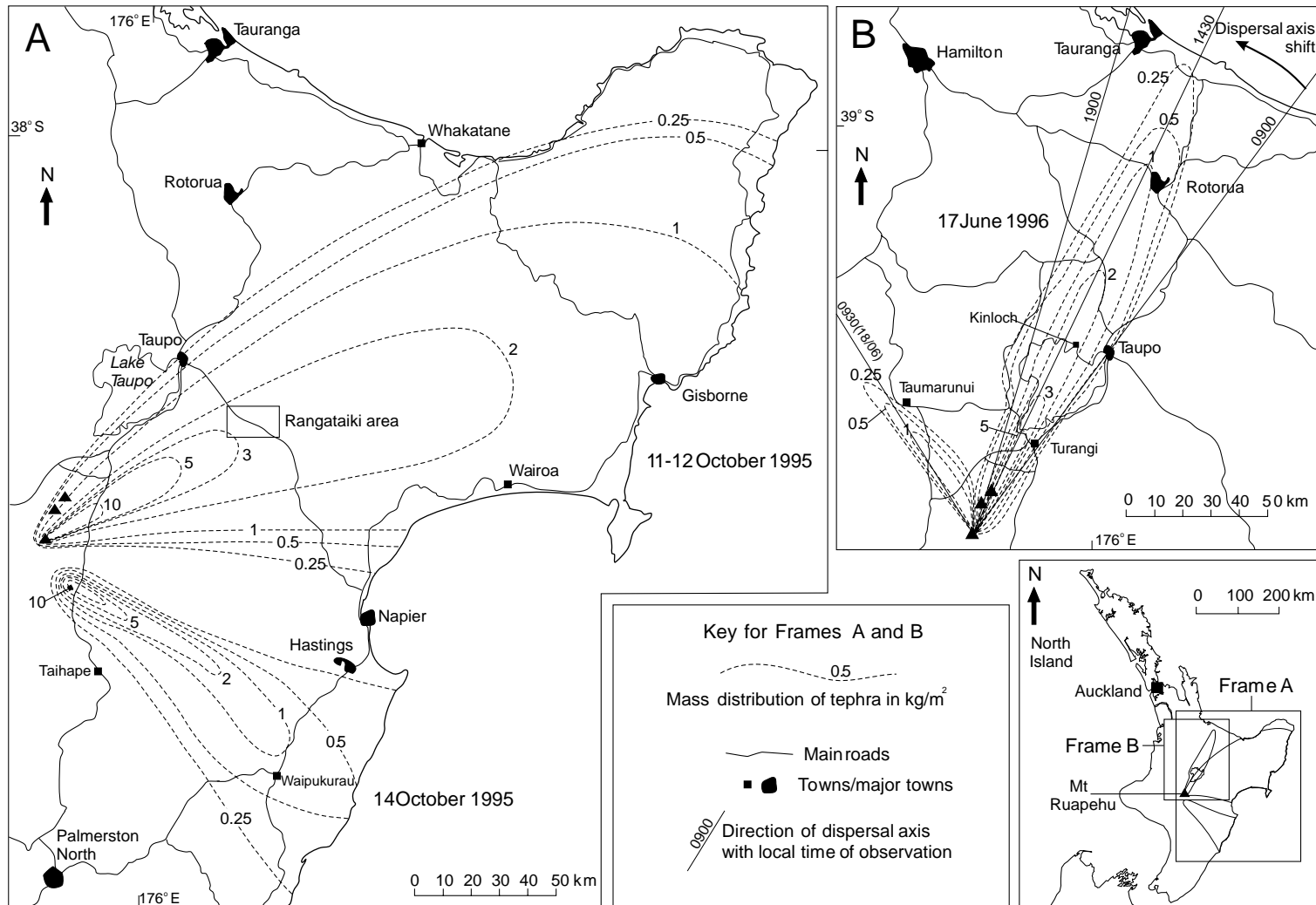
Fig. 2. Mass distribution maps of the major 1995 and 1996 tephra falls from Ruapehu based upon field measurements made by S.J.C., V.E.N. and J.A.L. along with assistance in 1995 from R. Stewart, J. Palmer, A. Palmer and S. Donoghue and in both years from farmers and civil defence officers throughout the North Island. (A) 11 and 14 October 1995 events, with the position of the Rangataiki area marked. (B) 17–18 June 1996 event with the approximate position of the dispersal axis marked for various times during the eruption.

Table 1
Chronology of explosive eruptions leading to tephra falls during the 1995–1996 activity of Ruapehu volcano

Date	Eruption type	Lahar produced?	Eruption column[a] (km)	Dispersal direction and distance (km)	Tephra volume ($\times 10^6$ m^3)	Tephra samples	Comments
18 Sept 1995	Phreatomagmatic	Y	negligible		–		
20 Sept	Phreatomagmatic	Y	negligible		–		
23 Sept	Phreatomagmatic	Y	10	NE, 12	< 0.01		Light dusting visible on snow
24 Sept	Phreatomagmatic (continuous)	Y	8–10	E, 15	< 0.01		
25 Sept	Phreatomagmatic (continuous)	Y	8–10	E, 20	c. 0.01	95/1, 95/3	0.5 mm fall 18 km from vent
26 Sept	Phreatomagmatic	N	< 5	E, 6	< 0.01		
27 Sept	Phreatomagmatic	Y	5–10	SE–E, 25	< 0.01	95/2	Minor ashfall in Waiouru
29 Sept	Phreatomagmatic	Y	5–6	S–SW, 4	< 0.01		
3 Oct	Phreatomagmatic	N	1–6	S, N–E, 10	< 0.01		
4 Oct	Phreatomagmatic	N	< 5	S–SE, 15	< 0.01		
5 Oct	Phreatomagmatic	N	7–8	SE, 15	< 0.01		
6 Oct	Phreatomagmatic	Y	7–8	E, 20	< 0.01		Minor ashfall on Desert Rd.
7 Oct	Phreatomagmatic	Y	7–9	NE, 20	< 0.01		
8 Oct	Phreatomagmatic	N	7–8	E, 20	< 0.01		Minor ashfall on Desert Rd.
9–10 Oct	Phreatomagmatic	N	< 5	Various, 5	< 0.01		
11–12 Oct	Phreatomagmatic–magmatic	Y	8–10	ENE, > 220	25	95/4–6, 10, 12	Crater Lake emptied, eruption for c. 8 h[b] Winds changing from SW to from W during eruption
13 Oct	Dry–magmatic?	N	< 5	E, 10	< 0.01		
14 Oct	Dry–magmatic?	N	10–11	ESE, > 140	5	95/7–9	Eruption for c. 5 h[b] Strong winds from NW
15–17 Oct	Dry–magmatic?	N	1–2	N–NE, 3	< 0.01		
18 Oct–9 Nov	Dry–magmatic?	N	< 1	Various, 3	< 0.01		Minor ashfall restricted to upper cone
10 Nov 1995–March 1996	Gas emissions	N	< 2	–	–		Minor lava extrusion viewed in crater in late March 1996
16 June 1996	Phreatomagmatic	Y	< 5	N	< 0.01		
17 June 1996	Phreatomagmatic–magmatic	N	7–10	ENE–NE, > 300	5	96/1–7, 96/10–14, 96/37, 96/45	Crater Lake emptied during eruption, winds from SW changing to S
18 June 1996	Magmatic, strombolian	N	2–5	NW, > 70	1	96/8–9	
19–20 June	Strombolian	N	< 2	S, < 5	< 0.01		
21–26 June	Gas emission	N	< 2	negligible	–		
27–28 June	Strombolian	N	6	E–SE	< 0.01		Minor ashfall on Desert Rd.
29 June–5 July	Gas emission and strombolian	N	< 2	Various, < 4	< 0.01		

Table 1 (*Continued*).

