

Secondary mineral formation in the White River tephra in grassland and forest soils in central Yukon Territory

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¹College of Science and Management; ²Canada Research Chair-Soil and Environmental Sciences, University of Northern British Columbia, 3333 University Way, Prince George, British Columbia, Canada V2N 4Z9; and ³Agriculture and Agri-Food Canada, Summerland, British Columbia, Canada V0H 1Z0. Received 6 January 2005, accepted 15 July 2005.

Strickland, A. J., Arocena, J. M., Sanborn, P. and Smith, C. A. S. 2005. **Secondary mineral formation in the White River tephra in grassland and forest soils in central Yukon Territory.** *Can. J. Soil Sci.* **85**: 637–648. Selected surface horizons of grassland and forest soils formed under a cold, semi-arid climate were investigated to evaluate the formation of secondary minerals within the White River tephra, a Late Holocene rhyolitic tephra (~1150¹⁴ C yr BP) veneer that overlies the soil landscapes of central Yukon. Concentrations of extractable Fe (< 0.48%), Al (< 0.26%) and Si (< 0.082%) concentrations in surface tephra-containing horizons of grassland and forest pedons are low. The high amount of exchangeable calcium in grassland soils is likely due to cycling by vegetation and perhaps, aeolian inputs of Ca and Mg carbonates. Al is incorporated into Al-humus complexes in forest pedons and allophane in grassland pedons. Allophane content is low (< 0.56%) in all soils as is ferrihydrite (< 0.34%). Mineral composition of the sand fraction from tephra horizons is dominated by volcanic glass, plagioclase feldspars, amphiboles, epidote, pyroxenes and very limited quantities of quartz and primary Fe oxides. Chlorite and an expanding phyllosilicate were also detected and are assumed to be of detrital origin. Clay mineralogy is dominated by volcanic glass, quartz, feldspars and minimal quantities of kaolinite and dehydrated halloysite in surficial horizons. Kaolinite is assumed to be of detrital origin while dehydrated halloysite is a product of a low leaching and dry environment where limited resilication occurs. Scanning electron microscopy (SEM) investigation indicates the presence of opaline silica in surface horizons from forest pedons which has likely formed due to freezing of the soil solution in combination with dehydration and resilication. Overall, the soil horizons formed within the veneer of White River tephra have experienced minimal weathering and very little silicate clay mineral development.

Key words: Tephra, glass, Yukon, minerals (secondary), weathering

Strickland, A. J., Arocena, J. M., Sanborn, P. et Smith, C. A. S. 2005. **Formation de minéraux secondaires dans les tephra de la rivière White sur les brunizems et les sols forestiers du centre du Yukon.** *Can. J. Soil Sci.* **85**: 637–648. Les auteurs ont examiné certains horizons de surface des brunizems et des sols forestiers formés en climat froid semi-aride afin d'établir la présence de minéraux secondaires dans les tephra de la rivière White, placage de tephra rhyolitique datant de la fin de l'Holocène (~1 150 ans BP) qui couvre le sol dans la région centrale du Yukon. Les résultats indiquent que la concentration de Fe (< 0,48 %), d'Al (< 0,26 %) et de Si (< 0,082 %) extractibles dans l'horizon de surface du tephra des pédons de prairie et de forêt est faible par nature. La forte concentration de calcium échangeable dans les brunizems vient sans doute du cycle de la végétation et éventuellement d'un apport éolien de Ca- et de Mg- des carbonates. Dans les pédons forestiers, l'Al est intégré aux complexes Al de l'humus alors que dans les pédons des prairies, on le retrouve dans l'allophane. Les sols renferment peu d'allophane (< 0,56 %) et de ferrihydrite (< 0,34 %). Dans la fraction sableuse des tephra, les minéraux sont dominés par du verre volcanique, du feldspath plagioclase, de l'amphibole, de l'épidote, des pyroxènes et une très petite quantité de quartz et d'oxydes ferreux primaires. Les auteurs ont aussi découvert du chlorite et un phyllosilicate d'expansion qu'on suppose avoir une origine détritique. La minéralogie de l'argile révèle surtout du verre volcanique, du quartz, des feldspaths et une petite quantité de kaolinite ainsi que d'halloysite déshydratée dans les horizons de surface. On pense que la kaolinite a une origine détritique, mais l'halloysite déshydratée pourrait venir d'une lente lixiviation et de l'aridité d'un milieu où la resilication est limitée. Les examens au MEB révèlent la présence de silice opaline dans les horizons de surface des pédons forestiers. On la doit vraisemblablement à la congélation de la solution de sol parallèlement à sa déshydratation et à la resilication. Dans l'ensemble, les horizons formés dans le placage de tephra de la rivière White ont été très peu altérés, ce qui a restreint la formation des minéraux de l'argile à silicate.

Mots clés: Tephra, verre, Yukon, minéraux (secondaires), altération

Tephra is a "collective term for all clastic volcanic materials that are ejected from a vent during an eruption" (Soil Science Society of America 1997); it is non-sorted and ranges in size from fine dust to massive blocks and often consists largely of volcanic glass. Volcanic glass exhibits little resistance to chemical weathering compared with crystalline silicate min-

erals (Smith et al. 1999). The susceptibility of volcanic glass to breakdown imparts unique geochemical and physical properties to the clay mineral assemblage of tephra-derived soils (Shoji et al. 1993). The rate of weathering leads to high concentrations of Al, Fe and Si in soil solutions (Dubroeuq et al.

Abbreviations: CEC, cation exchange capacity; EG, ethylene glycol; Gly, glycerol; RH, relative humidity; SEM, scanning electron microscopy

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1998); these solutions are over-saturated and favor the formation of metastable, poorly ordered solid phases dominated by allophane, ferrihydrite, and opaline silica (Takahashi et al. 1993; Dahlgren et al. 1993).

The formation of allophane in the soil environment is favored under humid, temperate climatic conditions (Wada 1989) or in an environment with udic moisture regimes, good drainage and a soil solution $\text{pH}(\text{H}_2\text{O}) > 5.0$ (Parfitt and Kimble 1989). Halloysite is thought to replace allophane as the dominant clay fraction mineral in environments with low rainfall ($<1350 \text{ mm yr}^{-1}$), minimal ($<250 \text{ mm yr}^{-1}$) leaching and abundant mobile Al (Parfitt et al. 1984; Nizeyimana et al. 1997). At $\text{pH}(\text{H}_2\text{O}) < 5.0$, metal-humus complexes, ferrihydrite and opaline silica are considered to be the main colloidal constituents (Shoji et al. 1993). As the soil solution becomes less saturated with respect to the poorly ordered solid phases, Ostwald ripening (dehydration with subsequent increase in crystallinity) may lead to the formation of more crystalline phyllosilicates such as smectite, gibbsite and kaolinite (Chadwick and Chorover 2001).

The presence of other weathering products in tephra such as 2:1 or hydroxy interlayered 2:1 silicates, kaolinite and gibbsite (Ugolini and Dahlgren 1991; Takahashi et al. 1993; Ndayiragije and Delvaux 2003) is controversial (Dahlgren et al. 1993). Tephra typically contains few precursor minerals such as chlorite and mica, which can weather directly to 2:1 and 1:1 phyllosilicate minerals (Shoji et al. 1993). Parfitt and Saigusa (1985) determined that the presence of 2:1 phyllosilicates and their intergrades in tephra-derived soils is a result of the alteration of volcanic glass under strongly acidic conditions. However, alternative hypotheses have been proposed to account for their presence. Several scientists (e.g., Inoue and Naruse 1990; Ugolini et al. 1991; Dahlgren et al. 1997) attributed the presence of smectite and trioctahedral vermiculite to a detrital origin. Another theory on the origin of 2:1 layer silicates in tephra-derived soils attributes their presence to alteration of mafic minerals such as pyroxenes and amphiboles in the tephra (Mizota 1976). Tephra-derived soils may also contain aeolian-transported materials such as quartz, feldspar, kaolinite and mica (Dahlgren et al. 1993; Shoji et al. 1993).

