

**Comparing volcanic glass shards in unfertilized and fertilized Andisols  
derived from rhyolitic tephtras, New Zealand: evidence for accelerated  
weathering and implications for land management**

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## **Highlights**

- We examined glass shards from two Andisols of different age and fertilizer history
- The average sizes and angularities of the glass shards decreased with soil age
- The shard size and angularity decreases were more marked in the fertilized soils
- Additions of phosphatic, F-containing fertilizer had enhanced the glass dissolution

## **Keywords**

Dealumination, clay minerals, allophane, fluoride, Udands, Vitrand

## **Abstract**

Enhanced weathering associated with the use of phosphate fertilizers has been identified in some of the major farming areas of New Zealand and an evaluation of its effects on soil properties and the implications for soil management are needed. We assessed changes in the character of volcanic glass shards in topsoils (0–10 cm depth) of two tephra-derived Andisols of differing ages (Udivitrands, Hapludands), and with and without long-term fertilization, to test if fertilizing accelerates the weathering of soil constituents. Using visual assessment based on scanning electron microscopy and electron microprobe analyses of glass shards from samples from paired sites, we showed that the average sizes of the shards and the sharpness of the glass-shard edges (angularity) diminished with the age of the soil, and that these decreases were more marked in the soils that had been fertilized. Silica polymorphs were observed only in the older soil (Hapludand) that had been fertilized. We concluded that the addition of phosphate-containing fertilizer enhanced the dissolution of volcanic glass, consistent with phosphoric acid and F<sup>-</sup>-induced dealumination and desilication, and thus soil weathering has been accelerated. The Al and Si may subsequently coprecipitate as secondary minerals, such as allophane. However, silica polymorphs may form where Al activity is low. The occurrence of neogenic silica in topsoils (despite high annual rainfall that should result in desilication of the topsoil and reprecipitation of silica deeper in the soil) is explained by the seasonality of fertilizer application and the spring-summer climate, where the soil remains moist for periods sufficiently long enough for the dissolution of volcanic glass (and possibly of other aluminosilicates), the formation of Al-humus complexes, and the subsequent precipitation of silica in dry periods. Implications of the accelerated weathering for soil and land management are discussed.

## 1. Introduction

Dealumination of clay minerals is a phenomena not often described in soils. Jackson et al. (1952) proposed that the reduction in charge of dioctahedral micas may occur from dealumination, being, in this case, substitution of Si for Al in the tetrahedral layer, while Gjems (1970) reported dealumination during the pedogenic weathering of clays in a podzol when the pH dropped below 4.5. More recently, Egli et al. (2004) reported F- and humus-mediated dealumination of 2:1 clay minerals and consequent formation of smectites.

In New Zealand, dealumination has also been described in some volcanic-ash (tephra) derived soils. Taylor et al. (2012) and Taylor and Kim (2009) presented evidence for the dealumination of soil minerals by accelerated weathering or chemical attack on aluminosilicates. Increased concentrations of acid-extractable Al were observed in soils obtained from the Bay of Plenty, Auckland, and Waikato regions of northern North Island, New Zealand, for farmed land that had receive substantial inputs of phosphate fertilizers since about 1950, but not for unfertilized forested land. Two specific mechanisms were proposed: (1) partial dissolution of clay minerals by local areas of temporal high acidity associated with phosphate fertilizer granules; and (2) surface complexation and extraction by the fluoride and residual hydrofluoric acid present in phosphate fertilizers (superphosphate may contain up to 2% F: Cronin et al., 2000; Mirlean and Roisenberg, 2007).

The likelihood that nitrogen fertilisers had a role in accelerated weathering was discussed in Taylor and Kim (2009) and rejected. Briefly, soil acidification because of nitrification of urea may be caused by N inputs greater than those assimilated by biota and stored either in biota or soil organic matter, the imbalance of cation over anion uptake by plants, loss of  $\text{NO}_3\text{-N}$  due to leaching, and incomplete return to soil of the alkalinity of organic anions removed in products (Bolan et al., 1991; Barak et al., 1997). Soil acidification

is also partly neutralised by  $\text{OH}^-$  released when  $\text{NO}_3^-$  is taken up and assimilated by biota (Bouman et al., 1995). Thus, the net reaction of nitrogen addition, nitrification, and uptake by biota is acid/base neutral (Barak et al., 1997). Hence, although Bouman et al. (1995) recorded pH values as low as 4.3, the solubility of Al did not increase substantially as pH decreased. In addition, soil acidification is managed by application of lime in New Zealand farm systems. Monitoring of New Zealand soils shows that farm management, generally, ensures soil pH levels are meeting the optimum required by the plants grown under the different land uses in New Zealand, and pH rarely drops below 5.5 (e.g. Taylor, 2015). A variety of hydroxyl groups are found on the surface of the soil matrix as  $\text{OH}^-$  replacement of  $\text{O}^{2-}$  on the surface of Al, Fe, Si, and Mn oxides in clay minerals results in reactive  $\text{OH}^-$  on the mineral surfaces. The reactive  $\text{OH}^-$  may be released from the mineral surface by complexation with oxianions. So, as  $\text{H}_2\text{PO}_4^-$  ions are adsorbed onto the surface functional groups of soil colloids, i.e. by ligand exchange, part of the soil acidity produced is neutralised (Parfitt, 1978; Goldberg and Sposito, 1985).

