

THERMAL CONDUCTIVITY AND THE UNFROZEN WATER CONTENTS OF VOLCANIC ASH DEPOSITS IN COLD CLIMATE CONDITIONS: A REVIEW

ELENA KUZNETSOVA

Norwegian University of Science and Technology, Trondheim, Norway

Abstract—Layers of volcanic ash and Andosol soils derived from the ash may play an important role in preserving snow and ice as well as in the development of permafrost conditions in (a) the immediate vicinity of volcanoes at high elevations or at high latitudes and (b) land areas that are often distant from volcanic activity and are either prone to permafrost or covered by snow and ice, but have been affected by subaerial ash deposition. The special properties of volcanic ash are critically reviewed, particularly in relation to recent research in Kamchatka in the Far East of Russia. Of special importance are the thermal properties, the unfrozen water contents of ash layers, and the rate of volcanic glass weathering. Weathering of volcanic glass results in the development of amorphous clay minerals (*e.g.* allophane, opal, palagonite), but occurs at a much slower rate under cold compared to warm climate conditions. Existing data reveal (1) a strong correlation between the thermal conductivity, the water/ice content, and the mineralogy of the weathered part of the volcanic ash, (2) that an increase in the amounts of amorphous clay minerals (allophane, palagonite) increases the proportion of unfrozen water and decreases the thermal conductivity, and (3) that amorphous silica does not alter to halloysite or other clay minerals, even in the Early Pleistocene age (Kamchatka) volcanic ashes or in the Miocene and Pliocene deposits of Antarctica due to the cold temperatures. The significance of these findings are discussed in relation to past climate reconstruction and the influence of volcanic ash on permafrost aggradation and degradation, snow and ice ablation, and the development of glaciers.

Key Words—Allophane, Amorphous Clay, Climate Change, Cold Climate, Opal, Palagonite, Permafrost, Thermal Conductivity, Unfrozen Water, Volcanic Ash.

INTRODUCTION

Volcanic ash is associated with a considerable proportion of the Earth's land surface. At the same time, an estimated 15% of the land surface is affected by permafrost and glacial ice. Consequently, volcanic ash may play an important role in the aggradation and degradation of cold regions (Kellerer-Pirklbauer *et al.*, 2007; Froese *et al.*, 2008). An understanding of the influence of volcanic ash on these frozen areas will allow for a more accurate prediction of the stability of cold areas in the future and provide a better understanding of the factors that affect past climates, soils, and soil stability. Vital to making accurate predictions is an understanding of the thermal properties of volcanic ash, which are thermal conductivity, thermal diffusivity, and heat capacity (Juen *et al.*, 2013). The available measurements on the thermal properties of various types of volcanic ash in different geographic and climatic settings is limited and this means that inappropriate assumptions are being used and empirical comparisons are currently being made using insufficiently 'representative' natural soils. Such empirical comparisons can be seriously misleading because the comparisons do not take into account the unique mineralogical and chemical

properties of volcanic glass as well as the different climatic conditions. For example, even for the same region of Kamchatka in eastern Russia, the volcanic ash may not only have different ages and the glass different chemical compositions, but also different weathering stages, mineralogical compositions, and degrees of water saturation. These ashes may be permanently frozen or unfrozen and all of these characteristics may affect the thermal properties (Braitseva *et al.*, 1997; Ponomareva *et al.*, 2007; Kuznetsova, 2011; Kuznetsova *et al.*, 2011, 2013; Kyle *et al.*, 2011; Kuznetsova and Motenko, 2014). These differences may be why the critical thickness of tephra on the top of glaciers may act to either insulate or enable the ablation of different volcanoes. The measured critical tephra thickness values ranged from 24 mm for the glaciers at Mt. St. Helens, USA, (Driedger, 1980) and for the tephra that erupted in 1996 at Mt. Ruapehu, New Zealand, (Manville *et al.*, 2000) to <5.5 mm for the tephra from the 1947 eruption of the Hekla volcano, Iceland, (Kirkbride and Dugmore, 2003) and the tephra from the Villarica volcano in Chile (Brock *et al.*, 2007). The reasons for this disparity in critical tephra thicknesses are unknown. Ayris and Delmelle (2012) assumed that the particle size and porosity of the tephra might be the reason. Taking into consideration that the tephra cover on glaciers is wet during periods of ablation, the thermal conductivity (λ) of this material should not be overlooked. For most models, the dry thermal conductivity of tephra is used

* E-mail address of corresponding author:

elena.kuznetsova@ntnu.no

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(Brock *et al.*, 2007). For the same degree of saturation, the λ values can vary by a factor of 2–3 (Kuznetsova *et al.*, 2012; Kuznetsova and Motenko, 2012).

The unfrozen water content is of particular importance in understanding the thermal and mechanical behavior of frozen soils at temperatures near the melting point. Unfrozen water exists naturally in silts and clays, but is absent in sands and granular soils (Ershov *et al.*, 1978; Andersland and Ladanyi, 2004; Yershov and Williams, 2004). In glacier interlayers, the unfrozen water between ice and mineral particles can act as a lubricant to modify the stress transfer between ice-particle and particle-particle contacts by relaxing the interactions between the particles and the ice (Moore, 2014). In permafrost areas, unfrozen water controls ice segregation processes at freezing temperatures, which are responsible for frost heaving in soils and rock disintegration mechanisms (Ershov *et al.*, 1978; Andersland and Ladanyi, 2004; Yershov and Williams, 2004; French, 2013).

The present review summarizes existing data regarding: (1) the thermal properties and unfrozen water contents of frozen volcanic ash and cinders, (2) the effects of cold temperatures on the weathering processes of volcanic glass, and (3) the relationships between frozen volcanic deposit mineralogy and the thermal properties. This review is based on published data from studies in Kamchatka, Eastern Russia, where investigations considered the effects of climate change on permafrost and the response of glaciers, the properties of volcanic soils in cold regions, and numerical modelling of glaciers and permafrost thermal behavior (Kellerer-Pirklbauer *et al.*, 2007; Abramov *et al.*, 2008; Ayriz and Delmelle, 2012; Juen *et al.*, 2013; Kuznetsova and Motenko, 2014; Langmann, 2014).

MATERIALS AND METHODS

Materials

The majority of the World's volcanoes are within the active subduction zones of oceanic and continental plates. The geographic spread of volcanic ash and pumice deposits derived from areas of active and recently extinct volcanoes occurs where climates can range from cold-humid temperate to the humid to semi-arid tropics, and elevations can range from deep ocean bottoms to high altitude mountains (Wada, 1987; Neall, 2006). The distribution of tephra (*i.e.* volcanic ejecta) from a particular volcanic eruption depends on the force and the dominant wind direction at the time. Before deposition, fine-grained tephra can travel hundreds of kilometers. Volcanic gases and the particles from the eruptions produced by high latitude volcanoes may quickly encompass the poles due to a shorter pathway and a higher wind speed. For example, volcanic emissions from Mt. Hudson and Puyehue-Cordon Caulle, Chile, or from Kasatochi, Alaska, were trans-

ported around the pole within 10–14 days (Barton *et al.*, 1992; Schoerberl *et al.*, 1993; Langmann, 2014).