Date	Eruption type	Lahar produced?	Eruption column[a] (km)	Dispersal direction and distance (km)	Tephra volume ($\times 10^6$ m^3)	Tephra samples	Comments
July 6	Strombolian	N	2–3	W–SW, < 6	< 0.01	96/18	
July 7	Strombolian	N	5	N–NE, 10	c. 0.01	96/19–20	
July 8	Strombolian	N	3–5	N–NW, > 50	c. 0.1	96/23–30, 96/38	Ashfall in Taumarunui
July 9–10	Strombolian	N	2–3	NE, 40	c. 0.01	96/31–35, 96/44	Ashfall at Waihi and Turangi
July 11–15	Strombolian and gas emission	N	2–4	E, 9	< 0.01		
July 16	Strombolian	N	6	SE, 25	c. 0.01		Ashfall at Waiouru
July 17–19	Gas emission and minor strombolian	N	2.4	E–SE, 9	< 0.01		
July 20	Strombolian	N	6–10	S–SE, 20	c. 0.01	96/46	Ashfall in Karioi Forest
July 21	Strombolian	N	4	E, 9	< 0.01		
July 22–23	Strombolian	N	2–6	E, 20	< 0.01		
July 24	Strombolian	N	5–8	NE, 40	< 0.01		Minor ashfall in Turangi
July 25	Strombolian	N	< 4	E, 5	< 0.01		
July 26	Strombolian	N	9–10	E–SE, 120	c. 0.01		Minor ashfall in Napier
July 27–30	Strombolian	N	2–5	N–NE, 5	< 0.01		
July 31–Aug 4	Strombolian	N	< 3	S–SW, 5	< 0.01		
Aug 5	Strombolian	N	5	E, > 20	c. 0.01		Minor ashfall on the Desert Rd. and Napier
Aug 6–20	Quiet gas emission and strombolian	N	< 3	Various, 5	< 0.01		
Aug 21–31	Gas emission	N	negligible	–	-		
Sept 1	Strombolian	N	< 3	SE–SW, 5	< 0.01		
Sept 2–9	Gas emission and strombolian	N	< 3	Various, 5	< 0.01		

[a] Combined from New Zealand Meteorological Service reports at the time, estimations reported by pilots and calculations from satellite imagery (Turner and Hurst, 2001) and field observations made by S.J.C., J.A.L. and V.E.N.

[b] Eruption duration estimated from duration of wideband tremor; Bryan and Sherburn (1999).

around 3000 yr B.P. (Donoghue et al., 1997). The most characteristic aspect of the late Holocene Ruapehu eruptions, including at least 13 since AD 1860, is the ejection of lake water to form lahars (e.g. Cronin et al., 1997b,c).

Since 1879, the Ruapehu Crater Lake has disappeared only briefly three times: following the 1945 eruption (Johnston et al., 2000), at some stage between the 11 and 14 October 1995 eruptions, and during the 17 June 1996 eruption (it began to refill soon after 14 October 1995). In 1991 the lake was estimated to have a volume of about 9 million m^3 (Christenson et al., 1992). The lake temperature cycles between 10 and 60°C and its chemical composition changes, due to variable rates of volcanic gas input (Hurst et al., 1991). The waters are rich in $SO_4 > Cl > Al > Ca > Fe > Na$, $Mg > F > SiO_2$, with F concentrations ranging between 90 and 450 μg g^{-1} between 1971 and 1991 (Christenson and Wood, 1993; Christenson, 2000). Sulphur gases are thought to have condensed at the bottom to form a pool of molten elemental S up to 10 m deep (Christenson et al., 1992).

Christenson and Wood (1993) modelled chemical and physical dynamics of the vent–hydrothermal system (Fig. 1B). Gases released from a convecting magma body, including HF, rise through a single-phase region, where sublimates (halides and sulphides) may form at above 750°C. As the temperature decreases, acid condensates, including HF, begin to form. Reactions between the condensate and wall rock, either andesite or earlier formed alteration products, begin also at this stage. The long-term absolute decline of F between 1971 and 1991 indicated that it was possibly bound in fluorite-CaF_2 or fluorapatite-$Ca_5(PO_4)_3F$), although these were not detected in ejecta of this period.

In summary, the Ruapehu Crater Lake hydrothermal system represents a huge F store, contained either within the acidic lake water, probably as Al–F complexes (cf. Wenzel and Blum, 1992), or within mineral phases.

4.2. Eruptions and tephra distribution

Mass deposition maps of the main 1995–1996 fallout (Fig. 2) were constructed by combining our own systematic measurements of tephra thickness and mass/unit area with those of farmers, fertiliser agents, regional and district council staff, schools, and civil defence members throughout the country.

During the climactic phases of 1995 Ruapehu activity, two tephra plumes were distributed east of the volcano on 11/12 October and 14 October (Table 1, Fig. 2A). Prior to October 11, most of the water within Crater Lake had been expelled in a series of smaller lahar-producing explosions that were accompanied by minor fallout within 15 km of the vent (Table 1; Cronin et al., 1997c). It is assumed that the last of the water was removed in the c. 8-h sustained eruption over the night of 11/12 October. This event produced an eruption column to altitudes of 10–12 km, which distributed at least 25 million m^3 of tephra over a broad area ENE of the volcano (Fig. 2A). Rain accompanied and/or soon followed this eruption in many areas. A second sustained eruption of c. 5 h duration occurred on October 14, from an essentially dry vent. An eruption column up to 10–12 km distributed at least 5 million m^3 of tephra in a narrow lobe ESE of the volcano (Fig. 2A).

Following a pause in explosive activity for several months, water began to pond in the crater and vigorous degassing continued in the vent area. Explosive eruptions began on 17 June 1996. A 24-h eruptive period ensued during which at least 5 million m^3 of tephra was distributed in a narrow lobe NE of Ruapehu (Fig. 2B), and toward the end of this phase a further 1 million m^3 fell in a smaller lobe to the northwest. Smaller rhythmic eruptions continued over the next few months from a dry vent area (Table 1). Most of these involved a series of blasts c. 2–15 min apart, each producing a small eruption column 1–5 km above the volcano that was normally blown away before the next formed. In high-frequency events (2–3-min intervals), the eruption clouds formed a continuous plume, whereas separate clouds formed during less frequent events coalesced more slowly. Fallout from these latter eruptions was restricted to mostly within 50 km of the vent.

4.3. Fragmentation and particle size distributions

Tephra samples were wet-sieved through a 63-µm sieve, with coarser material being sieved at half-ϕ intervals and finer material segregated either using a sedigraph autoanalyser or via standard pipette methods.