Exposure of aluminosilicates to the two specific mechanisms proposed above results in dealumination, namely the extraction of Al, and presumably Si, from the mineral or mineraloid matrix. The process of dealumination is important because the breakdown of primary minerals and volcanic glass results in elements that were normally retained inside the residual phases of aluminosilicates becoming more mobile and potentially bioavailable (Taylor and Kim, 2009). Such elements include the environmentally sensitive trace elements Ag, Bi, Sn, Tl, and U.

Much of the central North Island has been blanketed with deposits of silica-rich rhyolitic tephras derived from eruptions of the Taupo, Okataina, and Tuhua volcanic centres (Lowe and Palmer, 2005), which weather mainly to allophane or halloysite, or both,

depending on a range of factors, forming mainly Andisols (Ugolini and Dahlgren, 1991; Dahlgren et al., 2004; Hiradate and Wada, 2005; McDaniel et al., 2012). Andesitic tephras have also been deposited but these are much less voluminous and thinner than the rhyolitic tephras by several orders of magnitude. Rhyolitic tephras typically contain abundant fragments (pyroclasts) of Si-rich glass and glassy vesicular pumice clasts relatively low in Al (compared with basaltic glass). Such fragmental, glassy materials in soils can weather through hydrolysis even more readily than accompanying crystals or lithics because of the high surface area, vesicularity, and thermodynamic instability of glass (Churchman and Lowe, 2012), thereby releasing Si, Al, and other elements for mineral neogenesis (Hiradate and Wada, 2005).

Volcanic glasses dissolve through sequential removal of metals from the glass structure via proton exchange reactions (Hiradate and Wada, 2005; Gislason and Oelkers, 2003; Declercq et al., 2013). The overall dissolution rate is controlled by the detachment of Si tetrahedral that have been partially liberated from the glass structure through the removal of adjoining Al and the concomitant transformation of Al from its tetrahedral to octahedral state (Hiradate and Wada, 2005). Strongly adsorbing anions such as  $\text{PO}_4^{2-}$  and  $\text{F}^-$  can act in the same way as  $\text{OH}^-$  and increase glass dissolution rate, even in acidic conditions. The potential role of  $\text{F}^-$  is discussed further below. If F-containing phosphate fertilizer additions are accelerating the weathering of soil constituents then such changes should be observable by examining changes in the character of volcanic glass. In our study, we evaluated the effect of long-term fertilizer additions on the character of volcanic glass fragments in topsoils (0 to 10 cm depths) of two Andisols (Soil Survey Staff, 1999) derived from weathered rhyolitic tephras in central North Island, one, an Udivitrand, being much younger than the other, a Hapludand.

## 2. Materials and methods

### 2.1 Materials

Topsoil samples from paired sites under dairy pasture farmland fertilized with superphosphate and urea, and unfertilized forest were taken from two extensive soil types derived from either Late Holocene or Late Quaternary rhyolitic (silica-rich) tephras: (1) Taupo sandy loam (an Udivitrund, Late Holocene in age), and (2) Tirau silt loam (a Hapludand, Late Quaternary in age) (Table 1). Samples for each soil comprised a composite of 50 cores, 2.5 cm diameter taken from 0–10 cm depth, on a 50 m transect. Rainfall was very similar at both sites (about 1600 and 1650 mm per annum), both were formed under native broadleaf-podocarp forest until the arrival of Polynesians around AD 1280, after which bracken fern *Pteridium* spp. and scrub replaced much of the forest after burning, and both are well drained (Bakker et al., 1996, Lowe and Palmer, 2005; McGlone et al., 2005).

The *Taupo soil* is derived from rhyolitic tephra from the Taupo eruption (AD 232  $\pm$  10, Hogg et al., 2012) and is dominated by glassy pumice clasts and glass shards, which have weathered to form about 4% clay dominated by allophane. This amount of allophanic clay is consistent with a period of weathering of only ~1800 years (Hodder et al., 1990). The topsoil textures are sandy loams.

The *Tirau soil* is derived from intermixed, multiple tephra layers, chiefly rhyolitic in composition, derived from a very thin deposit (~1–2 cm) from the Taupo eruption (c. AD 232) overlying a composite (>50 cm in thickness) of mainly Holocene and Late Pleistocene tephras post-dating the deposition of the Rotorua tephra (c. 15,600 calendar years ago, Lowe et al., 2013) (Table 1; Pullar and Birrell, 1973). The Tirau soil has thus had about ten times

longer to weather through developmental upbuilding pedogenesis (Lowe and Tonkin, 2010) than the Taupo soil, and so the topsoils have finer silt loam textures with clay contents of about 19%, dominated by allophane. The volcanic glass content of the Tirau soil accordingly is lower than that of the Taupo soil (Table 1; Bakker et al., 1996).