Despite active volcanism, permafrost (*i.e.* ground that remains at or below 0°C for 2 or more years) and glaciers often exist on the slopes of high elevation or high latitude volcanoes (Kellerer-Pirklbauer *et al.*, 2007). Examples of the coexistence of volcanism, permafrost, and glaciers are known from Argentina (Liaudat *et al.*, 2014), Chile (Brock *et al.*, 2007; Reid and Brock, 2010), Hawaii (Woodcock, 1974), Iceland (Etzelmüller *et al.*, 2007), Kamchatka (Bäumler, 2003; Abramov *et al.*, 2008), Mexico (Palacios *et al.*, 2007), New Zealand (Manville *et al.*, 2000), North America (Froese *et al.*, 2008), and Antarctica (Gow and Williamson, 1971). Extraterrestrially, Mars has an average surface temperature of -63°C, ice caps, and permafrost conditions that cover more than half of the surface, but Mars is covered by rocks of volcanic origin and other evidence of volcanism (Allen *et al.*, 1981; Carr, 2007).

Volcanic eruptions are one of the major causes of ice and snow burial in volcanic areas. This has been demonstrated on volcanoes in Iceland, the USA, New Zealand, and Chile, where the combination of a climate favorable to permafrost and a thin tephra layer (with a low thermal conductivity) is sufficient to reduce snow ablation in the layer beneath the tephra and to cause substantial ground ice formation and permafrost aggradation (Gow and Williamson, 1971; Driedger, 1980; Major and Newhall, 1989; Kirkbride and Dugmore, 2003; Kellerer-Pirklbauer *et al.*, 2007; Reid and Brock, 2010; Liaudat *et al.*, 2014).

Properties of volcanic ash and pumice, as well as volcanic soils, have been widely investigated due to the unique properties. Paleoscientists and tephrochronologists use volcanic ash as a tool for linking and dating geological, paleoecological, paleoclimatic, and archaeological sequences or events (Braitseva *et al.*, 1993; Marchant *et al.*, 1996; Ponomareva *et al.*, 2007; Lowe, 2010, 2011; Jaramillo *et al.*, 2015). Soil scientists are concerned with the unique physical, chemical, and mineralogical properties of soils formed on volcanic ash (or Andisols) with respect to the high permeability, organic matter, secondary minerals, and high specific surface areas as well as other aspects (Nanzyo, 2002; Karpachevskii *et al.*, 2009; Shoba and Ivanov, 2011). In cold environments, volcanic ash is an important factor in (1) processes that influence permafrost aggradation and degradation of the carbon in peat accumulations and (2) volcanic ash use as a chronological marker in studies of rock glaciers, glacial moraines, glacier fluctuations, moraine development, and glaciofluvial deposition (Denton and Karlén, 1977; Driedger, 1980; Robinson and Moore, 2000; Bäumler, 2003; Froese *et al.*, 2008). The influence of tephra is important to snow and ice ablation, permafrost aggradation, and the energy balance at the glacier–atmosphere interface (Greuell and

Oerlemans, 1986; Manville *et al.*, 2000; Hock, 2005; Brock *et al.*, 2007; Kellerer-Pirklbauer *et al.*, 2007; Pellicciotti *et al.*, 2009; Richardson and Brock, 2010; Juen *et al.*, 2013; Möller *et al.*, 2016). Terrestrial volcanoes in permafrost areas provide analogous information that can be used to develop volcanic permafrost models for Mars (Anderson *et al.*, 1967; Allen *et al.*, 1981; Arvidson *et al.*, 2004; Squyres *et al.*, 2006; Demidov and Gilichinsky, 2009).

Methods

Many authors (Ershov *et al.*, 1978; Farouki, 1981a; Smith and Tice, 1988) presented reviews of the existing test methods to determine the thermal properties of soils and unfrozen water. Most common methods to measure the unfrozen water contents of frozen volcanic soils include nuclear magnetic resonance (NMR) (Tice *et al.*, 1978), time domain reflectometry (TDR) (Smith and Tice, 1988), contact methods, and cryoscopic methods (Ershov *et al.*, 1978). The most common methods to measure thermal properties include the thermal probe method (Conner *et al.*, 1997) and the thermal regular regime method (Dulnev, 1960; Yershov and Williams, 2004).

RESULTS AND DISCUSSION

Thermal conductivity of volcanic ash

An analysis of heat transfer and frost action in soils with a pyroclastic cover requires a knowledge of the thermal properties of each layer. Thermal conductivity is a key input parameter in heat transfer modelling and indicates the ability of the material to transmit heat. Heat capacity is the ability of soils to retain heat. Thermal diffusivity, the quotient of thermal conductivity and heat capacity per unit volume, is usually used to calculate the time required to initially freeze an unfrozen soil. A comprehensive review of thermal properties with an emphasis on the factors that influence soil thermal conductivity was presented by Farouki (1981b). The thermal properties of a soil are strongly influenced by the density and the water content, particularly because of the contrasting properties of these basic components. For instance, the thermal conductivities of solid mineral particles generally varies from 1 to 8 W/(m·K). Quartz has a thermal conductivity of about 8 W/(m·K), while other minerals, such as feldspars and micas, have thermal conductivities of around 2 W/(m·K). In addition to grain mineralogy, texture also must be considered. For example, the thermal conductivities of soils with the same water contents and dry densities that contain solids with different thermal conductivities (2 and 8 W/(m·K)) can differ by a factor of 2.5 (Johansen, 1977).

Most methods to predict soil thermal conductivity are based on the degree of saturation, dry density, and/or the thermal conductivity of the solid particles (Kersten, 1949; van Rooyen and Winterkorn, 1957). Due to the presence of amorphous phases in volcanic soils, such as

volcanic glass and clay minerals, the use of these models to calculate the thermal conductivity of volcanic ash is difficult. In addition, the thermal properties of volcanic ash soils is very different from other soils (Kasubuchi, 1975). Amorphous volcanic glass develops from a very viscous, undercooled solid solution, in which the arrangements of atoms or groups of atoms appears to be random as in liquids. The dispersion of heat waves in the random atomic network of volcanic glass proceeds more intensively than in crystalline atomic networks and considerably reduces the thermal conductivity (λ) (Chudnovsky, 1962). The angular particle shapes, higher porosities, and greater unfrozen water contents of volcanic ash also contribute to the lower thermal conductivity compared to sedimentary sands with the same grain size (Bovesecchi and Coppa, 2013; Kuznetsova and Motenko, 2014).

For the same degree of saturation (S_r), the thermal conductivities of sedimentary sands can be larger than volcanic ash by a factor of 2–3. For example, the thermal conductivity of volcanic ash with $S_r = 0.8$ in the frozen state can be 0.8–1.2 W/(m·K) and 1.8–2.8 W/(m·K) for quartz sand (Figure 1) (Ershov and Motenko, 2001; Kuznetsova *et al.*, 2012). Results indicated that volcanic glass composition and secondary minerals affect the thermal properties of volcanic soils, especially in the frozen state. Thus, the thermal conductivities and thermal diffusivities of ash samples with rhyolitic glass (line 5, Figure 1) were higher than for ash samples with andesitic and basaltic glass (line 6, Figure 1).