Particle size distributions depended as strongly on phreatic water influence as they did on the distance from the vent. The earliest minor tephras of the 1995 sequence were poorly to very poorly sorted fine ashes ($\sigma_1 = 2.1$–2.4) at 10–15 km from source. Tephra from the largest event on 11 October 1995, when a diminished Crater Lake was still present, also displayed very poor sorting ($\sigma_1 = 2.2$–2.7) at all sampled locations. Tephra fall samples from the following magmatic eruption on 14 October were generally better sorted ($\sigma_1 < 2$).

The best observed and sampled tephra lobe was erupted in clear weather on 17 June 1996. The variable influence of the disappearing Crater Lake that occurred during this eruption provides a key to the grain size distributions of other eruptions.

Shifting wind direction from SW to SE during the 17 June 1996 eruption allows a detailed examination of the eruption processes. The fallout dispersal axis swept from a bearing of c. 35 east of Grid North, westwards across the central North Island, depositing tephra produced at successive stages of the eruption along progressively northerly bearings (Fig. 2B). Hence grain size parameters can be analysed with increasing distance from source and with time, represented here as decreasing angle east of Grid North. In the earlier stages the partially re-formed Crater Lake was dispersed and the eruption style was phreatomagmatic. Later stages were progressively dominated by magmatic eruption styles.

Phreatomagmatic influence is represented by the poorly sorted and multi-modal grain size distributions (cf. Walker and Croasdale, 1972; Wohletz, 1983) in tephra samples deposited at greatest angles east of Grid North (Fig. 3). The effect is strongest at c. 40 km from source, but is still noticeable at up to c. 140 km from the volcano, where crosswinds and mixing within the plume
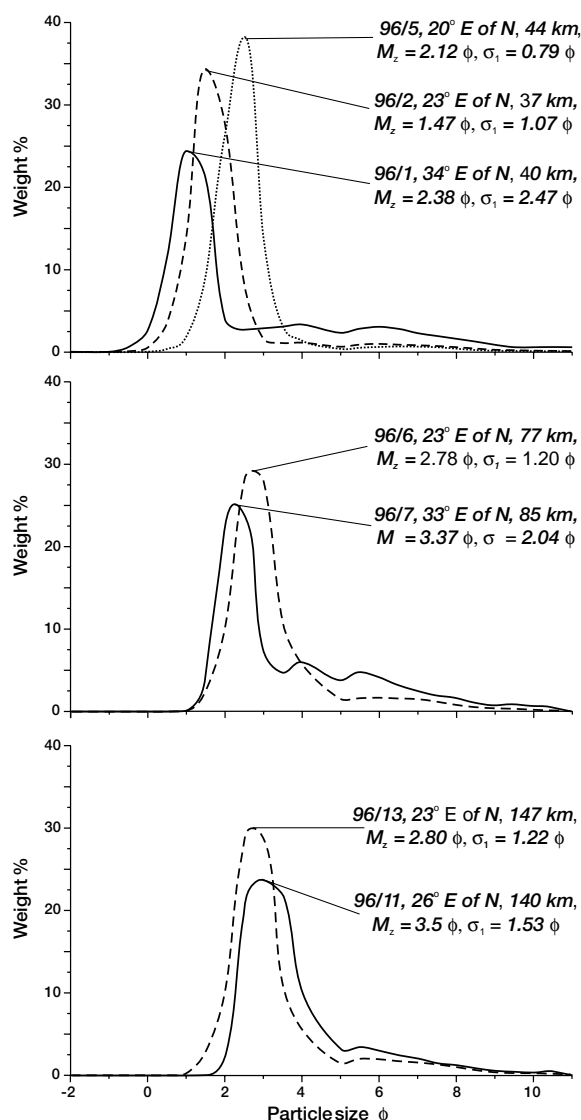

Fig. 3. Comparison of grain size distribution curves for 17 June 1996 tephra samples erupted at various distances from source, and at various dispersal angles from Ruapehu. Whole deposit graphic means and standard deviations (M_z and σ_1; after Folk and Ward, 1957) are given for each sample.

probably reduced the differentiation. The phreatomagmatic deposits are not only more poorly sorted, but at c. 40 and 80 km from source also have a coarser primary mode compared to magmatic eruptives deposited at the same distance within a few hours. This reflects the field observa-

tions of decreasing column heights and eruption vigour during the day. The overall trends observed at three distances from source (Fig. 3) are that the deposits become better sorted and more strongly unimodal with distance.

There are two trends noted in grain size with increasing distance from the vent (Fig. 4A). The poorly sorted tephra from the initial phreatomagmatic phase shows a steep improvement in sorting with distance, whereas the sorting of the tephra from the magmatic phase does not. Some of the tephra from the initial phreatomagmatic phases fell as accretionary lapilli. This early-phase tephra generally fell wet, with coarser particles being coated by a pale steel-grey film of fine ash, and elemental sulphur, whereas later tephra had the appearance of dark greyish brown friable sand.

The graphic grain size parameters of the sub-populations within 17 June 1996 tephra samples collected between 9.2 and 182 km from source (Table 2) were analysed with the aid of the K-Ware SFT program (v. 2.14.0120; Wohletz, 2001). Apart from the strong primary mode of all tephra samples, up to two other modes are noted. The second and third sub-populations are most important in the phreatomagmatic tephra (Fig. 4B), although they are also significant in many of the magmatic tephra samples beyond 40 km from source. The primary sub-population becomes finer with distance from source (Fig. 4C), as would be expected for particle fallout, and the phreatomagmatic samples define a parallel, but consistently coarser, trend. The second sub-population, present only in samples >40 km from source, also defines a fining trend for both magmatic and phreatomagmatic samples, while the third sub-population remains constant throughout the dispersal distance. In both the latter sub-populations, the phreatomagmatic samples are generally coarser than magmatic samples at medial distances, but similar at around 140 km from source.

The coarser modes of all the sub-populations in the phreatomagmatic samples are consistent with the higher eruption column produced in the early high-energy steam explosions. In addition, the phreatomagmatic fragmentation processes probably also lead to a greater proportion of fines
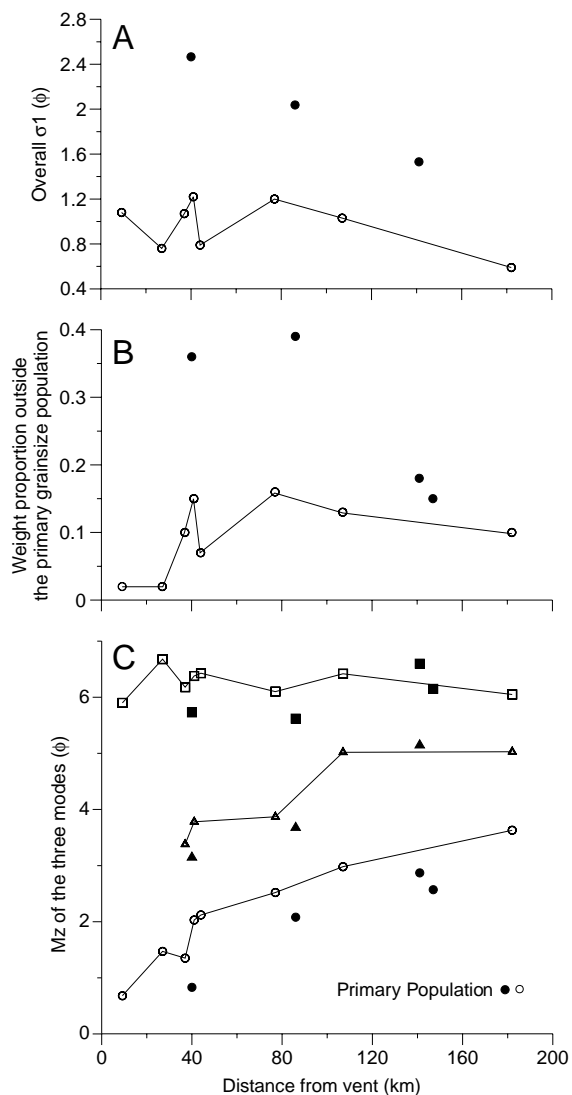