**Table 1** Characteristics of the two soil types

<b>Soil type</b>	Taupo sandy loam	Tirau silt loam
<b>Location</b>	38° 15.7', 175° 57.7' and 38°16.0', 175° 58.6'	37° 57.6', 175° 41. 7' and 37° 58.0, 175° 42.3'
<b>New Zealand Soil Classification<sup>a</sup></b>	Immature Orthic Pumice Soil	Typic Orthic Allophanic Soil
<b>Soil Taxonomy<sup>b</sup></b>	Typic Udivitrand, ashy/pumiceous, mesic	Typic Hapludand, medial, thermic/mesic
<b>Parent material and age</b>	Taupo Tephra (c. 1718 cal. yr BP) <sup>d</sup>	Taupo (c. 1718 cal. yr BP) and post-Rotorua rhyolitic tephra (<c. 15,600 cal. yr BP)
<b>Dominant mineralogy<sup>c</sup> (topsoil)</b>	Low (5%) clay content dominated by allophane. Glassy mineralogy class	20% clay content dominated by allophane. Abundant glass in sand fraction
<b>Landform</b>	Undulating crest in rolling landscape	20 m below crest in strongly rolling landscape
<b>Current landuse</b>	Unfertilized site: long-term pine forest Fertilized site: pasture	Unfertilized site: long-term pine forest Fertilized site: pasture
<b>Topsoil morphology</b>	Unfertilized site: 0-10 cm, dark brown 7.5YR 3/2  Fertilized site: 0-17 cm, very dark brown 10YR 2/2  Both sites: slightly sticky, non-plastic, moderately weak, friable sandy loam	Unfertilized site: 0-18 cm, dark greyish brown 10YR 3/2  Fertilized site: 0-15 cm, dark greyish brown 10YR 3/2  Both sites: non-sticky, non-plastic, weak, friable loamy silt
<b>Fertilizer history</b>	Unfertilized site: none known  Fertilized site: 300 kg h <sup>-1</sup> superphosphate per year, plus regular lime (1.5 t ha <sup>-1</sup> 3-yearly)	Unfertilized site: none known  Fertilized site: 700 kg h <sup>-1</sup> superphosphate per year, plus regular lime

<sup>a</sup>Hewitt (2010)

<sup>b</sup>Soil Survey Staff (2014)

<sup>c</sup>Bakker et al. (1996)

<sup>d</sup>Calendar years before present (present = 1950 AD)



## 2.2 Methods

Wet chemical analyses were carried out at IANZ-accredited laboratories, Landcare Research of Palmerston North (pH-water), AgResearch of Hamilton (hot-water carbon), and Hills Laboratory of Hamilton (anaerobically mineralised nitrogen, total F, and acid extractable Al and P), according to the Land and Soil Monitoring Manual (Hill and Sparling, 2009; Kim and Taylor, 2009). Samples were air dried at 35° C and sieved, with the <2 mm fractions used for analyses. Nitric/hydrochloric acid digestion (US EPA 200.2) followed by ICP-MS at the trace level was used for acid extractable Al and P. Total F was analysed using the alkali-fusion/ion-selective electrode method (McQuaker and Gurney, 1982).

Visual assessments of the degree of roundness of glass shards (i.e. sharpness of the edges and corners, essentially angularity), based on Powers (1953), were undertaken using scanning electron microscopy and electron microprobe analysis at paired sites.

All the electron micrographs were acquired at Braunschweig Technical University using a Jeol 6700F cold field emission scanning electron microscope with an attached backscattered-electron detector using composition-mode. Chemical analyses were carried out using an adapted EDAX energy dispersive spectrometer system including a SiLi-detector and the Genesis software package (v 5.21). The field emission electron gun probe currents were small (20 kV and current values near  $5^{-10}$  A) and the probe diameter was in a nanometre range. Areas (average of some thousand points) were analysed instead of single points to optimise the examination of glass grains to minimise loss of sodium and potassium through volatilisation during analysis (e.g. Lowe et al., 2008).

The samples were dried at 60° C and hand ground with an agate mortar. The resulting powder was held on a conducting carbon-pad fixed on a brass sample holder. Specimens were sputter coated with a thin conductive Au layer of 10 to 20 nm thickness. All the analyses were normalised to dry substance and without the non-analysed elements (Li, Be, B

etc.). All the SEM/EDX combination quantifications of glass have about 5% instrument error because analysis are of non-perfect surfaces with inhomogenities and other small particles in the vicinity. Thus, the results are presented to only two significant places.

### 3. Results

Selected analytical data from the paired sites are presented in Table 2. Compared with the background sites, long-term fertilizer application has resulted in increased P, F, and acid-extractable Al, whereas the addition of lime has increased the pH. Because pH has increased, the increase in acid-extractable Al clearly cannot be attributed to a lowering of the pH.