While many studies have examined clay mineral formation in tephra-derived soils (Wada et al. 1987; Ping et al. 1988; Ugolini et al. 1991; Dahlgren et al. 1997; Nizeyimana et al. 1997; Malucelli et al. 1999), few have examined the transformation of tephra in a cold and dry continental climate, especially in soils lacking present-day permafrost. A previous study in the Yukon Territory (Smith et al. 1999) examined the weathering and transformation of the White River tephra in Cryosolic soils under mixed spruce forest. The objective of this paper is to compare the transformation of the White River tephra in soils under grassland and forest vegetation in a permafrost-free environment in the Yukon Territory.

MATERIALS AND METHODS

Study Area and Sampling Methods

The study area is located along the Klondike Highway between Whitehorse and Carmacks in the Yukon Territory,

Canada (Fig. 1). The White River tephra is the most likely origin of the tephra considered in this study based on the distribution pattern documented by Lerbekmo and Campbell (1969), Richter et al. (1995), Clague et al. (1995) and Robinson (2001). The White River tephra is distributed over an area of $\sim 540\,000 \text{ km}^2$ with a plume volume of 27 km^3 (Robinson 2001). There are two separate lobes of volcanic ejecta (Lerbekmo and Campbell 1969) consisting of a northern deposit (1900–1500 ^{14}C yr BP) along the Alaska/Yukon border and the eastern deposit (1147 ^{14}C yr BP) (Clague et al. 1995). The tephra deposits within our study area in central Yukon range from a few centimetres (2–3) on colluvial slopes to $\sim 40 \text{ cm}$ thick at lower elevations and in valley bottoms. The tephra deposit decreases in thickness eastward from its source, Mount Churchill (4766 m), Alaska (Richter et al. 1995), across the southern and central Yukon, extending into the western District of Mackenzie in the Northwest Territory (Clague et al. 1995). The eastern lobe tephra (within the study area) is classified as rhyolitic and the proportion of glass increases with distance from the source (Lerbekmo and Campbell 1969).

The climate of the study area is estimated (Wahl et al. 1987) to be transitional between Whitehorse and Pelly Ranch weather stations (Table 1), with a mean annual air temperature of $\sim -2.5^\circ\text{C}$ and mean annual precipitation of $\sim 290 \text{ mm}$ (Environment Canada 2003). The soil temperature regime is cold and permafrost is discontinuous, while the soil moisture regime is semi-arid to sub-arid moist unsaturated (Soil Classification Working Group 1998; Froese et al. 2001). The climate is dry enough that grasslands form on warm aspects and are particularly well developed on steep, south-facing slopes. Upland areas support mixed forests. Poorly drained valley bottom positions and some north-facing aspects are underlain by near-surface ($<2 \text{ m}$ depth) permafrost and support open stands of black spruce and Sphagnum moss. For a more complete description of the environmental conditions of the central Yukon readers are referred to Smith et al. (2004).

Vegetation of the grassland sites is composed of *Penstemon gormanii* (Greene), *Artemisia frigida* (Willd.), *Plantago canescens* (M.F. Adams), *Calamagrostis purpurascens* (R. Br.), *Poa glauca* (Vahl) and a cryptogamic crust consisting of lichen, cyanobacteria, algae, mosses and fungi (Belnap et al. 2001). Forest sites are dominated by *Picea glauca* (Moench) Voss, *Populus tremuloides* (Michx.), and *Shepherdia canadensis* (L.) Nutt.

The uppermost horizons formed within a surface veneer of tephra from three grassland and three forest pedons (Table 2) were sampled and described according to the Soil Classification Working Group (1998). Pedons 02-02, 02-03, 02-04, and 02-28 were collected in July 2002 while pedons 03-01 and 03-02 were collected in August 2003. Grassland pedons (02-02, 03-01 and 03-02) generally had a southwest aspect and $\sim 50\%$ slope with a Ah horizon $<10 \text{ cm}$ thick overlying a horizon of apparently unweathered tephra (C horizon) typically 5-cm thick. All grassland pedons are classified as Orthic Melanic Brunisols based on horizon morphology within the colluvium beneath the tephra veneer where a IIAhb horizon, a IIBm horizon and a IICk occur.

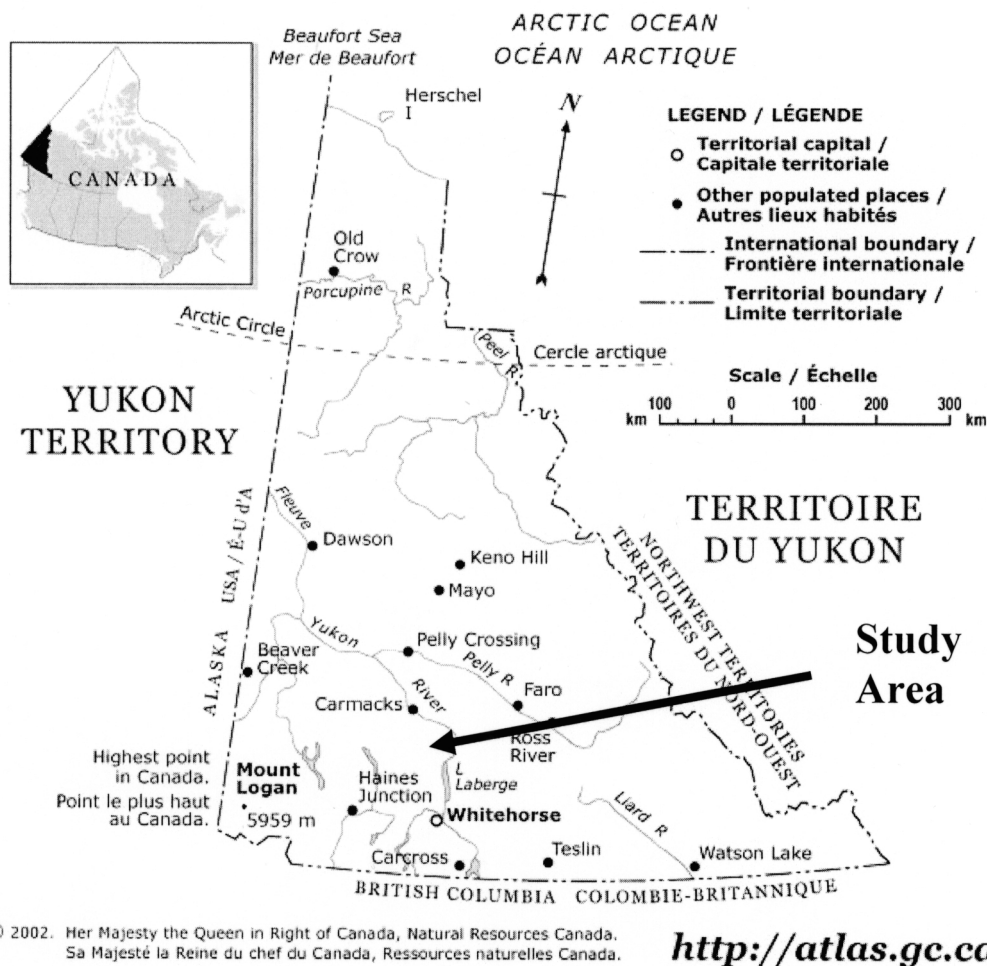


Fig. 1. Location of the study area along the Klondike Highway between Whitehorse and Carmacks, Yukon Territory, Canada (Government of Canada 2002).