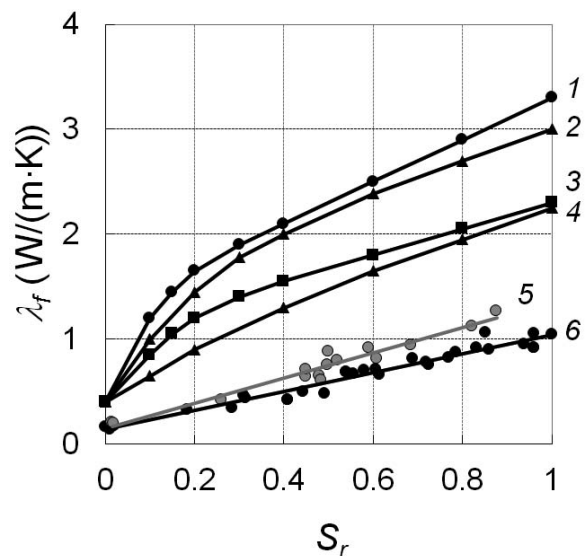


Figure 1. The dependence of the thermal conductivity in the frozen state (λ_f) on the degree of saturation (S_r) for the following deposits: 1 – a 0.25–0.65 mm quartz sand, 2 – a fine quartz sand, 3 – a 0.1–0.5 mm polymineral sand, 4 – a fine polymineral sand, 5 – a volcanic ash with rhyolitic glass, and 6 – a volcanic ash with basaltic glass. 1–4 data from the Department of Geocryology, Moscow State University, Russia.

Table 1. Thermal properties of volcanic ash and cinder samples.

	Area	Additional parameters	λ , W/(m·K)	$a \times 10^{-6}$, m ² /sec	C, J/(kg·K)	Literature reference
Volcanic soil	Memuro (Japan)	$W = 0\%$	0.14	-*	-*	(Clark, 1966)
		$W = 20\%$	0.26			
		$W = 40\%$	0.42			
		$W = 60\%$	0.61			
		$W = 80\%$	0.64			
Allotphanic soils Piece of pumice	Japan Kamchatka	$W = 30-33\%$	0.5-0.7	-*	-*	(Maeda <i>et al.</i> , 1977) (Nasedkin <i>et al.</i> , 1987)
		Glass = const (85%), $p=2840 \text{ kg/m}^3, n = 0$	0.92			
		$p = 2400 \text{ kg/m}^3, n = 0.15$	0.66			
		$p=1400 \text{ kg/m}^3, n = 0.50$	0.31			
		$p = 600 \text{ kg/m}^3, n = 0.80$	0.13			
Basaltic cinder and scoria	Kamchatka	$W = 0\%$	0.21	-*	-*	(Connor <i>et al.</i> , 1997)
Allotphanic soils Volcanic ash soil	Chile Columbia	$W = 30-33\%$	0.84-0.94	-*	-*	(Antilén <i>et al.</i> , 2003) (Yun and Santamarina, 2005; Herrera <i>et al.</i> , 2007)
		$W = 115\% n = 0.13$	0.71	-*	-*	
Volcanic tephra	Villarrica volcano (Chile)	$W = 0\%$	0.35	-*	-*	(Brock <i>et al.</i> , 2007; Reid and Brock, 2010)
Volcanic tephra	Kamchatka, Munovsky geothermal field	-*	0.28-0.93	-*	625-1839	(Kiryukhin <i>et al.</i> , 2013)
Basaltic tephra Pozzolanic soil based on volcanic ash	Etna volcano (Italy) Lazio, Italy	-*	0.6 (0.25-0.54)	-*	-*	(Juen <i>et al.</i> , 2013) (Bovesecchi and Coppa, 2013)
		-*	0.14 - 0.18**	-*	-*	
		-*	0.15 - 0.31***	-*	-*	
Volcanic ash and cinder (scoria)	Kluchevskaya volcano group, Kamchatka	$W = 10 - 80\%$	0.3 - 1.0**	0.12 - 0.4**	1000 - 2300**	(Kuznetsova, 2011; Kuznetsova <i>et al.</i> , 2012; Kuznetsova <i>et al.</i> , 2013)
		$P_d = 0.7 - 1.65 \text{ g/cm}^3$	0.41 - 1.3***	0.13 - 0.7***	800 - 1500***	
Volcanic tephra (1-2 and 2-4 mm)	Grimsvötn volcano, Iceland	-*	0.104	-*	-*	(Möller <i>et al.</i> , 2016)

Notes: -* - not specified; 0.4** - in thawed state; 0.7*** - in frozen state; W - water content, n - porosity, p - density, P_d - dry density, λ - thermal conductivity, a - thermal diffusivity, C - heat capacity.

Most published data on the thermal properties of volcanic ash and pumice, as well as volcanic soils, are for dry samples and do not show the variations in soil mineralogy, chemical composition, water content, or dry density (Table 1). Values for λ range from 0.10–1.3 W/(m·K).

The thermal conductivity of a single piece of pumice depends on the sample density and porosity (Nasedkin *et al.*, 1987). With a constant glass content, increasing the porosity by a factor of 5 leads to a five-fold decrease in the thermal conductivity. Highly porous volcanic materials can protect the ice from melting much more effectively than a less porous, mica schist layer of similar thickness (Juen *et al.*, 2013).

A four-fold increase in the water content increased the thermal conductivity of a volcanic ash and volcanic soil by a factor of 2 to 2.5 (Clark, 1966; Kuznetsova *et al.*, 2012; Kuznetsova and Motenko, 2012). The maximum water content, however, does not necessarily lead to maximum thermal conductivity. Laboratory studies showed that the thermal conductivity of an ash sample with a water content of $W = 80\%$ and a dry density of $\rho_d = 0.9 \text{ g/cm}^3$ might be lower than a sample with $W = 20\%$ and $\rho_d = 1.6\text{--}1.7 \text{ g/cm}^3$ due to the chemical composition, volcanic ash weathering processes, and the unfrozen water (Motenko and Kuznetsova, 2011; Kuznetsova *et al.*, 2013).

The mass heat capacities (C_m) of volcanic materials were found to be quite low in comparison to traditional soils. Under dry conditions, C_m ranged from 625 to 840 J/(kg·K), under wet and frozen conditions C_m increased up to 1500 J/(kg·K), and under thawed and wet conditions C_m increased up to 2300 J/(kg·K). For the wet samples from Kamchatka, the thermal diffusivity varied between $0.12\text{--}0.40 \times 10^{-6}$ in the thawed state and $0.13\text{--}0.70 \times 10^{-6} \text{ m}^2/\text{sec}$ in the frozen state (see Table 1).

Several models have been developed to estimate the effect of porosity variations on the thermal conductivity and each of the models make different assumptions about particle shape. One of the challenges in the use of these models is that the fragments of the ash and pumice (scoria) are angular rather than spherical as is assumed in some models (Brailsford and Major, 1964). Heat flow in scoria is due both to conduction through the solids and to convection by water or air in the pore spaces. Heat conduction by water through the pore system in scoria, however, is a relatively minor factor in comparison to convection (Conner *et al.*, 1997).