**Table 2** Selected analytical data from the paired unfertilized and fertilized sites

Analysis	Site	Taupo sandy loam (Udivitrond)	Tirau silt loam (Hapludand)
Acid extractable P /mg kg <sup>-1</sup>	Unfertilized <sup>a</sup>	290	610
	Fertilized <sup>b</sup>	2600	2800
Total F /mg kg <sup>-1</sup>	Unfertilized	240	250
	Fertilized	690	570
Acid extractable Al /mg kg <sup>-1</sup>	Unfertilized	9700	19000
	Fertilized	8900	36000
pH	Unfertilized	5.3	5.3
	Fertilized	5.7	6.2
Total C (%)	Unfertilized	7.8	4.3
	Fertilized	10.6	10.8
Anaerobically mineralised N /mg kg <sup>-1</sup>	Unfertilized	95	80
	Fertilized	210	200
Hot water carbon /mg kg <sup>-1</sup>	Unfertilized	3150	3050
	Fertilized	6250	6350

<sup>a</sup>Pine forest (background)

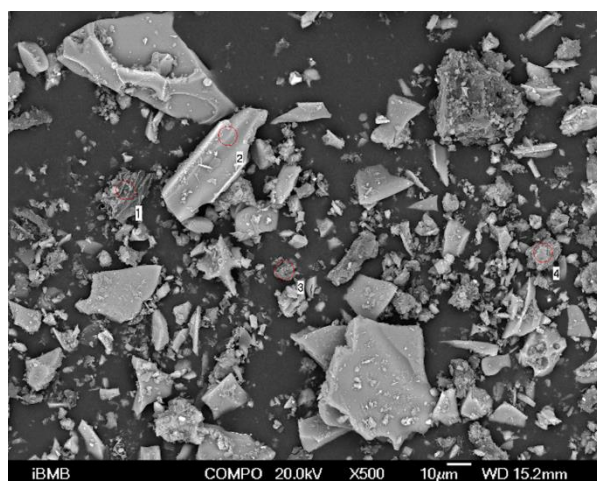
<sup>b</sup>Pasture

The older and longer-fertilized soils showed a decrease in the average size of the glass shards: the average grain size of the Taupo-soil shards was reduced after fertilization from 39 to 31  $\mu\text{m}$  in diameter, and that of the Tirau-soil shards was reduced after fertilization from 37 to 24  $\mu\text{m}$  (Table 3). Most shards were angular or very angular (i.e. grain edges were sharpest)

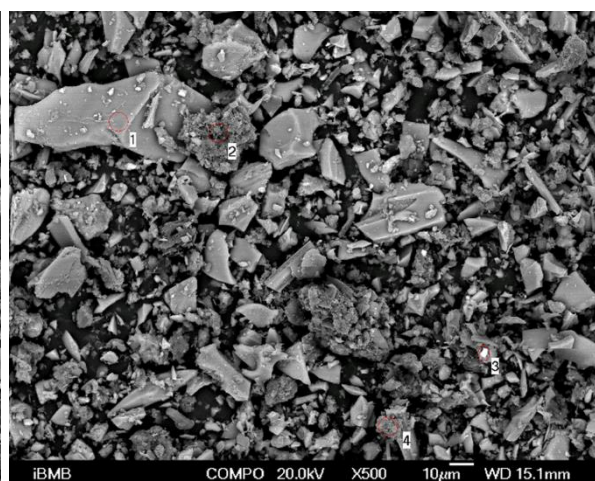
in the unfertilized Taupo soil, while those of the older Tirau soil were sub-angular or sub-rounded (Table 3), and pitting in shards was present for the fertilized Tirau soil (Figs. 1–2), consistent with phosphate fertilizer-induced accelerated dissolution imposed over natural weathering (cf. Hodder et al., 1990, 1991).

**Table 3** Comparison of glass-shard sizes for samples from fertilized and unfertilized soils, and roundness classes (range 0 to 6) of Powers (1953), and presence of neogenic silica polymorphs

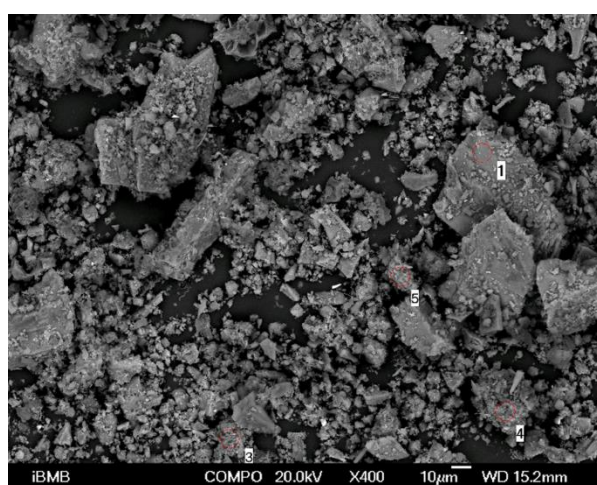
	<b>Taupo sandy loam (Udivitrond)</b>				<b>Tirau silt loam (Hapludand)</b>			
	Average µm	Median µm	Range µm	<i>n</i>	Average µm	Median µm	Range µm	<i>n</i>
Unfertilized	39	33	12-231	104	37	25	22-252	101
Fertilized	31	23	7-246	102	24	22	8-94	100
Roundness	Mainly classes 0 & 1 (very angular to angular) with class 1 predominant in fertilized soil				Mainly classes 2 & 3 (subangular to subrounded) with class 3, and pitting, predominant in fertilized soil			
Neogenic SiO <sub>2</sub> polymorph	Not present in either unfertilized or fertilized soils				Present in fertilized soil only			



