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Arsenic Mobility and Compositional Variability in High-Silica Ash Flow Tuffs

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by

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ABSTRACT

Volcanic rocks typically have only low to moderate arsenic concentrations, none-the-less, elevated levels of arsenic in ground waters have been associated with pyroclastic and volcaniclastic rocks and sediments in many parts of the world. The potential for arsenic leaching from these deposits is particularly problematic as they often comprise important water-bearing units in volcanic terrains. However, the role that chemical and mineralogical variations play in controlling the occurrence and mobility of arsenic from pyroclastic rocks is largely unexplored.

This study uses chemical and X-ray diffraction data to characterize and classify 49 samples of ash-flow tuffs, and 11 samples of tuffaceous sediments. The samples exhibit a range of devitrification and chemical weathering. Total and partial digestion, and water extractions of samples are used to determine the total, environmentally available, and readily leachable fractions of arsenic present in all tuff samples. Leaching experiments were also performed with buffered solutions to determine the influence of elevated pH levels on arsenic mobility.

The 49 tuff samples have a mean arsenic content of 7.5 mg kg^{-1}, a geometric mean arsenic content of 4.8 mg kg^{-1}, a median arsenic content of 5.2 mg kg^{-1}, and a maximum arsenic concentration of 81 mg kg^{-1}. The mean and median values are 2.8 – 4.4x the average crustal abundance of 1.7 mg kg^{-1} (Wedepohl, 1995), and consistent with previously reported values for volcanic glasses and felsic volcanic rocks (Onishi and Sandell, 1955; Wedepohl, 1995), although the maximum arsenic content is higher than

previously reported (e.g., Casentini et al., 2010; Fiantis et al., 2010; Nobel et al., 2004). In addition, the arsenic concentrations of tuffs were found to be highly heterogenous, both between and within individual units, and in some cases, individual outcrops.

Results of whole rock and leachate analyses indicate that there is no significant difference in the total arsenic content of tuffs as a result of devitrification or weathering, but both devitrified and weathered tuffs contain higher levels of environmentally available arsenic than unweathered glassy tuffs. Glassy tuffs did not produce any readily leachable arsenic, while individual devitrified and weathered tuffs both generated aqueous concentrations that exceeded regulatory limits after 18 hours. Leaching of weathered tuffs produced higher levels of arsenic at high (~9-11) pH than in tests conducted at circum-neutral pH. Devitrified and glassy tuffs showed no increase in leachable arsenic with increasing pH.

The results of this study indicate that devitrification and weathering processes determine the host phases, degree of adsorption, and overall mobility of arsenic from ash-flow tuffs. Tuffs that have undergone different types of alteration are likely to have different host phases of arsenic, and different mechanisms that mobilize arsenic into the environment. Potential host phases and mobility mechanisms are discussed, and a conceptual model of arsenic behavior in ash-flow tuffs is proposed.

ACKNOWLEDGMENTS

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CHAPTER 1: INTRODUCTION AND BACKGROUND

INTRODUCTION

The occurrence of groundwater containing elevated arsenic concentrations has emerged as a major health concern throughout the world. Arsenic is known to cause cancer of the skin, bladder, and lungs, damage to the circulatory and nervous systems, hypertension, and diabetes (Brown and Ross, 2002; Ng et al., 2003). Arsenic levels exceeding the World Health Organization Maximum Contaminant Level (MCL) of 50 μg/L occur in many locations worldwide including Bangladesh, India, Cambodia, Argentina, the United States, Hungary, and China, among others, and is likely to occur in additional regions where reliable data regarding drinking water is currently unavailable (Amini et al., 2008). Within the United States, where approximately half the population depends on groundwater sources for drinking water, arsenic concentrations exceeding the Environmental Protection Agency MCL of 10 μg/L are found in 5-11% of groundwater sourced drinking water systems (Ryker, 2003).

Elevated arsenic concentrations in drinking water supplies in several locations within the United States, Argentina, Greece, Turkey, Chile and Italy have been associated with volcanic rocks and ash-flow tuffs (Casentini et al., 2010; Johannesson and Tang, 2009; Welch et al., 2000). Proximity to volcanic rocks has been found to be statistically predictive of arsenic contamination of water supplies (Amini et al., 2008). Felsic tuffs have been identified as primary hydrologic units in ~25% of the regions in the United States known to contain high groundwater arsenic levels and in at least one case, dissolution of volcanic glass has been identified as the primary geochemical source of arsenic in groundwater (Johannesson and Tang, 2009; Welch et al., 2000). Several studies have identified volcanic tuffs or tuffaceous sediments as the source of groundwater arsenic in the southern Willamette Valley of Oregon (Goldblatt et al., 1963; Hinkle and Polette, 1999; Nadakavukaren et al., 1984; Whanger et al., 1977).

Despite the widespread association of elevated groundwater arsenic levels with ash-flow tuffs, the mechanisms of arsenic release and the role that compositional variations play in the mobility of arsenic is largely unexplored in the literature. Tuffs vary considerably in composition and can experience both high- and low-temperature alteration, the degree of which can vary considerably, even within a single unit. The goal of my study is to quantify the degree to which chemical composition, devitrification, and low-temperature alteration control the mobility of arsenic and other trace elements from high-silica (> 70% SiO_2) ash-flow tuffs under varying environmental conditions. Developing a better understanding of arsenic-mineral associations in tuffs and identifying the characteristics and conditions that promote high dissolved arsenic concentrations will improve the predictive modeling of arsenic behavior in volcanic terrain and aid in the identification of aquifers that are likely to yield high arsenic groundwaters.

BACKGROUND

Arsenic Geochemistry

Arsenic in groundwater exists primarily as As(III) or As(V). The arsenic species present is dependent of the pH and redox conditions of the specific water systems in question (Figure 1).

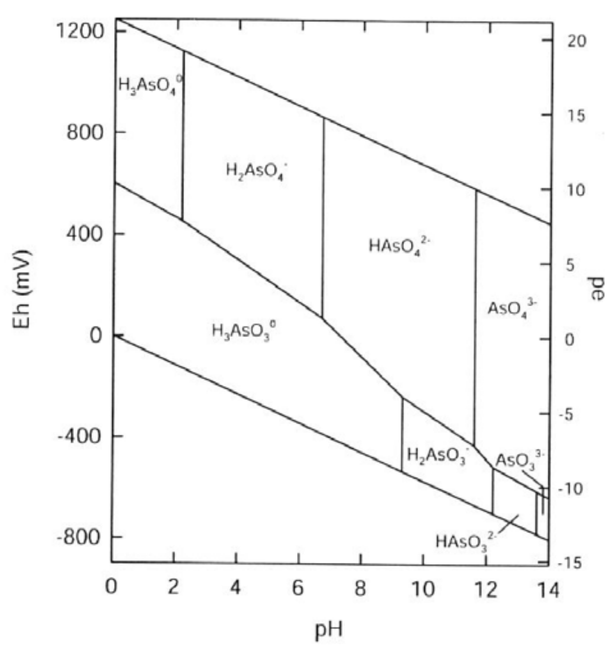

Figure 1. Eh-pH diagram for aqueous arsenic species at 25ºC and 1 bar pressure, from (Smedley and Kinniburgh, 2002).

Under circum-neutral pH, arsenate occurs primarily as $HAsO_4^{-2}$ or $H_2AsO_4^-$ and is the dominant form of arsenic in oxidizing environments, while arsenite occurs predominantly as $H_3AsO_3^0$ and is the dominant form under reducing conditions. Both oxidation states are commonly found in natural water systems (Cullen and Reimer, 1989; Welch et al., 2000). The occurrence of arsenate as an oxyanion contributes to its mobility at pH values typically found in groundwaters. Most toxic trace metals occur as cations which have limited mobility at circumneutral pH due to the tendency of cations to become more strongly sorbed as pH increases (Smedley and Kinniburgh, 2002). In contrast, toxic trace elements that occur as oxyanions become less strongly sorbed as pH increases.

Redox Behavior of Arsenic

The speciation of arsenic is controlled by redox conditions and plays a major role in arsenic mobility mechanisms. As(III) is thermodynamically unstable in aerobic conditions, but the oxidation process proceeds slowly, with a half life of one to three years, unless mediated by microbial action (Rhine et al., 2008; Stollenwerk, 2003). The rate of oxidation under atmospheric conditions has also been observed to increase at pH > 9 (Manning and Goldberg, 1997). In contrast, the reduction of As(V) to As(III) proceeds rapidly under both biotic and abiotic conditions (Stollenwerk, 2003).

Redox conditions also influence the mobility of arsenic by affecting arsenic bearing minerals, and major sorbents of arsenic. Arsenic is frequently hosted in sulfide minerals, and Fe-oxides and oxyhydroxides are a major sorbent of arsenic. Reduction of Fe(III) present primarily as oxides and oxyhydroxides to Fe(II) present primarily as free cations, and oxidation of sulfide minerals are both processes associated with arsenic contamination of groundwater systems. Fe(III) reduction occurs after the reduction of O_2, NO_3^-, and MnO_2, at an Eh close to 0 mV, and before the reduction of As(V) and SO_4^{2-} (Langmuir, 1997; Smedley and Kinniburgh, 2002).

SORPTION BEHAVIOR OF ARSENIC

Sorption and coprecipitation processes are the primary mechanisms controlling the mobility of dissolved arsenic in natural waters (Dixit and Hering, 2003; Welch et al., 2000). Adsorption processes are controlled by aquifer mineralogy, arsenic concentrations and speciation, pH, and concentrations of competing anions (Stollenwerk, 2003). Adsorption of arsenic is positively correlated with the Fe- and Al-oxide and clay content of aquifer solids, and these minerals act as the primary sorbents of arsenic, although solid organic matter and carbonate minerals may act as sorbents as well (Goldberg, 2002; Stollenwerk, 2003).

Common Sorbents

Iron, aluminum, and manganese oxides are the most prevalent sorbents for arsenic in aquifer sediments, occurring both as discrete particles and as coatings on other mineral surfaces (Stollenwerk, 2003; Welch et al., 2000). Iron oxides and oxyhydroxides are the most abundant sorbent in aquifer solids, and occur in varying compositions and degrees of crystallinity including hydrous ferric oxides (HFO), goethite, and magnetite (Dixit and Hering, 2003; Jang and Dempsey, 2008). Poorly crystalline oxyhydroxides that form by precipitation of Fe(III) from solution have the highest sorption capacity due to the decrease in surface area and surface complexation sites as the degree of crystallinity increases (Stollenwerk, 2003). Aluminum oxides and oxyhydroxides are structurally similar to Fe minerals and display similar sorption capacity and behavior for arsenic but are generally less abundant in aquifer solids (Stollenwerk, 2003) .

Clay minerals are another potential sorbent of arsenic. Kaolinite, illite, chlorite, and halloysite have all been observed to sorb both As(III) and As(V) (Stollenwerk, 2003). Overall clay minerals have negative surface charges, but surface metal cations at the edges of particles, most commonly aluminum, have the capacity to form surface complexes with arsenic (Davis and Kent, 1990). The dependence of arsenic sorption on Al-OH sites at clay mineral edges results in some similar responses of clay minerals and aluminum oxides to geochemical parameters including pH (Stollenwerk, 2003). One major area where clay minerals differ from each other and aluminum oxide minerals is in the concentration of sorption sites. Kaolinite has been observed to adsorb greater amounts of arsenic than equal amounts of illite and montmorillonite with larger surface areas, indicating that the number of sorption sites of a specific clay mineral plays a larger role than surface area (Manning and Goldberg, 1996).

pH Dependence

For all potential adsorbents the sorption of arsenic is pH dependent. For Fe oxide minerals, sorption of As(V) is highest at low pH and begins declining near pH 4 while sorption of As(III) increases to a maximum at circum-neutral pH conditions (pH 5 to 9), decreasing under alkaline conditions (Figure 2) (Dixit and Hering, 2003). Both aluminum oxides and clay minerals display similar sorption patterns with respect to pH, with As(V) declining with increasing pH and As(III) reaching a maximum at circum-neutral pH (Goldberg, 2002). When both As(III) and As(V) are present in a system, the sorption behavior of As(V) is largely unchanged, while As(III) increases until it reaches a maximum at pH 10 for Fe-oxides, and then rapidly decreases (Jang and Dempsey, 2008).

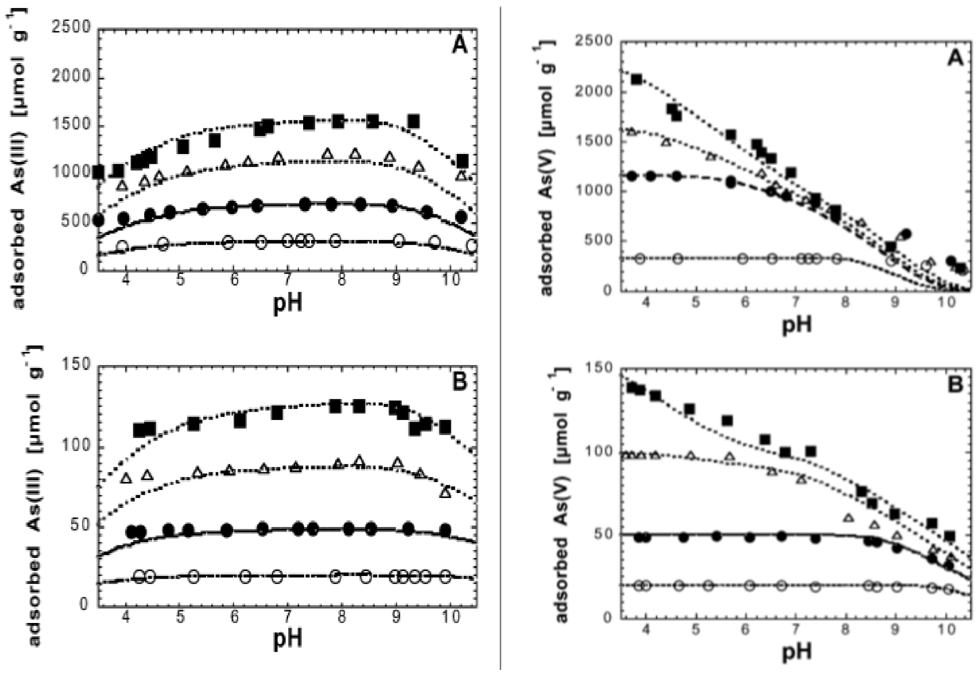

Figure 2. Adsorption of arsenate and arsenite onto A) amorphous iron oxide and B) goethite as a function of pH. Arsenic concentrations range from 100 μM (■) to 10 μM (○). From Dixit & Hering (2003).

Competing Anions

Competing anions, chiefly phosphate, can decrease the adsorption of arsenic. The influence of phosphate on arsenic sorption is well documented, and elevated arsenic concentrations are correlated with high phosphate concentrations in a number of locations throughout the world (Dixit and Hering, 2003; Welch et al., 2000). Phosphate will decrease the adsorption of both As(V) and As(III), but a higher degree of similarity between P(V) and As(V) results in more effective competition with As(V) (Stollenwerk, 2003). Competition with phosphate will decrease the adsorption of As(V) over the full pH range, while phosphate primarily decreases the adsorption of As(III) at pH < 9 (Jain and Loeppert, 2000).

Silicic acid is a less effective competitor than phosphate, but is known to compete with arsenic for sorption sites at pH values greater than 8 (Dixit and Hering, 2003; Stollenwerk, 2003). Dissolved organic matter (DOC) may also compete with arsenic for sorption sites. In sufficient quantities, DOC, chiefly humic and fulvic acids, may cause oxyhydroxides to which arsenic is adsorbed to dissolve. However, high DOC concentrations tend to occur in reduced waters so these effects likely would impact only adsorbed As(III) (Ravenscroft et al., 2009).

Reducing Groundwater Systems

Arsenic contamination of reducing groundwater systems is known to occur in Bangladesh, Taiwan, Vietnam, and Hungary and Romania (Ravenscroft et al., 2009; Smedley and Kinniburgh, 2002). In all of these locations the contaminated aquifers are composed of Quaternary sedimentary deposits containing high proportions of organic matter, with waters characterized by high Fe, Mn, and NH_4 concentrations (Smedley and Kinniburgh, 2002). The primary geochemical trigger for arsenic mobility in these reducing environments is reductive dissolution of Fe-oxides that act as a sink for arsenic. As Fe^{3+} that comprises the oxides and oxyhydroxides is reduced to Fe^{2+} both crystalline and amorphous forms of Fe oxide minerals dissolve, releasing any adsorbed or coprecipitated arsenic (Ravenscroft et al., 2009; Welch et al., 2000). During the process of dissolution arsenic may be released and immediately readsorbed to the residual oxide surfaces, preventing arsenic contamination until all or most of the Fe-oxides are reduced (Ravenscroft et al., 2009). In environments with exceptionally high organic matter concentrations, such as Bangladesh, elevated phosphate concentrations are found as well, which may contribute to the mobilization of arsenic adsorbed to clays or aluminum oxides.

Oxidizing Groundwater Systems

Arsenic contamination of oxidizing groundwater systems is known to occur in Italy, Argentina, Chile, Mexico, and the Southwestern United States (Casentini et al., 2010; Smedley and Kinniburgh, 2002; Welch et al., 2000). These environments are frequently, but not always, arid, and the groundwater systems are characterized by high pH, and often high salinity and elevated F or B concentrations (Smedley and Kinniburgh, 2002). The geology of these aquifers is more variable than contaminated aquifers with reducing groundwater systems, and include volcanic rocks and sediments as well as alluvial sediments (Smedley and Kinniburgh, 2002). In oxidizing environments the primary geochemical trigger for mobilizing arsenic is alkali desorption, which describes the tendency of As(V) to desorb as pH increases in alkaline oxic waters (Ravenscroft et al., 2009). The occurrence of alkali desorption in arid environments and the presence of high salinity in many waters contaminated by alkali desorption indicates that it may operate in conjunction with evaporative concentration of arsenic in some environments, with evaporation increasing the concentrations of arsenic and the alkalinity of these waters.

Chemical and Mineralogical Variations in Ash-Flow Tuffs

Although elevated arsenic levels in groundwaters have often been associated with ash-flow tuffs, there has been little investigation in the role that variations in tuffs may play in either the occurrence or mobility of arsenic from these units. Compositional variations in high-silica ash-flow tuffs can be divided into three primary categories: chemical variations in the source material, high-temperature alteration that occurs immediately after deposition, and low temperature alteration to zeolites and clays. Unaltered ash-flow tuffs display the same range of compositional variation found in high-silica igneous rocks, but for the purposes of this project the primary variation investigated will be the Al/(Na_2O+K_2O) ratio. Peralkaline (e.g. low Al/ (Na_2O+K_2O)) ash-flow tuffs have been observed to weather at higher rates than tuffs with higher Al/ (Na_2O+K_2O) ratios and equal SiO_2 concentrations (Streck, M., personal communication). Both alkali and aluminum content are likely to play a role in weathering and arsenic mobility, since aluminum is necessary for the formation of low temperature alteration products, and the release of alkalis will influence the pH of groundwaters in peralkaline tuff units.

High-temperature alteration processes that occur immediately after deposition of an ash-flow tuff include devitrification and vapor phase alteration. Devitrification occurs during slow cooling within the interior of thick tuffs deposited at high temperatures, resulting in the glassy ash and pumice particles crystallizing into fine-grained feldspars, primarily sanidine, and other silica minerals including cristobalite, quartz and tridymite (Ross and Smith, 1980; Vaniman, 2006). Vapor-phase alteration is distinguished from devitrification in that it occurs primarily in pore spaces rather than within individual glass particles and will often result in larger crystals (Ross and Smith, 1980). Vapor-phase alteration produces the same primary minerals as devitrification, but can also include a wide variety of minor minerals that can incorporate elements expelled from glass particles during devitrification (Vaniman, 2006). High temperature alteration processes typically occur in the interior of individual cooling units, and produce distinct zonation within the body of the tuff (Figure 3). Element mobility during high-temperature alteration of peralkaline silicic lavas occurs during crystallization and is attributed to both expulsion of the vapor phase and groundwater leaching (Weaver et al., 1990). Na, F, Cl, Cs, Y, and rare earth elements (REE) have been observed to be depleted during crystallization (Weaver et al., 1990).