The degree of saturation (S_r) is the generalized parameter used to interpret the thermal conductivity properties of deposits that have the same grain size distributions and is affected by water content, ice content, density, and porosity. The degree of saturation is calculated using the formula $S_r = W \cdot \rho_s / (e \cdot \rho_w)$ for unfrozen samples and the formula $S_r = (1,1W_{ic} + W_w) \cdot \rho_s / (e \cdot \rho_w)$ for frozen samples, where W_{ic} is the ice content, W_w is the unfrozen water content at a particular

temperature, e is the void ratio defined as $e = (\rho_s - \rho_d) / \rho_d$, ρ_s is the density of solid particles in g/cm^3 , ρ_d is the dry density in g/cm^3 , and ρ_w is the water density of 1 g/cm^3 (GOST25100-95, 1995; Andersland and Ladanyi, 2004; Trofinov *et al.*, 2005).

Heat flow in volcanic ash takes place mostly by conduction because the particle size is smaller than scoria and the water content becomes important. Increasing the value of S_r leads to an increase in thermal conductivity and thermal diffusivity in both unfrozen and frozen materials due to the replacement of low conductivity air with more conductive water and/or ice in the pores (Figure 2). A void ratio (e) increase leads to a decrease in the thermal conductivity. A two-fold increase in the S_r value for a material with the same porosity, however, leads to a two-fold increase in the thermal conductivity (Figure 3) (Kuznetsova *et al.*, 2012; Kuznetsova and Montenko, 2012).

Unfrozen water content

The engineering properties of frozen soils are temperature dependent between 0°C to -10°C , which is the temperature range where the phase composition of water (ice, water, and vapor) changes appreciably. All thermophysical processes in freezing and frozen soils are connected to some extent with the unfrozen water content. The effect of temperature on thermophysical processes is greater in soil types that contain large quantities of unfrozen water. Unfrozen water contents increase as particle size decreases, giving the order sand < silt < clay. The presence of unfrozen water in frozen soils is an integral part of frost heave theory, permafrost studies, and frozen ground engineering (Andersland and Ladanyi, 2004).

Unfrozen water was first identified by Bouyoucos (1917, 1921) and numerous different methods have been used since then to measure unfrozen water (Williams, 1964; Low *et al.*, 1968a, 1968b; Ershov *et al.*, 1978; Tice *et al.*, 1981; Smith and Tice, 1988; Yoshikawa and Overduin, 2005). Various empirical correlations of the unfrozen water content in wet soils with specific surface area, temperature, and soil physical properties have been reported in the literature (Fukuo and Ariga, 1967; Low *et al.*, 1968a, 1968b; Nakano and Brown, 1971; Anderson and Tice, 1973; Tice *et al.*, 1978; Lunardini, 1981; Civan, 2000; Yoskikawa and Overduin, 2005). Similar films of unfrozen water may play an important role in surface weathering of Martian rocks (Anderson *et al.*, 1967). The presence of unfrozen water films is an important factor in weakening rock/ice mixtures for a subtle climate sensitivity (Moore, 2014).

Numerous investigations have demonstrated that in addition to external influences, such as temperature, the main factors that determine the unfrozen water contents of frozen soils are: a) the specific surface areas of the solid phases in the soil systems, b) the chemical and mineralogical compositions of the soils, c) the nature of

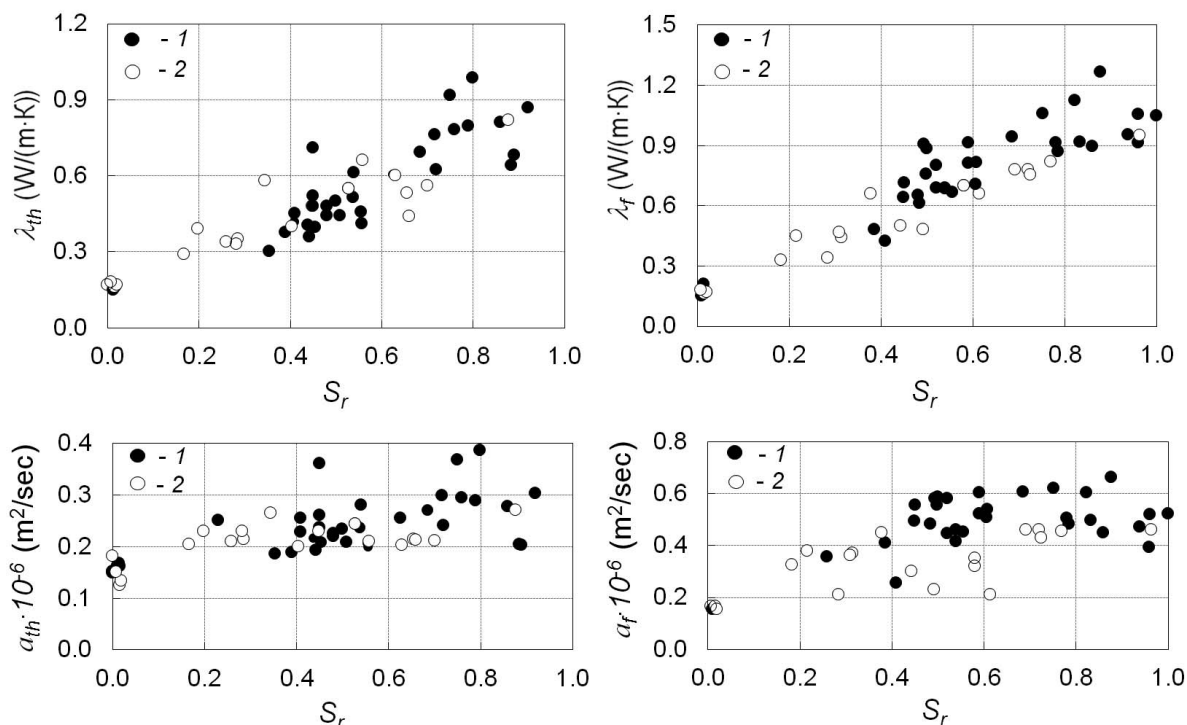


Figure 2. The dependence of the thermal conductivities (λ_{th} and λ_f) and thermal diffusivities (a_{th} and a_f) on the degree of saturation (S_r) for the thawed and frozen states: 1 – data for cinder and scoria, 2 – data for volcanic ash.

the exchange cations, and d) the contents and compositions of water soluble compounds (Nersesova and Tsytoch, 1963; Yershov and Williams, 2004). Data on the unfrozen water contents of frozen volcanic ash soils are published infrequently. Anderson and Tice (1973) and Smith and Tice (1988) mentioned volcanic ash soils among 17 other soils and showed a relationship between the dielectric constants and the volumetric unfrozen water contents. Akagawa and Fukuda (1991)

demonstrated using pulsed nuclear magnetic resonance (NMR) that the unfrozen water contents of the Ohya tuff depended on temperature over a measured temperature range below zero. Even at -5°C , the sample contained 7.5% unfrozen water by weight, which reflected the rough surface microstructure of the pores and the large specific surface area. For volcanic ash collected in Kamchatka and Iceland, the unfrozen water contents varied from 0 to 27% for temperatures below -3°C and