Fig. 4. Grain size distribution trends with distance within the 17 June 1996 tephra lobe; for all graphs, solid symbols denote phreatomagmatic-phase samples and open symbols, magmatic-phase. (A) Overall sample graphic standard deviation/sorting (σ_1) with distance from source. (B) Weight proportion of samples that lie outside the primary sub-population, plotted against distance from source. (C) Calculated graphic means (M_z) of the three grain size sub-populations within the tephra samples with distance from source.

within these samples (cf. Wohletz, 1983). The early phreatomagmatic phase also entrained a much greater xenolithic component as the blasts eroded the hydrothermal system and lake sedi-

Table 2
Summary grain size parameters (after Folk and Ward, 1957) describing sub-populations present within 17 June 1996 tephra samples collected between 9.2 and 182 km from source

Sub-popula-tion	M_z (ϕ)	σ_1 (ϕ)		Mode (ϕ)		Weight proportion
1	0.68–3.63	0.42–0.98	Well–moderately sorted	0.62–3.59	Coarse sand–very fine sand	0.61–0.98
2	3.17–5.27	0.32–0.67	Well–moderately well sorted	3.22–5.88	Very fine sand–medium silt	0.00–0.07
3	5.9–6.68	0.53–1.97	Moderately well–poorly sorted	5.29–6.68	Medium silt	0.02–0.29
Overall	0.67–3.70	0.59–2.47	Moderately well–very poorly sorted	–	–	–

ments and incorporated lake water with its suspended sediments.

4.4. Mineralogy/lithology

Grain mounts of sieved separates from the 2–3-ϕ and 3–4-ϕ fractions were analysed under a polarising microscope. In addition fine-silt and clay fractions were analysed by X-ray diffractometry, following the procedures of Whitton and Churchman (1987).

The common phases of the tephra are: vesiculated glass > plagioclase ≫ orthopyroxene (hypersthene) ≫ clinopyroxene(augite) ≫ titanomagnetite with occasional rare resorbed olivine. In addition a variable proportion of rock fragments occurred,

Table 3
Modal mineral assemblages (%) determined from combined point counts (2×300 grains) of 2–3-ϕ and 3–4-ϕ sieved fractions from three 1995 tephra falls and the 17 June 1996 tephra lobe

Sample	Date/Bearing	Distance (km)	Glass	Pl[a]	Opx	Cpx	Tm	Ol	S°	Rock fragments
Early minor phreatomagmatic event										
95/3	25/9/95	4	23	23	10	4	<0.5	0	9	31
95/1	25/9/95	15	11	21	13	3	<0.5	<0.5	12	40
Largest tephra eruption, phreatomagmatic–magmatic										
95/4	11/10/95	10	22	26	15	5	<0.5	0	3	29
95/5	11/10/95	15	19	31	16	5	<0.5	<0.5	2	27
95/10	11/10/95	130	26	21	4	2	0	0	<0.5	47
95/6	11/10/95	155	30	32	12	<0.5	0	0	<0.5	26
Large tephra eruption, magmatic										
95/8	14/10/95	18	22	30	16	4	<0.5	0	0	28
95/11	14/10/95	48	20	34	11	4	0	0	0	31
95/9	14/10/95	114	22	30	12	2	0	0	0	34
17/6/96, early phreatomagmatic stage										
96/1	34° E of N	40	37	27	17	6	<0.5	<0.5	2	11
96/12	26° E of N	140	65	23	11	<0.5	0	0	<0.5	<0.5
17/6/96, magmatic stage										
96/3	20° E of N	27	36	27	30	4	<0.5	0	0	3
96/5	20° E of N	44	58	28	11	1	<0.5	0	0	2
96/6	23° E of N	77	56	29	11	3	1	0	0	<0.5
96/10	21° E of N	107	70	20	9	<0.5	<0.5	0	0	<0.5
96/14	23° E of N	182	81	13	5	<0.5	<0.5	0	0	0
18/6/96, latest sporadic strombolian eruptions										
96/9	35° W of N	14	51	28	10	3	1	0	0	7

[a] Pl = plagioclase, Opx = orthopyroxene, Cpx = clinopyroxene, Tm = titanomagnetite, Ol = olivine, S° = elemental sulphur spheroids.

Table 4
XRF major element analyses of tephra samples from the main 1995–1996 eruptions

Sample	95/3[a]	95/1	95/5	Gisborne	95/8	96/1	96/7	96/3	96/2	96/4	96/5	96/6	96/10	96/13	96/9
Date	25/09/95	25/09/95	11/10/95	11/10/95	14/10/95	17/06/96	17/06/96	17/06/96	17/06/96	17/06/96	17/06/96	17/06/96	17/06/96	17/06/96	18/06/96
Distance (km)	4	15	15	225	18	40	85	27	37	41	44	77	107	147	14
Eruption style[b]	P	P	P–M	P–M	M	P	P	M	M	M	M	M	M	M	M
SiO_2	63.49	63.38	58.56	64.11	59.31	58.50	57.82	57.22	57.18	57.35	57.30	57.83	58.44	58.67	57.69
TiO_2	0.71	0.8	0.6	0.81	0.66	0.71	0.71	0.64	0.66	0.66	0.65	0.68	0.80	0.78	0.69
Al_2O_3	16.10	16.12	16.25	14.81	16.61	15.52	15.50	15.81	15.35	15.42	15.87	16.30	16.75	16.83	16.25
Fe_2O_3	5.46	6.44	7.36	6.05	7.16	7.81	7.76	7.78	8.13	8.10	7.75	7.31	6.93	6.88	7.52
MnO	0.01	0.08	0.12	0.08	0.11	0.11	0.10	0.11	0.12	0.11	0.11	0.12	0.10	0.11	0.11
MgO	3.32	2.27	5.55	2.88	4.76	5.43	5.28	6.26	6.67	6.55	6.15	5.25	4.41	4.10	5.47
CaO	6.79	7.3	7.36	6.90	7.24	7.54	8.17	7.79	7.83	7.64	7.73	7.73	7.48	7.36	7.71
Na_2O	2.49	1.86	2.84	2.63	3	2.89	3.18	3.07	2.83	2.90	3.13	3.30	3.53	3.68	3.21
K_2O	1.50	1.62	1.23	1.57	1.42	1.31	1.32	1.16	1.12	1.13	1.17	1.30	1.40	1.44	1.20
P_2O_5	0.12	0.13	0.1	0.15	0.12	0.18	0.16	0.16	0.12	0.12	0.14	0.19	0.16	0.17	0.14

Major elements recalculated to 100% on a H_2O- and S-free basis (wt%).
[a] All 1995-series samples determined by I.E.M. Smith, University of Auckland, New Zealand, other samples by Spectra-Chem analytical, Lower Hutt, New Zealand, 'Gisborne' analysis provided by the Gisborne District Council.
[b] Eruption style: P = phreatomagmatic phase, M = magmatic phase.

along with grey spheres and globules of elemental S and rare white fragments of altered andesite and hydrothermal precipitates, particularly in the 1995 tephras and the phreatomagmatic samples of the 17 June 1996 tephra (Table 3).