Table 1. Temperature and precipitation recorded at Whitehorse and Pelly Ranch, Yukon Territory. All values from 1971 to 2000 normals (Environment Canada 2003)

Site location	Elevation (m)	Latitude	Longitude	Mean air temperature °C			Mean precipitation (mm)		
				Annual	January	July	Annual total	Annual rainfall	Annual snowfall
Whitehorse, YT	706	60°42'N	135°4'W	-0.7	-17.7	14.1	267.4	163.1	145.0
Pelly Ranch, YT	454	62°49'N	137°22'W	-3.9	-27.5	15.5	310.3	197.5	112.8

Table 2. Location, vegetation type and elevation of grassland and forest pedons, Yukon Territory

Pedon no.#	Vegetation type	Soil classification	Elevation (m)	Latitude	Longitude
02-02	Grassland	Orthic Melanic Brunisol	650	61°49.079'N	136°03.462'W
03-01	Grassland	Orthic Melanic Brunisol	710	61°52.339'N	136°06.323'W
03-02	Grassland	Orthic Melanic Brunisol	550	62°21.249'N	136°25.100'W
02-03	Forest	Orthic Dystric Brunisol	620	61°49.079'N	136°03.462'W
02-04	Forest	Orthic Dystric Brunisol	560	62°28.316'N	136°33.107'W
02-28	Forest	Orthic Dystric Brunisol	490	62°28.316'N	136°42.284'W

The forest pedons (02-03, 02-04 and 02-28) had a south westerly aspect, average surface slopes of 10% and typically forest litter layers over a Bm horizon and an unweathered tephra (C) horizon. Tephra horizons totaled 20 to 30 cm

thick. Forest pedons are classified as belonging to the Orthic Dystric Brunisol subgroup, again based on the morphology of the underlying buried soil typically comprised of a Hb, IIBm and IIBC horizons. Permafrost was not observed at

any of the study sites. Horizons were not noted to have mixed with underlying buried soils. The data that will be presented in this paper are limited to the surface tephra-derived horizons.

Geochemical Analyses

Soil samples were air dried and passed through a 2-mm sieve prior to analysis and results presented on an oven-dried (105°C) basis. Particle size distribution was determined by the pipette method (Kalra and Maynard 1991) with prior sonic dispersion (6 min. at 400 W) treatment.

Soil pH in water (1:2) was measured according to the procedure outlined by Kalra and Maynard (1991) using an Orion™ pH meter. The cation exchange capacity (CEC) and the exchangeable cations were determined using 1 M unbuffered NH_4Cl ; CEC is estimated by the amount of exchangeable NH_4^+ replaced by Na^+ and then determined by titration following distillation (Kalra and Maynard 1991). The total amounts of exchangeable Ca, Mg, Na and K were determined from the NH_4Cl extract using Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES).

Other geochemical analyses were determined by ICP-AES following methods according to Kalra and Maynard (1991). Al (Al_p) and Fe (Fe_p) associated with metal-humus complexes were extracted using 0.1 M sodium pyrophosphate. Al (Al_o) associated with amorphous or allophanic constituents and Al-humus complexes, Fe (Fe_o) associated with ferrihydrite and Si (Si_o) associated with allophanic constituents (Parfitt and Saigusa 1985) were extracted with 0.2 M acid ammonium oxalate solution adjusted to pH 3.0 and shaken in the dark for 4 h. Fe (Fe_d) associated with crystalline oxides and fractions from metal-humus complexes and poorly ordered constituents (Shoji et al. 1993) were extracted using dithionite-citrate solution, which was shaken overnight.

Total carbon and nitrogen (pedons 03-01 and 03-02) were determined by LECO C and N analyzer and organic carbon was estimated by the difference between total C and inorganic carbon determined by the CaCO_3 equivalent method (Kalra and Maynard 1991). These analyses were performed by the British Columbia Ministry of Forests Research Branch Laboratory (Victoria, British Columbia). Additional analyses of total carbon, organic carbon and total nitrogen (pedons 02-02, 02-03, 02-04 and 02-28) were performed by the Agriculture Canada Laboratory (Swift Current, Saskatchewan) following methods outlined in Sheldrick (1984).

Mineral Analysis

Mineral composition of the clay (<0.002 mm) and sand (0.05–2.0 mm) fractions was determined using X-ray diffraction analysis. Clay fraction samples were prepared according to Theisen and Harward (1962) for K- and Ca-saturated samples. The Ca-saturated clay samples were scanned at 54% relative humidity (RH) and solvated with ethylene glycol (EG) and glycerol (Gly). The K-saturated clay samples were scanned at 0% and 54% RH (ambient temperature) and after heating at 300°C and 550°C. Sand fractions from grassland and forest tephra horizons were ground to ~ 0.05 mm diameter to enhance random orientation and facilitate mineral identification. The sand fractions

of the forest pedons were subjected to an overnight 100°C treatment and scanned at 0% RH to determine the presence of expanding 2:1 phyllosilicates. Clay fraction and sand fraction minerals were identified according to their characteristic X-ray reflections using Bruker EVA™ diffraction software and standard references (Dixon and Weed 1989).

Allophane content was estimated from the ratio of ($\text{Al}_o - \text{Al}_p$)/ Si_o and the associated Si_o (%) content (Parfitt 1990). Ferrihydrite was estimated from the Fe_o (%) content (Childs 1985). The proportion of Fe and Al in poorly ordered constituents or metal-humus complexes was estimated from Al_p/Al_o and Fe_p/Fe_o ratios (Shoji et al. 1988a,b), the proportion of Fe in crystalline or poorly ordered oxides and oxyhydroxides was estimated from Fe_o/Fe_d (Shoji et al. 1988a,b) and the ratio of Al:Si in poorly ordered constituents was estimated using ($\text{Al}_o - \text{Al}_p$)/ Si_o (Parfitt 1990).

Microscopy

Scanning electron microscopy was performed on the sand fraction (0.05–2.0 mm) using a Philips XLS-30 scanning electron microscope to identify the presence of volcanic glass and to determine the morphology of weathered glass shards. All samples were sputter coated with gold prior to SEM observation. Semi-quantitative ($\pm 10\%$) elemental analysis of samples was performed using EDAX DX-4 microanalysis; total elemental analyses were normalized to 100%. Samples were not washed prior to sputter coating and SEM investigation.

Statistical Analysis

The physical and geochemical data were analyzed using the Student's *t*-test statistic for significant differences between means using Microsoft Excel for Windows XP.

RESULTS

Physical and Geochemical Properties

The silt contents of the tephra-derived soil horizons are significantly lower under grassland than forest soils. Clay contents increase slightly with depth in the forest pedons, which typically contain higher clay contents than the grassland soils. The mean clay contents of tephra (C horizons) under forest (16%) cover are greater than for grassland tephra C horizons (11%); a similar pattern was observed for surficial Ah or Bm horizons (Table 3).

The mean soil pH(H_2O) for tephra and surficial horizons is significantly greater ($p < 0.05$) in grassland (pH 6.3) than forest (pH 5.1 and pH 4.6) pedons (Table 3). Organic carbon concentration is <3.5% for all horizons, and is higher in grassland than forest pedons (Table 3). Total nitrogen concentrations are greater in all grassland horizons.

Exchangeable Ca and Mg concentrations are significantly greater in grassland pedons than those under forest vegetation for tephra (13 vs. 2.1 cmol (+) kg^{-1}) and surficial horizons (22 vs. 5.2 cmol (+) kg^{-1}). Exchangeable K decreases throughout each profile and is significantly higher in grassland than forest surficial horizons (1.0 vs. 0.49 cmol (+) kg^{-1}), while exchangeable Na increases with depth under grassland vegetation and displays a slight decrease with

Table 3. Selected physical and chemical properties of tephra horizons (C) and surficial (Ah and Bm) horizons for grassland and forest pedons

Selected physical and geochemical property	Grassland pedons tephra horizon (C)	Forest pedons tephra horizon (C)	Grassland pedons surficial horizon (Ah)	Forest pedons surficial horizon (Bm)
% sand	48 (±9.0)	33 (±2.2)	58 (±3.0)	42 (±7.7)
% clay	11 (±5.0)	16 (±0.99)	9.0 (±3.1)	13 (±4.0)
% silt	41* (±4.2)	51* (±1.9)	34* (±2.1)	45* (±3.8)
Texture	Sandy loam	Silt loam	Sandy loam	Silt loam
Munsell color	10YR 6/2	10YR 8/1	10YR 4/2	10YR 6/3
% total C	2.2 (±0.30)	0.99 (±0.85)	3.4 (±0.46)	2.9 (±0.43)
% organic C	2.1 (±0.30)	0.92 (±0.77)	3.3 (±0.42)	2.6 (±0.42)
% total N	0.18* (±0.020)	0.044* (±0.032)	0.29 (±0.045)	0.13 (±0.015)
pH (H ₂ O)	6.3* (±0.29)	5.1* (±0.23)	6.3* (±0.25)	4.6* (±0.086)
CEC cmol (+) kg ⁻¹	14 (±1.9)	7.6 (±2.6)	17 (±2.9)	14 (±2.4)
Exchangeable Cations cmol (+) kg ⁻¹				
Na	0.16 (±0.044)	0.095 (±0.0091)	0.072 (±0.018)	0.10 (±0.012)
Ca	13* (±1.2)	2.1* (±0.86)	22* (±0.76)	5.2* (±1.2)
Mg	1.7* (±0.27)	0.21* (±0.091)	2.8* (±0.31)	0.58* (±0.16)
K	0.44 (±0.19)	0.40 (±0.14)	1.0* (±0.17)	0.49* (±0.097)

* Denotes significantly different means ($P < 0.05$) among similar horizons, (±) indicates standard error of the mean ($n = 3$).

depth under forest vegetation (Table 3). The concentrations of exchangeable Ca and Mg in grassland pedons are significantly higher than the forested pedons, both in tephra and surficial horizons (Table 3).