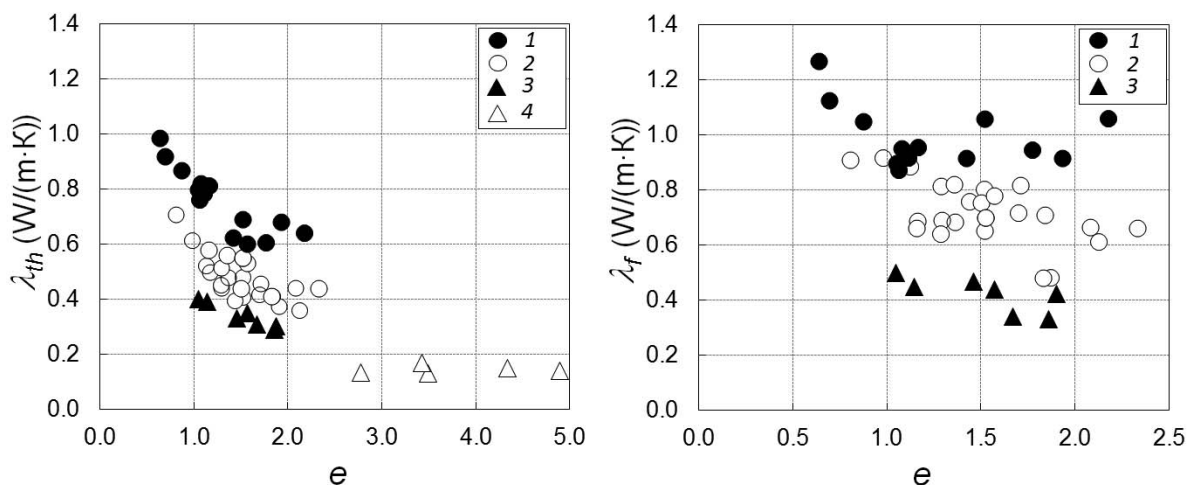


Figure 3. The thermal conductivities (λ) vs. the void ratios (e) in the thawed and frozen states for volcanic ash samples with different degrees of saturation (S_r): 1 – $S_r > 0.6$, 2 – $S_r = 0.4-0.6$, 3 – $S_r = 0.2-0.4$, and 4 – $S_r < 0.2$.

the amounts depended on the deposit age, chemical composition, salinity, amorphous clays, and the weathering conditions. The unfrozen water contents (W_w) were higher in volcanic ash samples that contained allophane ($W_w = 2\text{--}13\%$) than in ash samples that contained opal ($W_w = 0\text{--}3\%$). The highest proportion of unfrozen water (27%) occurred in an ash sample with a high soil water salinity (Kuznetsova, 2011; Kuznetsova and Motenko, 2014). For Icelandic samples that contain palagonite, which is the alteration product of basaltic glass found in association with sideromelane, the unfrozen water contents may reach 2–3% for temperatures below -3°C (Kuznetsova, 2011; Kuznetsova *et al.*, 2013). Palagonite is used as a terrestrial analog for the soils of Mars (Allen *et al.*, 1981) and studies on palagonite behavior at temperatures $<0^\circ\text{C}$ may be helpful in understanding weathering mechanisms. One of the weathering models used for Martian rocks suggested that a slow geochemical alteration occurs due to unfrozen water films, while thin ice layers can cover rock surfaces in winter (Allen *et al.*, 1981; Allen and Conca, 1981).

Influence of mineralogy on thermal properties and unfrozen water content

The sensitivity of permafrost and glaciers to energy and mass exchanges at the surface is controlled to a great extent by the thermal conductivity of the thin soil or debris layer that is exposed to seasonal freezing and thawing. The thermal offset between the average ground surface temperature and the ground temperature is directly related to the damping factor produced by the active layer. This damping factor combines the average thermal conductivities and thermal diffusivities in the active layer in the thawed and frozen states (λ_{th} , λ_f , a_{th} , a_f) as λ_f/λ_{th} or a_f/a_{th} (Osterkamp and Romanovsky, 1999). The thermal conductivity of water ($\lambda_w \approx 0.56 \text{ W}/(\text{m}\cdot\text{K})$) is approximately 4 times less than the thermal conductivity of ice ($\lambda_{ice} \approx 2.2 \text{ W}/(\text{m}\cdot\text{K})$); thus, the presence of unfrozen water at $<0^\circ\text{C}$ temperatures can make dramatic changes in all the physical properties of frozen ground. Various models of surface energy use thermal conductivity values in frozen and thawed states to predict heat transfer, freeze/thaw depth, permafrost/glacier stability, and to recover heat flux histories (Anisimov *et al.*, 1997; Hinzman *et al.*, 1998). In

addition, the thermal conductivity of soils depends on various factors, which include seasonal variations, mineralogical changes, unfrozen water content, and ice content.

Effect of volcanic glass alteration on thermal properties, ice, and unfrozen water content

A strong correlation between the unfrozen water content and the amorphous mineral content for a range of temperatures below zero was demonstrated in samples from Kamchatka (Kuznetsova and Motenko, 2014). For temperatures below -3°C where variations in unfrozen water content are not significant, the unfrozen water contents ranged from 2 to 11% for volcanic ash samples that contained allophane and from 0 to 3% for volcanic ash samples that contained opal. This correlation was related to the active surface area, which was higher for allophane ($800 \text{ m}^2/\text{g}$) than opal ($0.5 \text{ m}^2/\text{g}$) and to the presence of micropores in the allophane structure (Henmi and Wada, 1976; Theng *et al.*, 1982). The total water content of the soil sample (W) can be divided into two categories: unfrozen water, W_w , and ice, $W - W_w$. Due to the differences in the thermal conductivities of $0.56 \text{ W}/(\text{m}\cdot\text{K})$ for water and $2.2 \text{ W}/(\text{m}\cdot\text{K})$ for ice, changes in the ratio of unfrozen water to ice, $W_w/(W - W_w)$, directly affect the thermal conductivities of frozen soils. Just as the unfrozen water contents were correlated with the opal or allophane contents, a similar relationship was found between the thermal conductivities in the frozen state to the water/ice ratios and mineral formation. Five groups were distinguished that depended on (1) whether opal or allophane were present and (2) the unfrozen water contents at temperatures below -3°C (Figure 4, Table 2). In the volcanic ashes that contained opal (lines I and II, Figure 4), little unfrozen water was present and the water/ice ratio $W_w/(W - W_w)$ varied from 0 to 0.08. Line I (Figure 4) contains data for samples with almost no unfrozen water and line II (Figure 4) summarizes the data for samples with W_w values that ranged from 0.5 to 1.1%. In volcanic ashes that contained allophane (lines III, IV, and V in Figure 4), the unfrozen water contents ranged from 2 to 11% and the $W_w/(W - W_w)$ ratios varied from 0.08 to 0.58. In Figure 4, lines III, IV, and V contain the averaged data from samples with unfrozen water contents of 0.8–3%, 2–4 %, and 10–11%,

Table 2. The ratios of unfrozen water (W_w) to ice ($W - W_w$) contents at -10°C for ash samples that contain allophane and opal.