In the 1996 phreatomagmatic eruptives (dispersed on the most easterly bearing, Table 3), glass fragments are mostly highly vesicular and pale brown, with a minor proportion ($< 5\%$) being dark brown. In later erupted samples, the relative proportions of dark brown glass rise, up to c. 50% of the glass population. The latest eruptives (dispersed northwest on 18 June 1996, Tables 1 and 3) differ in being dominated (c. 90%) by dark brown to sometimes opaque vesicular glass. Plagioclase and pleochroic, green hypersthene laths show strong oscillatory zoning with common dark brown glass inclusions and rare sieve-textured cores. The pale green clinopyroxene also shows some degree of core–rim zoning, along with common glass inclusions, while rare olivine crystals are highly resorbed, with only small core portions remaining unaltered. Opaque minerals, dominantly titanomagnetite, generally occur in association with pyroxene grains. The rock fragments are non-vesicular or poorly vesicular, equant and highly angular in outline, and comprise dark brown glassy matrices with common, dominantly plagioclase microlites and plagioclase and orthopyroxene phenocrysts. Similar rock fragments have been found in several of the prehistoric, post-2000 yr B.P. tephra deposits from Ruapehu and were interpreted to represent phreatomagmatic fragmentation processes (Donoghue et al., 1997). This is in agreement with our observations of the eruptions as well as other mineralogic and grain size parameters of the 1995–1996 tephras.

Variations in mineralogy within the June 1996 tephra lobe (Table 3), typical of all the eruptives, relate to both phreatomagmatic influences (larger proportions of glassy rock fragments) and the progressive relative loss of mineral phases of higher specific gravity with greater distance from source.

Volumetrically the silt and clay components are most important from samples of the early 1995 tephras (up to the 11 October 1995 event), as

well as those from the phreatomagmatic phase of the 17 June 1996 event. Crystalline silt and clay components within the tephras are often obscured on X-ray patterns by large background 'hump' signals from amorphous components within the samples (mostly glass and amorphous silica). Typical assemblages found in clay fractions are glass/amorphous silica phases ≽ smectite ≥ natro-alunite ≥ elemental S > kandite > feldspar, cristobalite, anhydrite, pyrite > quartz. Fluoride-bearing mineral phases were not unequivocally identified, although chemical equilibrium studies of Crater Lake (Christenson and Wood, 1993) indicate they may be present in small quantities.

4.5. Geochemistry – results

The composition of several tephra samples was determined by X-ray fluorescence (XRF) (Table 4). Total S content (Table 5) was estimated by atomic absorption spectrometry (ICP-AAS) after digestion in hot nitric acid (Cronin et al., 1998) and in dry powder with a LECO CNS autoanalyser. Water-extractable S (SO_4^{2-}) was estimated by ICP-AAS following shaking 1 g of tephra with 40 ml of water for 24 h (Table 5). LECO and nitric acid digestion methods agree well for S contents, but XRF measurements appear consistently slightly higher for the S-rich samples (c. 3 wt%), and around double for the S-poor samples (c. 1 wt%). The former two methods, designed to determine agriculturally useful element concentrations, are probably not extracting S contained within primary mineral phases and glass, and hence probably underestimate total S contents, an effect especially noticeable in the magmatic-phase eruptives.

Total F (Table 6) was measured after fusing

Table 5
Estimates of sulphur concentration of the Ruapehu 1995 and 1996 tephra layers

Sample	Date	Distance (km)	Phase[a]	S XRF[b] (wt%)	S HNO₃[c] (wt%)	S LECO[d] (wt%)	SO_4^{2-}[e] (wt%)
95/1	25/09/95	15	P	6.81	n.d.	n.d.	3.10
95/5	11/10/95	15	P–M	n.d.	3.04 (0.05)	3.06 (0.20)	0.47 (<0.01)
95/10	11/10/95	130	P–M	n.d.	3.57 (0.08)	3.06 (0.03)	1.00 (0.01)
95/6	11/10/95	155	P–M	n.d.	n.d.	2.78 (0.06)	n.d.
Gisborne[f]	11/10/95	225	P–M	4.57	n.d.	n.d.	n.d.
95/8	14/10/95	18	P–M?	n.d.	0.91 (0.12)	0.77 (0.04)	0.34 (>0.01)
95/11	14/10/95	48	M	n.d.	0.47 (0.02)	0.35 (0.06)	n.d.
95/9	14/10/95	114	M	n.d.	0.64 (0.02)	0.49 (<0.01)	n.d.
95/12	14/10/95	116	M	n.d.	0.55 (0.03)	0.45 (<0.01)	n.d.
96/1	17/06/96	40	P	3.60	3.26 (0.01)	n.d.	0.73 (0.01)
96/7	17/06/96	85	P	3.39	2.83 (0.16)	n.d.	0.82 (0.07)
96/11	17/06/96	140	P–M	n.d.	1.41 (0.01)	n.d.	0.53 (0.01)
96/3	17/06/96	27	M	0.99	n.d.	n.d.	n.d.
96/2	17/06/96	37	M	1.62	0.71 (0.08)	n.d.	0.28 (0.01)
96/4	17/06/96	41	M	1.49	n.d.	n.d.	n.d.
96/5	17/06/96	44	M	1.19	n.d.	n.d.	n.d.
96/6	17/06/96	77	M	1.80	0.92 (0.15)	n.d.	0.41 (<0.01)
96/10	17/06/96	107	M	1.66	0.76 (0.25)	n.d.	0.33 (<0.01)
96/13	17/06/96	147	M	1.12	0.43 (0.09)	n.d.	0.33 (<0.01)
96/9	18/06/96	14	M	1.54	0.39 (0.11)	n.d.	0.18 (<0.01)

Replicated measurements (three times) are shown as means with standard deviations in parentheses.
n.d. = not determined.
[a] P = phreatomagmatic, M = magmatic.
[b] Calculated as if all were in elemental form, analysis sources as indicated in Table 4.
[c] Total S from digestion of ground tephra in hot conc. nitric acid (method reported in Cronin et al., 1998).
[d] Measured with ground tephra on a LECO CNS autoanalyser, model FP2000.
[e] 1 g of tephra to 40 ml water, shaken for 24 h, measured by ICP-AAS.
[f] Data supplied by Gisborne District Council.