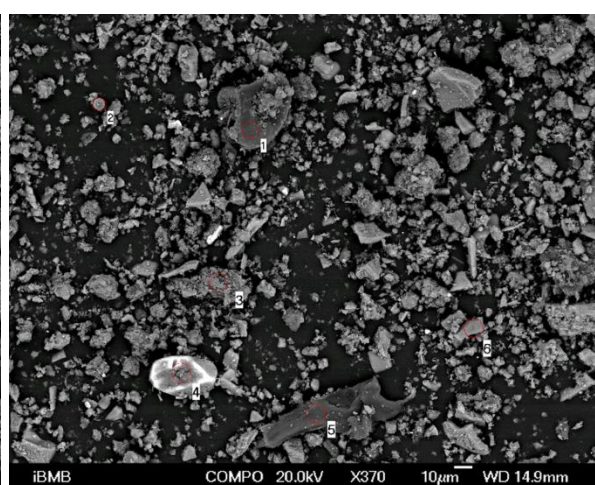
A. Taupo sandy loam, unfertilized



B. Taupo sandy loam, fertilized

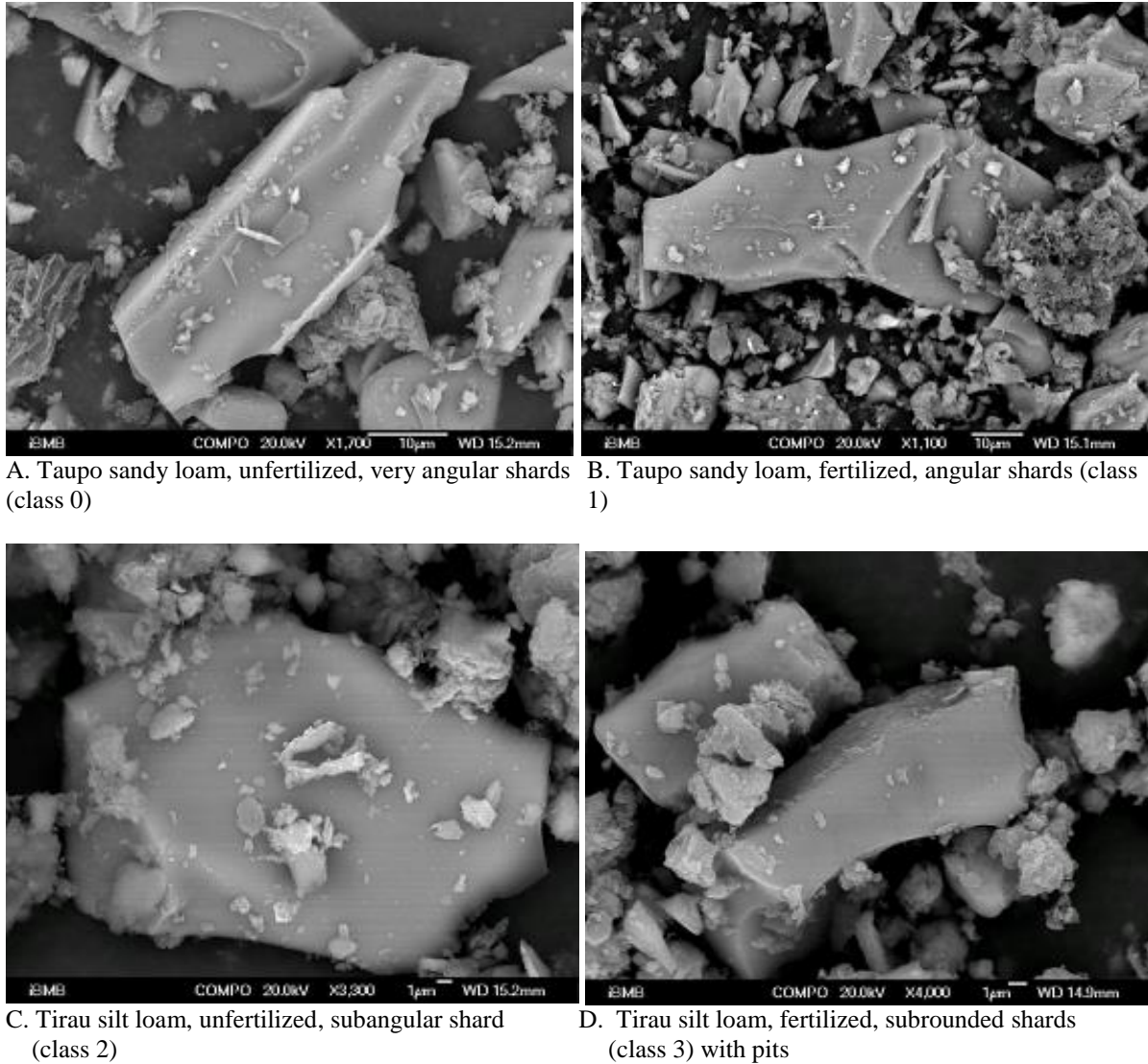


C. Tirau silt loam, unfertilized



D. Tirau silt loam, fertilized

**Fig. 1** Electron micrographs of glass shards from the four soils (<2 mm fractions). Also present in small amounts are crystals or crystal fragments (mineral grains including felsic and ferromagnesian minerals, and Fe-Ti oxides), and clay aggregates. The numbers represent microprobe analysis sites



**Fig. 2** Micrographs of representative glass shards from the four soils showing differences in roundness classes (Powers 1953).