Group	$W_w/(W - W_w)$	Secondary mineral	W_w
I			$<0.5\%$
II	0–0.8	opal	0.5–1.1%
III			0.08–3%
IV	0.08–0.58	allophane	2–4%
V			10–11%

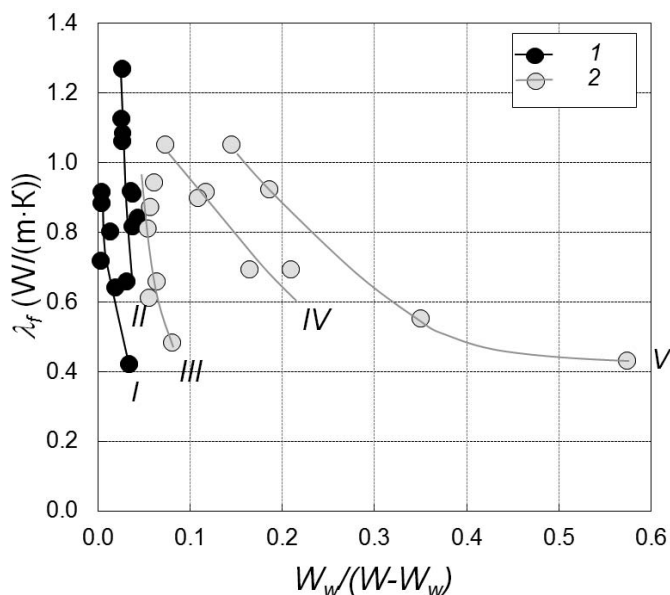


Figure 4. Thermal conductivities vs. the unfrozen water/ice ratios at -10°C . The lines plot the data for: (I) the (I and II) ash samples with opal and (2) the (III, IV and V) ash samples with allophane at the unfrozen water contents of I – $W_w < 0.5\%$, II – $0.5 < W_w < 1.1\%$, III – $0.8 < W_w < 3$, IV – $2 < W_w < 4$, and V – $W_w = 10-11\%$ (Kuznetsova and Motenko, 2014).

respectively. For example, in volcanic ash samples that contained opal, a small change in the water/ice ratio $W_w/(W-W_w)$ from 0.02 to 0.04 decreased thermal conductivity by a factor of 2. For volcanic ash samples that contained allophane, thermal conductivity decreased by a factor of 3 due to the greater variation of 0.19 to 0.58 in the water/ice ratios. The thermal conductivity and thermal diffusivity ratios in the frozen and unfrozen states (λ_{th}/λ_f , a_{th}/a_f) control the thermal offsets between the average ground surface temperature and the ground

temperature by regulating the damping factor of the active layer. The dependence of λ_f/λ_{th} and a_f/a_{th} ratios on water content were grouped into three curves: curve 1 approximates data for volcanic ash samples that contained opal, curve 2 for samples that contained both opal and allophane, and curve 3 for samples that contained only allophane (Figure 5). The slopes of the curves are defined by the correlations between the thermal conductivities and the water/ice ratios from Figure 4: curve 1 corresponds to lines I and II

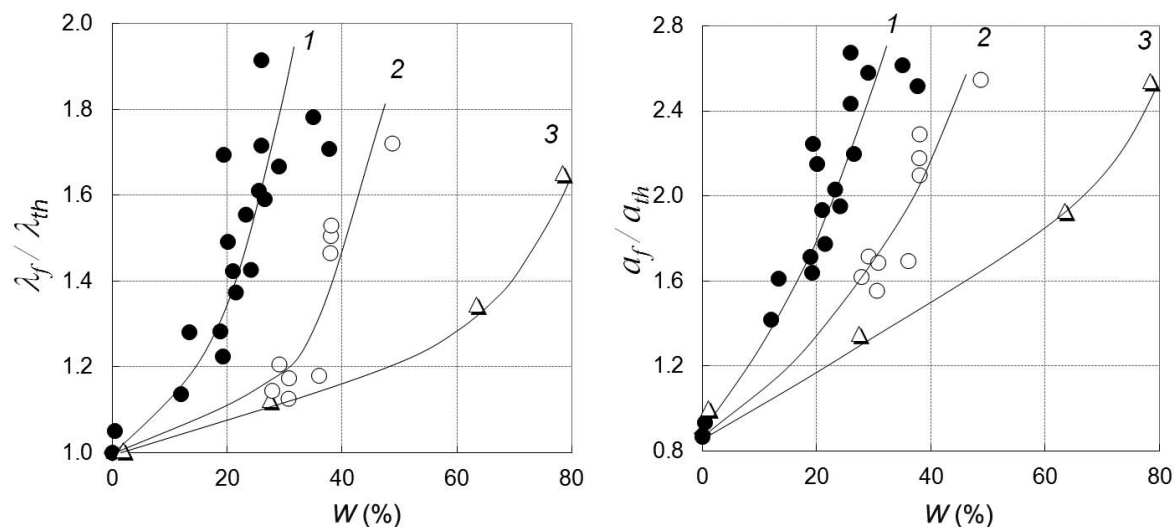


Figure 5. Plots of the thermal conductivity ratios λ_f/λ_{th} and the thermal diffusivity ratios a_f/a_{th} of volcanic ash samples in the frozen and thawed states vs. the water contents. The lines show the data for: 1 – volcanic ash with opal, 2 – volcanic ash with both opal and allophane, and 3 – volcanic ash samples with only allophane.

($W_w < 3\%$); curve 2 corresponds to lines III and IV ($W_w = 2\text{--}4\%$); and curve 3 corresponds to line V ($W_w = 10\text{--}11\%$).

Effect of altitude on the unfrozen water contents of layers that seasonally freeze and thaw

Altitude related patterns in volcanic ash sample properties have been described, such as volcanic glass alteration and unfrozen water contents (Kuznetsova and Motenko, 2014). Four distinct altitude groups were reported, two were associated with the high altitude of zone Z_1 (1600 m), zone Z_2 (1000–1300 m), zone Z_3 (700–800 m), and zone Z_4 (290 m) (Figure 6).

Zone Z_1 . The volcanic ash samples had a similar age of around 1500 years old and were collected from the tundra zone at an altitude of 1600 m where permafrost is widespread. Three samples were from the seasonal melting layer (the active layer) at the top of the soil where cryogenic weathering plays an important role. These samples have experienced radical temperature fluctuations with repeated freezing and thawing cycles that have been a controlling factor in composition and structural changes which occurred in this layer. All the samples were characterized by andesitic glass, were associated with allophane, and contained various amounts of unfrozen water. These samples varied in color and grain size distribution. The sample with the highest unfrozen water content was collected from just above the existing freeze/thaw boundary and had been most affected by freeze/thaw cycles. The sample with the lowest unfrozen water content was collected from a borehole in the permafrost and had been permanently frozen. Two other samples were collected from the upper part of the active layer where the temperature does not alternate from warm to freezing during the warm season.

Zone Z_2 . This group of samples were collected from the tundra zone at an altitude of 1000–1300 m. The age of the volcanic ash samples was nearly 35 years. The glass from three of the samples was of rhyolitic composition and was associated with opal, but one sample had a basaltic composition and was associated with allophane. The unfrozen water content was low (0–0.5%).

Zone Z_3 . These samples were collected from an altitude of 700–800 m from an area within the tundra zone with seasonal permafrost. The glass composition was either (1) rhyolitic and associated with opal, (2) andesitic and associated with allophane, or (3) basaltic and associated with allophane (Kuznetsova and Motenko, 2014). Correlations between the unfrozen water contents, sample age, and allophane or opal presence were observed with unfrozen water contents that tended to be higher in the older samples or in samples that contained allophane.