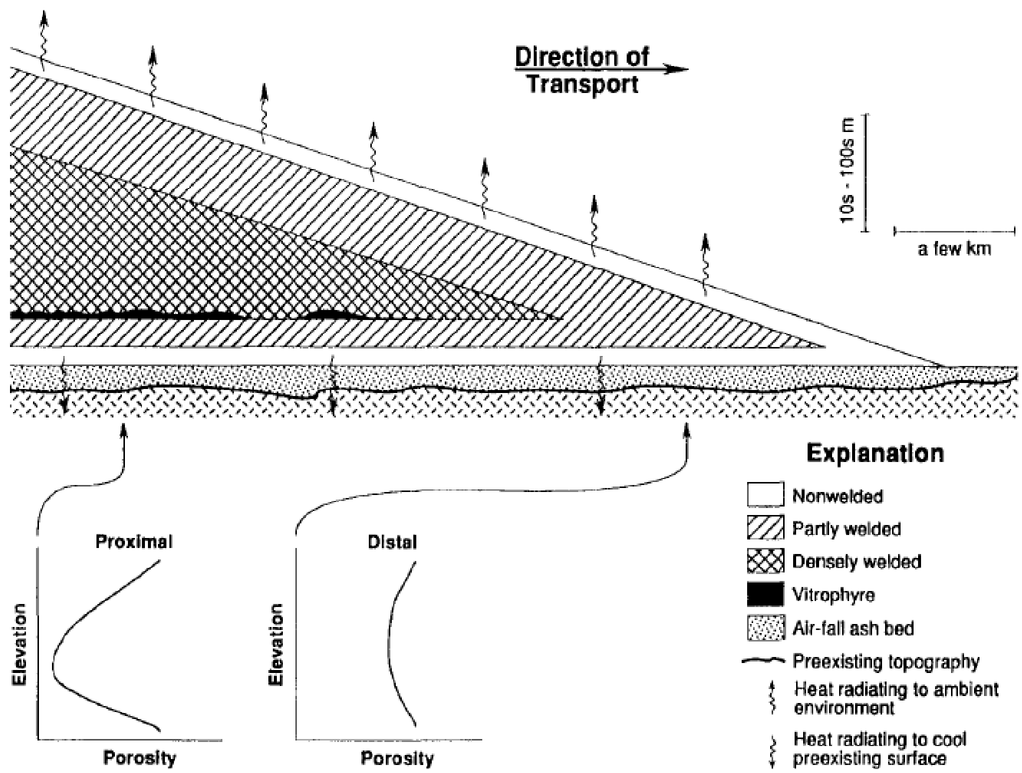

Figure 3. Conceptual model of cooling ash-flow unit showing zonation and vertical porosity variation (Istok et al., 1994).

Low-temperature alteration processes occur over longer time periods than high temperature alteration. As ash-flow tuffs are exposed to low-temperature waters, the unstable volcanic glasses are altered first to clay minerals, often smectites (Vaniman, 2006). As alteration progresses the relative abundance of illites and chlorites increases (Fisher and Schmincke, 1984). At high pH and ionic strength large quantities of zeolites are also formed during low temperature alteration of tuffs (Vaniman, 2006). Clinoptilolite is the most common zeolite produced outside of saline lake environments, but mordenite, chabazite and phillipsite are also common and the specific minerals formed will be influenced by the Si/Al ratio of the tuff (Vaniman, 2006). During low-temperature alteration, elements can be depleted by groundwater leaching or enriched by structural incorporation in minerals, ion exchange, and adsorption (Zielinski, 1982).

Arsenic in Tuffs

Surprisingly little information is available regarding the range of arsenic concentrations in volcanic glass. The most oft-cited source, even today, is Onishi and Sandell (1955), who report an average arsenic concentration of 5.9 mg/kg based on 12 volcanic glass samples. Nicolli et al. (1989) found arsenic concentrations ranged between 6.8 and 10.4 mg/kg with a geometric mean of 8.7 mg/kg in 10 samples of volcanic glass isolated from volcanically derived loess. These mean values are approximately four times the average crustal abundance of 1.7 mg/kg (Wedepohl, 1995). There are some indications that arsenic concentrations increase with silica content in volcanic rocks, although it is unclear if this holds true for volcanic glasses (Onishi and Sandell, 1955). The upper limit of arsenic in volcanic glass appears be ~20 mg/kg (Casentini et al., 2010;

Fiantis et al., 2010), although Noble at al. (2004) reported arsenic concentrations of up to 65 mg/kg in glassy calc-alkalic volcanic rocks from Peru.

The concentrations of arsenic in ash-flow tuffs is relatively modest in comparison to shales, which often have mean arsenic contents in excess of 10 mg/kg (Onishi and Sandell, 1955), but which are not typically sources of groundwater arsenic. Thus, the association of tuffs with elevated groundwater arsenic levels must be due to one or more processes that allow for mobilization, not simply elevated arsenic concentrations. Possible mechanisms include: 1) the relatively rapid dissolution of reactive glasses (Nadakavukaren et al., 1984; Nicolli et al., 1989); 2) dissolution of other readily soluble arsenic-bearing phases, possibly vapor phase alteration products or lithic fragments; 3) alkali desorption wherein weathering of volcanic glass causes an increase in solution pH which promotes release of arsenic from mineral surfaces (Smedley and Kinniburgh, 2002); and or 4) the dissolution of minerals containing competing anions that promote desorption of arsenic via anion exchange (Casentini et al., 2010).

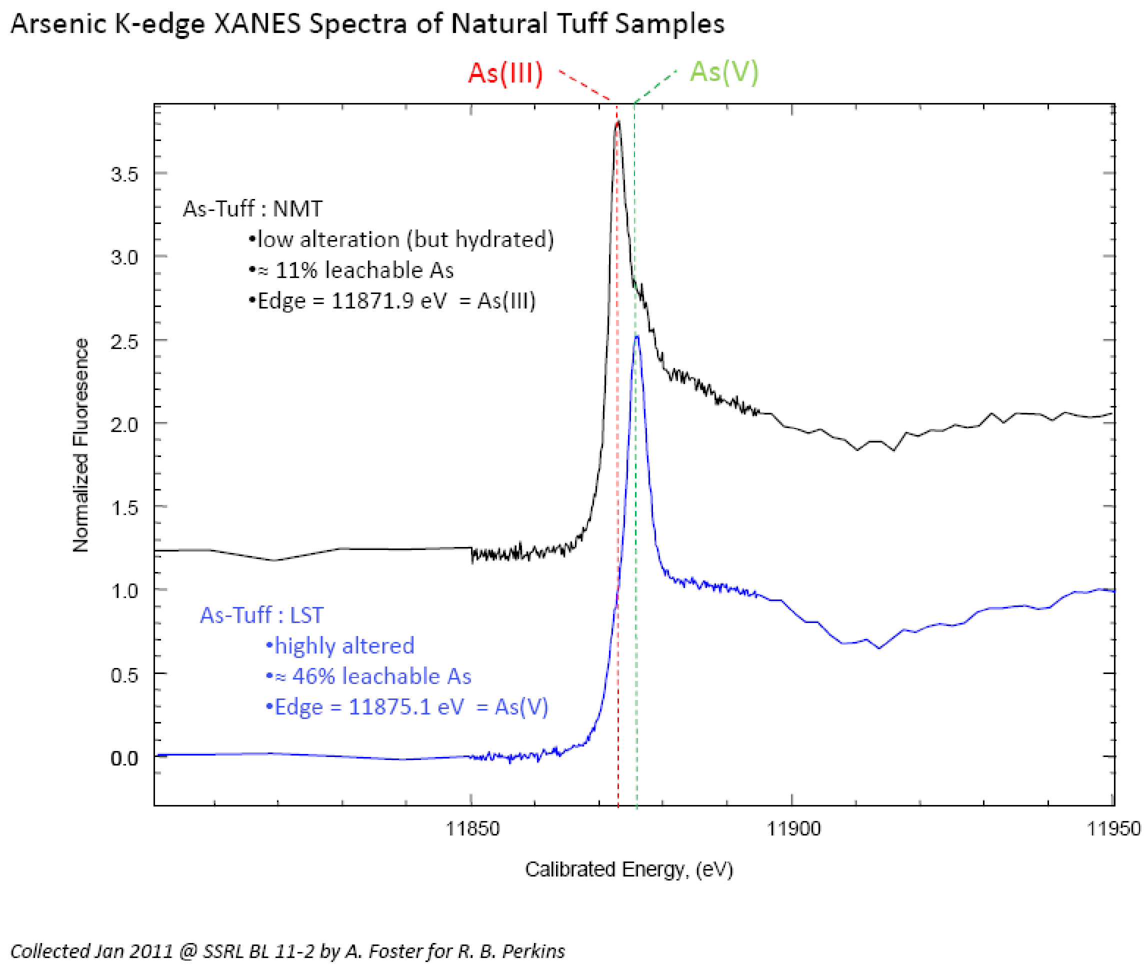

Figure 4. Arsenic K-edge XANES spectra of selected tuff samples from preliminary As leaching study. The less altered tuff contained primarily As(III) while the highly altered tuff contained primarily As(V).

Preliminary data suggest that arsenic in unaltered glassy tuffs is present predominantly as As(III) while arsenic in altered tuffs is predominantly As(V) (Figure 4). Results of a preliminary arsenic leaching study suggest that arsenic is more easily leached from altered tuffs that unaltered tuffs (Table 1, Figure 5). Altered tuffs present far more complications in terms of identifying the residence of oxidized arsenic because a variety of new hosts are possible, including secondary silica, secondary iron/manganese oxides or aluminum hydroxides, and various clays and zeolites. The host phase plays an important role in terms of sorption characteristics and stability under varying conditions.

Table 1. Total and environmentally available arsenic concentrations of select tuff samples used in preliminary As leaching study. Available arsenic refers to arsenic present in phases other than glasses and silicate mineral phases such as feldspars and quartz. Note: total As concentrations from previous INAA analysis. Errors = 1 σ from replicate analysis.

	Total As ($\mu g\ g^{-1}$)	**"Available" As ($\mu g\ g^{-1}$)**	**Available/Total**	**Degree of Alteration**
Little Butte	~4?	2.18 ± 0.07	0.55	Highly Altered
LST	~4?	1.85 ± 0.03	0.46	Highly Altered
San Luis (NM)	1.9 ± 0.5	0.64 ± 0.04	0.34	Intermediate
San Luis (RC)	2.3 ± 0.4	0.39 ± 0.03	0.17	Intermediate
NMT	4.2 ± 0.3	0.48 ± 0.01	0.11	Hydrated Glass
RST	4.1 ± 0.4	0.26 ± 0.03	0.06	Fresh Glass

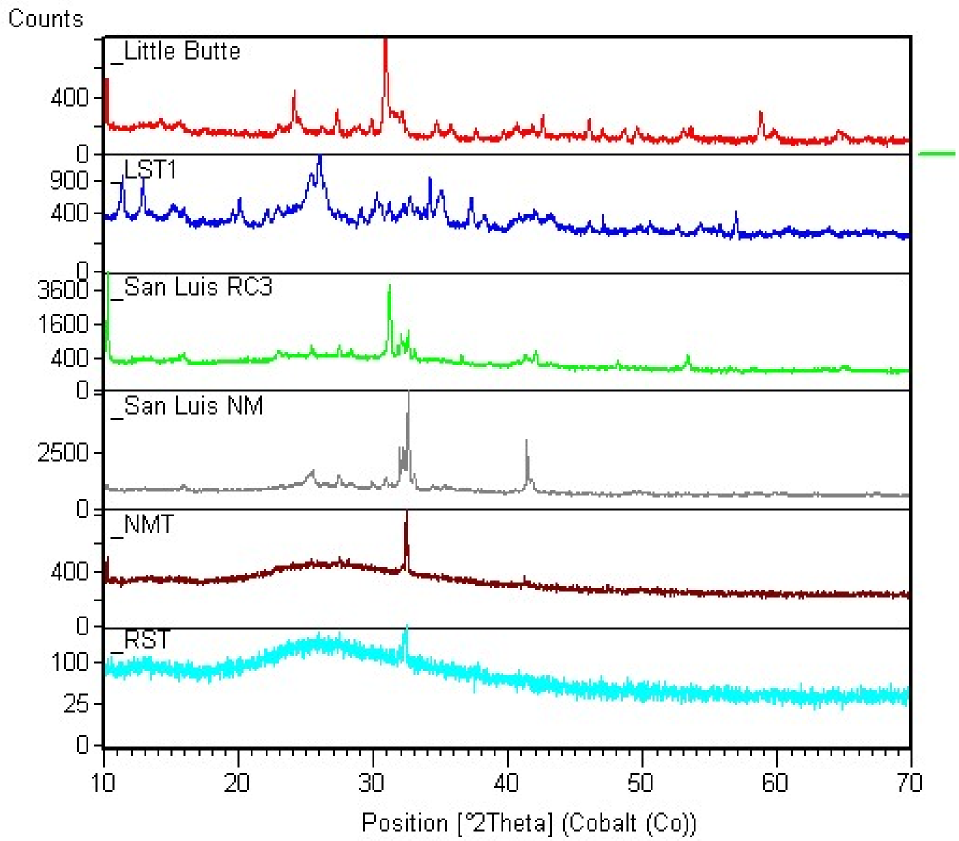

Figure 5. XRD analysis of six tuff samples used in preliminary As leaching study displaying increasing degrees of low-temperature alteration. More altered tuffs contain a larger number of mineral phases, which increases the number of potential host phases of arsenic in altered tuffs relative to unweathered glassy samples.

CHAPTER 2: ARSENIC OCCURRENCE IN ASH-FLOW TUFFS AND ASSOCIATED SEDIMENTS

INTRODUCTION

Despite the widespread association between ash-flow tuffs and arsenic contamination, surprisingly little is known about arsenic occurrence in these units. Previously reported values for mean arsenic concentrations are based on only 10-12 samples of volcanic glasses, and there has been little effort to identify arsenic host phases or to correlate arsenic with other elements in these rocks (Onishi and Sandell, 1955; Nicolli et al., 1989). Ash-flow tuffs are complex geologic units that can display multiple types and degrees of alteration, but most research involving arsenic and tuffs focuses on glassy tuffs, and does not consider devitrification and weathering.

In this study, 49 tuff samples spanning a range of chemical and mineralogical compositions, as well as 11 samples of tuffaceous sediments were used to investigate the behavior of arsenic in ash-flow tuffs. Specific objectives of the study are 1) to better quantify the levels of arsenic found in tuffs, 2) to determine if bulk chemical composition, particularly alumina-alkali ratios, influence levels of arsenic found in tuffs, and 3) to determine if devitrification and weathering influence arsenic concentrations in tuffs.

METHODS

Sample Collection and Preparation

For this study, 42 hand samples of tuffs and tuffaceous sediments were collected from various locations throughout Oregon. Eight samples were collected from the Southern Willamette Valley, and 23 samples were collected from Central and Eastern Oregon. As both tuffs and tuffaceous sediments have been suggested as sources of groundwater arsenic, 11 samples of tuffaceous sediments were collected from Eastern Oregon. Wherever possible, samples displaying different alteration states were obtained from the same unit, and in some cases the same location. Full sections of unweathered samples were collected from single outcrops for two units, the Dinner Creek Tuff and the Rattlesnake Tuff. An additional 18 samples obtained from the existing collection of Dr. Martin Streck collection were also analyzed. Sample locations can be found in Table 2.

To prepare samples for analysis, visibly altered exteriors were chipped away with a rock hammer, and approximately fist-sized or smaller chunks of sample were fed through a Braun jaw-crusher until the largest pieces were between ~2 cm and ~5 mm. Early samples were hand split, and one quarter of the sample was then run through a disc grinder, until the largest pieces were ~5 mm. For later samples this step was eliminated in favor of using a finer setting on the crusher to achieve a smaller grain size. (~5 mm). In all cases, the equipment was thoroughly cleaned between samples.

Crushed samples were hand split and ~ 5-15 g portions were sent to either the Washington State University Geoanalytical Lab, in Pullman, WA, or Activation

Laboratories Ltd., in Ontario, Canada for bulk chemical analysis. The remainder of each crushed sample was split up to four times using a small (Jones-type) riffle splitter, and split portions (~5 – 10 g) ground to a fine powder using a Fisher alumina ceramic mortar grinder. Samples were ground for 20 – 30 minutes. If grains larger than ~0.5 mm remained after 30 minutes, grinding was finished by hand with a ceramic mortar and pestle.

X-ray Diffraction (XRD)

To characterize the mineralogy of the tuffs samples were analyzed using a Phillips (now PANalytical) Theta-Theta PW3040 X-ray diffractometer equipped with a standard scintillation counter and copper anode X-ray lamp. Samples were further ground by hand using an agate mortar and pestle until they passed through a 65 μm sieve. A random powder mount was prepared using a side-pack aluminum sample holder. Diffraction patterns were obtained in continuous mode using a step size of 0.020 degrees two theta (º2θ) and scan step times of 1.00 second from 5 to 75 º2θ.

Table 2. Locations and ages of samples used in this study.

Sample ID	Unit	Formation	Age	Latitude	Longitude	Age Source
BC1	Bully Creek Tuff	Bully Creek	15.66 +- 0.7 Ma	44.07925	-117.5435833	Nash and Perkins, 2012
BC2	Bully Creek Tuffaceous Sediments	Bully Creek		44.07925	-117.5435833	
BC3	Bully Creek Tuffaceous Sediments	Bully Creek		44.07925	-117.5435833	
DC1	Dinner Creek	Hog Creek Sequence	15.9 – 15.4 Ma			Streck at al., 2011
DC4	Dinner Creek	Hog Creek Sequence	15.9 – 15.4 Ma	43.766139	-118.030167	Streck at al., 2011
DC5	Dinner Creek	Hog Creek Sequence	15.9 – 15.4 Ma	43.766139	-118.030167	Streck at al., 2011
DC6	Dinner Creek	Hog Creek Sequence	15.9 – 15.4 Ma	43.766139	-118.030167	Streck at al., 2011
DC7	Dinner Creek	Hog Creek Sequence	15.9 – 15.4 Ma	43.766139	-118.030167	Streck at al., 2011
DC8	Dinner Creek	Hog Creek Sequence	15.9 – 15.4 Ma	43.766139	-118.030167	Streck at al., 2011
DC9	Dinner Creek	Hog Creek Sequence	15.9 – 15.4 Ma	43.32795	-118.1321	Streck at al., 2011
DS1	Drip Springs Tuffaceous Sediments	Drip Springs	Late Miocene to Pliocene	43.98541667	-117.5765	Walker and MacLeod, 1991
DS2	Drip Springs Tuffaceous Sediments	Drip Springs	Late Miocene to Pliocene	43.98541667	-117.5765	Walker and MacLeod, 1991
DS3	Drip Springs Tuffaceous Sediments	Drip Springs	Late Miocene to Pliocene	43.98541667	-117.5765	Walker and MacLeod, 1991
DT1	Dale Tuff	Tower Mountain/ Eastern John Day facies	28.5 Ma			Ferns et al., 2001
DT2	Dale Tuff	Tower Mountain/ Eastern John Day facies	28.5 Ma			Ferns et al., 2001
DT3	Dale Tuff	Tower Mountain/ Eastern John Day facies	28.5 Ma			Ferns et al., 2001
DVC1	Devine Canyon		9.68 Ma	43.77685	-119.00065	Streck et al., 1999

Sample ID	Unit	Formation	Age	Latitude	Longitude	Age Source
DVC2	Devine Canyon		9.68 Ma	43.7124	-119.0078	Streck et al., 1999
DVC4	Devine Canyon		9.68 Ma	43.77275	-118.127611	Streck et al., 1999
FD1	Foster Dam	Little Butte Volcanics	26.28 Ma	44.41991667	-122.6653167	McClaughry et al., 2010
FD2	Foster Dam	Little Butte Volcanics	26.28 Ma	44.41991667	-122.6653167	McClaughry et al., 2010 (McClaughry, 2010)
FD3	Foster Dam	Little Butte Volcanics	26.28 Ma	44.41991667	-122.6653167	McClaughry et al., 2010
FD4	Foster Dam	Little Butte Volcanics	26.28 Ma	44.41991667	-122.6653167	McClaughry et al., 2010
LB1	Little Butte	Little Butte Volcanics?				
LG1	Tuff of Leslie Gulch		15.5 +- 0.5 Ma	43.322389	-117.315806	Vander Meulen et al., 1987
LG2	Tuff of Leslie Gulch		15.5 +- 0.5 Ma	43.322389	-117.315806	Vander Meulen et al., 1988
LG3	Tuff of Leslie Gulch		15.5 +- 0.5 Ma	43.322389	-117.315806	Vander Meulen et al., 1989
LG4	Tuff of Leslie Gulch		15.5 +- 0.5 Ma	43.314111	-117.218944	Vander Meulen et al., 1990
LST1	Lower Sanidine Tuff	Turtle Cove Member of the Painted Hill Unit of the John Day Formation	29.75 Ma			Retalleck et al., 2000
MA1	Member A	John Day	39.17 Ma			Smith et al., 1998
MK1	Tuff of Mohawk (Intracaldera)	Little Butte Volcanics	30.9 Ma	44.09558333	-122.9628833	McClaughry et al., 2010
MK2	Tuff of Mohawk (Intracaldera)	Little Butte Volcanics	30.9 Ma	44.08903333	-122.9740167	McClaughry et al., 2010
MTA1	Mount Angel					
PG1	Picture Gorge	John Day	28.65 ±0.07 Ma	44.02693	-119.18415	Retalleck et al., 2000
PG2	Picture Gorge	John Day	28.65 ±0.07 Ma	44.02693	-119.18415	Retalleck et al., 2000
PG3	Picture Gorge	John Day	28.65 ±0.07 Ma			Retalleck et al., 2000
RST1	Rattlesnake Tuff		7.1 Ma			Streck and Grunder, 1995
RST2	Rattlesnake Tuff		7.1 Ma			Streck and Grunder, 1995
RST4	Rattlesnake Tuff		7.1 Ma			Streck and Grunder, 1995
RST5	Rattlesnake Tuff		7.1 Ma	43.709694	-119.464167	Streck and Grunder, 1995
RST6	Rattlesnake Tuff		7.1 Ma	43.716028	-119.630972	Streck and Grunder, 1995