Electron microprobe analyses ( $n = 22$ ) of major elements for the unfertilised and fertilised Taupo soils are consistent with those obtained previously on glass from Taupo and other rhyolitic tephra in New Zealand (e.g. Gehrels et al., 2006; Lowe et al., 2008), with normalized mean ( $\pm 1$  sd) data for the most abundant oxides as follows:  $\text{SiO}_2$   $72.5 \pm 1.4$  wt%;  $\text{Al}_2\text{O}_3$   $13.3 \pm 0.6$  wt%;  $\text{TiO}_2$   $0.3 \pm 0.1$  wt%;  $\text{FeO}$   $3.0 \pm 0.8$  wt% (total iron expressed as FeO);  $\text{MnO}$   $0.2 \pm 0.1$  wt%;  $\text{MgO}$   $0.6 \pm 0.1$  wt%;  $\text{CaO}$   $1.9 \pm 0.4$  wt%;  $\text{Na}_2\text{O}$   $3.7 \pm 0.8$  wt%; and  $\text{K}_2\text{O}$   $4.6 \pm 0.9$  wt%. No glass shards large enough for satisfactory microprobe analysis were found



in the fertilized Tirau soil. The analyses showed a peak where F would be expected, but it was related in size to Fe and was attributed to Fe interference.

Silica polymorphs ( $\text{SiO}_2$ ) were identified in the Tirau fertilized soil (Fig. 3), but not in samples from the other soils (Table 3).



**Fig. 3** Example of neogenic silica in the Tirau silt loam, fertilized soil

## 4. Discussion

### 4.1. *Enhanced dissolution of volcanic glass, induced by the addition of phosphate fertilizer*

The weathering of volcanic glass and the formation of comminuted residues and clay minerals have been previously reported by Bakker et al. (1996) in a micromorphological

study that included examination of both the Taupo and Tirau soils. They found pumiceous glass fragments decreased in amount and size towards the soil surface, and that these fragments were altered with some of the vesicles broken or opened and filled with non-crystalline isotropic, i.e. nanocrystalline, clay-sized material. Our study shows enhanced dissolution of volcanic glass, induced by the addition of phosphate fertilizer, is an additional process to that of natural chemical weathering (by hydrolysis) and clay-mineral synthesis. The effects of chemical weathering are seen in plant production of acids and chelating ligands to accelerate chemical alteration of soil minerals and compounds (Churchman and Lowe, 2012; Sparks, 2012). Alekseeva et al. (2011) reported soil acidification under a tea plantation accelerated not only the transformation of silicate minerals, but also changes in ferromagnetic minerals in the soil. Although acidification enhances the mobility of many metal cations, Taylor and Kim (2009) found the acid extractable fraction was enhanced only in some metals and not in Cr or Fe, suggesting an additional mechanism is occurring. F is known as an aggressive extractant for Al from within the soil matrix and enhances aluminosilicate dissolution rates (Elrashidi and Lindsay, 1987).

Dissolution rates of glass increase monotonically with increasing fluoride concentration because of the formation of Al-fluoride complexes, which decrease the activity of  $\text{Al}^{3+}$  (Wolff-Boenisch et al., 2004). In addition, Sigfusson et al. (2008) showed that the chemical weathering rates of Andisols were influenced by the external supply of anions, such as F, capable of complexing  $\text{Al}^{3+}$ . Consequently, it is not surprising that a similar process takes place around a phosphate fertilizer granule that supplies phosphoric acid and ligands such as  $\text{F}^-$ . The importance of F is emphasised. Acidity alone would dissolve acid-soluble compounds and would not explain the increase in acid-soluble Al seen by Taylor et al. (2012) and Taylor and Kim (2009). Also, the acidity around a phosphate fertilizer granule is temporary as  $\text{PO}_4^{3-}$  exchanges with  $\text{OH}^-$  on the soil matrix. Tuttle et al. (2009) reported that

neutralisation of the weathering solution from a shale-derived soil in streams and groundwater resulted in elements being adsorbed and precipitated.

The formation of Al-fluoride complexes and subsequent decrease in  $\text{Al}^{3+}$  activity around a phosphate fertilizer granule pushes the equilibrium in favour of more dealumination and probably more desilication. As loading of the pore water increases and pH increases (with  $\text{PO}_4^{3-}$  sorption), the complexes become increasingly insoluble. Thus, increased amounts of Si and Al are available for the neogenesis of (acid soluble) secondary minerals, or Al could occupy exchange sites on mineral surfaces (Pawluk and Dudas, 1978), or both. Al remains in the surface horizon but is now readily acid soluble.