Zone Z_4 . These samples were collected from an altitude of 290 m within the upper part of the forest zone, where only seasonal freezing has taken place. The highest unfrozen water content was associated with samples with andesitic glass that contained allophane and the lowest unfrozen water content was associated with rhyolitic glass that contained opal. The highest unfrozen water content was found in the first and last elevation groups (Z_1 and Z_4) in samples that contained allophane. The main feature of the first group was that all samples were in a seasonal thawing layer and in permafrost. The ages of the samples were around 1500 years. A distinctive feature of group Z_4 was that it contained the oldest deposits among the investigated samples (6000–9000 years old) and it occurred in the forest zone with warmer annual temperatures. This suggests that the seasonal freeze/thaw cycles in permafrost areas lead to a more rapid alteration of volcanic glass and, thus, to an increased unfrozen water content.

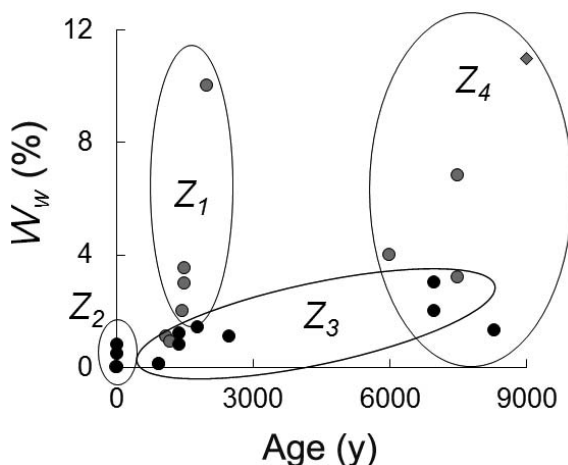


Figure 6. Plots of the unfrozen water contents vs. the sample ages. The zones indicated by the ellipses group samples based on altitude: Z_1 – 1600 m, Z_2 – 1000–1300 m, Z_3 – 700–800 m, and Z_4 – 290 m (Kuznetsova and Motenko, 2014).

Weathering aspects of volcanic glass in cold climates

The glass fraction in volcanic ejecta is the most readily altered silicate component (Parfitt *et al.*, 1983; Shoji *et al.*, 1993), which makes it a potentially sensitive indicator of climate as long as the alteration environment is identified and the time framework when alteration occurred can be deduced. The rate of volcanic ash weathering or subsurface alteration depends not only on the glass chemistry, but more importantly on temperature and water availability. At subzero temperatures in heavily frozen ground, the decomposition rate of glass is minimal, which reflects the very slow rates of chemical reactions as well as the lack of free water. In topographically varied terrains, the situation is complicated. In areas with a mean annual temperature (MAT) below -1°C and a mean annual precipitation (MAP) of <500 mm, clay minerals in volcanic soils are scarce (Table 3) and the volcanic glass

Table 3. Selected characteristics of volcanic materials from cold volcanic regions.

Location	Climate	MAP (mm)	MAT (°C)	Source of the material	Deposit age	Clay formation	Vegetation zone	Literature reference
<i>Permafrost area</i>								
Kamchatka	Humid cold	500–1000	>–1 (1000–1500 m) –2...–8 (1500–3000 m)	Kamchatka	Holocene, Early Pleistocene	Allophane, little evidence	Tundra, forest	(Abramov <i>et al.</i> , 2008; Kuznetsova and Motenko, 2014)
Yukon, Canada	Cold dry	350	–5	Mt. Bon, Alaska	1200 B.P.	Allophane, little evidence	Boreal/subarctic Forest	(Smith <i>et al.</i> , 1999; Robinson and Moore, 2000)
Dry valleys, Antarctica	Cold-desert hyperarid	45–100	–20 ... –35	Alkali volcanoes of Erebus Volcanic Province	Miocene, Pliocene	<5%	–	(Marchant <i>et al.</i> , 1993; Marchant & Denton, 1996; Marchant <i>et al.</i> , 1996)
<i>Seasonal frozen ground</i>								
Commander Islands	Humid cold	470	2.1	Kamchatka	Holocene	Allophane	Tundra	(Shoba and Ivanov, 2011; Ivanov <i>et al.</i> , 2014)
Iceland	Humid cold to low arctic	500–2000	2–5	Iceland	Holocene	Palagonite, allophane, imogolite, ferrhydrite.	Tundra, forest	(Farbrót <i>et al.</i> , 2007; Kellerer-Pirkbauer <i>et al.</i> , 2007; Arnalds, 2008; Sigfusson <i>et al.</i> , 2008; Stoops <i>et al.</i> , 2008)
Mt. Cotacachi, Ecuador	High-altitude	900 (2500 m) 1500 (4000 m)	~3 (4400 m) ~15 (2400 m)	Volcano Cotacachi, Ecuador	Holocene	Allophane (soils at elevations 3200–4050 m) Halloysite (below 2700 m)	Tundra, forest	(Zehetner <i>et al.</i> , 2003; Zehetner and Miller, 2006)
Towada, Japan	Humid, cold	>1800 (900–1400 m) 1200–1800 (400–900 m) 1000–1200 (400 m)	7–9 (900–1400 m) 9–11 (<900 m)	Japan	1000–2000 year	Allophane, imogolite, 2:1 layer silicates	Subalpine, montane, forest	(Wada, 1987; Ugolini and Dahlgren, 1991)
New Zealand	Humid	200–14000	3.7–13.8		Up to 50,000 years			(Dixon <i>et al.</i> , 2016)

is mostly preserved in the unaltered state. With a higher MAT, the alteration rate of volcanic glass increases and leads to the development of amorphous clays, such as allophane, immogolite, and palagonite. Parfitt *et al.* (1983) proposed a weathering pattern for rhyolitic glass, where halloysite is the dominant clay mineral in areas with MAPs <1500 mm and allophane dominates at MAPs >1500 mm. At high elevations, the higher rainfall and less evaporation due to lower temperatures creates a strong leaching environment and amorphous clays dominate the colloidal fractions of these volcanic soils with no halloysite. In the mountains of northern Ecuador, allophane is dominant in the colloidal fraction of volcanic soils above 3200 m, whereas allophane is absent at <2410 m where precipitation is higher. In the drier conditions of soils at intermediate elevations (3200–2700 m), allophane is found in smaller quantities, and in soils at <2700 m halloysite is often dominant in the fine fraction (Zehetner *et al.*, 2003). Similar slow rates of glass weathering are associated with cold or hot and dry deserts because the absence of available water for weathering reactions is the controlling factor. Still, the repeated heating and cooling in frozen and hot deserts, however, accelerates physical weathering by fracturing volcanic glass, which thereby increases the surface area available for chemical alteration. In contrast, the alteration of volcanic glass in warm or hot humid climates is rapid. Not only are these reactions easier to study, but the reactions are also associated with agriculturally important soils and much greater economic pressure is applied to understand these soils. Within the warm humid zones and depending on the chemical composition of the volcanic glass, the following reaction series have been suggested (Shoji and Masui, 1971; Nagasawa, 1978; Parfitt and Wilson, 1985; Wada, 1987; Parfitt, 1990; Stoops *et al.*, 2008):

volcanic glass → allophane → halloysite
 volcanic glass → opal → allophane → halloysite
 volcanic glass (sideromelane) → palagonite

The most obvious academic use for understanding the factors that control the alteration of volcanic ash is the ability to use it to reconstruct past climates and the weathering environments of the more recent geological past. More immediately, however, it has important roles to play in predicting (1) the effects of volcanic glass alteration on the regional stability of landscapes in relation to long and short term climate change and (2) help in the geological exploration of Mars.