Sample ID	Unit	Formation	Age	Latitude	Longitude	Age Source
RST7	Rattlesnake Tuff		7.1 Ma	43.716028	-119.630972	Streck and Grunder, 1995
RST8	Rattlesnake Tuff		7.1 Ma	43.659278	-118.99875	Streck and Grunder, 1995
RST9	Rattlesnake Tuff		7.1 Ma	43.659278	-118.99875	Streck and Grunder, 1995
RST10	Rattlesnake Tuff		7.1 Ma	43.659278	-118.99875	Streck and Grunder, 1995
RST11	Rattlesnake Tuff		7.1 Ma	43.659278	-118.99875	Streck and Grunder, 1995
RST13	Rattlesnake Tuff		7.1 Ma	43.659278	-118.99875	Streck and Grunder, 1995
RU1	Round Up	John Day	<28.7 Ma			Patridge, 2010
SLNM	Nelson Mountain Tuff	San Luis Caldera Complex	26.1 Ma			Lipman, 2006
SLRC	Rat Creek Tuff	San Luis Caldera Complex	25.47 Ma			Lipman, 2006
SR1	Smith Rock Tuff - Haystack Reservoir Outflow Lobe	Smith Rock Tuff	29.53 Ma	44.4967	-121.1547	Smith et al., 1998
SR2	Smith Rock Tuff - Haystack Reservoir Outflow Lobe	Smith Rock Tuff	29.57 Ma	44.4967	-121.1547	Smith et al., 1998
TS1	Tuffaceous Sediments		Late Miocene to Pliocene	43.940833	-118.132806	Walker and MacLeod, 1991
TS3	Tuffaceous Sediments		Late Miocene to Pliocene	43.868833	-118.507583	Walker and MacLeod, 1991
TS4	Tuffaceous Sediments		Late Miocene to Pliocene	44.41805556	-118.11275	Walker and MacLeod, 1991
TSD1	Tuffaceous Sandstone		Late Miocene to Pliocene	43.82997222	-118.4250556	Walker and MacLeod, 1991
TSD2	Tuffaceous Sandstone		Late Miocene to Pliocene	43.82997222	-118.4250556	Walker and MacLeod, 1991
TW1	Tuff at Willamette Street	Fisher Formation	Middle Eocene	43.95128	-123.13797	McClaughry et al., 2010
TW2	Tuff at Willamette Street	Fisher Formation	Middle Eocene	43.93903333	-123.20682	McClaughry et al., 2010
WU1	Winema Unnamed		Miocene	43.33941	-121.61758	Sherrod and Pickthorn, 1992

Diffraction patterns were analyzed using PANalytical X'Pert Highscore Plus software package, to obtain semi-quantitative mineral compositions. When possible AutoQuan software was used to perform non-standardized Reitveld analysis and obtain more accurate semi-quantitative compositional percentages. In some cases the software database was missing one or more of the mineral phases present in the samples, and Reitveld analysis was not performed. Amorphous phases were not included in these results, and the proportion of amorphous phases (glass) was estimated based on deviations in the background of XRD patterns from a straight line, particularly between approximately 10 and 40 º2θ, where the presence of amorphous phases produces a wide curved deviation of the background pattern from a straight line.

The XRD used produces wide low-intensity peaks at approximately 4-5 º2θ and 8-9 º2θ that are consistently present in XRD patterns. These peaks were determined to be instrument artifacts, possibly due to misaligned slits and peaks at these positions were excluded from analysis unless significantly larger than that measured on a blank holder.

Optical Microscopy

Thin sections of selected samples were examined in order to confirm the XRD results and identify any potential minor mineral phases that were not identified in the XRD patterns. In addition, particular textures were considered to be indicative of different alteration processes (

Figure 6).

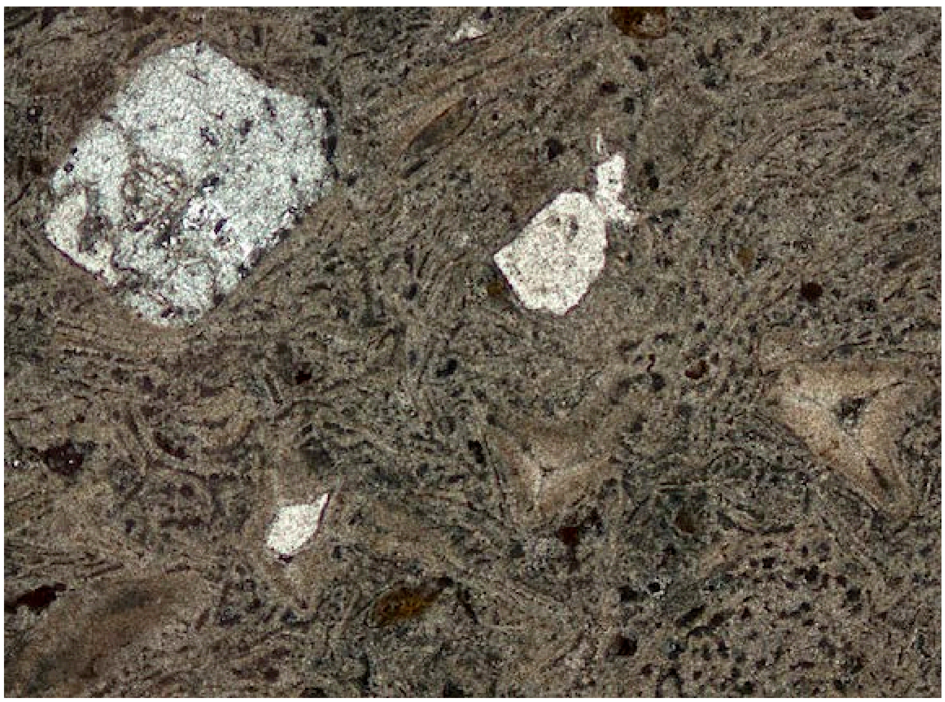

Figure 6. Sample PG2, under plane light at 5x magnification, displaying axilotic texture produced during devitrification, where minerals crystallized perpendicular to the boundaries of glass shards.

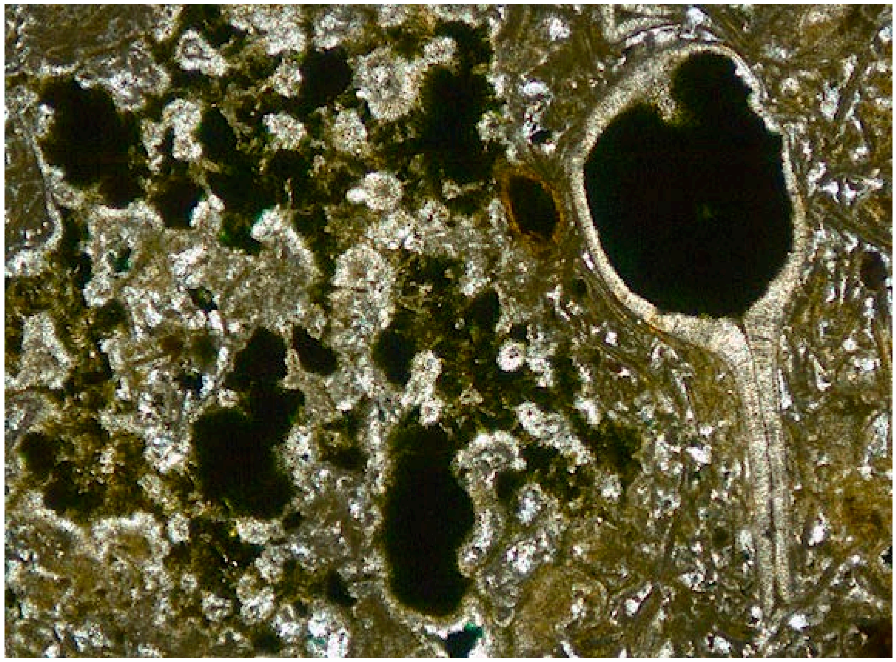

Figure 7. Sample PG1 under plane light at 5x magnification, displaying both axiolitic texture and alteration to green and brown clay minerals.

Bulk Chemistry

Crushed samples were hand split, and ~ 5-10 g portions were sent to either the Washington State University Geoanalytical Lab, in Pullman, WA, or Activation Laboratories Ltd., in Ontario, Canada for bulk chemical analysis. At both labs, values for major elements were obtained via X-ray fluorescence (XRF). For samples sent to WSU, selected trace elements (Ni, Cr, V, Ba, Rb, Sr, Ga, Cu, Zn, Pb, La, Ce, Th, and Nd) were obtained via XRF. For samples sent to Activation Laboratories trace elements were determined via ICP-MS (Cu, Cd, Mo, Pb, Ni, Zn, S, Be, Li, Sr, V, Y) or Instrumental Neutron Activation Analysis (INAA) (As, Ba, Co, Cr, Cs, Eu, Rb, Sb, Sc, Se, Th, La, Ce, Nd, Sm, Sn, Yb, Lu).

Total Arsenic

For samples where arsenic values were not obtained via INAA at Activation Laboratories, samples were digested following US EPA Method 3052 (US Environmental Protection Agency, 1996b). Sample aliquots were weighed to 0.250 ± 0.001 g and placed in Teflon vessels that had been cleaned with concentrated nitric acid and repeatedly rinsed with deionized water (18.2 MΩ cm). Subsequently, 1.5 mL trace-metal grade HF, 4.5 mL trace-metal grade HNO_3^-, and 1 mL trace-metal grade HCl were added to the vessels. Samples were digested using a Milestone Ethos EZ microwave digester for 40 minutes reaching a final temperature of 240ºC for 20 minutes. Method blanks and certified reference materials (JR1 from the Japanese Geological Survey, and SRM 1633a from the National Bureau of Standards) were run every 20 samples, and duplicate digests were carried out on three samples. After digestion samples were poured into 50 mL plastic centrifuge tubes. Vessels were rinsed three times with 18.2 MΩ cm distilled water, and the water was added to the samples. Centrifuge tubes were filled with water to 25 mL.

Samples were further diluted to a total of 50.0 mL in test tubes (1:1 dilution) and analyzed using an Agilent 700 Series ICP-OES with an inert sample introduction system (a V-groove nebulizer with Sturman–Masters spray chamber and alumina injector). Detailed operating conditions for the analysis are listed in Appendix A.

RESULTS: BULK ROCK CHARACTERIZATION

Major Mineralogy

The major mineralogy of all samples was determined based of the results of XRD analysis in concert with examination of thin sections and hand samples. The percentage of glass present in all samples was estimated based upon deviations in background levels of the XRD patterns from a straight line, particularly between approximately 10 and 40 º2θ (Figure 8), coupled with examination of thin sections and hand samples to confirm the XRD results.

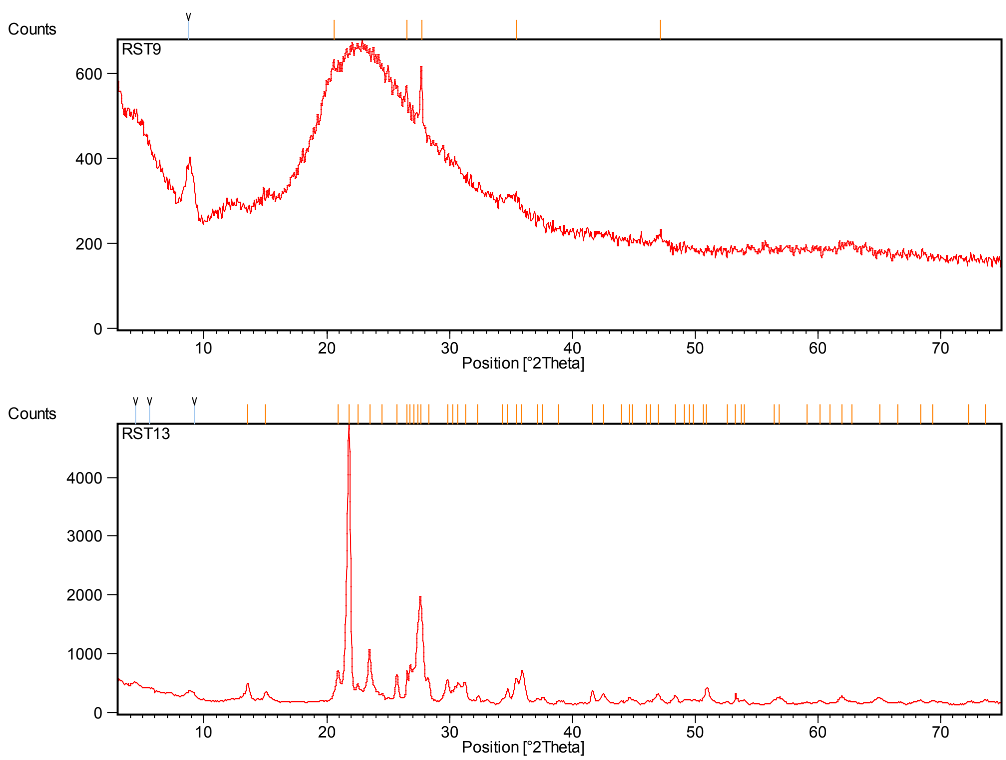

Figure 8. XRD patterns for unweathered glassy (RST9) and devitrified samples (RST13). Glass content of samples was estimated based upon the deviation of background levels from a straight line between approximately 10 and 40 º2θ, coupled with visual examination of hand samples and thin sections.

The majority of minerals identified in XRD patterns fell into four categories; feldspars, low pressure silica polymorphs, zeolites, and clay minerals (Table 3). Sanidine was the most common feldspar identified followed by albite, but anorthoclase, microcline, and labradorite were all identified in at least one sample. In many cases multiple feldspars were acceptable matches to the XRD patterns, and especially in devitrified samples with very small crystals, the specific alkali feldspar present could not be identified in thin section. In these cases, the feldspar that best matched the XRD pattern was selected.

Quartz, cristobalite, and tridymite were all identified in multiple samples, and many samples contained more than one silica phase. Quartz can occur as a phenocryst in glassy samples, while cristobalite and tridymite occur exclusively as devitrification products. The presence of multiple silica polymorphs in a single sample may indicate either devitrification of a glassy rock that contains quartz phenocrysts, or multiple phases forming as the temperature decreases during the devitrification process.

Clays and zeolites are both common alteration products found in weathered tuffs. The most common clays identified in XRD patterns were smectites, particularly saponite and montmorillonite. Illite, kaolinite, and sepiolite were also identified in multiple samples. The clay mineral tosudite, a 1:1 interstratified chlorite-smectite mineral known to be a product of alteration of tuffs and tuffaceous sediments (Shimoda, 1969), was identified in a number of tuffaceous sediment samples. The zeolite minerals most commonly identified were heulandite, mordenite, and clinoptilolite.

Table 3. Major mineralogy and categorization of tuff samples, based on semi-quantitative XRD results, optical microscopy, and examination of hand samples. Percentages of amorphous material (glass) was not included in semi-quantitative XRD results, and was instead estimated solely from examination of XRD patterns, thin sections, hand samples

Sample ID	Primary Minerals / Glass (>30%)	Secondary Minerals (30% - 10%)	Minor Minerals (<10%)	Devitrification Classification	Weathering Classification
BC1	Saponite Anorthoclase			Glassy	Weathered
BC2	Cristobalite	Tridymite Kaolinite	Sanidine	Sediment	Sediment
BC3	Montmorillonite	Sanidine	Quartz	Sediment	Sediment
DC1	Glass Anorthoclase	Quartz Montmorillonite	Sepiolite	Glassy	Unweathered
DC4	Glass	Labradorite		Glassy	Unweathered
DC5	Cristobalite Sanidine Albite			Devitrified	Unweathered
DC6	Cristobalite Sanidine	Albite	Tridymite	Devitrified	Unweathered
DC7	Cristobalite	Sanidine Albite	Tridymite	Devitrified	Unweathered
DC8	Glass Saponite Labradorite			Glassy	Weathered
DC9	Sanidine Tridymite		Albite	Devitrified	Unweathered
DS1	Saponite	Albite	Tridymite Cristobalite Quartz	Sediment	Sediment
DS2	Tosudite	Kaolinite Tridymite Cristobalite	Calcite Quartz	Sediment	Sediment
DS3	Tridymite Cristobalite		Kaolinite	Sediment	Sediment
DT1	Albite	Cristobalite Glass		Glassy	Unweathered
DT2	Glass Albite		Illite	Glassy	Unweathered
DT3	Sanidine Cristobalite		Pigeonite Quartz Cordierite	Devitrified	Unweathered
DVC1	Sanidine	Cristobalite Quartz		Devitrified	Unweathered
DVC2	Sanidine	Quartz Saponite	Cristobalite	Devitrified	Weathered
DVC4	Glass	Albite Quartz		Glassy	Unweathered
FD1	Heulandite	Quartz Mordenite	Montmorillonite	Glassy	Weathered

Sample ID	Primary Minerals / Glass (>30%)	Secondary Minerals (30% - 10%)	Minor Minerals (<10%)	Devitrification Classification	Weathering Classification
FD2	Heulandite	Mordenite Quartz	Montmorillonite	Glassy	Weathered
FD3	Heulandite	Mordenite Quartz	Montmorillonite	Glassy	Weathered
FD4	Heulandite	Mordenite Quartz		Glassy	Weathered
LB1	Illite	Quartz Sanidine	Kaolinite Zeolite ZSM-11	Glassy	Weathered
LG1	Heulandite Mordenite		Quartz	Glassy	Weathered
LG2	Sanidine	Quartz	Cristobalite Pyrite	Devitrified	Weathered
LG3	Quartz Microcline		Palygorskite Cristobalite	Devitrified	Weathered
LG4	Quartz	Albite	Calcite	Devitrified	Weathered
LST1	Clinoptilolite Montomorillonite	Albite Glass	Calcite	Glassy	Weathered
MA1	Saponite Sanidine	Cristobalite Illite		Devitrified	Weathered
MK1	Albite	Quartz Montmorillonite		Devitrified	Unweathered
MK2	Albite Quartz		Montmorillonite	Devitrified	Unweathered
MTA1	Glass Anorthoclase		Illite	Glassy	Weathered
PG1	Quartz	Sanidine Illite Cristobalite		Devitrified	Weathered
PG2	Cristobalite Sanidine	Albite		Devitrified	Unweathered
PG3	Glass		Sanidine Saponite	Glassy	Unweathered
RST1	Glass		Montmorillonite Quartz	Glassy	Unweathered
RST3	Glass			Glassy	Unweathered
RST4	Sanidine Cristobalite		Biotite	Devitrified	Unweathered
RST5	Sanidine	Tridymite Quartz Cristobalite Albite		Devitrified	Unweathered
RST6	Glass	Sanidine Quartz		Glassy	Unweathered
RST7	Sanidine Cristobalite			Devitrified	Unweathered

Sample ID	Primary Minerals / Glass (>30%)	Secondary Minerals (30% - 10%)	Minor Minerals (<10%)	Devitrification Classification	Weathering Classification
RST8	Glass		Sanidine Quartz	Glassy	Unweathered
RST9	Glass		Albite Quartz	Glassy	Unweathered
RST10	Glass		Albite Quartz	Glassy	Unweathered
RST11	Sanidine Tridymite	Cristobalite	Helvite	Devitrified	Unweathered
RST13	Sanidine Cristobalite			Devitrified	Unweathered
RU1	Clinoptilolite Montmorillonite	Glass	Quartz	Glassy	Weathered
SLNM	Albite Montmorillonite		Illite Cristobalite Quartz	Devitrified	Weathered
SLRC	Illite	Saponite Glass	Anorthite Albite	Glassy	Weathered
SR1	Clinoptilolite	Quartz Albite Mordenite		Glassy	Weathered
SR2	Quartz	Albite Orthoclase		Devitrified	Unweathered
TS1	Tosudite	Sanidine	Cristobalite Quartz	Sediment	Sediment
TS3	Tosudite		Cristobalite	Sediment	Sediment
TS4	Tosudite Montmorillonite			Sediment	Sediment
TSD1	Anorthite Tosudite			Sediment	Sediment
TSD2	Albite Tosudite		Quartz	Sediment	Sediment
TW1	Albite	Quartz	Cristobalite Illite Montmorillonite	Devitrified	Unweathered
TW2	Heulandite	Albite Stilbite	Illite Chlorite Quartz	Sediment	Sediment
WU1	Anorthoclase	Cristobalite Quartz		Devitrified	Unweathered

Sample Categorization

Major mineralogy and bulk chemical analysis were used to categorize each sample. Each sample was placed into a category for two different compositional variables: degree of devitrification (devitrified or glassy), and degree of weathering (unweathered or weathered) (Table 3).