Extractable Al_p , Fe_d , Fe_o , and Fe_p decrease with depth through each grassland and forest pedon with all concentrations consistently low (Table 4). Mean Al_o values are greater for forest surficial horizons (0.26%) than grassland horizons (0.13%) while grassland tephra contents (0.18%) are greater than those for the forest pedons (0.11%). Al_p values exhibit a large but not statistically significant difference in the mean values between surficial grassland (0.039%) and forest (0.15%) horizons. Si_o values are very low but are higher in grassland pedons (Table 4).

The mean Fe_o/Fe_d ratios are greater for surficial (0.49) and tephra (1.5) horizons of the forest pedons than the grassland pedons (<0.4). Fe_p/Fe_o ratios are significantly lower in grassland (0.27) than forest pedons (0.65). The Al:Si atomic ratio (of poorly ordered weathering products) estimated from $(Al_o - Al_p)/Si_o$ ratio shows that for tephra horizons, grassland and forest pedons have ratios 1.5 and 2.0, respectively; ratios for surficial horizons are 1.6 and 3.5 for grassland and forest pedons, respectively (Table 4).

Soil Mineralogy and Microscopy

X-ray diffraction patterns of the sand fraction of tephra horizons from grassland and forest pedons (Fig. 2) show the presence of the following minerals, in decreasing order of abundance based on intensities of the dominant reflections (nm): plagioclase feldspars (0.321, 0.404) > amphiboles (0.313, 0.83) > epidote (0.29) > pyroxenes (0.332, 0.318) >> quartz (0.426, 0.33) = magnetite = ilmenite (0.148, 0.173). The sand fractions of the grassland pedons also contain chlorite as evidenced by the 001 reflection at 1.45 nm with an associated weak 002 peak at 0.72 nm and a strong 004 reflection at 0.363 nm (Fig. 2). The forest pedons contain an expanding 2:1 phyllosilicate as evidenced by the collapse of the 1.41 nm peak to 1.0 nm after heating overnight at 100°C and 0% RH (Fig. 3). The clay fractions of the grassland and

forest pedons contain few silicate clay minerals and have nearly identical XRD patterns (Figs. 4 and 5). Mica was identified based upon a 1.0-nm spacing in all treatments and was present in limited quantities, predominantly in surficial horizons (Fig. 4). The 1.0-nm reflection did not disappear or collapse to 0.7 nm upon heating at K-300°C or K-550°C, which is evidence for mica and not hydrated halloysite, which also gives a 1.0-nm spacing (Dixon and Weed 1989). Quartz and feldspar are present in all samples.

Kaolinite and/or dehydrated halloysite occur in limited quantities in surficial horizons. Kaolinite is identified based upon a 0.71-nm spacing, which disappears at K-550°C, whilst dehydrated halloysite is identified by the additional 0.445-nm peak with intensity equal to half or more that of the 0.7-nm peak (Brindley 1961). The pedons containing kaolinite/halloysite display a weak peak at 0.445-nm (Fig. 4). However, it is difficult to ascertain its intensity compared with that of the 0.7-nm peak due to the characteristic broad X-ray reflection of the volcanic glass; it can be inferred that the soils contain both minerals.

The allophane content is low for all horizons (<0.6%) and is higher in tephra C horizons under grassland than forest vegetation, while the reverse occurred for the surface horizons (Table 4). Ferrihydrite content is also very low with the forest pedons containing slightly greater quantities (Table 4).

SEM examination of the tephra from surficial and tephra horizons identifies the dominant component to be volcanic glass mixed with organic materials and few grains of feldspar, quartz and amphibole. The glass particles are vesicular (Fig. 6a) and are primarily angular in shape with minor rounded and tear-like particles with diameters ranging from 200 to 400 µm. Elemental analysis (Table 5) of the glass surface reveals an elevated C content and higher level of Al than exchangeable bases. Evidence of weathering is limited to etching of the glass surface (Fig. 6b), predominantly in the forest pedons, and is positively correlated with elevated C levels, low proportion of Si and high amounts of Na and Mg (Table 5). Opaline silica (Fig. 6c) was observed under the forest pedons on the surface of glass spheres and

Table 4. Mean extractable Fe, Al and Si concentrations for tephra (C) horizons and surficial (Ah and Bm) horizons of grassland and forest pedons

Selected extractable Fe, Al and Si properties	Grassland pedons tephra horizon(C)	Forest pedons tephra horizon (C)	Grassland pedons surficial horizon (Ah)	Forest pedons surficial horizon (Bm)
% Fe _d	0.25 (±0.069)	0.12 (±0.062)	0.48 (±0.13)	0.43 (±0.11)
% Fe _o	0.10 (±0.030)	0.14 (±0.087)	0.12 (±0.015)	0.20 (±0.068)
% Fe _p	0.032 (±0.014)	0.030 (±0.014)	0.034 (±0.0039)	0.14 (±0.058)
% Al _o	0.18 (±0.043)	0.11 (±0.041)	0.13 (±0.017)	0.26 (±0.067)
% Al _p	0.073 (±0.020)	0.065 (±0.033)	0.039 (±0.0083)	0.15 (±0.054)
% Si _o	0.082 (±0.034)	0.022 (±0.0046)	0.058 (±0.0040)	0.034 (±0.0090)
(Al _o -Al _p)/Si _o	1.5* (±0.28)	2.0* (±0.38)	1.6* (±0.25)	3.5* (±0.69)
Fe _o /Fe _d	0.39 (±0.034)	1.5 (±0.80)	0.28 (±0.066)	0.49 (±0.12)
Fe _p /Fe _o	0.33 (±0.090)	0.35 (±0.21)	0.27* (±0.021)	0.65* (±0.053)
Al _p /Al _o	0.42 (±0.097)	0.57 (±0.081)	0.31 (±0.083)	0.55 (±0.081)
% allophane	0.49 (±0.20)	0.15 (±0.031)	0.35 (±0.024)	0.56 (±0.14)
% ferrihydrite	0.17 (±0.063)	0.24 (±0.15)	0.21 (±0.025)	0.34 (±0.12)

* Denotes significantly different means ($P < 0.05$) among similar horizons, (±) indicates standard error of the mean ($n = 3$). Fe_d = dithionite-citrate extractable Fe; Fe_o, Al_o and Si_o = acid ammonium oxalate extractable Fe, Al and Si; Fe_p and Al_p = sodium pyrophosphate extractable Fe and Al.