#### *4.2. Reactions with soil organic matter*

As with reactions with F, organic matter can form complexes with Al and may have a role in regulating Al release rates in natural weathering and dissolution of glass and minerals in tephras (Dahlgren and Walker, 1993; Nanzyo, 2002; McDaniel et al., 2012) – for example, speciating  $\text{Al}^{3+}$  with oxalate increased dissolution rates in basaltic glass (Sigfusson et al., 2008). In our study, significant amounts of organic matter, as measured as total C, were present in the soils at both the fertilized and unfertilized sites but considerably more was present at the fertilized sites (Table 2). Also, leaching of major base cations by dissolved organic matter has been reported by Egli et al. (2008) and Antweiler and Drever (1983), and Mg and Na depletion at the fertilized sites compared with the unfertilized sites was observed by Taylor and Kim (2009). Calcium and K were not depleted because of lime and fertilizer additions.

It is likely both  $\text{F}^-$  and organic matter form complexes with Al, influencing chemical weathering rates (Ugolini et al., 1988). Organic and fluoride complexes were the dominant forms of Al in all soil solutions and through-flow from hardwood and conifer sites in the



Adirondack Mountains, New York (David and Driscoll, 1984), while Al-fluoride complexes were the predominant fraction of labile Al in Adirondack surface waters (Driscoll et al., 1987), even though these sites are unlikely to receive F-containing fertilizers. The addition of F in fertilizer is likely to increase the proportion of Al as fluoride complexes.

#### 4.3. *Formation of clay minerals*

A consequence of enhanced weathering may be enhanced formation of clay minerals through the redistribution of Al. This is because the dissolution of volcanic glass plays an important role in formation and transformation processes and as a cation supplier (Kawano et al., 1997). This process redistributes constituents originally bound within the glass, such as base cations, trace elements, and Al, potentially increasing their mobility and bioavailability. The redistribution of Al may aid the formation of clay minerals, such as allophane or halloysite. Where silica is rapidly removed by leaching, allophane formation is favoured; where silica activity in soil solution is high ( $>10 \text{ mg L}^{-1}$ ), halloysite forms in preference to allophane (Parfitt et al., 1983, 1984; Singleton et al., 1989; Parfitt, 1990, 2009; Churchman and Lowe, 2012).

#### 4.4. *Possible biochemical weathering of volcanic glass*

Alternatively, enhanced biochemical weathering could be caused by the increased activity of microorganisms as indicated by the increased anaerobically mineralised N and hot-water carbon analyses (Table 2). It might be that microbial activity is strongly increased by the addition of P-fertilizer and, as a consequence, biochemical weathering of the glass is increased. Although microbially-derived etch pits and biogenic grooves reported in Staudigel et al. (1995) and Thorseth et al. (1995) were not seen in our samples, that some of dissolution was due to microbes cannot be ruled out (cf. Cockell et al., 2009). If microorganisms assist in

reducing angularity, then the hypothesis still holds in that the addition of fertilizers, arguably, could enhance microbial activity.

Ploughing of farmland can also enhance microbial activity by making labile soil organic matter more available (e.g. see Goh, 2004). In rhyolitic glass, there are also potential nutrients, such as K, Mg, and Ca, which can, if released, increase microbial activity. However, biological activity, as measured by anaerobically mineralized N in Taylor and Kim (2009), followed soil organic C concentration ( $r = 0.545$ ) rather than being a consequence of fertilizer application or not.

#### 4.5. *Silica polymorphs*

Another consideration is the presence of neogenetic silica polymorphs in the topsoil of the fertilized Tirau soil alone. Annual rainfall at all sites is relatively high (average 1600–1650 mm) and leaching should result in desilication of the topsoil, with silica reprecipitated (or combined with Al) deeper in the soil environment according to the silica-leaching model established for soils developed on tephras described above (e.g. Lowe, 1986, 1995; Singleton et al., 1989). An explanation for the contrasting observation – the precipitation of silica polymorphs despite high rainfall – may relate to the seasonality of fertilizer application. Most phosphate fertilizer is applied in the Waikato region annually in late spring when soil through-flow is diminishing. Although rainfall averages about 100 mm/month over spring-summer, drainage through to the subsoil does not occur except in extreme weather events, i.e. soil solution movement is minor or static. Thus, the soil remains moist for a period long enough for the dissolution of volcanic glass (and possibly other alumina-silicates), the formation of Al-humus complexes, and the precipitation of silica in the form of silica polymorphs. In addition, the supersaturation of silica by surface evaporation and plant transpiration in the A horizon, and thus potential for its precipitation, would

potentially be at a maximum during late summer or early autumn when the soil generally is driest (Lowe, 1986; Drees et al., 1989).

An alternative mechanism for the formation of the silica polymorphs could be through the uptake and biocycling of Si by plants (Lowe, 1986; Henriot et al., 2008; Churchman and Lowe, 2012; Clymans et al., 2015). Farmer et al. (2005) postulated that plant phytoliths provide a sink, hence short-term nutrient uplift, for Si from soil solutions during the growing season that is released back to solutions during winter and spring. This mechanism could be important for increased cultivation safety for growing Si-accumulating plants (e.g. rice, sugar cane, and sorghum).