Samples were categorized as devitrified or glassy based on XRD results and optical microscopy. Samples containing glass were categorized as glassy, while samples lacking glass and containing cristobalite, tridymite, or quartz were categorized as devitrified. For highly weathered samples containing neither glass nor cristobalite, alteration products were used to distinguish between the categories. Both clays and zeolites are common alteration products found in tuffs, with zeolites forming specifically from the alteration of glass (Vaniman, 2006). Samples containing both clays and zeolites were categorized as originally glassy, and samples containing clays but lacking zeolites were categorized as originally devitrified. Although weathered samples were given a categorization of either glassy or devitrified, they were mineralogically distinct enough that they were excluded from the Devitrified and Glassy categories for the purposes of data analysis, and all subsequent references to those categories include only unweathered samples.

The degree of weathering was determined using the semi-quantitative XRD results, and was based on the proportion of alteration products (clays + zeolites) in each sample. When compared to observation of both hand samples and thin sections the proportions of clays and zeolites determined via AutoQuan software appeared to greatly exceed the actual amount of alteration products present, and the categories defined reflect that. Therefore, samples for which the estimated content of clays + zeolites was ≤ 30% were categorized as "Unweathered" while samples with estimated clay + zeolite contents ≥ 31% were categorized as "Weathered." A few exceptions to these categories were made, particularly for highly glassy rocks. Since the amount of glass present was not included in the semi-quantitative XRD results, samples composed primarily of glass produced results that contained very high percentages (>90%) of clays, despite the rocks themselves obviously not being clay-rich. In these cases, the weathering categorization was determined primarily based on observation of hand samples, and thin sections if available.

Categorizations were compared to major element chemistry, particularly Loss on Ignition (LOI) values (Table 8). Samples classified as Unweathered that contained LOI values higher than 5% were re-examined, since high LOI values are a potential indicator of the presence of hydrated alteration products. Two samples with semi-quantitative clay percentages near the classification limit of 30% were reclassified as Weathered based on LOI values exceeding 5%.

RESULTS: BULK ROCK CHEMISTRIES

QA/QC Results

For samples digested via EPA Method 3052 and analyzed via ICP-OES recoveries of As from certified reference standards ranged from 82.7% to 94.6%, but were inconsistent for a number of other trace elements (Table 4).

Table 4. Recoveries for certified reference materials analyzed via ICP-OES. Arsenic recoveries ranged from 82.7% to 94.6%. S had recovery percentages within ± 5%, but other elements were more variable.

	JR-1			SRM 1633a		
Element	Measured Value (ppm)	Certified Value (ppm)	Recovery %	Measured Value (ppm)	Certified Value (ppm)	Recovery %
As	13.48	16.30	82.7	137.13	145.00	94.6
Be*	2.64	3.34	78.9	11.72	12.00	97.7
Mo*	2.57	3.25	79.1	24.93	29.00	86.0
Sb	1.64	1.19	138.2	11.42	6.80	167.9
Sm	< 0.70	6.03	< 11	< 0.70	NA	

* Values for SRM 1633a are not certified values.

Three samples were prepared and analyzed in duplicate. Relative percent differences (RPDs) between arsenic concentrations in the duplicate samples ranged from 1.4 to 12% (Table 5).

Table 5. Relative percent differences for duplicate samples analyzed via EPA Method 3052.

Element	MA1a (µg/L)	MA1b (µg/L)	RPD (%)	RST4a (µg/L)	RST4b (µg/L)	RPD (%)	MK2a (µg/L)	MK2b (µg/L)	RPD (%)
As	41.69	36.99	11.95	19.70	18.19	7.96	46.17	45.53	1.38
Be	13.67	14.05	-2.74	12.58	12.28	2.42	6.04	6.02	0.25
Mo	3.83	3.31	14.41	6.84	6.93	-1.32	1.98	2.58	-26.03
Sm	19.96	15.74	23.59	18.38	18.29	0.50	ND	ND	NA

Check standards were run during ICP-OES analysis as a check on instrumental accuracy. All elements reported produced values that were within ± 5% of the standard value (Table 6).

Table 6. Recoveries from Method Blank and check standards analyzed via ICP-OES. Check standard QC1 had a concentration of 100 ug/L for all elements except Sb and Sn, and check standard QC2 had a concentration of 50 ug/L for all elements except Sb and Sn.

Element	QC Blank1 (µg/L)	QC1a (µg/L)	QC2a (µg/L)	QC Blank2 (µg/L)	QC1b (µg/L)	QC2b (µg/L)	Method Blank (µg/L)
As	ND	103.3	49.6	ND	103.9	50.2	ND
Be	ND	98.6	48.6	ND	95.4	47.1	ND
Mo	ND	92.5	46.9	ND	91.0	45.1	ND
Sm	ND	100.6	54.7	ND	95.8	49.6	ND

One sample, DT3, was analyzed at both the WSU Geoanalytical Lab and Activation Laboratories. The RPDs for the two analyses reached a maximum of 35% for major elements (P_2O_5), and 106% for trace elements (Cu) (Table 7).

Table 7. Relative percent differences for sample DT3, analyzed at the WSU Geoanalytical Lab (WSU) and Activation Laboratories (AL). Major elements are reported in weight percent, and trace elements are reported in mg/kg.

Element	DT3 WSU	DT3 AL	RPD
SiO2	75.00	75.21	-0.28
Al2O3	12.19	12.45	-2.11
FeO	1.13	1.25	-10.26
MnO	0.010	0.011	-9.52
MgO	0.29	0.35	-18.75
CaO	0.46	0.49	-6.32
Na2O	2.97	3.04	-2.33
K2O	4.61	4.62	-0.22
TiO2	0.07	0.08	-10.53
P2O5	0.014	0.02	-35.29
Ni[1]	2	3.00	-30.77
Cr[2]	2.80	< 2	NA
V[1]	6.00	5.00	18.18
Ba[2]	602.80	460.00	26.87
Rb[2]	103.90	95.00	8.95
Sr[1]	31.40	35.00	-10.84
Y[1]	18.50	16.00	14.49
Cu[1]	3.70	12.00	-105.73
Zn[1]	23.20	31.00	-28.78
Pb[1]	16.30	14.00	15.18
La[2]	33.00	32.90	0.30
Ce[2]	57.20	55.00	3.92
Th[2]	11.20	8.30	29.74
Nd[2]	20.20	22.00	-8.53

[1]Analyzed via ICP-MS at Activation Laboratories, and XRF at WSU.
[2]Analyzed via INAA at Activation Laboratories and XRF at WSU.

Bulk Chemistry

Major element chemistry for all samples is provided in Table 8. Among tuff samples, SiO_2 values ranged from a low of 52.8% in a weathered sample to a high of 81.8% in a devitrified sample. Total weight percents including Loss on Ignition (LOI) values ranged from a low of 97.7% to a high of 100.2%.

Table 8. Major element chemistry for tuff and tuffaceous sediment samples. All values were obtained via XRF, and reported in weight percent.

Sample	Devitrificat	Weathering	Lab	SiO2	Al2O3	MnO	FeO	MgO	CaO	Na2O	K2O	TiO2	P2O5	LOI	Total
BC1	Glassy	Weathered	AL	52.82	11.98	0.078	8.59	2.27	3.72	1.61	0.98	1.170	0.180	16.25	99.64
BC2	Sediment	Sediment	AL	84.17	2.80	0.013	1.59	0.55	0.50	0.08	0.12	0.220	0.010	9.12	99.18
BC3	Sediment	Sediment	AL	50.60	14.97	0.037	5.97	1.73	1.99	0.53	0.53	1.240	0.080	21.49	99.17
DC1*	Glassy	Unweath.	WSU	71.48	11.85	0.04	1.75	0.13	0.57	2.36	5.81	0.17	0.02		94.17
DC4	Glassy	Unweath	AL	72.71	11.84	0.056	2.14	0.11	0.53	2.77	5.79	0.170	0.020	3.2	99.34
DC5	Devitrified	Unweath	Al	75.14	12.23	0.005	1.69	0.13	0.31	4.16	3.82	0.170	0.030	1.98	99.67
DC6	Devitrified	Unweath	AL	76.07	11.48	0.012	2.31	0.11	0.28	4.10	3.51	0.160	0.080	1.57	99.68
DC7	Devitrified	Unweath	AL	77.73	10.65	0.044	1.98	0.09	0.30	3.93	3.22	0.150	0.020	1.55	99.67
DC8	Glassy	Weathered	AL	65.39	12.77	0.115	2.76	1.58	1.10	2.18	3.44	0.180	0.030	9.11	98.65
DC9	Devitrified	Unweath	AL	76.49	12.60	0.005	0.70	0.04	0.22	4.73	3.81	0.170	0.030	0.31	99.11
DS1	Sediment	Sediment	AL	67.63	7.41	0.005	2.84	1.21	3.39	0.37	0.23	0.450	0.050	15.97	99.55
DS2	Sediment	Sediment	AL	77.97	4.53	0.005	1.73	0.86	2.82	0.13	0.09	0.270	0.020	10.61	99.03
DS3	Sediment	Sediment	AL	88.96	1.67	0.005	0.47	0.21	0.47	0.06	0.19	0.100	0.010	6.41	98.55
DT1	Glassy	Unweath	WSU	71.38	12.27	0.028	1.73	0.16	0.97	2.62	3.97	0.216	0.032	4.32	97.70
DT2	Glassy	Unweath	WSU	73.48	12.27	0.019	0.99	0.08	0.62	2.05	5.50	0.081	0.018	4.23	99.34
DT3	Devitrified	Unweath	AL	75.21	12.45	0.011	1.25	0.35	0.49	3.04	4.62	0.080	0.020	2.01	99.53
DVC1	Devitrified	Unweath	WSU	74.53	11.65	0.036	2.82	0.17	0.24	4.04	4.47	0.294	0.049	1.14	99.44
DVC2	Devitrified	Weathered	WSU	68.51	12.95	0.067	2.65	0.82	0.75	2.72	3.74	0.290	0.032	5.75	98.28
DVC4	Glassy	Unweath	AL	74.02	10.65	0.062	2.81	0.05	0.21	3.71	5.25	0.180	0.010	2.87	99.82
FD1	Glassy	Weathered	WSU	64.08	12.43	0.049	3.98	0.63	3.64	1.67	1.30	0.454	0.080	11.33	99.64
FD2	Glassy	Weathered	WSU	64.08	12.40	0.060	3.18	0.34	3.62	2.18	1.28	0.361	0.058	11.50	99.06
FD3	Glassy	Weathered	WSU	64.26	12.08	0.065	3.04	0.43	3.67	2.03	0.76	0.304	0.053	12.55	99.24
FD4	Glassy	Weathered	WSU	63.88	12.59	0.048	4.06	0.90	2.79	1.46	2.34	0.425	0.056	10.09	98.64
LB1	Glassy	Weathered	WSU	73.05	13.53	0.017	1.83	0.17	0.40	0.92	4.35	0.174	0.011	4.26	98.71
LG1	Glassy	Weathered	AL	63.89	11.48	0.005	2.31	0.01	1.72	3.73	2.48	0.240	0.010	13.53	99.40
LG2	Devitrified	Weathered	AL	67.80	14.18	0.005	0.69	0.05	1.30	2.42	6.74	0.310	0.010	5.97	99.48
LG3	Devitrified	Weathered	AL	75.51	8.71	0.005	1.64	0.10	1.18	1.57	3.91	0.170	0.020	6.6	99.41
LG4	Devitrified	Weathered	AL	76.56	10.68	0.033	2.39	0.15	0.48	4.39	2.34	0.230	0.010	2.3	99.56
LST1*	Glassy	Weathered	WSU	63.84	10.53	0.78	2.06	0.36	3.72	1.77	3.03	0.26	0.03		85.67
MA1*	Devitrified	Weathered	WSU	69.09	12.30	0.13	2.95	0.66	2.08	3.04	1.76	0.47	0.12		92.60
MK1	Devitrified	Weathered	WSU	71.11	14.00	0.041	2.69	0.25	2.39	4.31	1.62	0.371	0.089	2.18	99.05
MK2	Devitrified	Weathered	WSU	70.00	14.58	0.007	2.35	0.32	2.06	4.05	1.58	0.382	0.017	3.74	99.09

Sample	Devitrificat	Weathering	Lab	SiO2	Al2O3	MnO	FeO	MgO	CaO	Na2O	K2O	TiO2	P2O5	LOI	Total
MTA1	Glassy	Weathered	WSU	60.52	15.37	0.120	5.05	1.65	3.67	2.93	2.19	0.759	0.219	6.35	98.83
PG1	Devitrified	Weathered	WSU	77.79	8.80	0.033	2.51	0.10	1.54	2.27	4.78	0.160	0.058	1.78	99.82
PG2	Devitrified	Unweath	AL	74.27	13.03	0.010	1.61	0.10	0.48	4.37	3.81	0.210	0.020	1.58	99.49
PG3	Glassy	Unweath	AL	70.57	12.04	0.044	2.23	0.63	0.92	2.26	5.43	0.220	0.030	4.88	99.26
RST05	Devitrified	Unweath	AL	77.21	11.82	0.085	1.64	0.03	0.08	3.93	4.92	0.120	0.030	0.22	100.08
RST06	Glassy	Unweath	AL	72.85	11.94	0.097	1.84	0.21	0.54	3.50	4.75	0.200	0.050	2.98	98.95
RST07	Devitrified	Unweath	AL	75.12	12.34	0.081	1.98	0.19	0.41	4.14	4.30	0.210	0.050	0.7	99.52
RST08	Glassy	Unweath	Al	73.21	12.11	0.075	1.34	0.07	0.24	2.78	5.92	0.130	0.150	3.18	99.21
RST09	Glassy	Unweath	AL	73.21	12.74	0.091	1.48	0.08	0.23	3.10	5.47	0.140	0.020	3.44	100.00
RST1	Glassy	Unweath	WSU	73.62	12.00	0.085	1.33	0.05	0.32	3.58	4.74	0.146	0.009	3.52	99.40
RST10	Glassy	Unweath	AL	74.15	11.72	0.074	1.45	0.07	0.22	3.27	5.52	0.130	0.040	2.95	99.59
RST11	Devitrified	Unweath	AL	79.16	10.33	0.091	1.49	0.10	0.24	3.54	3.82	0.130	0.020	1.31	100.23
RST13	Devitrified	Unweath	AL	76.32	11.92	0.112	1.80	0.19	0.35	4.19	4.30	0.180	0.060	0.71	100.13
RST2	Glassy	Unweath	WSU	73.49	11.75	0.070	1.34	0.03	0.32	3.32	5.04	0.145	0.015	3.42	98.94
RST4	Devitrified	Unweath	WSU	76.04	12.03	0.075	1.56	0.05	0.30	4.24	4.40	0.169	0.035	0.28	99.18
RU1*	Glassy	Weathered	WSU	64.45	11.92	0.05	2.49	0.68	2.40	3.48	1.12	0.29	0.50		86.93
SLNM	Devitrified	Weathered	WSU	69.64	13.56	0.139	2.27	0.78	2.08	3.46	4.28	0.327	0.535	2.16	99.23
SLRC	Glassy	Weathered	WSU	63.47	15.49	0.112	2.44	1.44	2.14	2.74	4.30	0.457	0.098	6.03	98.72
SR1	Glassy	Weathered	WSU	68.94	11.48	0.041	1.43	0.67	2.49	1.07	2.08	0.147	0.036	10.53	98.91
SR2	Devitrified	Unweath	WSU	81.80	8.98	0.042	1.48	ND	0.06	2.52	4.26	0.125	0.066	0.64	99.97
TS1	Sediment	Sediment	AL	69.94	10.02	0.005	2.96	1.01	0.98	1.17	0.28	0.560	0.030	12.73	99.69
TS3	Sediment	Sediment	AL	76.32	6.70	0.005	2.43	0.63	0.55	0.43	0.23	0.280	0.020	12.38	99.98
TS4	Sediment	Sediment	AL	66.09	14.56	0.088	2.77	1.23	0.50	3.33	3.14	0.170	0.040	6.16	98.08
TSD1	Sediment	Sediment	AL	49.89	16.00	0.212	8.23	2.89	7.23	1.83	0.76	1.150	0.420	10.62	99.23
TSD2	Sediment	Sediment	AL	55.71	16.21	0.144	7.08	2.91	6.57	2.20	1.34	1.090	0.220	6.19	99.67
TW1	Devitrified	Weathered	WSU	68.05	15.05	0.096	3.14	0.21	2.77	4.53	1.89	0.833	0.209	2.49	99.27
TW2	Sediment	Sediment	WSU	51.74	14.43	0.189	11.06	3.35	6.40	3.56	0.24	1.665	0.162	6.51	99.31
WU1	Devitrified	Weathered	WSU	67.77	14.95	0.126	3.72	0.43	1.32	5.55	2.81	0.540	0.109	2.26	99.59

* Bulk chemistry for samples was obtained during the course of prior studies, and LOI values were unavailable.

The majority of samples had alumina/alkali ratios >1, which is likely a result of loss of alkalis during alteration, rather than being representative of original magmatic composition. There was no correlation between alumina/alkali ratios and arsenic in any category of ash-flow tuffs (Figure 9).

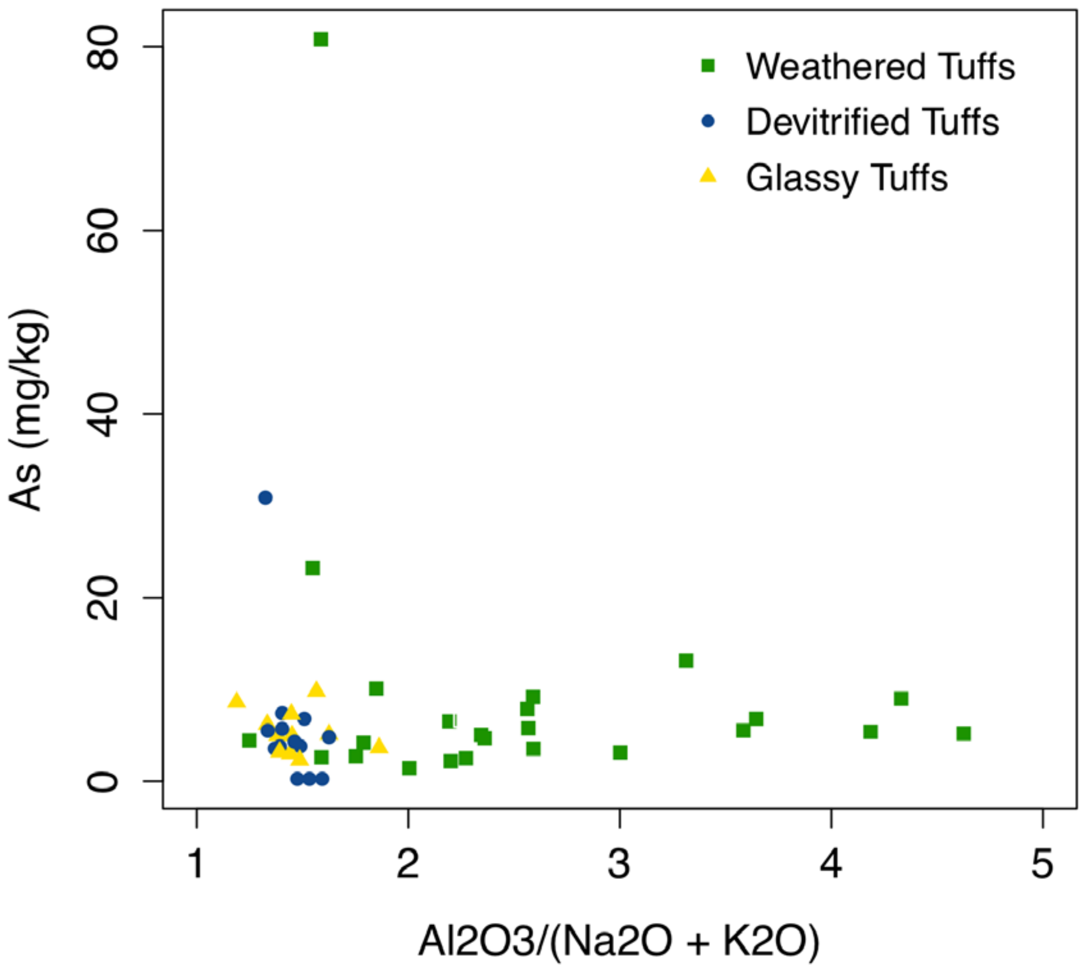

Figure 9. Arsenic as a function of alumina/alkali ratios of tuff samples. The majority of the samples have ratios > 1, and there is no correlation between alumina/alkali ratios and arsenic concentrations.