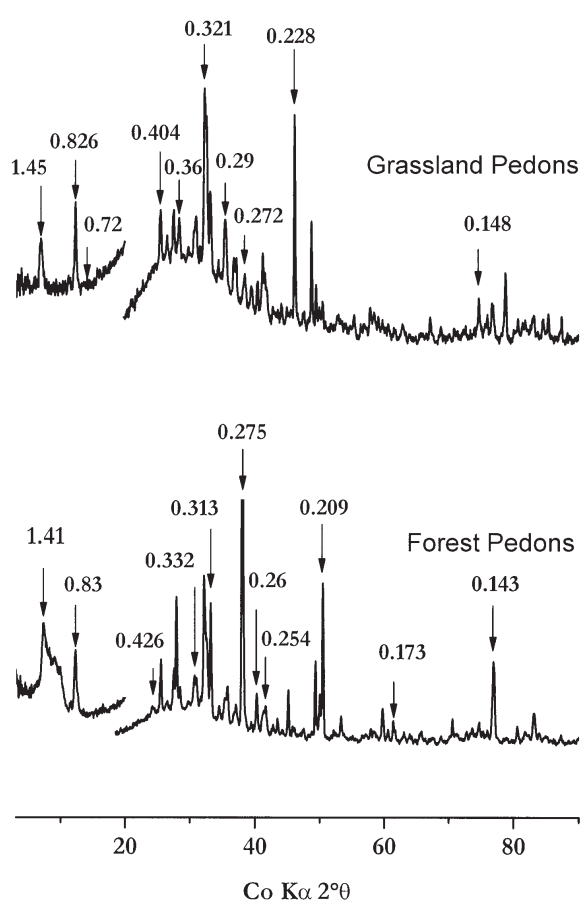


Fig. 2. X-ray diffraction patterns of sand fraction (0.05–2.00 mm) from tephra horizons of grassland and forest pedons (d-spacing in nm).

in a very small quantity. Elemental analysis of the opaline spheres (Table 5) shows a small quantity of Na and K, and high concentrations of silicon, oxygen and Al similar to that of the glass surface. Particles (<10 μm) as seen in Fig. 6a were noted to a greater extent under the forest pedons and are dominated by higher levels of Fe, Al and exchangeable bases like Ca (Table 5).

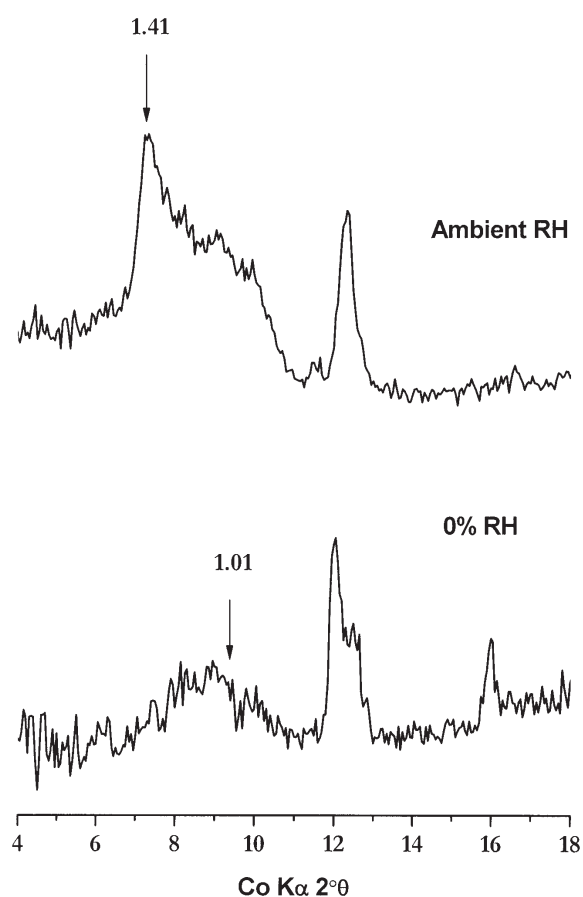


Fig. 3. X-ray diffraction patterns of sand fraction (0.05–2.00 mm) from tephra horizons of the forest pedons: scanned at ambient relative humidity (RH) and at 0% relative humidity (RH) after overnight heating (d-spacing in nm).

DISCUSSION

Soil Physical and Geochemical Properties

Clay contents are low in all horizons (<19%) and increase marginally with depth suggesting limited translocation through the soil profiles and limited weathering (Wada et al. 1987; Malucelli et al. 1999). The influence of vegetation is

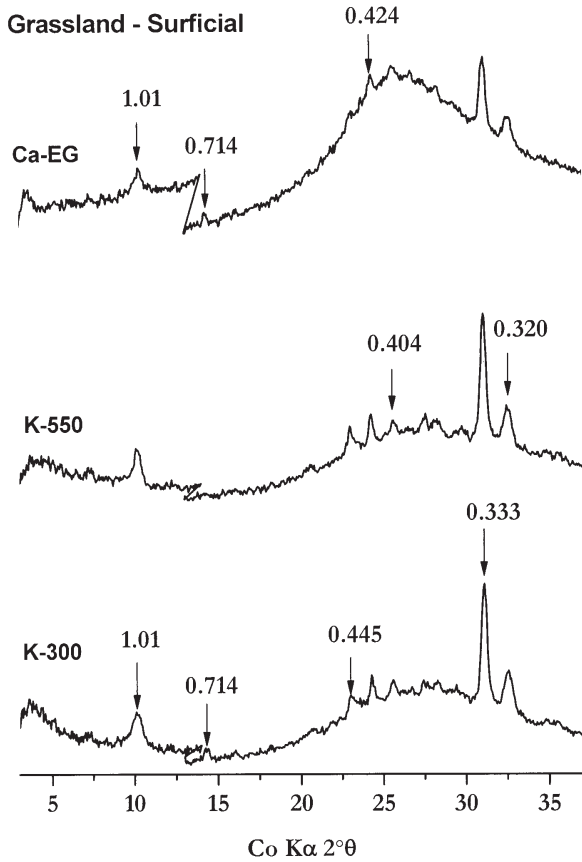


Fig. 4. Representative X-ray diffraction patterns [K-saturated heating to 300°C and 550°C and treatment of Ca-saturated sample with ethylene glycol (EG)] of the clay fraction (<0.002 mm) from surficial horizons of grassland and forest pedons (d-spacing in nm). The anomaly at 13–14 2°θ is due to band overlap.

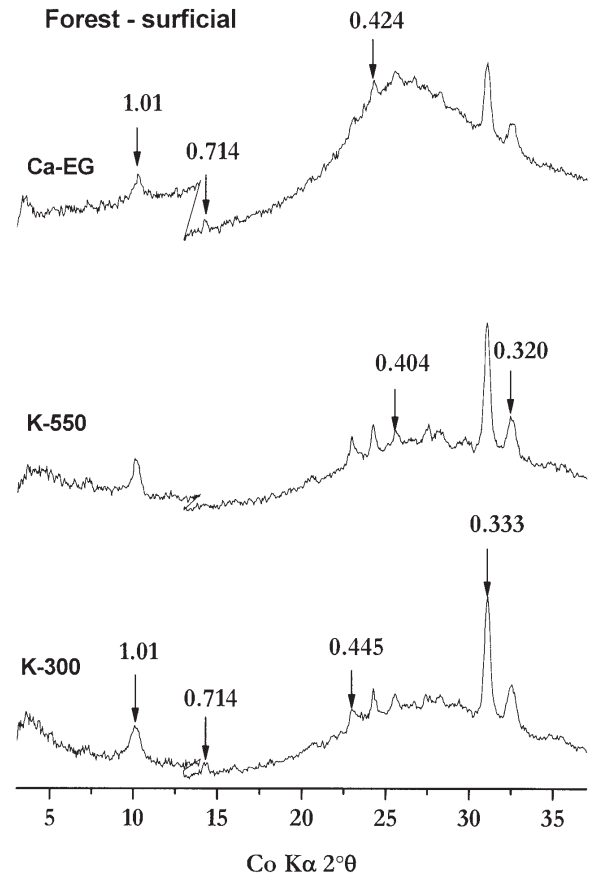


Fig. 5. Representative X-ray diffraction patterns [K-saturated heating to 300°C and 550°C and treatment of Ca-saturated sample with ethylene glycol (EG)] of the clay fraction (<0.002 mm) for tephra horizons of grassland and forest pedons (d-spacing in nm). The anomaly at 13–14 2°θ is due to band overlap.

evident in higher pH values and high concentrations of exchangeable Ca, K and Mg in the grassland pedons, which is related to the ability of grasses to cycle base cations (Ugolini et al. 1988). The higher CEC values in grassland horizons are attributed to the mixing of organic matter into the soil profile as evidenced by the greater organic carbon content for grassland tephra horizons (Table 3). In a similar study by Ugolini et al. (1988), exchangeable cation cycling was five times greater under grassland vegetation than forest. In coniferous ecosystems, soils have lower pH values, due to the polyphenol-rich litter (Ugolini and Dahlgren 1991; Nanzyo et al. 1993).