Table 6
Fluoride concentrations of Ruapehu tephras

Sample	Date	Distance (km)	Phase	Total F	Soluble F extraction 1[a] (mg kg^{-1})	Soluble F extraction 2 (mg kg^{-1})	Soluble F extraction 3 (mg kg^{-1})
TFS16	TF5[b], c. 650–830 yr B.P.	18	M?	117	3.6		
TFS1	TF5[b], c. 650–830 yr B.P.	21	M?	146	3.0		
TFS6	TF8[b], c. 500–650 yr B.P.	9	M?	138	1.0		
TFS14	TF8[b], c. 500–650 yr B.P.	18	M?	231	6.2		
95/3	25/09/95	4	P	1797	59.1	28.6	33.9
95/1	25/09/95	15	P	547 (10)	23.0 (0.1)	8.4	11.4
95/4	11/10/95	10	P–M	438	27.8		
95/5	11/10/95	15	P–M	367 (11)	11.2		
95/10	11/10/95	130	P–M	439 (23)	23.4		
95/6	11/10/95	155	P–M	969	23.7 (0.1)	10.0	20.8
95/8	14/10/95	18	M	493 (5)	15.7		
95/11	14/10/95	48	M	370 (16)	1.6		
95/12	14/10/95	116	M	423 (19)	0.4 (< 0.1)	18.8	6.3
96/1	17/06/96	40	P	810 (32)	46.1	16.1	29.6
96/7	17/06/96	85	P	794	44.8		
96/45	17/06/96	87	P	784	52.9 (1.7)	0.0	22.7
96/11	17/06/96	140	P–M	591 (32)	15.9	7.8	34.9
96/3	17/06/96	27	M	335	5.3		
96/5	17/06/96	44	M	287	7.9		
96/6	17/06/96	77	M	405	8.9		
96/10	17/06/96	107	M	351	24.3		
96/14	17/06/96	180	M	408	17.3		
96/9	18/06/96	14	M	375 (35)	58.8		
96/20	07/07/96	9	M	331 (18)	67.9 (2.7)	31.8	15.0
96/22	08/07/96	9	M	319	14.7		
96/27	08/07/96	47	M	346 (38)	39.3		
96/28	08/07/96	59	M	329	26.3		
96/31	09/07/96	9	M	354	55.4		

Duplicated samples are shown as means with standard deviations in parentheses.

[a] Extraction from 1.5 g of ground sample to 30 ml of water, 24 h shaking; sequential extractions are on the same tephra sample.

[b] Tufa Trig tephra members 5 and 8 (after definition of Donoghue et al., 1997).

ground samples with 17 M NaOH at up to 600°C in a muffle furnace, followed by dissolution of the fused cake in water, removing interfering Fe and Al ions by adjusting the pH to 8.5 ± 0.1 with conc. HCl (McQuaker and Gurney, 1977; Frankenberger et al., 1996), and determining F in filtrates using an F ion-selective electrode after addition of a total ionic strength adjustment buffer (Larsen and Widdowson, 1971). This method is proven accurate and reliable for determination of F concentrations within soils and fertilisers with a range of compositions and F concentrations broader than those within the Ruapehu tephras (e.g. Cronin et al., 2000).

Environmentally available F in the tephras was primarily estimated by extraction in water (1.5 g ground tephra to 30 ml water, shaken for 24 h) at unmodified pH. Measurement of F within the resulting solutions (after adjusting pH as described above) was made by either F ion-selective electrode or by ion chromatography (IC) (Landcare Research, New Zealand), both producing comparable results. Attempts to use varying combinations and strengths of acids and alkali extractants produced unreliable results, due to pH-related ionic interferences with the F ion-selective electrode, and total ionic strength interferences with the IC method. Hence a three-step sequential

water extraction (using the same 1.5-g ground sample and three successive 24-h shakings with 30 ml water) was used for a representative subset of samples (Table 6).

For both total and soluble F determinations two pre-historic (c. 500–800 yr B.P.) Ruapehu tephras of similar chemical composition (TF 5 and 8 of Donoghue et al., 1997) were used for reference.

4.6. Geochemistry – discussion

4.6.1. Major elements/oxides

Tephra samples of the phreatomagmatic stage of the 17 June 1996 eruption and deposited at c. 40 km from source have lower MgO and Fe_2O_3 contents and higher K_2O compared to the magmatic eruptives deposited at similar distances a few hours later. The earliest erupted tephras in 1995 also show the highest SiO_2 contents. Together these variations presumably represent a greater altered xenolithic content in the vent-opening/clearing phreatomagmatic-phase eruptives and slightly more fractionated magma within the roof of the erupting chamber.

Changes in chemistry with distance within individual tephra lobes are best demonstrated by the 17 June 1996 deposit, with increasing SiO_2, K_2O, Na_2O and Al_2O_3, and decreasing MgO, CaO and Fe_2O_3 contents, these being consistent with the mineral assemblage trends of decreasing pyroxene content (dense particles) and increasing glass with distance from source. These bulk tephra analyses naturally represent a range of intermediate chemistries between that of 'whole-rock' analyses from bombs (as reported by Gamble et al., 1999) and electron microprobe-determined glass chemistry (reported partly by Donoghue et al., 1997).

4.6.2. Sulphur and fluorine

Even with the analytical limitations described above, the relative differences in 'total S' concentrations are dramatic between magmatic- and phreatomagmatic-phase samples, corresponding to the petrological observation of spherical elemental S particles in the latter.

Sulphur concentrations reach around 3 wt% in phreatomagmatic-phase samples up to 80 km from source (Fig. 5B) and, like in the much lower magmatic-phase samples, show a decreasing trend with distance. The S concentrations of initial-phase tephras are generally between 3 and 10 times those of the later magmatic-phase samples (Table 5). Observations of elemental sulphur in the phreatomagmatic samples imply that this is the major S phase, although other phases such as natro-alunite, anhydrite and pyrite are identified by XRD, and primary gypsum may also occur according to Christenson and Wood (1993). Soluble S shows no strong systematic trends with distance from source (Table 5), but appears more strongly dependent on the influence of the eruptive style (phreatomagmatic versus magmatic).

Trends of soluble element concentration with distance from source are overshadowed by the differences between tephras of the phreatomagmatic and magmatic eruption stages. Water-soluble phases are expected to relate to surface area of tephra (i.e. increase with finer grain size/distance from source). Using the example of the 17 June 1996 tephra lobe, soluble concentrations of Al and Mg show little systematic trend with distance in magmatic-phase samples (Fig. 5A). However, phreatomagmatic-phase samples begin with considerably higher concentrations, which rapidly decrease with distance.

A subtle trend of rising F concentrations (Table 6; Fig. 5C) with distance in magmatic samples may be related to increasing glass contents with distance. A similar subtle trend in the soluble F concentrations of magmatic samples (Fig. 5D) is probably related to increasing surface area of the tephra as its particle size decreases with distance. These trends are, however, eclipsed by the substantially higher contents of both total and soluble F in phreatomagmatic samples, which in the former case show a decreasing trend with distance.