Trace element concentrations of tuff and tuffaceous sediment samples are located in Table 9. For samples analyzed via INAA at Activation Laboratories, five samples produced arsenic levels below the MDL of 0.5 mg kg^{-1}. For samples analyzed via ICP-OES, only one sample was below the MDL of 1.2 mg kg^{-1}.

Table 9. Selected trace element concentrations (mg kg^{-1}) for tuff and tuffaceous sediment samples. Full trace element results can be found in Appendix C. For samples analyzed at Activation Laboratories the elements Cu, Mo, Pb, Ni, Zn, S, Li, Be, Sr, and V were obtained via ICP-MS, and the elements As, Ba, Cr, Rb, and Sb were obtained via INAA. For samples analyzed at WSU the elements Ba, Cr, Cu, Ni, Pb, Rb, Sr, V, and Zn were analyzed via XRF and the elements As, Be, and Mo were analyzed via ICP-OES at Portland State University. Blank entries indicate that values were not analyzed.

Sample	Devit..	Weathering	Lab	As	Ba	Be	Cr	Cu	Li	Mo	Ni	Pb	Rb	S	Sb	Sr	V	Zn
BC1	Glassy	Weathered	AL	5.20	820	1.00	9	11		0.5	9	5	7.5	300	0.8	206	78	128
BC2	Sediment	Sediment	AL	<0.5	25	0.50	1	9	8	0.5	3	1.5	7.5	50	0.6	31	54	50
BC3	Sediment	Sediment	AL	4.80	690	3.00	18	12	23	0.5	8	13	7.5	200	0.9	154	43	144
DC1	Glassy	Unweathered	WSU	4.97	1351	2.39	3	1		5.3	0	17	87			29	3	142
DC4	Glassy	Unweathered	AL	5.00	1220	3.00	1	6	12	7.0	6	13	76	100	1.1	27	4	204
DC5	Devitrified	Unweathered	Al	<0.5	1150	3.00	1	5	2	0.5	2	8	7.5	50	0.8	35	5	185
DC6	Devitrified	Unweathered	AL	6.80	950	3.00	1	6	5	1.0	2	10	7.5	50	1	30	24	134
DC7	Devitrified	Unweathered	AL	3.80	1000	3.00	1	6	6	2.0	3	6	55	50	0.9	34	12	102
DC8	Glassy	Weathered	AL	2.50	930	3.00	1	5	18	4.0	2	14	47	50	0.7	50	13	241
DC9	Devitrified	Unweathered	AL	<0.5	1190	3.00	1	3	7	1.0	0.5	13	160	50	1	30	6	129
DS1	Sediment	Sediment	AL	20.50	25	2.00	23	30	6	0.5	8	4	7.5	9700	2.7	122	149	47
DS2	Sediment	Sediment	AL	5.00	250	1.00	7	11	4	0.5	5	1.5	7.5	300	2.8	71	74	58
DS3	Sediment	Sediment	AL	<0.5	110	1.00	11	6	<1	0.5	0.5	1.5	7.5	50	0.5	33	34	10
DT1	Glassy	Unweathered	WSU	3.64	626	2.04	13	16		2.6	5	16	86			92	18	35
DT2	Glassy	Unweathered	WSU	5.09	615	2.19	6	8		3.5	2	16	123			38	2	32
DT3	Devitrified	Unweathered	AL	4.80	603	3.00	3	4	16	1.0	2	16	104	50	0.9	31	6	23
DVC1	Devitrified	Unweathered	WSU	3.55	170	3.36	9	12		1.8	5	24	85			23	15	159
DVC2	Devitrified	Weathered	WSU	1.43	262	2.48	10	7		1.5	4	15	43			52	15	128
DVC4	Glassy	Unweathered	AL	8.60	25	8.00	17	7	37	7.0	3	28	185	50	1.6	4	3	284
FD1	Glassy	Weathered	WSU	5.39	539	1.64	6	10		0.1	2	9	26			191	29	101
FD2	Glassy	Weathered	WSU	5.51	505	1.51	6	8		0.6	1	10	39			132	23	102
FD3	Glassy	Weathered	WSU	8.98	466	1.65	4	7		0.1	1	11	29			151	15	103
FD4	Glassy	Weathered	WSU	13.13	713	1.70	4	10		0.2	3	9	76			783	29	100
LB1	Glassy	Weathered	WSU	5.77	733	0.32	6	5		0.7	4	12	104			33	12	35
LG1	Glassy	Weathered	AL	10.10	1100	5.00	1	3	5	0.5	0.5	15	122	600	0.6	27	1	169
LG2	Devitrified	Weathered	AL	23.20	1220	5.00	1	5	6	0.5	0.5	9	172	50	0.9	22	1	89
LG3	Devitrified	Weathered	AL	2.60	380	3.00	1	3	43	0.5	1	14	65	400	0.9	7	2	127
LG4	Devitrified	Weathered	AL	80.80	640	4.00	1	5	32	2.0	0.5	9	7.5	50	0.4	34	1	153

Sample	Devit..	Weathering	Lab	As	Ba	Be	Cr	Cu	Li	Mo	Ni	Pb	Rb	S	Sb	Sr	V	Zn
LST1	Glassy	Weathered	WSU	6.52	483	2.25	4	11		1.0	2	16	63			331	17	111
MA1	Devitrified	Weathered	WSU	7.87	1298	2.77	10	20		0.7	5	18	54			176	33	129
MK1	Devitrified	Weathered	WSU	4.68	405	1.12	20	20		0.9	8	6	35			184	24	63
MK2	Devitrified	Weathered	WSU	9.17	421	1.21	3	7		0.5	3	6	31			178	24	27
MTA1	Glassy	Weathered	WSU	3.13	553	1.17	24	19		1.6	8	13	47			310	67	75
PG1	Devitrified	Weathered	WSU	4.44	641	1.90	4	7		0.3	2	11	132			27	10	131
PG2	Devitrified	Unweathered	AL	<0.5	1280	3.00	1	6	8	0.5	1	11	7.5	50	0.9	43	11	147
PG3	Glassy	Unweathered	AL	9.80	720	5.00	16	8	7	5.0	2	7	89	100	1.4	49	9	173
RST1	Glassy	Unweathered	WSU	3.00	605	2.88	5	3		4.0	3	19	90			10	6	108
RST10	Glassy	Unweathered	AL	6.20	400	4.00	1	5	31	5.0	4	14	79	50	1.4	6	4	132
RST11	Devitrified	Unweathered	AL	5.70	600	4.00	1	8	29	3.0	5	11	140	50	2	17	12	101
RST13	Devitrified	Unweathered	AL	7.40	1080	4.00	13	7	11	1.0	6	11	110	200	1.6	34	12	131
RST2	Glassy	Unweathered	WSU	3.29	721	2.71	6	2		3.7	2	19	85			11	5	120
RST4	Devitrified	Unweathered	WSU	3.79	739	2.49	5	4		1.4	4	14	88			16	6	96
RST5	Devitrified	Unweathered	AL	5.50	480	3.00	10	7	24	2.0	2	16	143	50	1.1	5	10	127
RST6	Glassy	Unweathered	AL	7.30	560	4.00	22	9	26	5.0	4	12	107	50	1.7	25	11	124
RST7	Devitrified	Unweathered	AL	4.30	530	4.00	1	38	25	2.0	11	12	7.5	50	1.8	27	19	107
RST8	Glassy	Unweathered	AL	3.20	370	4.00	1	5	14	5.0	1	16	99	50	1.6	13	4	138
RST9	Glassy	Unweathered	AL	2.30	290	4.00	1	4	20	6.0	3	17	7.5	50	1.4	9	4	138
RU1	Glassy	Weathered	WSU	3.55	552	1.03	5	8		0.1	0	10	20			155	15	73
SLNM	Devitrified	Weathered	WSU	2.72	770	3.74	9	12		2.0	2	28	158			265	42	98
SLRC	Glassy	Weathered	WSU	2.17	1819	1.86	4	21		1.5	4	21	106			440	20	70
SR1	Glassy	Weathered	WSU	6.80	571	3.96	4	10		0.6	1	19	92			97	9	164
SR2	Devitrified	Unweathered	WSU	30.89	374	3.10	5	10		2.0	2	16	128			9	16	128
TS1	Sediment	Sediment	AL	13.90	25	2.00	32	26	15	2.0	16	3	18	3500	0.4	74	152	87
TS3	Sediment	Sediment	AL	4.90	25	0.50	30	21	11	2.0	6	1.5	7.5	1400	0.2	39	69	36
TS4	Sediment	Sediment	AL	6.70	25	5.00	1	5	18	3.0	6	20	7.5	2400	0.9	56	20	179
TSD1	Sediment	Sediment	AL	2.60	880	0.50	164	65	6	0.5	81	1.5	7.5	400	0.05	224	128	70
TSD2	Sediment	Sediment	AL	<0.5	600	1.00	139	66	9	0.5	79	6	7.5	400	0.4	190	100	77
TW1	Devitrified	Weathered	WSU	5.06	351	1.24	7	26		0.6	3	8	33			218	43	49
TW2	Sediment	Sediment	WSU	< 1.2	154	0.42	16	161		0.1	15	3	5			274	290	110
WU1	Devitrified	Weathered	WSU	4.19	875	1.97	11	16		1.2	9	14	53			135	41	85

Total Arsenic Concentrations

The 49 tuff samples have a mean arsenic content of 7.5 mg kg^{-1}, a geometric mean arsenic content of 4.8 mg kg^{-1}, a median arsenic content of 5.2 mg kg^{-1}, and a maximum arsenic content of 81 mg kg^{-1} (Table 10). The mean and median values are 2.8 – 4.4x the average crustal abundance of arsenic of 1.7 mg kg^{-1} (Wedepohl, 1995), and consistent with previously reported mean values for both felsic volcanic rocks (3.5 mg kg^{-1}) and volcanic glasses (5.9 mg kg^{-1}) (Onishi and Sandell, 1955; Wedepohl, 1995).

Table 10. Total arsenic contents of tuffs and tuffaceous sediments. Numbers in parentheses indicate values that include samples identified as outliers.

	Mean (mg/kg)	Geometric Mean (mg/kg)	Median (mg/kg)	Standard Deviation (mg/kg)	Median Absolute Deviation (mg/kg)
All Tuffs n = 45 (49)	5.2 (7.5)	4.2 (4.8)	5.0 (5.2)	3.4 (11)	2.5 (2.8)
Weathered Tuffs n = 18 (20)	6.0 (10.0)	5.2 (6.2)	6.0 (5.6)	3.3 (16)	3.2 (3.8)
Unweathered Tuffs n = 28 (29)	4.7 (5.7)	3.4 (3.7)	4.6 (4.9)	2.6 (5.8)	1.9 (2.2)
Devitrified n = 15 (16)	4.3 (9.6)	2.4 (2.9)	4.3 (4.7)	2.6 (17)	2.1 (2.3)
Glassy n = 13	6.1	4.9	6.0	3.1	2.8
Tuffaceous Sediments n = 10 (11)	4.5 (6.3)	2.0 (2.5)	4.3 (5.6)	4.9 (7.7)	4.8 (7.3)

Arsenic values were normalized to 100% on an anhydrous basis. Four samples (LG4, LG2, SR2, and DS1) were identified as outliers using Grubbs test for outliers. Arsenic concentrations in tuffs were positively skewed, and appeared to be lognormally distributed, so the data were log transformed, and Shapiro-Wilk tests of normality were performed on arsenic concentrations for tuffs, tuffaceous sediments, and the different categories of tuff samples. At a significance level of $\alpha = 0.05$, unweathered tuffs, glassy tuffs, and tuffaceous sediments were still found to be non-normally distributed after log transformation and removal of outliers (Table 11). Details of statistical methods can be found in Appendix B.

Table 11. Test statistics (W) and p-values for Shapiro-Wilk tests of normality.

	W	p-Value
All Tuffs n = 45	0.782	7.93E-07
Weathered Tuffs n = 18	0.985	0.974
Unweathered Tuffs n = 28	0.711	1.41E-05
Devitrified n = 16	0.971	0.917
Glassy n = 13	0.699	0.0008
Tuffaceous Sediments n = 10	0.844	0.050

Brown-Forsythe tests for equality of variances were performed on log transformed arsenic concentrations for all groups of samples with outliers removed (Table 12). At a significance level of α = 0.05, the variance of all tuffs was found to be different than the variance of tuffaceous sediments. Both devitrified and glassy and weathered and unweathered tuffs were found to have statistically indistinguishable variances.

Table 12. Test statistics, number of samples, and p-values for Brown-Forsythe tests of equal variances.

	Test Stat	n1	n2	p-Value
Tuffs v. Tuffaceous Sediments	8.12	46	10	0.006
Weathered v. Unweathered Tuffs	0.800	18	28	0.380
Devitrified v. Glassy	2.30	15	13	0.143

Non-parametric Mann-Whitney-Wilcoxon tests were performed on log transformed arsenic values, and the arsenic concentrations were not found to be significantly different between the different categories of samples (Table 13).

Table 13. Test statistic (U), number of samples, and p-values for Man-Whitney-Wilcoxon tests of equality performed on sample categories.

	U	n1	n2	p-Value
Tuffs v. Tuffaceous Sediments	273	46	10	0.367
Weathered v. Unweathered Tuffs	213	18	28	0.270
Devitrified v. Glassy	59	15	13	0.478

Although the categories are not statistically distinguishable, devitrified and weathered samples contain a larger range of arsenic concentrations than glassy samples, and higher maximum arsenic concentrations (Figure 10). Although 10% of all samples have arsenic concentrations in excess of 10 mg kg^{-1} no fresh glassy samples contain arsenic at those levels.

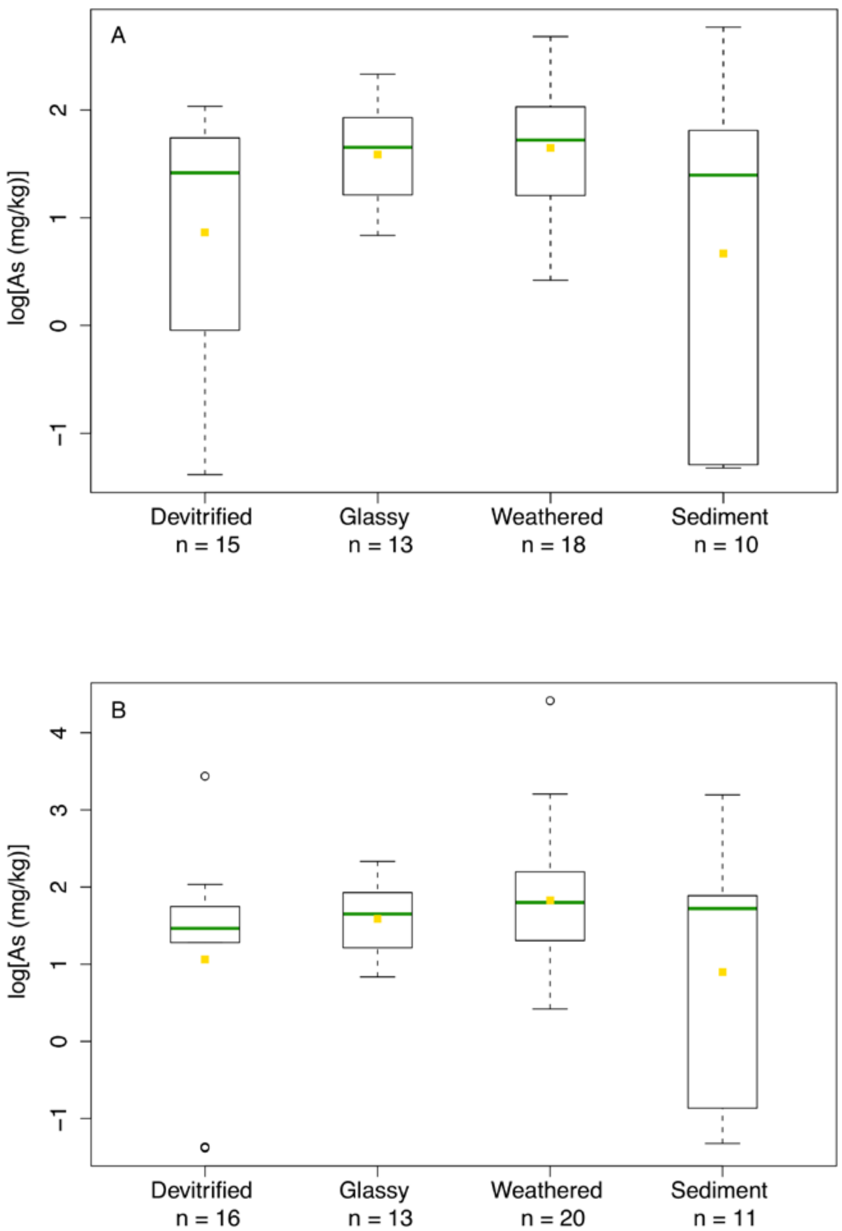

Figure 10. Log transformed distributions of total arsenic concentrations for samples divided by category. A: without outlying values. B: with outlying values. Yellow squares indicate mean values.

Variability Within Units

Total arsenic concentrations can vary substantially within individual units (Figure 11). The most extreme example is the Tuff of Leslie Gulch, which has a maximum arsenic concentration or 81 mg kg^{-1}, about 30 times greater than its minimum arsenic concentration of 2.6 mg kg^{-1}.

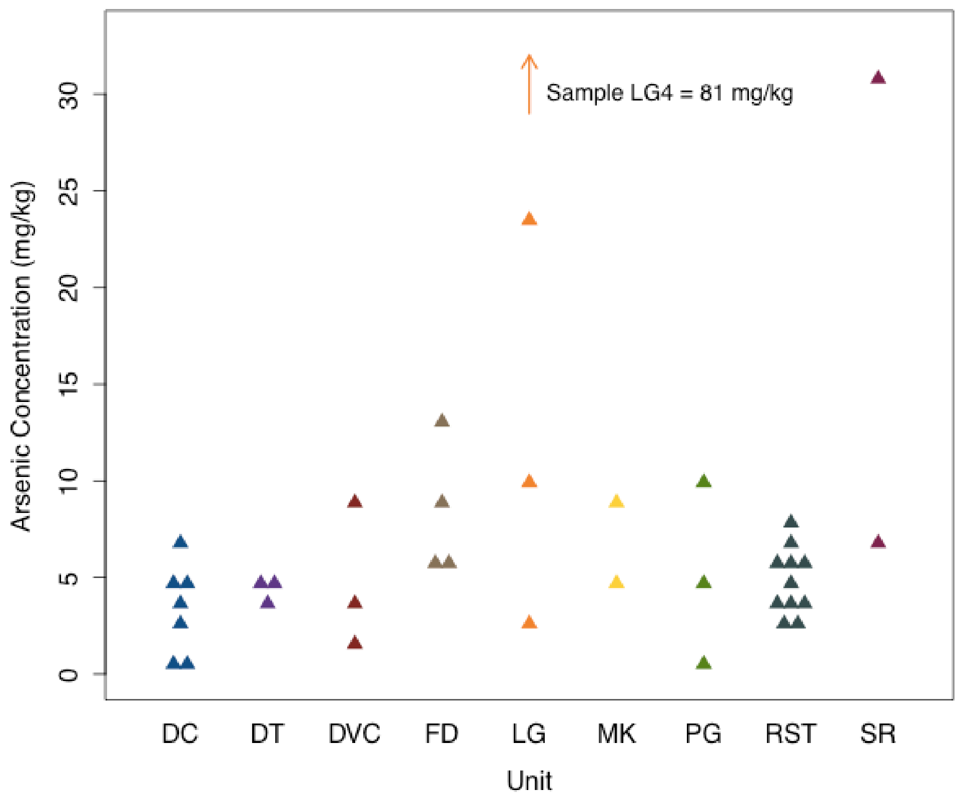

Figure 11. Ranges of arsenic found in individual geologic units. DC = Dinner Creek Tuff, DT = Dale Tuff, DVC = Devine Canyon Tuff, FD = Tuff of Foster Dam, LG = Tuff of Leslie Gulch, MK = Tuff of Mohawk, PG = Picture Gorge Tuff, RST = Rattlesnake Tuff, SR = Tuff of Smith Rock.