The CEC values for grassland pedons are less than the sum of exchangeable cations due to the use of unbuffered NH_4Cl in the CEC determination, the variable charge of the soil and the high levels of exchangeable Ca^{2+} and Mg^{2+} . The presence of soil components with variable charge might have contributed to the CEC values of the grassland and forest pedons (Nanzyo et al. 1993). The high levels of exchangeable Ca^{2+} and Mg^{2+} correspond to those reported by Smith et al (1999) in a permafrost-affected White River

tephra-derived soil, suggesting the presence of a mild weathering environment. Aeolian deposition of glacial-derived loess containing Ca- and Mg-carbonates may also contribute to the high levels of Ca and Mg in the study area. We observed the presence of calcareous layers in several colluvial sites in Central Yukon indicating the likelihood of the deposition of calcareous materials.

Secondary Mineral Formation

The difference in $\text{pH}(\text{H}_2\text{O})$ between grassland and forest pedons is important in its relation to the preferential formation of metal-humus complexes versus allophanic constituents (Parfitt and Kimble 1989; Nanzyo et al. 1993; Takahashi et al. 1993). The surficial horizons of the forest pedons have a $\text{pH}(\text{H}_2\text{O}) < 5.0$ suggesting that Fe and Al are present as metal-humus complexes (Shoji et al. 1993). Al_p and Fe_p values support this (Table 4), as they are highest in the surficial horizons under forest vegetation and decrease as the $\text{pH}(\text{H}_2\text{O})$ increases and the organic matter content decreases in the tephra horizon. The Fe_p/Fe_o and Al_p/Al_o ratios > 0.5 (Table 4) also indicate the preferential formation

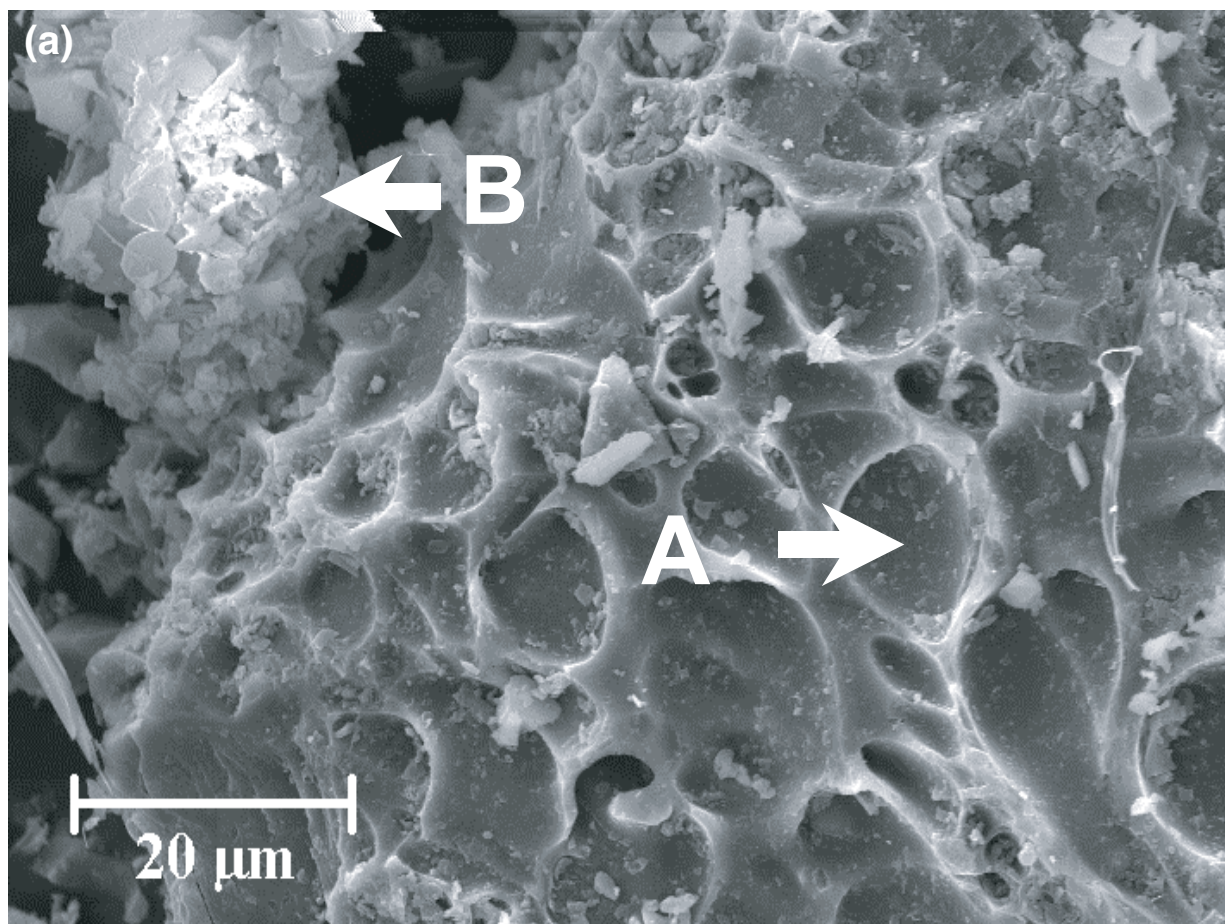


Fig. 6. (a) SEM micrograph of vesicular glass structure noted at [A] and Fe-rich particles $<10\ \mu\text{m}$ as noted at [B] in forest pedons. (b) SEM micrograph of etching on glass surface as noted at [A], and (c) SEM micrograph of opaline silica spheres on glass surface in forest pedons as noted at [A].

of metal-humus complexes in the surficial horizons of the forest pedons. These conditions lower Al activity and limit the formation of allophane (Shoji et al. 1988b). The Fe_o/Fe_d ratio (0.49) for surficial forest horizons indicates similar amounts of crystalline Fe and poorly ordered oxyhydroxides; iron in oxide form has greater stability than iron in Fe-humus complexes (Dahlgren et al. 1993; Shoji et al. 1993). Incorporation of Al into Al-humus complexes and possibly into allophane is suggested by the Al_p/Al_o ratio of 0.57 in tephra horizons. Fe occurs as poorly ordered constituents (ferrihydrite), suggested by the Fe_o/Fe_d ratio of 1.5. This ratio may not accurately reflect the incorporation of Fe into ferrihydrite due to isomorphous substitution of $\text{Fe}^{(\text{III})}$ for $\text{Al}^{(\text{III})}$ in Al-oxides which are not extractable in dithionite-citrate solution (Dixon and Weed 1989) resulting in a higher value of Fe_o than Fe_d .

In grassland horizons, the low Fe_p and Al_p values and the $\text{pH}(\text{H}_2\text{O}) > 5.0$ suggest that Fe and Al are present as poorly ordered materials, presumably allophane and ferrihydrite (Ugolini and Dahlgren 1991; Nanzyo et al. 1993). This is sup-

ported by the Fe_p/Fe_o and Al_p/Al_o ratios of < 0.5 in surficial and tephra horizons. Fe_o/Fe_d ratios < 0.5 for grassland pedons suggest that secondary Fe is predominantly in the form of crystalline oxides. However, Fe-oxyhydroxides were not identified by XRD in forest or grassland pedons probably due to extremely low levels of acid-oxalate extractable Fe ($< 0.31\%$) not only for grassland pedons but also forest pedons. The formation of crystalline Fe-oxyhydroxide may be due to seasonal moisture deficits within the grassland study area and to a lesser degree in the forested study area. Smith et al. (1999) suggest that Si_o values $> 0.10\%$, in addition to Al_p/Al_o ratios < 0.5 , are essential for reliable estimates of allophane content; these conditions do not exist in tephra or surficial horizons in the study (Table 4). The estimates for allophane are comparable to Parfitt and Kimble (1989) who equate a Si_o content of 0.2% to $\sim 1\text{-}2\%$ allophane. Allophane content was very low ($< 0.57\%$) in all horizons despite conditions favoring its formation in the grassland pedons. The availability of Al is limited due to neither complexation with humus nor the formation of 2:1 layer silicates, but rather due to its slow release by carbonic acid weathering (Dahlgren et al. 1993). This is in