#### 4.6. *Elemental fluxes*

The hydration and hydrolysis of glass should result in fluxes of Al, Si, base cations, and traces of other elements from the glass into interstitial pore waters (Hodder et al., 1991, 1996). Proton exchange and the release of base cations should result in acid buffering and contribute to the very rapid precipitation of secondary minerals from such solutions as well as replacement of glass shards by new secondary minerals (Hodder et al., 1990; Dahlgren et al. 2004; Churchman and Lowe, 2012). Consistent with such fluxes, acid-recoverable concentrations of several trace elements that were normally retained inside residual phases of aluminosilicates were shown by Taylor and Kim (2009) to be also significantly higher in fertilized than in nonfertilized soils. These include (with enrichment-to-background factors) Li (2.5), La (2.1), Mn (1.5), and Ag, Bi, Mo, Sn, and Tl (1.4). Also, this process may have contributed one-quarter of the observed increase in acid-recoverable U in Taylor and Kim (2009).

Another consequence of enhanced weathering may be enhanced leaching of the more mobile elements and concentration of relatively immobile elements, such as Ti, Cr, and V.

Generally, larger cations, such as Al, would be expected to remain fixed within the soil profile, although these can be redistributed to lower horizons, while smaller cations, such as Ca, Na, and Sr, may be preferentially leached (Churchman and Lowe, 2012). Similarly, lighter isotopes may be preferentially leached and the chemical signature of the soil may be changed. As chemical and isotopic signatures are ultimately transferred to the sedimentary record, changes in soil elemental and isotopic composition may affect the element geochemistry and mineralogy of sediments.

#### *4.7. Implications for soil and land management*

In general, Andisols are noted for their distinctive physical properties such as high water-holding capacity, free drainage, low bulk density and high porosity and hence good aeration, stable aggregation, friability, and good tilth (e.g. Ugolini and Dahlgren, 2002; McDaniel et al., 2012; Yuan and Wada, 2012). These features are manifest in Andisols in New Zealand, including the Tirau and Taupo soils (Parfitt et al., 1981; Allbrook, 1985; Neall, 2006; Lowe and Palmer, 2005; Hewitt, 2010). Consequently, they are usually excellent media for seedling emergence and root growth and proliferation. It should be emphasized, however, that these properties may be altered through management (Candan and Broquen, 2009; Neall, 2006; McDaniel et al., 2012). From our study, several implications for soil management and health emerge as a consequence of the accelerated weathering. For example, some trace elements, such as Co, are already at levels below optimum for animal health in these soils (e.g. Cornforth, 1998; Lowe et al., 2014) and increased leaching of these could reduce the efficiency of corrective fertilizer additions. Increased direct dosing of animals with essential trace elements may be required in the future.

Other implications for soil management include changes in soil permeability and water storage capacity. Loss of mass may lead to increased porosity of the soil and enhanced

permeability, if it is undisturbed by further cultivation. Tuttle and Breit (2009) reported enhanced permeability because of a 14% loss of the original mass in parent material for a shale-derived soil. Conversely, precipitation of clays within pore spaces may reduce soil permeability but increase water storage. Changes in porosity are also likely to cause changes in surface area and capacity to store cations and anions (Notario et al., 1995).

At a global scale, there may be a significant feedback mechanism between climate and weathering processes. Enhanced weathering could result in enhanced removal of CO<sub>2</sub> from the atmosphere, as soil carbon derived ultimately from photosynthesis is converted into dissolved HCO<sub>3</sub><sup>-</sup> (Berner, 1997). Also, weathering releases divalent cations to the ocean via groundwater and riverine transport. Once there, divalent cations promoting the drawdown of CO<sub>2</sub> from the atmosphere by the precipitation and subsequent burial of carbonate minerals (Gislason et al., 2009). If the enhancement of weathering is significant, it may provide some mitigation for climate change.

It is often taken for granted that soil processes over relatively short time spans, i.e. decades, will continue to behave as they have in the past. However, the impact of a “new” development may change processes and hence soil properties and soil functioning, potentially leading to a threat to food security. Given that this enhanced weathering has been identified in some of the most extensive farming areas of New Zealand, there is some urgency in ascertaining its effects on soil properties in greater depth.

## **5. Conclusions**

The hypothesis tested in this study is that the addition of F-containing phosphate fertilizers enhances the dissolution of volcanic glass, as shown by a marked decrease in shard size and

angularity, and an increase in dissolution pitting on shard surfaces, through production of phosphoric acid and F<sup>-</sup>-chelating ligands increasing amounts of Si and Al available for neogenesis. Al and Si may subsequently coprecipitate as secondary minerals, such as allophane. However, neogenic silica may form where Al activity is low through the formation of Al-fluoride or Al-humus complexes, coupled possibly with seasonal climatic effects.

The occurrence of neogenic silica in topsoil of the fertilized Tirau soil, when the annual rainfall indicated leaching should result in desilication of the topsoil and the reprecipitation of silica deeper in the soil, could be explained by the seasonality of fertilizer application and the spring-summer climate, where the soil remains moist for a period long enough in spring for the dissolution of volcanic glass (and possibly other alumina-silicates), the formation of Al-humus complexes, and then the precipitation of silica in late summer or early autumn when conditions are driest.

As this enhanced weathering has been identified in some of the major farming areas of New Zealand, there is a growing need to ascertain further its effects on soil properties and impacts on soil and land management.

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