Arsenic concentrations varied within individual outcrops as well as individual units. Complete sections from unwelded bases through devitrified tops were collected from single outcrops of the Rattlesnake Tuff and the Dinner Creek Tuff (Figure 12). Both sections contained ranges of arsenic concentrations >5 mg kg^{-1}.

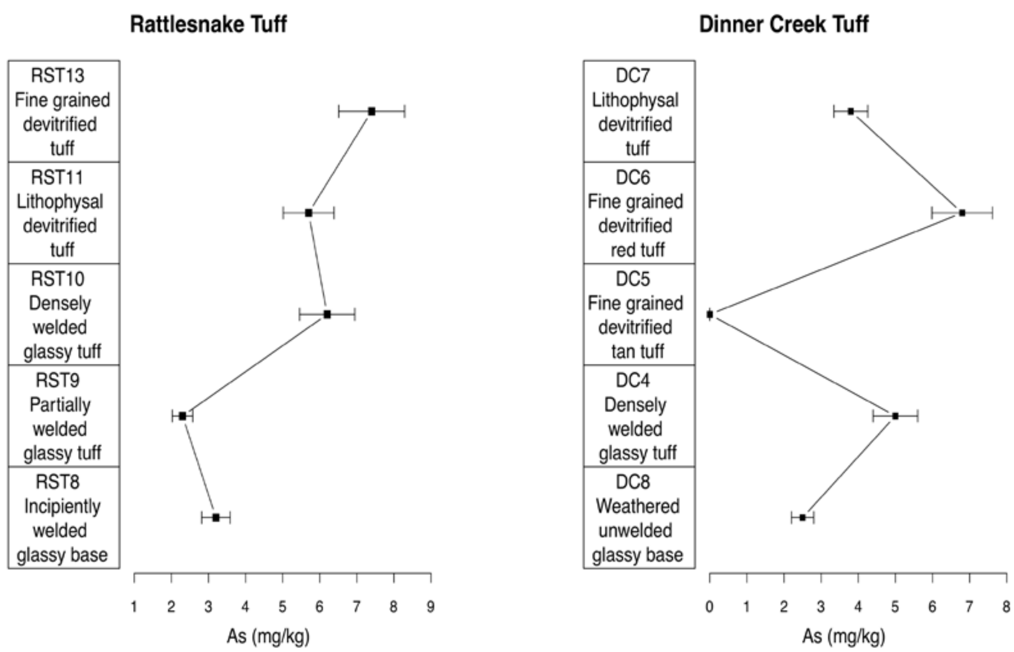

Figure 12. Stratigraphy and corresponding arsenic concentrations for two sections of individual tuff units. The type section of the Rattlesnake tuff shows higher arsenic levels upsection in the less porous sections of the unit. The Dinner Creek section shows arsenic concentrations ranging from <0.5 mg kg^{-1} (non-detect value plotted as 0 mg kg^{-1}) to 6.8 mg kg^{-1}, with no apparent relationship between arsenic concentration and position within the section. Error bars are based on INAA recovery percents from certified reference materials from Activation Laboratories, Ltd.

In the Rattlesnake Tuff arsenic concentrations generally increased upsection, with lower arsenic levels in the incipiently and partially welded glassy samples at the base, and higher values in both the densely welded glassy sample and devitrified samples. In contrast, the Dinner Creek Tuff did not display any apparent relationship between arsenic concentration and vertical position within the section.

Elemental Correlations

Tests of correlation between arsenic and other elements were performed on log transformed data with outliers excluded using the non-parametric Spearman's rank correlation coefficient, which was chosen over Pearson's product moment correlation coefficient due to both the non-normal distribution of the data and the comparative robustness of Spearman's rank correlation coefficient when dealing with outliers. Details of statistical calculations can be found in Appendix B. Arsenic displayed statistically significant ($p < 0.05$) correlations with a few of the elements in the samples used in this study (Table 14).

Table 14. Statistically significant ($p < 0.05$) elemental correlations with arsenic. Italicized items showed a negative correlation with arsenic, while un-italicized items showed a positive correlation.

	Significant Correlations with Arsenic
All Tuffs (df = 44)	*Al_2O_3*, FeO, Sb
Weathered Tuffs (df = 16)	*K_2O, Mo*
All Unweathered Tuffs (df = 26)	*Al_2O_3*, Cu, FeO, Sm
Devitrified Tuffs (df = 13)	MnO, Sm
Glassy Tuffs (df = 11)	Cr, FeO
Tuffaceous Sediments (df = 8)	None

Arsenic in all tuff samples was negatively correlated with Al_2O_3, and positively correlated with FeO and Sb. Different categories of tuffs displayed different correlations between arsenic and other elements, although a positive correlation with FeO was present in multiple categories. The majority of the statistically significant correlations, including the correlation with FeO, were not reflective of strong linear relationships between elements, with R^2 values < 0.15 (Figure 13).

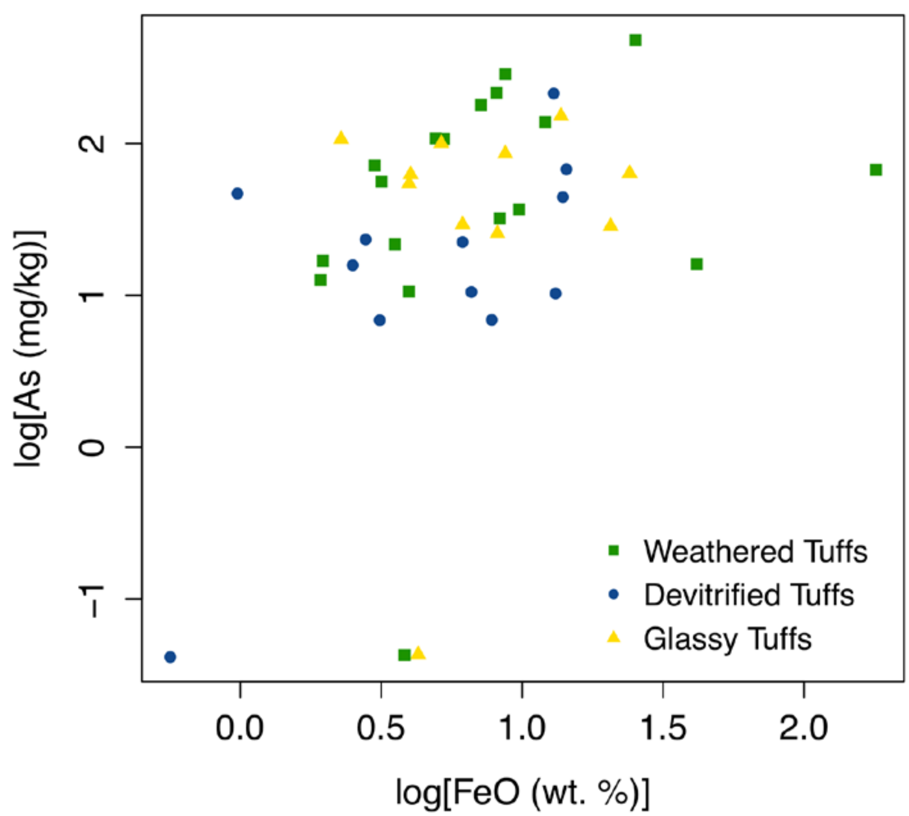

Figure 13. Log transformed Arsenic and FeO concentrations in tuffs and tuffaceous sediments. Although statistically significant positive correlations were found between arsenic and FeO, there is not a strong linear relationship between the elements

DISCUSSION

Arsenic concentrations in ash-flow tuffs are higher than previously reported values, and highly heterogenous between and within individual units. Although the median arsenic concentrations do not differ between categories of tuffs, the range of arsenic, particularly the maximum arsenic concentrations, is different between both weathered and unweathered tuffs and devitrified and glassy tuffs. Although 10% of the samples in this study had arsenic concentrations exceeding 10 mg kg^{-1} none of those samples were unweathered glassy samples. Together, these results suggest three distinct mechanisms that determine the arsenic concentrations of individual tuff samples: arsenic content of the original source magma, mobility of arsenic during deposition of the unit, and mobility of arsenic during post-depositional alteration processes, both devitrification and weathering.

Composition of Source Magma

The first factor in determining arsenic levels in a tuff sample is the arsenic content of the original source magma. Although no correlation was found between alumina/alkali ratios and arsenic, previous research has suggested that the arsenic content of volcanic rocks increases with silica content, and less felsic volcanic rocks have lower mean arsenic concentrations than ash-flow tuffs (Onishi and Sandell, 1955). Fractional crystallization of feldspars, other anhydrous silicates, and oxides produces melts enriched in volatiles and incompatible metals, including arsenic (Borisova, 2010). Enrichment driven by fractional crystallization is a likely mechanism for producing arsenic concentrations in high-silica tuffs that exceed both the average value of the continental crust, and values found in less silicic volcanic rocks.

Arsenic concentrations can also vary between different silicic magmas. Along with boron, arsenic has been suggested as an indicator of contributions from sedimentary materials and slab-derived fluids in subduction zone magmas (Noll, 1996). Magmas produced by melting of high arsenic sedimentary materials and magmas incorporating a high proportion of slab-derived fluids can contain higher arsenic concentrations than magmas produced in other tectonic settings.

Although the arsenic concentrations of tuff samples in this study displayed a high degree of heterogeneity within individual units it seems likely that the magmatic source plays some role in determining the final arsenic concentrations of individual samples. All of the units in this study that contained at least one sample with arsenic levels exceeding 10 mg kg^{-1} also contained samples with lower arsenic levels. However, the lower arsenic levels for these units still exceeded the median value of 5.0 mg kg^{-1} for all tuffs, which suggests that the original source magmas for these units were potentially more arsenic rich than units lacking high arsenic (>10 mg kg^{-1}) samples.

Depositional Processes

Pyroclastic volcanic eruptions that produce ash-flow tuffs involve substantial and rapid degassing of silicic magmas. Arsenic is known to preferentially partition into the vapor phase, and has been found to be enriched by factors of $10^2 – 10^3$ relative to the melt in studies of andesitic magma systems (Symonds, 1987). Unlike more effusive eruption mechanisms pyroclastic flows entrain both solid and vapor phase portions of a magma during deposition. The presence of arsenic in the vapor phase during deposition of ash-flow tuffs is likely to result in loss of some portion of arsenic from the system as well as heterogeneity of arsenic levels within the unit itself (Borisova, 2010).

While substantial heterogeneity was observed within units the results of this study do not provide definitive conclusions about spatial patterns of arsenic distribution that occur as a result of movement of the vapor phase. The arsenic concentrations in the type section of the Rattlesnake Tuff suggest one possible pattern of spatial distribution. Within a single outcrop samples taken higher in the section, representing the denser, less permeable interior of the unit, display higher arsenic concentrations than un- or partially welded samples from the base of the unit (Figure 12). This suggests that volatile arsenic entrained in the flow may have migrated from the permeable lower portions of the unit during deposition and cooling, and been trapped in the overlying less permeable interior. This same pattern is not seen in the Dinner Creek Tuff.

An additional hypothesis regarding the spatial distribution of arsenic within individual tuffs is that arsenic may decrease with increasing distance from the eruptive center, as a higher proportion of the volatiles are lost as the flow travels further from its source. Distance from the eruptive center is a variable worth exploring in further studies.

Post-Depositional Alteration Processes

Although the median values were not statistically different between categories of tuffs only weathered and devitrified tuffs included samples with arsenic concentrations that exceeded 10 mg kg^{-1}, and unweathered glassy samples contained a much smaller range of arsenic levels than the other categories of tuffs. This suggests that both devitrification and weathering have the potential to concentrate arsenic relative to unaltered tuffs.

The most likely mechanism to explain the potential for arsenic enrichment in devitrified tuffs relative to glassy tuffs is vapor phase mineralization. Vapor phase mineralization occurs primarily in the interiors of thick (>10 m) ash-flow tuffs, and can be driven by the degassing of H_2O, CO_2, S, and other volatile components from pyroclastic glasses during the process of devitrification (Vaniman, 2006). As a result of the wide variety of constituents that are excluded from the structure of feldspars and silicates that form during devitrification, vapor phase mineralogy can be very complex, and can differ substantially between tuffs. Vapor phase minerals include a variety of silicate minerals (alkali feldspar, tridymite, cristobalite, quartz, amphibole, biotite, zircon, monazite, and garnet have all been observed), as well as oxides, carbonates, phosphates, chlorides, and sulfides (Stimac, 1996; Vaniman, 2006). Oxides, phosphates, and sulfide minerals are all likely candidates for arsenic host phases. In addition, the fact that vapor phase mineralization occurs in some, but not all, tuffs may explain why only a portion of the devitrified samples in this study were enriched in arsenic relative to glassy samples.

Unfortunately, identification of vapor phase minerals is difficult, because they tend to be small (< 1-10 μm), present at low concentrations (< 1% by volume), fragile, and located on grain surfaces and boundaries between larger crystals (Stimac, 1996). The complexity of vapor phase mineralogy and difficulty of identifying individual vapor phase minerals makes the characterization of vapor phase minerals beyond the scope of the solid phase characterization performed in this study.

CHAPTER 3: ARSENIC MOBILITY IN ASH-FLOW TUFFS AND ASSOCIATED SEDIMENTS

INTRODUCTION

Despite the widespread association between ash-flow tuffs and elevated groundwater arsenic concentrations, surprisingly little is known about arsenic mobility from these units. Multiple mechanisms have been proposed to explain the mobilization of arsenic from tuffs, including dissolution of volcanic glasses (Nicolli et al., 1989; Johannesson and Tang, 2009), and alkali desorption of arsenic from mineral grain surfaces (Smedley and Kinniburgh, 2002). Although tuffs are typically highly heterogenous and include both glassy and devitrified sections as well as varying degrees of weathering, most research has focused solely on volcanic glasses, and has not considered the alteration processes of devitrification and weathering, or what role those processes may play in mobilizing arsenic.

This study uses 49 tuff samples spanning a range of chemical and mineralogical compositions, as well as 11 samples of tuffaceous sediments to investigate the mobility of arsenic in ash-flow tuffs. Specific objectives of the study are 1) to quantify the amount of arsenic present in tuffs that can be mobilized into the environment by determining total environmentally available arsenic levels and readily leachable arsenic levels and 2) to determine if and how devitrification and weathering influence the amounts of mobile arsenic present in tuffs.

METHODS

To investigate the relative mobility of arsenic in tuffs of varying compositions two fractions of arsenic were identified. Both environmentally available and readily leachable fractions were operationally defined. The environmentally available fraction refers to the portion of arsenic mobilized by microwave digestion with concentrated HNO_3^-, following USEPA Method 3051A, which results in the dissolution of solid phases that are susceptible to chemical alteration under a range of surface geochemical conditions. This method does not recover metals hosted in silicate phases (feldspars, silica polymorphs, or glass), and is frequently referred to a "total recoverable" analytical method, in contrast to USEPA Method 3052 using HF + HNO_3^- + HCl, which is a "total total" method (Chen, 1998; US Environmental Protection Agency, 1996a).

The readily leachable fraction refers to the fraction of arsenic (and other elements) mobilized by simple mixing with reagent-grade water for a relatively short period of time (18 hours), following ASTM D3987-85. This method is designed to produce a water extract that simulates conditions where the solid phase is the dominant factor in determining the final pH of the extract (Das, 2007).

Environmentally Available Arsenic

To determine the environmentally available fraction of elements, samples were digested following USEPA Method 3051A (US Environmental Protection Agency, 1996a). A subsample of crushed and powdered sample was weighed to 1.000 ±0.001 g and placed in a Teflon microwave vessel to which 10 mL of 17 M trace-metal grade

HNO_3^- was subsequently added. Samples were digested using a Milestone Ethos EZ microwave digester for 40 minutes, reaching a maximum temperature of 240ºC for 20 minutes. Method blanks and standard JR1 from the Japanese Geological Survey were run every 20 samples. Samples were decanted into 50-mL plastic centrifuge tubes and vessels were rinsed three times with 18.2 MΩ cm distilled water. The rinse was added to the digested samples, and the centrifuge tubes were filled to 40 mL with water. Samples were centrifuged at 3000 rpm for 10 minutes. Samples were further diluted (1:1 with water) in plastic test tubes immediately prior to analysis, and mixed by pouring the diluted sample into a second plastic test tube. Samples were analyzed using an Agilent 700 Series ICP-OES. Operating conditions for the analysis are listed in Appendix A.

Readily Leachable Arsenic

An additional aliquot of powdered sample was weighed to 1.000 ±0.001, placed in a 50-mL centrifuge tube and combined with 20.0 mL of 18.2 MΩ cm deionized water. Samples were mixed at 20 rpm for 18 hours. After mixing, samples were centrifuged at 3000 rpm for 15 minutes and ~15 mL of each solution was decanted into a fresh 50-mL centrifuge tube. Samples were acidified using 0.300 mL of trace-element grade HNO_3^- in order to preserve the solution for analysis. Samples were analyzed using an Agilent 700 Series ICP-OES. Operating conditions for the analysis are listed in Appendix A. For selected samples the pH of the resulting solution was determined from the unacidified sample.

pH Dependent Extractions

To determine how pH influences the leachability of arsenic from tuffs, the procedure for determining readily leachable arsenic was repeated with varying pH levels on selected samples. Five tuff samples with the highest total arsenic concentrations were selected from the glassy (BC1, DVC4, PG3, RST6, RST10), devitrified (DC6, MK2, RST11, RST13, SR2), and weathered (FD3, FD4, LG1, LG2, LG4) categories. Leaching experiments were performed at pH 3, 5, and 9 using Fisher Scientific buffer solutions, and at pH 11 using a buffer solution prepared in the lab using reagent grade NaOH and $NaHCO_3$ (Table 15). Specific buffers were selected primarily to avoid the use of potassium phosphate, a common component of buffer solutions, in order to avoid introducing phosphate anions into solution, as phosphate can behave as a competing anion and decrease the sorption of arsenic.

Table 15. Buffer solutions used to control pH levels in pH specific leaching experiments.

Name	Composition	pH
Fisher Chemical SB97-500 Buffer Solution	Potassium Acid Phthalate Hydrochloric Acid	3
Fisher Chemical SB102-1 Buffer Solution	Potassium Acid Phthalate Sodium Hydroxide	5
Fisher Chemical SB114-1 Buffer Solution	Boric Acid Potassium Chloride Sodium Hydroxide	9
	Sodium Hydroxide Sodium Bicarbonate	11

One gram of powdered sample was placed in a 50-mL centrifuge tube and combined with 20.0 mL of buffer solution. Samples were mixed at 20 rpm for 18 hours.

After mixing, samples were centrifuged at 3000 rpm for 15 minutes. Following centrifuging ~15 mL of solution was decanted into fresh 50-mL centrifuge tubes. Samples were acidified using 0.300 mL of trace element grade HNO_3^- to preserve the solution for analysis. Unfortunately, rectangular euhedral crystals were observed forming on the wall of the centrifuge tubes holding the pH 3 and pH 5 solutions, potentially the result of oxidation of the potassium acid phthalate in the buffer solutions by HNO_3^-, and the low pH extracts were not analyzed. The high pH solutions were analyzed using an Agilent 700 Series ICP-OES. Operating conditions for the analysis are listed in Appendix A.

RESULTS

QC Results

Check standards were run during ICP-OES analysis as a check on instrumental accuracy, and results are listed in Appendix A. For environmentally available arsenic samples, three analytical sessions were conducted, and results for individual elements varied slightly between sessions. Most elements consistently produced values that were within ± 10% of the standard value, with the exception Na and Si. Na was measured at values up to 118% of the check standard value during the first run, but was consistently within ± 10% of the standard value during subsequent runs. Si was not measured during the first run, but was measured at values exceeding the check standard value by up to 400% during subsequent sessions. Si values increased over the course of both runs, and values in excess of check standard values were likely the result of insufficient rinsing of the element between analyses of different samples. For the second and third sessions neither S and P were present in the check standard, but were still measured at low levels (up to 30 ppb for S) in check standard and blanks.

For readily leachable arsenic samples two analytical sessions were conducted. For both sessions the check standard results were similar to those for the environmentally available samples. Na and Si were consistently measured with values exceeding those of the check standards, and P and S were measured at low levels in check standards and blanks, despite not being present in those standards.