Kamchatka Peninsula, Far East of Russia

The Kamchatka Peninsula is a cold region with a rugged topography that contains numerous recent and extinct volcanoes over a large range of altitudes (580–4800 m), which had been a research focus long before the recent interest of society in global warming and the possible side effects. On the Kamchatka

Peninsula, the conditions are ideal to study the interplay between the weathering regime of volcanic ash (the dominant detritus) in permanently and temporarily frozen ground and the effects of various altitudes, local climatic conditions, and vegetative covers within a chronostratigraphic framework based on the radiometric dates of widespread ash falls. Research in the Kamchatka Peninsula started in the early 1960's and for the next 20 years much discussion and uncertainty ensued regarding the nature and the origin of the <5 μm fraction of volcanic ash samples. Gushchenko (1965), who worked on ashes from northern Kamchatka, concluded that (1) intensive processes of secondary mineral formation were ongoing and were mostly associated with the volcanic glass and (2) volcanic ash samples with halloysite and kaolin clay contents >80% in the <0.01 mm fraction had ages >3000 years. Braitseva *et al.* (1968) examined ancient volcanic ash deposits in the Central Kamchatka Depression and reported the absence of secondary minerals. Geptner and Ponomareva (1979) conducted thermal studies of the <0.01 and <0.001 mm fractions of volcanic ash and demonstrated that isotropic materials that had most likely formed from volcanic glass were present, but the samples contained no clay minerals. Markin (1980) conducted a thermal study of ash samples collected north of the Kluchevskaya volcano group using differential thermal analysis (DTA). Samples were taken from 0.3 m below the surface to a depth of 8 m. The radiometric ages of the oldest samples were >8500 years. The thermal analysis curves showed the presence of organic matter, but no endothermic characteristics of clay minerals (Markin, 1980). Almost 45 years later (Kuznetsova *et al.*, 2011; Kuznetsova and Motenko, 2014), infrared (IR) spectroscopic studies of volcanic ash were carried out on samples collected in Northern and Central Kamchatka. These volcanic ash samples had two amorphous phases, opal and allophane, as the products of volcanic glass alteration. Allophane is similar to some layer silicates in regard to the chemical composition and structure. Thermal analysis curves did not show the presence of clay minerals. At the present time, the oldest quaternary deposits found in Kamchatka are exposed in the banks of the Kamchatka River in Central Kamchatka. These deposits are referred to by the general term “blue clays” and consist mostly of pelitomorphous clay materials, diatom fragments, carbonaceous dust, and scraps of plant and pyroclastic materials. These deposits are of Lower Pleistocene age. Within these deposits are seams of a white vitroclastic ash that occurs at many locations in the banks of the river. Kuprina (1970) investigated volcanic ash collected from the “Polovinka” bank, where about 60% of the material consisted of volcanic glass fragments that ranged in size from 0.25 to 0.01 mm and contained 33% halloysite with an index of refraction in oriented units of 1.514 ± 0.002 . X-ray diffraction patterns of the

<0.001 mm fraction showed hydrated halloysite, meta-halloysite, and a mixture of feldspars. Thermogravimetric analysis proved that the clay material was halloysite. Rengarten and Kuprina (1968) believed that the halloysite was formed diagenetically during partial decomposition of the ash material. In contrast, mineralogical analyses of a volcanic ash layer in “blue clays” collected from the “Krutoy” river bank indicated only opaline silica and no clay minerals (Kuznetsova and Motenko, 2014). According to Kiryanov (1981), the volcanic ash in the “blue clays” is rhyolitic and consists of 97% volcanic glass and 3% plagioclase.

Analog for Martian soils.

The surface temperature of Mars averages about -63°C , water is absent, and the atmospheric pressure is considerably lower than on Earth (Carr, 2007). Volcanic ash appears to be widespread on Mars and understanding the manner and rate of ash alteration is an important aspect in interpreting the surface geology as well as in facilitating future robotic exploration. Gooding and Keil (1978) suggested that Martian rock alteration must depend on relatively inefficient mechanisms, such as solid/gas reactions, that are much less efficient than the solid/water reactions on Earth. The best Earth surface analogs for Martian conditions are the Dry Valleys of Antarctica, where some Miocene and Pliocene ash deposits are 15 million years old and yet still contain <5% clay (Marchant *et al.*, 1993, 1996). Allen *et al.* (1981) and Allen and Conca (1991) suggested that localized heating on Mars by volcanism or by impacts have set off hydrothermal reactions between water and rocks to develop clay minerals. A terrestrial analog on Earth of the alteration products of Martian basaltic glass is ‘palagonite,’ a complex and variable material that apparently consists of poorly crystallized phyllosilicates (smectite group or mixed layer clays). Points of resemblance between the two materials include the bulk chemical composition, particle size, reflectance spectra, and magnetic properties (Allen *et al.*, 1981). Visible and near IR spectra of the Mars landing sites were well matched by an Fe-rich palagonite, a clay like material produced by the weathering of volcanic soils (McCord *et al.*, 1982; Singer, 1982).

CONCLUSIONS

Many numerical models used to investigate and predict the evolution of cold regions as a result of changes in climate lack accurate data on thermal properties, such as thermal conductivity, heat capacity, and thermal diffusivity of the soil or debris layers that are involved. Because of the angular shape of the fragments that make up volcanic ash and scoria, it is not appropriate to use existing models to estimate the bulk thermal conductivity. The lack of experimental data on

the thermal conductivity of volcanic deposits hinders the development of realistic models. Many factors, such as water content, dry density, porosity, unfrozen water content, mineral composition, and volcanic ash weathering state affect the thermal conductivity and thermal diffusivity values in both the frozen and thawed states. Knowledge of the thermal properties of volcanic ash layers that cover permafrost and glacier slopes is essential to understand and predict the effects of layer thickness on permafrost aggradation/degradation, ice melting, and glacier ablation rates. The decreased thermal conductivity of volcanic ash in the frozen state is associated with the development and presence of unfrozen water films that can have a direct mechanical impact on the movement or slippage between ice and mineral particles and, thus, change the stress transfer. This becomes particularly significant during periods of climate change when increased temperatures and the associated melting could weaken polythermal glaciers, affect areas with warm and discontinuous permafrost, and induce ice or land movements. These changes could perhaps occur on a catastrophic scale. Future research should focus on developing a new model to calculate the thermal properties of volcanic materials that is based on not only porosity, but also on other parameters, such as water content, density, the mineralogical composition of amorphous phases, and unfrozen water content. Until the development of a new model has been achieved, one must be circumspect about any predictions made about the stability of the very large areas of Earth that are covered by snow and/or ice and/or permafrost and that are also affected by volcanic ash.

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