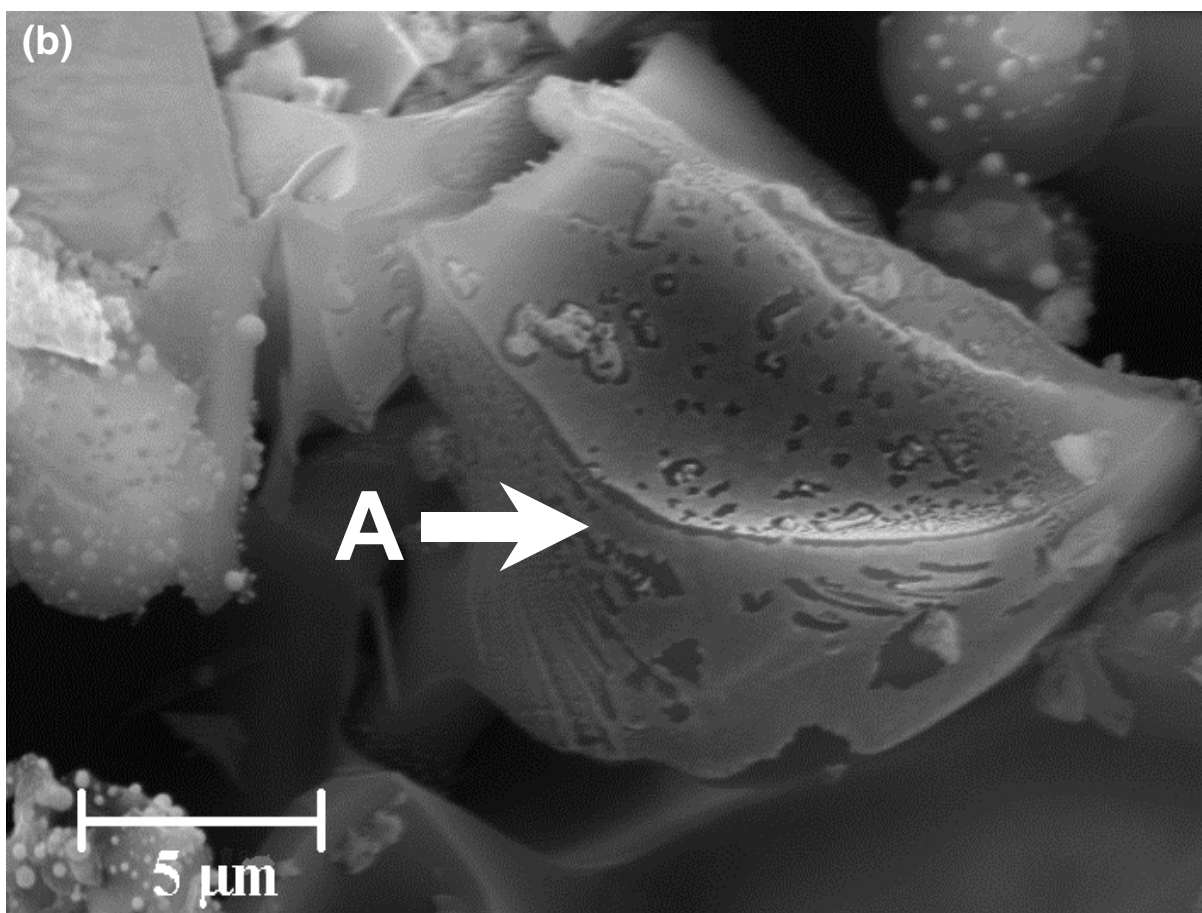


Fig. 6. Continued

contrast to the forest pedons where the organic acid-induced weathering, lower $\text{pH}(\text{H}_2\text{O})$ and Al_p/Al_o values > 0.5 , favor the formation of Al-humus complexes rather than allophane (Parfitt and Saigusa 1985). The Al_p/Al_o ratios in surficial horizons of the forest pedons are > 0.5 (Table 4), however, the estimate of allophane content is higher than that for grassland pedons. The higher estimate of allophane is due to the conversion factor (CF) = 16 for a $(\text{Al}_o - \text{Al}_p)/\text{Si}_o$ ratio of 3.5 as compared with $\text{CF} = 6$ for grassland pedons where atomic Al:Si ratios are ~ 1.5 (Parfitt 1990); CF were empirically derived by Parfitt and Wilson (1985) from volcanic soils in New Zealand. The atomic Al:Si ratios indicate that the grassland pedons favor the formation of an allophane intermediate between Si-rich and Al-rich, while the forest pedons favor the formation of an Al-rich allophane with a $(\text{Al}_o - \text{Al}_p)/\text{Si}_o$ ratio closer to 2 for tephra horizons.

Parfitt and Kimble (1989) suggest that allophanes with $\text{Al}:\text{Si} < 2.0$ form where the pH and Si concentration are high due to low rainfall and/or a lack of leaching for a considerable portion of the year. This condition is valid, in part, for the grassland pedons. Parfitt and Kimble (1989) also suggest that where the $\text{Al}:\text{Si} > 2$ and the pH is < 6.0 and Si is deficient due to leaching, an Al-rich allophane will form. These conditions partially coincide with the forest pedon environ-

ment. However, they are not heavily leached due to the dry environment, yet contain an Al-rich allophane. The high Al_o values potentially overestimate the Al:Si ratio and may not reflect accurately the allophane type and content present in the soil. It should also be considered that the Al-rich allophane may form when favorable leaching conditions exist, such as during spring snowmelt. The slight degree of resili-cation and subsequent evaporation and concentration of the soil solution would then form small amounts of opaline silica during summer months.

The presence of opaline silica indicates high silica activities in solution and a low leaching potential (Nizeyimana et al. 1997), which must be maintained if opaline silica is to remain stable in the soil environment (Dahlgren et al. 1993). High silica activity and low leaching may occur in the forest pedons which exhibit less movement of Si down the soil profile due to their finer textures than those of the grassland pedons, where no opaline silica was detected by SEM. Absence of opaline silica in grassland pedons is likely due to the conversion of solution Si into allophane as a result of slightly higher Al activity (Ping et al. 1988; Ugolini et al. 1991) associated with the low levels of Al-humus complexes. The small quantity of opaline silica in the surficial and tephra horizons of the forest pedons is linked to the formation of Al-humus complexes, thus leav-