Three samples analyzed for environmentally available arsenic were analyzed in duplicate. Relative percent differences for arsenic in the samples range from 2.5 to 7.6%.

Table 16. Relative percent differences for duplicate samples analyzed via EPA Method 3051a.

	WU1 RPD (%)	MK1 RPD (%)	MK2 RPD (%)
Al	0.24	1.18	0.37
As	7.64	3.53	2.49
Ba	0.06	0.83	0.45
Ca	0.41	1.62	0.38
Cd	4.07	1.72	5.17
Ce	0.03	0.94	0.91
Co	0.40	0.56	1.50
Cr	0.50	1.46	0.12
Cu	0.00	0.58	0.32
Fe	0.05	0.98	0.11
La	0.12	1.23	0.82
Mg	0.06	0.72	0.44
Mn	0.04	1.00	0.38
Na	0.61	1.10	0.01
Ni	0.45	0.79	2.00
P	0.03	0.36	0.42
Pb	1.31	4.04	1.66
S	0.92	2.54	0.41
Sm	2.01	0.54	0.00
Sr	0.05	1.11	0.49
V	0.18	1.09	0.46
Zn	0.20	0.74	0.62

All water extractions were performed in duplicate, and selected sample RPDs are displayed in Table 17, full RPD results can be found in Appendix A. Relative percent differences for arsenic ranged from 1.32% to 6.65%. The low levels of elements present in the water extracts produced many non-detections, as well as higher RPDs for many elements than occurred for other experiments.

Table 17. Relative percent differences for water extractions analyzed in duplicate.

	LG1 RPD (%)	RST10 RPD (%)	DST2 RPD (%)
Al	26.2	21	40.6
As	1.32	NA	6.65
Ba	32.1	13.5	18.1
Ca	20.5	12.5	0.59
Cu	1.18	8.16	4.36
Fe	7.29	19.6	46.9
La	16.5	NA	40.2
Mg	13.5	12.7	19.8
Mn	NA	NA	39.4
Mo	NA	NA	NA
Na	1.87	0.31	3.28
P	1.02	0.18	19.5
S	5.92	1.22	3.14
Si	1.65	10.6	9.03
Sr	30.6	15.7	14.4
Ti	0.46	18.4	35.9
V	18.5	0.29	1.70
Zn	6.99	13.0	43.9

Environmentally Available Arsenic

Complete results for the environmentally available fraction are listed in Appendix C. Two samples (LG4 and SR2) were identified as outliers using Grubbs test for outliers. Arsenic concentrations in tuffs were positively skewed and appeared to be lognormally distributed, so the data was log transformed, The mean environmentally available arsenic concentration present in all tuff samples, excluding the two outliers, is 2.2 mg kg^{-1}, the median environmentally available arsenic concentration is 1.8 mg kg^{-1}, and the geometric mean of arsenic present in the environmentally available fraction is 1.2 mg kg^{-1} (Table 18).

Table 18. Environmentally available fraction of arsenic present in ash-flow tuffs and tuffaceous sediments. Numbers in parentheses indicate values that include samples identified as outliers.

	Mean (mg/kg)	Geometric Mean (mg/kg)	Median (mg/kg)	Standard Deviation (mg/kg)	Median Average Deviation (mg/kg)
All Tuffs n = 47 (49)	2.2 (4.1)	1.2 (1.4)	1.8 (1.8)	2.1 (9.9)	2.3 (2.4)
Weathered Tuffs n = 19 (20)	3.3 (5.8)	2.4 (2.8)	2.9 (3.0)	2.3 (12.7)	2.4 (2.4)
Unweathered Tuffs n = 28 (29)	1.2 (2.3)	0.63 (0.74)	0.43 (0.57)	1.4 (5.7)	0.34 (0.54)
Devitrified n = 15 (16)	2.8 (6.6)	1.9 (2.4)	2.3 (2.4)	2.1 (13.8)	0.71 (0.78)
Glassy n = 13	1.8	0.23	0.7	2.1	0
Tuffaceous Sediments n = 11	2.4	1.1	1.4	3.1	1.7

Shapiro-Wilk tests of normality were performed on log transformed arsenic concentrations for all tuffs, tuffaceous sediments, and the different categories of tuff samples. At a significance level of $\alpha = 0.05$, all tuffs, unweathered tuffs, and glassy tuffs were found to be non-normally distributed (Table 19). Details of statistical methods can be found in Appendix B.

Table 19. Test statistics (W) and p-values for Shapiro-Wilk tests of normality.

	W	p-Value
All Tuffs n = 46	0.883	2.40E-04
Weathered Tuffs n = 18	0.935	0.137
Unweathered Tuffs n = 29	0.804	4.39E-04
Devitrified n = 16	0.935	0.467
Glassy n = 13	0.327	1.21E-06
Tuffaceous Sediments n = 10	0.918	0.306

Brown-Forsythe tests for equality of variances were performed on log transformed arsenic concentrations for all groups of samples (Table 12). At a significance level of $\alpha = 0.05$, both devitrified and glassy and weathered and unweathered tuffs were found to have unequal variances.

Table 20. Test statistics, number of samples, and p-values for Brown-Forsythe tests of equal variances.

	Test Stat	n1	n2	p-Value
Tuffs v. Tuffaceous Sediments	0.0471	47	11	0.829
Weathered v. Unweathered Tuffs	6.038	19	28	0.018
Devitrified v. Glassy Tuffs	5.282	15	13	0.051

Non-parametric Mann-Whitney-Wilcoxon tests were performed on the log transformed solid arsenic concentrations in the environmentally available fraction. Environmentally available arsenic was found to be significantly different between both weathered and unweathered tuffs and glassy and devitrified tuffs (Table 21). Unweathered tuffs have significantly less arsenic in the environmentally available fraction than weathered tuffs, and glassy tuffs have significantly less arsenic in the environmentally available fraction than devitrified tuffs.

Table 21. Test statistic (U), number of samples, and p-values for Man-Whitney-Wilcoxon tests of equality performed on sample categories.

	U	n1	n2	p-Value
Tuffs v. Tuffaceous Sediments	236	47	11	0.736
Weathered v. Unweathered Tuffs	101.5	19	28	3.15E-04
Devitrified v. Glassy	131	15	13	2.61E-05

Although unweathered tuffs are significantly different than weathered tuffs it appears that difference is driven primarily by the very low levels of environmentally available arsenic found in unweathered glassy tuffs in comparison to the other categories, rather than differences produced by weathering in both glassy and devitrified tuffs. When compared directly there is no significant difference between weathered tuffs and unweathered devitrified tuffs (Figure 14).

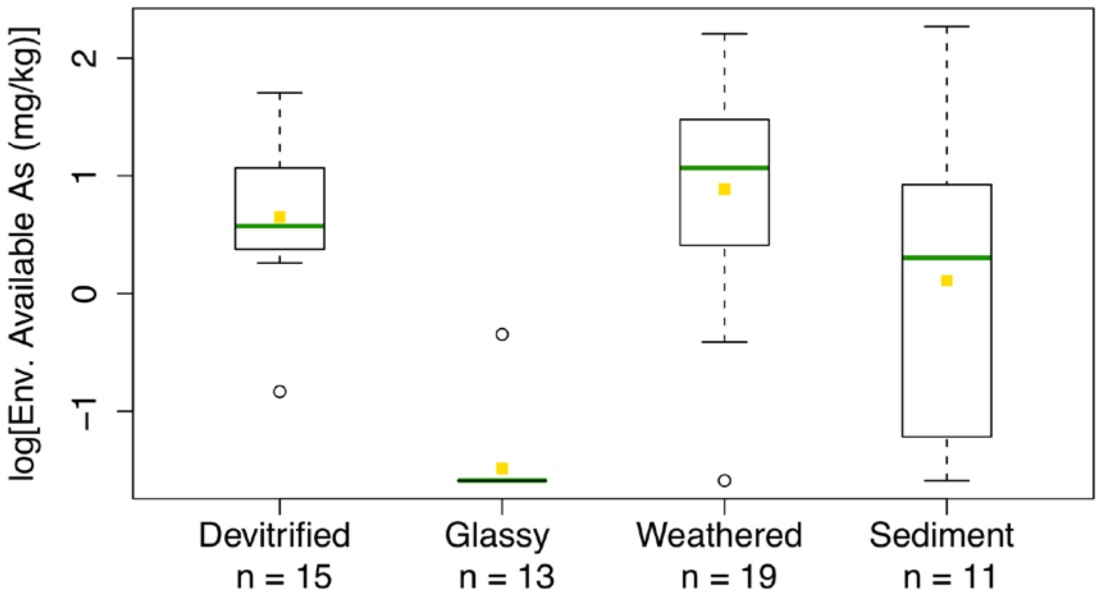

Figure 14. Environmentally available fraction of arsenic present in tuffs and tuffaceous sediments. Yellow squares indicate mean values. In unweathered glassy tuffs significantly less of the total arsenic is present in the environmentally available fraction than is found in devitrified or weathered tuffs, or tuffaceous sediments.

When the weathered tuff category is broken into originally glassy and originally devitrified samples the difference between glassy and devitrified samples is more apparent. Weathering does not produce a higher proportion of environmentally available arsenic in devitrified tuffs, but does produce a significantly higher proportion of environmentally available arsenic in glassy tuffs (Figure 15).

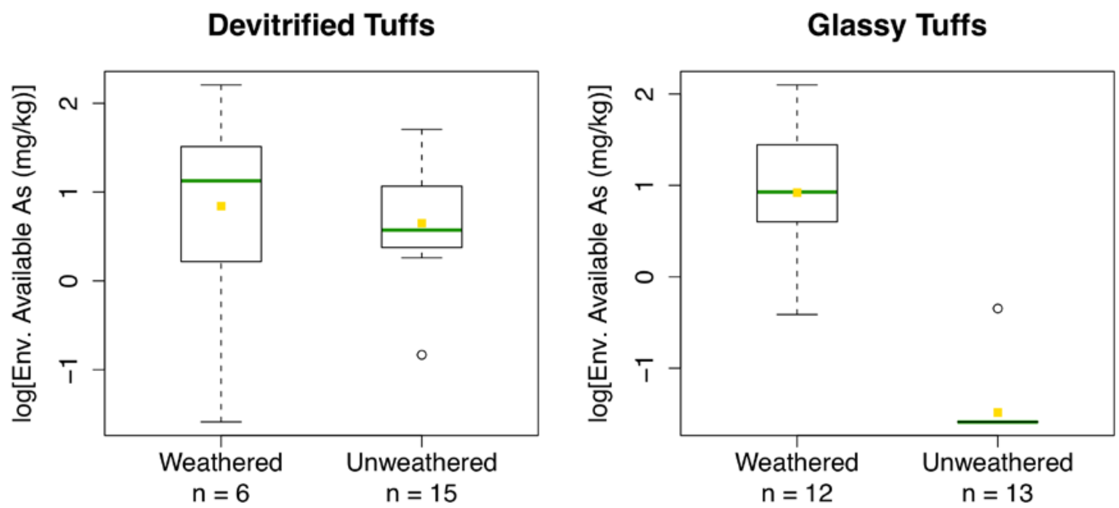

Figure 15. Environmentally available fraction of arsenic present in devitrified and glassy tuffs, by degree of weathering. Yellow squares indicate mean values. Weathering produces substantial differences in the environmentally available fraction of arsenic in glassy tuffs, but the difference between weathered and unweathered devitrified tuffs is not significant.

There are statistically significant positive correlations between environmentally available arsenic and total arsenic in all categories of samples except unweathered glassy tuffs (Figure 16). For devitrified and weathered tuffs, as well as tuffaceous sediments, regressions between total and available arsenic remain statistically significant ($p < 0.05$) even when samples identified as outliers are removed.

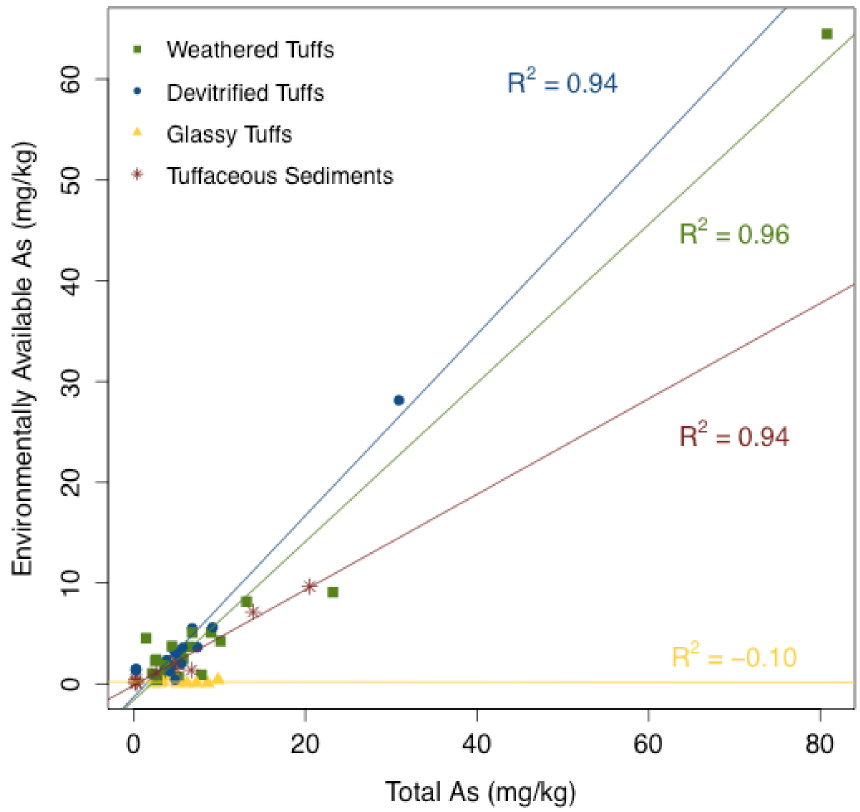

Figure 16. Environmentally available arsenic as a function of total arsenic concentrations. There is a direct relationship between total and available arsenic in all categories except glassy tuffs.

Readily Leachable Arsenic

The majority of tuff samples, including all unweathered glassy samples, produced levels of readily leachable arsenic below the method detection limit (MDL) of 102 µg kg^{-1}. Among the samples that produced detectable levels of arsenic, the geometric mean concentration was 236 µg kg^{-1}, and the median concentration was 219 µg kg^{-1} (Table 22).

Table 22. Readily leachable fraction of arsenic present in ash-flow tuffs and tuffaceous sediments. Values in parentheses indicate values that include samples below the MDL of 102 μg/kg.

	Mean (μg/kg)	Geometric Mean (μg/kg)	Median (μg/kg)	Standard Deviation (μg/kg)	Median Absolute Deviation (μg/kg)
All Tuffs n = 9 (49)	266 (90.5)	236 (67.6)	219 (51.1)	131 (99.6)	159 (0)
Weathered Tuffs n = 5 (20)	282 (109)	258 (76.5)	219 (51.1)	135 (120)	111 (0)
Unweathered Tuffs n = 4 (29)	245 (77.9)	212 (62.1)	248 (51.1)	143 (82.7)	178 (0)
Devitrified n = 4 (16)	245 (96.8)	212 (71.3)	248 (51.1)	143 (105)	178 (0)
Glassy n = 13	ND	ND	ND	ND	ND
Tuffaceous Sediments n = 7 (11)	1232 (1907)	1134 (367)	2174 (192)	1330 (1392)	1270 (208)

For statistical purposes non-detect values were replaced with a value of 0.5 x MDL (Antweiler, 2008; Clark, 1998). Arsenic levels in the leachable fraction were positively skewed, and appeared to be lognormally distributed, so values were log transformed and Shapiro-Wilk tests of normality were performed on arsenic concentrations for tuffs, tuffaceous sediments, and the different categories of tuff samples. At a significance level of α = 0.05, all categories of tuffs and tuffaceous sediments were found to be normally distributed, with the exception of glassy tuffs where all samples had identical values (Table 23). Details of statistical methods can be found in Appendix B.

Table 23. Test statistics (W) and p-values for Shapiro-Wilk tests of normality.

	W	p-Value
All Tuffs n = 46	0.498	1.03E-11
Weathered Tuffs n = 18	0.596	2.68E-06
Unweathered Tuffs n = 29	0.412	1.07E-09
Devitrified n = 16	0.554	3.84E-06
Glassy n = 13	NA	NA
Tuffaceous Sediments n = 10	0.787	0.006

Parametric F tests for equality of variances were performed on log transformed readily leachable arsenic values. At a significance level of $\alpha = 0.05$, tuffs and tuffaceous sediments, as well as devitrified and glassy tuffs, were found to have unequal variances. The variances of weathered and unweathered tuffs were not found to be statistically distinct (Table 24).

Table 24. Test statistics (F), numerator and denominator degrees of freedom, and p-values for F tests of eqaulity of variances.

	F	df1	df2	p-Value
Tuffs v. Tuffaceous Sediments	8.9	10	48	9.38E-08
Weathered v. Unweathered Tuffs	0.52	28	19	0.113
Devitrified v. Glassy	Inf	16	11	< 2.2 e-16

Two sample students t-tests were performed on log transformed arsenic levels in the different categories of samples. At a significance level of $\alpha = 0.05$, the means of glassy and devitrified tuffs were found to be unequal, while weathered and unweathered tuffs were not found to be statistically distinguishable (Table 25).

Table 25. Test statistic (t), number of samples, and p-values for two sample students t-tests of equality performed on sample categories.

	t	n1	n2	p-Value
Tuffs v. Tuffaceous Sediments	2.92	49	11	0.015
Weathered v. Unweathered Tuffs	-1.07	20	29	0.295
Devitrified v. Glassy	2.02	16	13	0.060

Unlike the total or environmentally available fractions, the readily leachable fraction did show a significant difference between tuffs and tuffaceous sediments (Figure 17, Table 25). Tuffaceous sediments contain both much higher arsenic concentrations and a much larger range of readily leachable arsenic concentrations than all categories of tuff samples. Both weathered and devitrified samples display a wider range of readily leachable arsenic levels than glassy tuffs (Figure 17).

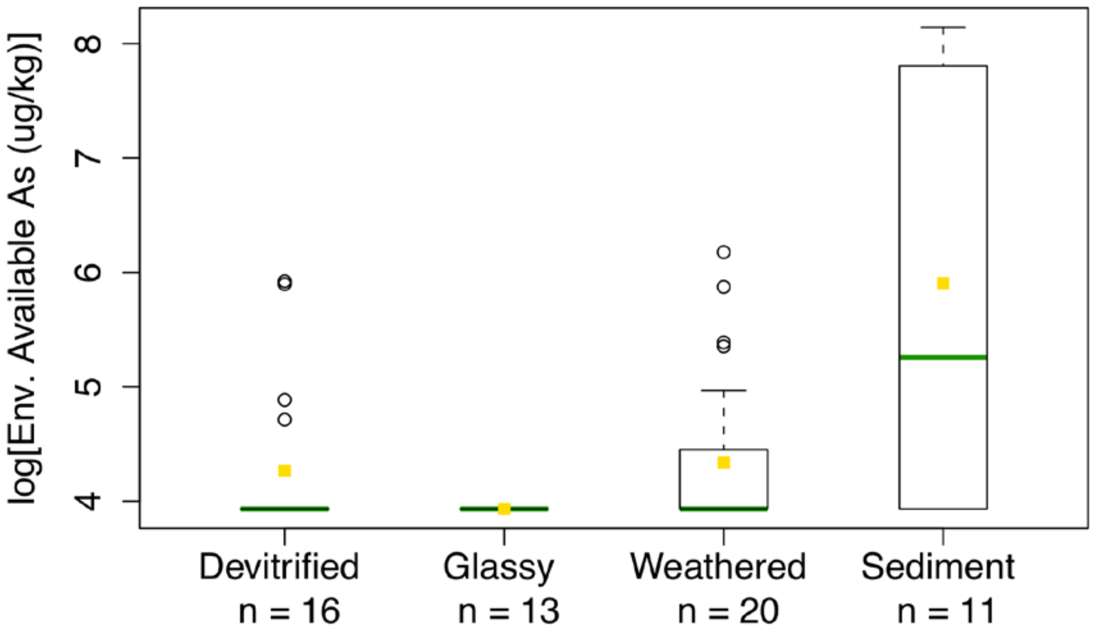

Figure 17. Readily leachable arsenic contents of ash-flow tuffs and tuffaceous sediments. Yellow boxes represent mean values. Tuffaceous sediments contained significantly more readily leachable arsenic than all categories of tuffs. Devitrified and weathered tuffs showed a greater range of readily leachable arsenic values than unweathered glassy tuffs.

Unlike the environmentally available fraction of arsenic, the readily leachable fraction shows no correlation with total arsenic for any category of sample (Figure 18).