The pre-historic tephra samples (TF 5 and 8) indicate that c. 100–200 mg F kg^{-1} is contained strongly bound within magmatic mineral phases (e.g. apatite) and fresh glass. The tephras erupted during July 1996 were produced by the final series of strombolian explosions and should have been influenced the least by the pre-existing hydro-
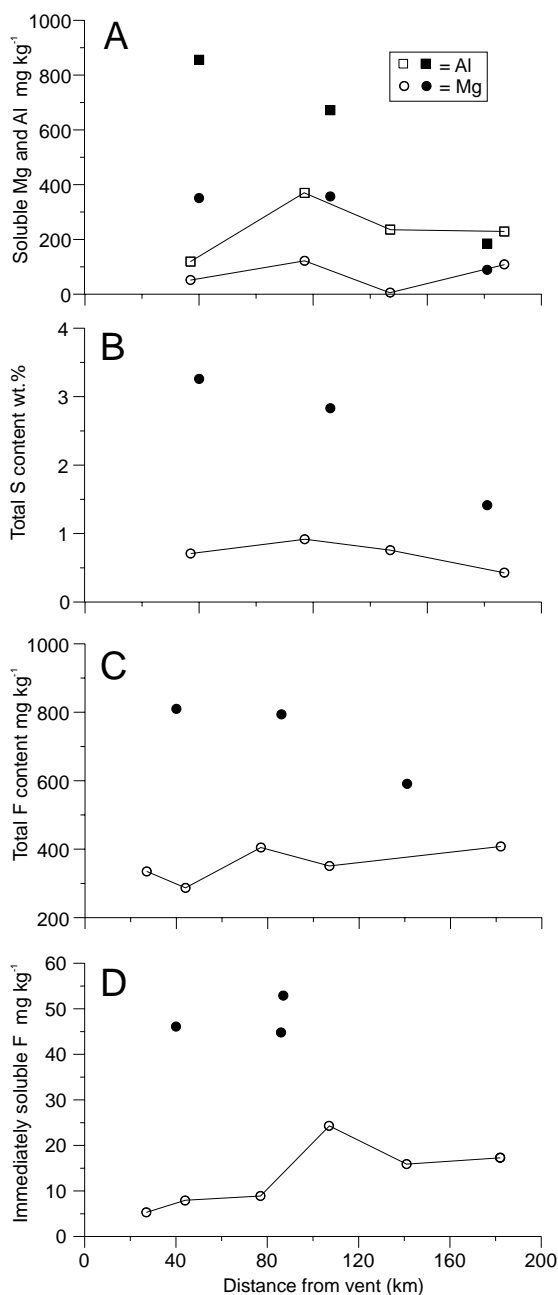
Fig. 5. Chemical composition trends with distance from source within the 17 June 1996 tephra lobe; for all graphs solid symbols denote phreatomagmatic-phase samples and open symbols, magmatic-phase. (A) Soluble Al and Mg with distance from source. (B) Total S content (measured by nitric acid digestion method), with distance from source. (C) Total F content with distance from source. (D) Immediately soluble (one 24-h leach) F with distance from source.

thermal system. Hence, their total F contents of c. 320–350 mg F kg^{-1} likely represent the mineral and glass F content before 500–800 years of weathering and diagenesis. This implies that c. 40–65% of the F in most phreatomagmatic-phase tephras is presumably derived from xenolithic components and Crater Lake water. In the earliest erupted units this non-magmatic component may reach 80%. These very high F concentrations correspond to the highest concentrations in S and soluble elements being related to the phreatomagmatic-phase samples and particularly higher weight fractions of the finer grain size populations (cf. Fig. 4B). Mineralogical evidence implies that the fine grain size populations include secondary materials from the Crater Lake hydrothermal system, lake sediments and suspended phases. Even though no discrete F-bearing phase was unequivocally identified, the concentration differences in total F content seem to suggest that much of it is carried within sediments and compounds associated with Crater Lake, such as amorphous silica.

In general, the latest-stage magmatic-phase tephras from Ruapehu have similar or higher total F concentrations to those of the major 1980 Mt St. Helens tephra (300 mg F kg^{-1}; Smith et al., 1983), and are higher than those in basaltic tephras from Vanuatu volcanoes (180–280 mg F kg^{-1}; Cronin and Sharp, 2002), but substantially lower than those from Hekla ($>$1000–2000 mg F kg^{-1}; Georgsson and Petursson, 1972; Óskarsson, 1980). The higher Ruapehu phreatomagmatic-phase F concentrations are comparable to or higher than those of tephras produced by phreatic eruptions through a hydrothermal system on Soufrière of Guadeloupe (540–800 mg F kg^{-1}; Le Guern et al., 1980). In this latter case, comparable to early-stage Ruapehu eruptions, fine ash was found to comprise mainly clays produced by hydrothermal alteration of primary volcanic rocks.

The F released in initial leaching experiments (Table 6; using ratios of 1:20 ash to water) are comparable to values reported by Christenson (2000) for various 1995–1996 tephra samples using a single leach at a 1:10 ash to water ratio, the one exception being a high value of 79 mg F kg^{-1}

of ash reported by Christenson (2000) for a sample of the 17 November 1995 tephra fall. The sequential water extractions we carried out on selected tephra samples of various eruptive events, however, indicate that not all the 'readily available' F is adequately estimated by a single extraction. Over the two successive extractions, for most samples, a further 70–270% of the original quantity of F was released (Table 6). This is probably one of the reasons why the F risk was underestimated soon after tephra fall. These results are in contrast with Óskarsson (1980), who found >90% of F with Hekla tephra was released immediately. Cronin and Sharp (2002) carried out an identical three-step leaching sequence on basaltic–andesitic tephras from strombolian eruptions (from visible lava lakes) at Yasur and Ambrym volcanoes in Vanuatu. In these cases consistently only <20% of the original F quantity was released in the two successive extractions. In the Hekla and Vanuatu cases, it appears almost all F was contained within highly soluble phases such as NaF, and $CaSiF_6$.

The Ruapehu leaching results imply that significant F, even in the magmatic-phase eruptives, is contained within slowly soluble phases. From the temperature and chemical conditions present in both eruption columns and the Ruapehu hydrothermal system, these phases probably include CaF_2 (fluorite), AlF_3, and $Ca_5(PO_4)_3F$ (fluorapatite). The first two of these phases are thermodynamically very stable and hence only poorly soluble at low temperatures, whereas fluorapatite is somewhat more soluble (e.g. Elrashidi and Lindsay, 1986). Other phases including various combinations of Na, K, Mg, Al, Si and F are similarly even less soluble at low temperatures.

4.7. 1995 fluorosis cases

Following the October 11–12 eruptions and ashfalls from Ruapehu volcano, sheep deaths occurred in the Rangataiki plains area, 90 km from the vent (Fig. 2) (Shanks, 1997). Approximately 2–3 kg m^{-2} of ash fell in this area. Heavy rainfall accompanied the ashfall and continued over the following days.

Approximately 2.5% of pregnant or lactating ewes died in the area, with 1250 dying on one property alone. This loss is greater when the numbers of associated newly born or still unborn lambs are also accounted for. The ashfall occurred near the end of winter, in an area where feed supply was short and the animals were facing high energy demands. Apart from several farms in the Rangataiki area, the only other stock that suffered such great effects was a flock of 1–2-year-old sheep that had been kept in yards for some time before the ashfall. Hence, in all cases the animals most severely affected were those having the greatest energy demands, grazing on short pastures covered by ash. This fasted state is a potential cause of particularly rapid F adsorption (cf. Cerklewski, 1997).