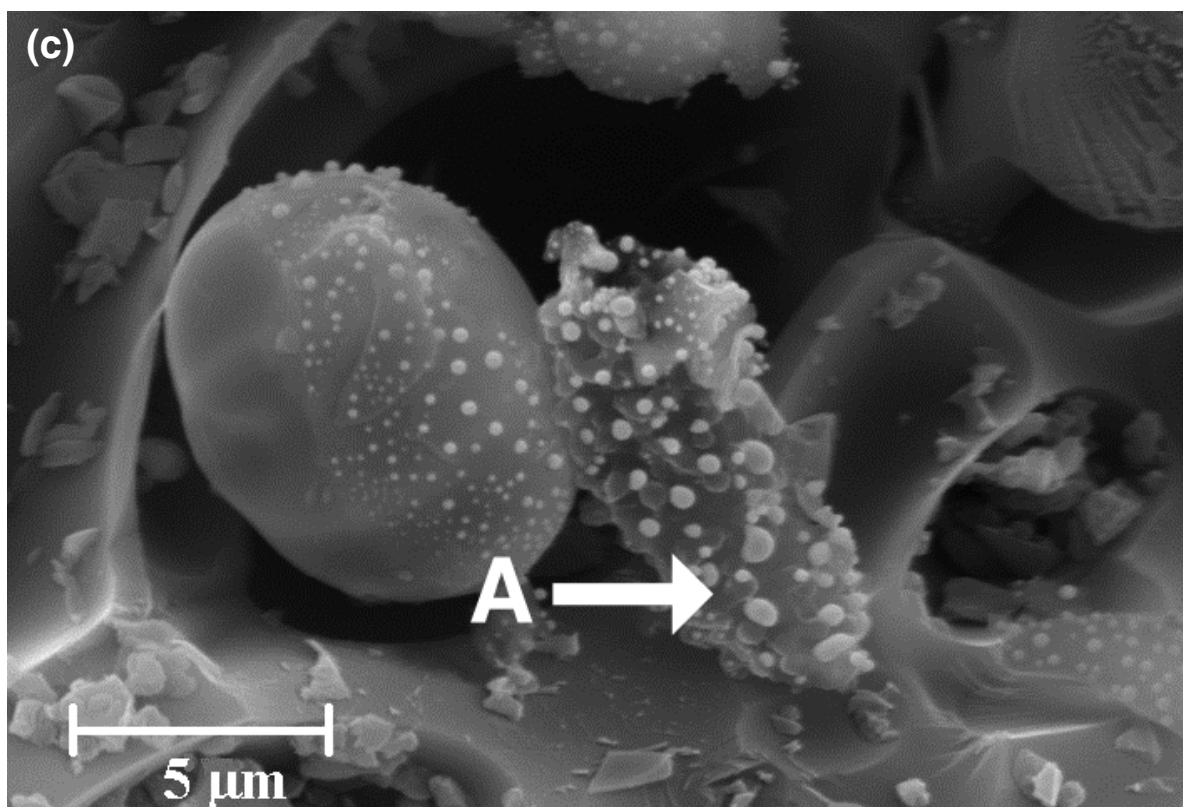


Fig. 6. Continued

Table 5. EDAX DX-4 -semi quantitative ($\pm 10\%$) microanalysis of opaline silica spheres ($n = 2$), volcanic glass surface ($n = 5$), organic film ($n = 3$) and particles $<10 \mu\text{m}$ ($n = 4$).

Element	Opaline silica spheres	Volcanic glass surface	Surface etching	Particles $<10 \mu\text{m}$
C	25 (± 0.16)	26 (± 3.9)	50 (± 6.2)	17 (± 3.2)
O	41 (± 0.85)	25 (± 7.4)	18 (± 7.3)	16 (± 6.7)
Na	2.0 (± 0.065)	3.5 (± 1.2)	17 (± 11)	1.1 (± 0.34)
Mg	0.79 (± 0.12)	1.3 (± 0.56)	6.2 (± 6.5)	5.0 (± 2.7)
Al	7.6 (± 0.14)	8.7 (± 0.75)	2.4 (± 1.6)	8.2 (± 1.7)
Si	20 (± 0.47)	26 (± 6.8)	1.3 (± 1.6)	25 (± 5.0)
K	1.3 (± 0.14)	2.5 (± 1.1)	0.14 (± 0.096)	1.1 (± 0.62)
Ca	0.98 (± 0.15)	1.8 (± 0.59)	0.20 (± 0.11)	5.8 (± 3.0)
Ti	0.13 (± 0.035)	0.34 (± 0.13)	0.19 (± 0.046)	1.6 (± 0.72)
Fe	1.1 (± 0.12)	2.9 (± 0.99)	1.6 (± 1.4)	17 (± 3.2)
Cu	0.51 (± 0.010)	1.8 (± 0.64)	2.8 (± 2.6)	2.6 (± 0.60)
Total	100	100	100	100

(\pm) indicates standard error of the mean.

ing a Si-rich environment (Ugolini et al. 1991) conducive to the formation of opaline silica during surface evaporation (Shoji et al. 1988a; Dahlgren et al. 1993). Opaline silica may also form during the freezing of the soil solution, as suggested by Shoji et al. (1988a) for situations in which opaline silica occurred in combination with Al-rich allophane.

The ferrihydrite content is low for all horizons but is higher in forest pedons, perhaps due to production of organic acids, which lower the pH, promoting the release of Fe from primary minerals (Nanzjo et al. 1993). The high affinity of organic acids and Si for the Fe oxide surface and limited dehydration has inhibited the further formation of

crystalline Fe-oxides in the forest pedons (Ugolini et al. 1991). Smith et al. (1999) noted the presence of poorly ordered Fe-oxyhydroxide coatings in White River tephra-derived soils. Overall, the low levels of Fe(III)-oxyhydroxides are indicative of a mild weathering regime (Malucelli et al. 1999) and the young age of these soils.

The XRD results show limited mineral formation in the clay fraction due to the cold and dry climate, short duration of weathering (~ 1150 yr) and the lack of precursor minerals in the rhyolitic tephra (Dahlgren et al. 1993). The absence of dehydrated halloysite, despite the indication of a Si-rich environment (in the forest pedons), which favors its forma-

tion (Dahlgren et al. 1993; Takahashi et al. 1993; Nizeyimana et al. 1997), is inconsistent with similar studies (Takahashi et al. 1993; Nizeyimana et al. 1997). Under low precipitation regimes halloysite can form directly from volcanic glass when silica activity in soil solution is high (Parfitt 1990). Halloysite formation is also favored in a weakly leached profile (Parfitt et al. 1984) such as occurs in the forest pedons, indicated by the presence of opaline silica and white (10YR 8/1), relatively unweathered tephra. The atomic Al:Si ratio (>2) of the forest pedons indicates the formation of an Al-rich allophane, which is commonly associated with a well-leached profile (Parfitt et al. 1984) rather than a Si-rich allophane or halloysite, typically associated with a low leaching environment. Allophanic materials may be a metastable precursor to halloysite when seasonal resilication takes place (Takahashi et al. 1993); this process of resilication may account for the minimal halloysite formation observed in the studied soils.

Repeated cycles of desiccation can transform poorly ordered weathering products into more ordered kaolin minerals (Takahashi et al. 2001). In our study area, this process is not likely to occur due to the low concentration of poorly ordered materials. With the short duration of soil formation, it is unlikely that kaolinite has formed pedogenically in this time period as it is commonly associated with low Si and base cation levels and high H_3O^+ concentrations under a high rainfall regime (Chadwick and Chorover 2001; Buol et al. 2002). Kaolinite may also be of detrital origin, or dispersed in loess in a relatively even pattern across the landscape (Ugolini et al. 1991). The kaolinite may be of detrital origin as it is not evenly distributed amongst the surficial horizons.

The presence of chlorite and an expanding phyllosilicate in the sand fractions of the tephra horizons is not pedogenic, as these minerals are absent from the clay fractions, nor are there sufficiently acidic conditions to favor 2:1 layer silicate formation (Parfitt and Saigusa 1985). Chlorite is considered unstable in horizons where organic acid-mediated weathering dominates (Dixon and Weed 1989; Ugolini et al. 1991), which may account for the presence of an expanding phyllosilicate in the forest pedons where organic acid weathering is potentially occurring. The presence of these minerals is likely a result of their incorporation as a detrital component of the tephra. It is possible that the aeolian deposition of fine grained quartz, mica and small amounts of detrital smectite and vermiculite have come to serve as precursor minerals (Dahlgren et al. 1993). As weathering is minimal, transformation from a precursor mineral is unlikely. The potential for contamination of the tephra horizons, from the buried horizons, which show greater clay mineral development (XRD patterns not shown), is low. Chlorite, smectite and hydroxy-interlayered vermiculite (detected in the buried soils) were not present in the clay fractions of the tephra and surficial horizons, suggesting that the mixing between tephra and buried horizons is minimal.

CONCLUSION

The formation of secondary minerals during the weathering of White River tephra under grassland and forest vegetation is quite limited due to several factors, including cold tem-

peratures combined with low precipitation and the young age of the deposit. The low contents of allophane and other metastable, poorly ordered solid phase constituents is a direct result of the low levels of Al, Fe and Si released from the volcanic glass. The soil environment has not favored 2:1 phyllosilicate mineral transformation or dehydrated halloysite, which is commonly associated with dry conditions similar to the study area. The grassland pedons favored allophane formation due to the carbonic acid weathering regime $pH(H_2O) > 5.0$. In forest pedons, the formation of Al-humus complexes and opaline silica was probably the result of the production of organic acids in the litter layer. The formation of opaline silica in an Al-rich environment is a result of the freezing of the soil solution (Shoji et al. 1988a). We believe that the extractable Fe is poorly ordered because crystalline Fe(III)-oxyhydroxides were not detected by the X-ray diffraction analysis indicating a juvenile stage of soil development. The phyllosilicates that were found in the White River volcanic ash soil contained in the sand fraction are thought to be of detrital origin. Organic acid production may have initiated the transformation of chlorite into an expanding phyllosilicate in the forest pedons. Kaolinite is also thought to be of detrital origin as the dry and cold environment is not favorable for its formation. Dehydrated halloysite is likely to occur in this dry environment but has not been definitely identified in the grassland or forest pedons.

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