The first animal deaths occurred 9 days after the tephra fall, and deaths continued for another 7–10 days. Surviving animals appeared weak and ataxic (Shanks, 1997). No polioencephalomalacia, as may be associated with high S intake, was noted.

Shanks (1997) found elevated rumen content F concentrations of 360–520 μg g^{-1} (normally <10 μg F g^{-1}; Shupe et al., 1963). This, along with the kidney histology, implies that many of the deaths were probably due to fluorine toxicity (Shanks, 1997). Blood serum F in three animals was not significantly elevated (0.14–0.23 μg F g^{-1}; Shanks, 1997), but this was sampled several days after onset of clinical signs of illness, and blood is known to be a very labile pool of F (Suttie et al., 1972).

Coote et al. (1997) examined the teeth of surviving animals (1 year old at the time of eruption) 6 months after the ashfall, using a proton microprobe. Teeth in the developmental stage during the eruption showed pitting of the enamel, a thin band of enamel enriched in fluoride (up to 1000 μg F g^{-1}), and a second layer within dentine containing around 4000 μg F g^{-1}.

Pasture samples collected in three paddocks, 10 days after ashfall (after heavy rain), contained 20, 30 and 90 μg F g^{-1} (normal NZ pasture concentrations <3 μg F g^{-1}; Loganathan et al., 2001), but the F concentration may have been much higher in the first few days after ashfall. These pasture compositions probably reflect F adhering

to pasture surfaces, since F is not readily taken up into pasture root systems (e.g. McLaughlin et al., 1997). Surface water samples collected at the same time showed F contents < 2 μg g^{-1}.

Following the 17 June 1996 eruption, sheep in the Kinloch area (70 km from Ruapehu) showed ataxia and inappetance. This area was covered by around 2–3 kg m^{-2} of ash, which was accompanied by dry weather for at least a week. All animals recovered.

5. Discussion

To understand the case of the October 1995 Rangataiki animal fluorosis occurrences several factors need to be considered. Firstly, an immediately toxic dietary F intake (in the form of NaF) for breeding ewes is ≥ 70 mg F kg^{-1} of dry diet, and for dairy cattle ≥ 60 mg F kg^{-1} (Thompson, 1978; NRC, 1980). Secondly, an acutely lethal dose for both would be ≥ 100 mg F kg^{-1} of animal weight (NRC, 1974), which equates to c. 5.5 g F for breeding ewes and c. 33 g F for cattle. Thirdly, it must be considered that the animals in the Rangataiki area were facing high stress levels at the time (due to feed shortage, cold and demands of pregnancy and lactation) and that the deaths took around 9 days to begin, hence these critical intake thresholds were likely to have been substantially lower.

During normal winter conditions in New Zealand, without tephra fall, it is known that sheep ingest around 260–275 g of soil per day (Lee et al., 1996), due to worm castings, soil splash and grazing on short pastures. For cattle, winter soil ingestion rates can be around 1200 g day^{-1} (Healy, 1968). Using these rates, over 9 days, sheep can easily consume up to 2.5 kg of soil, and cattle up to 11 kg. Ingestion rates of tephra coating pastures is likely to be substantially higher than these rates, especially since the 11 October 1995 tephra had a large silt–clay component that in conjunction with associated rain caused it to adhere strongly to pastures.

Using an estimate of 24–28 mg F kg^{-1} for immediately soluble F in the 11 October 1995 tephra (Table 6), around 200 kg of tephra is required to produce a full lethal dose for sheep. This is equivalent to the tephra cover over c. 80 m^2. Using an estimate of slowly soluble F from our data (c. 55 mg F kg^{-1}; Table 6), 100 kg or c. 40 m^2 of tephra is required, and even for the highly soluble F value of c. 78 mg F kg^{-1} reported by Christenson (2000), 70 kg is required (c. 28 m^2). Hence, the soluble concentrations within the Ruapehu tephras should not have been high enough to cause the deaths.

The bioavailability of CaF_2 in animals is considered to be around 50% of that from NaF (Clay and Suttie, 1985), and that of fluorapatite is probably even higher, due to its greater solubility. Hence, assuming the tephra at Rangataiki had a similar phreatomagmatic character to sample 95/6 (Table 6), a 'fixed' F concentration within glass of c. 300 mg kg^{-1}, and a minimum of 50% bioavailability of the remainder (= 335 mg F kg^{-1}), then around 15–16 kg of tephra would be required to provide an immediately lethal dose to sheep. It is clear that considering the lowered resistance of the grazing animals, the 9-day course of the disease, and other potential physical impacts of tephra ingestion, much less tephra would need to be consumed, which would be well within the range that the sheep are capable of eating. It is also apparent that the F-bearing component with the phreatomagmatic-phase eruptives of Ruapehu was still highly toxic to grazing animals, despite being poorly water-soluble.

6. Conclusions

The Ruapehu case study demonstrates the complexity of factors controlling the chemistry and consequent environmental impacts of tephra deposits. The role of phreatomagmatic versus magmatic fragmentation systems (as dependent on the presence of a large vent-hosted hydrothermal system) was overprinted on effects due to changing grain size (hence, total particle surface areas) with varying distances from source and wind parameters. Phreatomagmatic influences, including incorporation of hydrothermal system components within the tephras, were generally dominant for early-stage eruptives of the eruptive sequence.

Our results imply that for the many volcanoes with acid crater lakes, and the majority of strato-volcanoes that have some degree of vent-hosted hydrothermal system, environmental S and F hazard could be greater than previously realised. In particular, early-phase tephra deposits of an eruptive sequence, whether phreatic or phreatomagmatic, may include large fractions of secondary phases from adjacent or underlying hydrothermal systems that contain substantial amounts of F and S. In the Ruapehu case we estimate that, despite most of Crater Lake being expelled to form lahars (Cronin et al., 1997c), around 10^9–10^{10} g of F and $> 10^{12}$ g of S stored in the hydrothermal system were additionally distributed with the erupted tephras.

This mechanism can produce tephras with F concentrations up to two orders of magnitude greater than those simply estimated from their soluble F concentrations, and at least double those that would be expected from primary magma compositions. In addition, as demonstrated by the Ruapehu example and from theoretical considerations of F bioavailability, at least 50% of the F in such secondary phases (e.g. CaF_2, AlF_3, and $Ca_5(PO_4)_3F$) can be digested by grazing animals to cause fluorosis. Although S was not directly implicated as a problem in the Ruapehu case, with total concentrations exceeding 3 wt% in many cases, it may also prove to be a severe environmental hazard in agricultural systems (e.g. Rousseaux et al., 1991) and water supplies, especially since field studies showed that most had oxidised to SO_4^{2-} within 2 months of fall (Cronin et al., 1997a).

Sequential leaching studies on the Ruapehu tephras suggest that one-off estimates of soluble F concentration can be misleading for interpreting environmental F hazard from some eruptions. In strictly 'dry' magmatic systems, > 80–90% of F may be released in a single leaching. However, tephras containing hydrothermal components may continue to release F into water supplies and soils for days and possibly weeks following deposition. In many cases, F amounts released in later leaching events may exceed that of the first leachates by more than 200%.

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