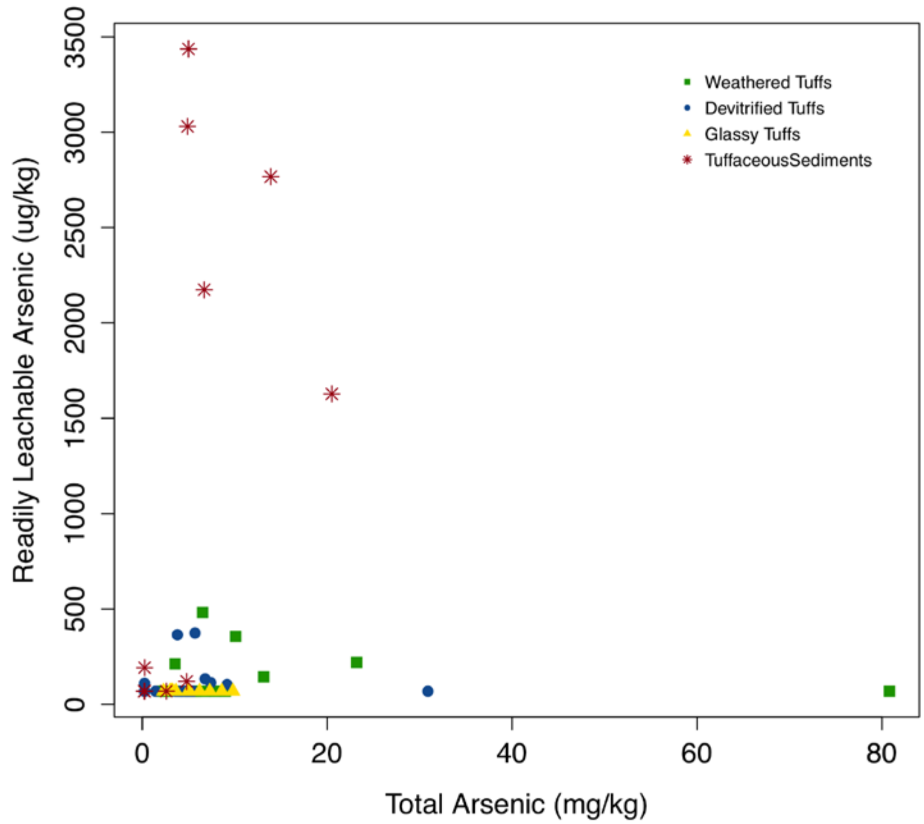

Figure 18. Readily leachable arsenic as a function of total arsenic present in samples. There is no correlation between the total amount of arsenic present in tuffs and sediments and the amount present in the readily leachable fraction.

Although the majority of tuff samples did not produce detectable levels of arsenic during water leaching experiments, individual samples of both devitrified and weathered tuffs and tuffaceous sediments did produce relatively high aqueous arsenic concentrations (Table 26).

Table 26. Aqueous arsenic concentrations produced by water leaching experiments. Descriptive statistical values only include samples that exceeded method detection limits.

	Mean (ug/L)	Median (ug/L)	Std Dev (ug/L)	Min (ug/L)	Max (ug/L)
Tuffs (n = 18)	8.1	5.3	7.1	1.7*	24.0
Weathered (n = 8)	9.7	8.9	8.0	2.0	24.0
Devitrified (n = 10)	6.8	4.4	6.3	1.7	18.7
Sediments (n = 7)	95.4	108.7	66.5	6.2	171.9

* Value is equivalent to the instrument detection limit of 1.7 ug/L, and should be considered semi-quantitative.

Overall, 12% of tuff samples and 45% of tuffaceous sediments produced aqueous arsenic concentrations exceeding EPA MCLs in only 18 hours, with some sediment samples approaching 20x the MCL of 10 ppb (Figure 19).

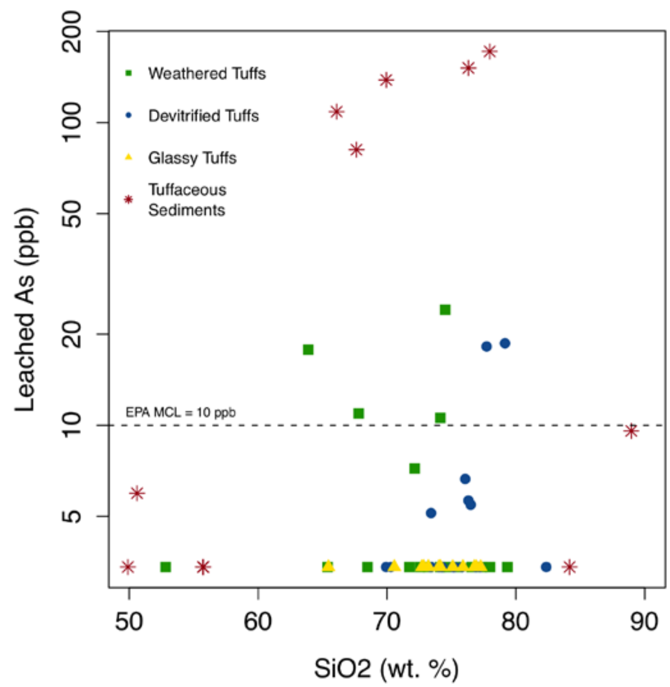

Figure 19. Aqueous arsenic concentrations produced by water leaching experiments. Weathered and devitrified tuffs and tuffaceous sediments all produced aqueous arsenic concentrations exceeding regulatory limits.

pH-Dependent Arsenic Mobility

Mean arsenic values increased as solution pH was increased between pH 9 and pH 11 for both devitrified and weathered tuffs, while glassy tuffs produced no arsenic concentrations above detection limits at either pH (consistent with the results from the unbuffered solutions). The increase in arsenic was minor for devitrified tuffs (92 to 124 $\mu g\ kg^{-1}$) but substantial for weathered tuffs (197 to 1068 $\mu g\ kg^{-1}$).

Patterns of arsenic mobility become clearer when the results of the controlled pH leaching experiments are compared with the readily leachable fraction of arsenic for the same samples. Unfortunately, the final pH of the readily leachable solutions was not measured for all samples. Of the solutions that were measured, pH levels varied between 6.2 and 8.9 with a mean value of 8.0. Arsenic concentrations of weathered tuffs at the circum-neutral pH conditions of the readily leachable extractions were slightly lower than arsenic concentrations at pH 9, and arsenic concentrations appear to increase at varying rates with increases in pH (Figure 20). In contrast, arsenic concentrations in devitrified tuffs actually decrease slightly between circum-neutral conditions and pH 9, and then increase slightly at pH 11, producing no clear relationship between pH and leachable arsenic in devitrified samples (Figure 20). Although the standard error bars for the devitrified and weathered samples overlap, a Mann-Whitney-Wilcoxon test confirms that the arsenic concentrations are significantly different ($p = 0.03$).

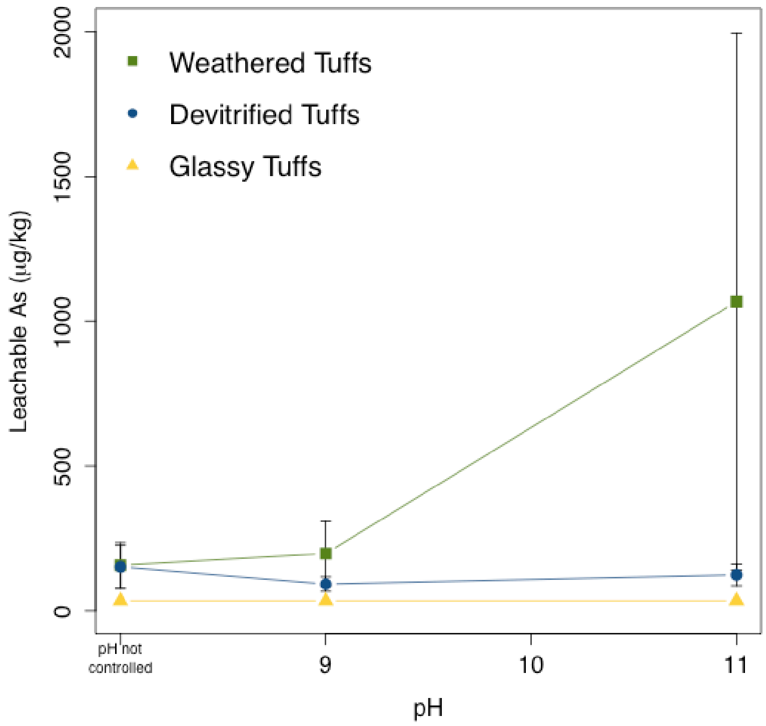

Figure 20. Arsenic concentrations from leaching experiments with uncontrolled pH compared with concentrations produced at pH 9 and 11. In weathered tuffs arsenic concentrations increased slightly from the circum-neutral conditions of the uncontrolled leachate experiments to pH 9, while arsenic concentrations decreased slightly between circum-neutral conditions and pH 9.

Elemental Correlations

For both fractions of mobile arsenic tests of correlation between arsenic and other elements were performed on log transformed data with outliers excluded using the non-parametric Spearman's rank correlation coefficient. In both the environmentally available fraction and the readily leachable fraction arsenic displayed statistically significant ($p < 0.05$) correlations with a variety of elements (Table 27).

Table 27. Statistically significant ($p < 0.05$) elemental correlations with arsenic. Italicized elements showed a negative correlation with arsenic, while un-italicized elements showed a positive correlation.

	Environmentally Available Fraction	Readily Leachable Fraction
All Tuffs (n = 47)	Al, Ca, Cd, Ce, Co, Cu, Fe, La, Pb, Sm, Sr, Ti, V, Zn	Al, Ba, Cu, Fe, Si, Ti, V, Zn
Weathered Tuffs (n = 19)	Ce, *Co*, La, *P, S, V*	Al, Fe, Si, Ti, Zn
Unweathered Tuffs (n = 28)	Ba, Cd, Ce, Co, Cu, Fe, La, Mn, Mo, *Na,* Ni, P, Pb, Sm, V, Zn	Mo, V
Devitrified Tuffs (n = 15)	Mn, S, V	Mo
Glassy Tuffs (n = 13)	None	None
Tuffaceous Sediments (n = 11)	Ce, S	Ca, Mo, S, Sr

In the environmentally available fraction, arsenic is positively correlated with a variety of elements including Al, Ca, Fe, Sr, and Zn. In the readily leachable fraction arsenic is positively correlated with Al, Fe, Si and Zn, among others. Tuffaceous sediments were positively correlated with S in both the environmentally available and readily leachable fractions. Although the correlation coefficients were statistically significant ($p < 0.05$), linear regression analysis determined that few of the correlations were reflective of strong linear relationships between arsenic and other elements ($R^2 < 0.60$). The two exceptions to this were the correlations between readily leachable arsenic and Fe in weathered samples, and readily leachable arsenic and Mo in devitrified samples (Figure 21).

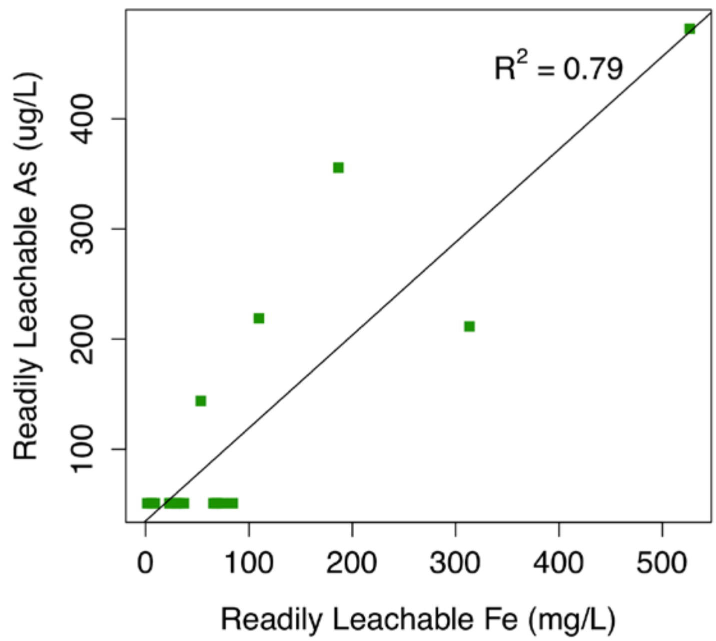

Figure 21. Linear relationship between readily leachable arsenic and iron in weathered tuff samples, p = 1.8e-07.

DISCUSSION

Potential Host Phases of Arsenic

The behavior of arsenic in both mobile fractions provides a number of indications that different host phases of arsenic exist in different categories of tuffs. My results indicate that in glassy tuffs arsenic is hosted in the glass phase. No glassy tuffs produced leachable arsenic under any pH conditions, indicating that arsenic is neither sorbed to mineral surfaces nor hosted in an easily soluble mineral phase. In addition, glassy tuffs contain significantly less environmentally available arsenic than other categories of tuffs, and are the only category of sample that does not show a positive correlation between total arsenic and environmentally available arsenic. This indicates that the bulk of the arsenic in glassy samples in bound in a silicate phase that is not dissolved in the partial digestions used to identify the environmentally available fraction. In glassy tuffs the most abundant silicate phase is the glass itself, which makes up the majority of the volume of glassy tuffs. Glass is also the most likely silicate phase to host arsenic since it is produced by quenching of lavas which can retain relatively high proportions of volatiles in comparison to silicate minerals.

In devitrified tuffs the most likely host phase of arsenic is a non-silicate mineral phase. Devitrified tuffs contain a relatively high percentage of their arsenic in the environmentally available fraction (median = 57%, max = 90%), and there is a strong positive correlation between total and environmentally available arsenic, which indicates that the bulk of the arsenic in these samples is not hosted in a silicate phase, because silicates are resistant to HNO_3^- treatment. The correlation between total and mobile arsenic is not seen in the readily leachable fraction, indicating that arsenic is not hosted in a highly soluble phase. Finally, leachable arsenic levels in devitrified tuffs do not increase with increasing pH, ruling out sorption to mineral surfaces as a potential host phase of arsenic in these samples.

While these results show that a non-silicate mineral phase is the most likely host of arsenic in devitrified tuffs it is not clear what specific mineral or minerals this might be. Vapor phase alteration that occurs during devitrification has the potential to produce a variety of minerals that would be likely host phases (particularly sulfides and phosphates), but as a result of their typical small size and low abundance, these minerals were not identified in the solid phase characterization performed during this study. Vapor phase mineralization is also highly variable, so it is possible that devitrified tuffs could contain multiple mineral phases enriched in arsenic and that these phases could differ between different tuffs.

In weathered tuffs the most likely host phase of arsenic is Fe-oxides and oxyhydroxides, as well as other alteration products including clay surfaces. Similarly to devitrified tuffs, weathered tuffs both contain a high percentage of their total arsenic in the environmentally available fraction and show a strong positive correlation between total and environmentally available arsenic, indicating a non-silicate host phase. In contrast to devitrified tuffs, weathered tuffs do show an increase in leachable arsenic with increasing pH, which indicates that sorption to grain surfaces likely plays a role in the behavior of arsenic. Weathering produces a range of alteration products that are potential sorbents for arsenic, including Fe-oxides and oxyhydroxides, kaolinite and illite clay minerals, and some zeolites, including clinoptilolite (Manning and Goldberg, 1996; Stollenwerk, 2003). Fe-oxides and oxyhydroxides are generally considered the most likely sorbent of arsenic, due to both their ubiquity and high concentration of surface sites. A positive correlation between Fe and arsenic was found in the readily leachable fraction, although the same relationship was not observed in the environmentally available fraction.

In glassy tuffs the weathering process produces higher levels of environmentally available arsenic than is present in unweathered tuffs, but this is not the case for devitrified tuffs. In glassy tuffs the relationship between weathered and unweathered samples is relatively straightforward. The differences between environmentally available arsenic in unweathered vs. weathered glassy tuffs, combined with the pH dependence of arsenic leachability from weathered samples suggests that during weathering arsenic is released from the glass phase and subsequently sorbs to alteration products.

The fate of arsenic during the weathering of devitrified tuffs is much less clear. One possible scenario is that arsenic behaves largely as it does in glassy tuffs, and is released from its non-silicate mineral phase and subsequently sorbs to alteration products. Another potential scenario is that only portions of the arsenic present in the non-silicate mineral host phase(s) is released and subsequently sorbed, producing weathered tuffs that contain both sorbed arsenic and arsenic hosted in minerals, resulting in two distinct arsenic host phases that both produce environmentally available arsenic.

In tuffaceous sediments the potential host phase or phases of arsenic remains more enigmatic than in tuffs themselves. Tuffaceous sediments display the same behavior of arsenic in the environmentally available fraction as weathered and devitrified tuffs (a high percentage of arsenic present in the environmentally available fraction and a strong correlation between total and environmentally available arsenic concentrations) that indicate a non-silicate host phase. In tuffaceous sediments the question of what that phase might be is more difficult to answer. The correlation between arsenic and S in both mobile fractions of the samples suggests that sulfide minerals are a likely host. However, tuffaceous sediments contain a high percentage (mean = 27%, max = 77%) of their total arsenic in the readily leachable fraction, and sulfide minerals are not highly soluble and would not be expected to produce high levels of leachable arsenic over short time periods in circum-neutral waters. Although contact with oxygenated waters would be expected to result in redox-driven dissolution of sulfide minerals, the 18 hour time period was likely insufficient for those reactions to fully occur.

One factor that is important to note is that with the exception of TW2, a volcaniclastic conglomerate from the Willamette Valley, all of the sediment samples in this study come from the Owyhee Upland physiographic province of Oregon and were formed in a similar arid climate. It is possible that environmental conditions and depositional processes played a significant role in determining both the overall arsenic concentrations and the host phase of arsenic in these samples. For example, evaporative concentration of arsenic during reworking of the tuffaceous material may have contributed to high levels of arsenic in some sediments. It may not be appropriate to use these samples to draw conclusions about arsenic in tuffaceous sediments from other regions, particularly if those regions have significantly different climates.

Potential Mechanisms of Arsenic Mobilization

Based on the different host phases tentatively identified for different categories of tuff, the mechanisms by which arsenic is mobilized from those categories will differ as well. In glassy tuffs the most likely mechanism of arsenic mobilization is the relatively slow dissolution of the glass phase. This is consistent with previous research that identified dissolution of volcanic glass as a primary geochemical control on arsenic levels in one groundwater system in the American Southwest (Johannesson and Tang, 2009). The fact that dissolution of glass is a relatively slow process, combined with the lack of arsenic concentrations exceeding 10 mg kg $^{-1}$ in glassy tuff samples, suggests that unweathered glassy tuffs present a lower risk of producing aqueous arsenic concentrations exceeding regulatory limits than other categories of tuff.

The most likely mechanism of mobilizing arsenic from devitrified tuffs is the dissolution of the non-silicate mineral host phase. Two of the unweathered devitrified samples in this study produced aqueous arsenic concentrations exceeding 10 μg L^{-1} in the water extraction experiment, indicating that at least some of the potential minerals hosting arsenic may be relatively soluble. Without a better understanding of what those minerals may be it is unclear what geochemical conditions might present greater risks of arsenic contamination sourced from devitrified tuffs.

In weathered tuffs the most likely mechanism of arsenic mobilization is desorption from mineral grain surfaces. The presence of sorbed arsenic in weathered tuffs means that a variety of geochemical conditions present increased risk of tuff-sourced arsenic contamination. Groundwaters with high pH, reducing conditions, and high concentrations of competing anions, particularly phosphate, can all result in desorption of arsenic from mineral grains and its release into solution.

CHAPTER 4: CONCLUSIONS

Conclusions and Conceptual Model

Arsenic concentrations in high silica ash-flow tuffs have a geometric mean value of 4.8 mg kg^{-1}, which is consistent with previously reported values and approximately 2.8 times the mean crustal abundance of 1.7 mg kg^{-1} (Onishi and Sandell, 1955; Wedepohl, 1995). Arsenic levels in tuffs are highly heterogenous both between and within units, and can reach levels exceeding 80 mg kg^{-1}. Additionally, 12% of ash-flow tuffs and 45% of tuffaceous sediments are capable of producing aqueous arsenic concentrations that exceed regulatory limits over a short period of time.

In addition to confirming the widespread idea that high silica ash-flow tuffs and tuffaceous sediments are a potential source of geogenic arsenic contamination, the results of this study indicate that the host phases and potential mechanisms of arsenic mobilization differ between categories of tuffs, and suggest a conceptual model for the behavior of arsenic in tuffs. The conceptual model suggested by these results includes factors influencing the total concentrations of arsenic in tuffs, changes in arsenic host phases during both devitrification and weathering, and potential mechanisms for the mobilization of arsenic into the environment (Figure 22).

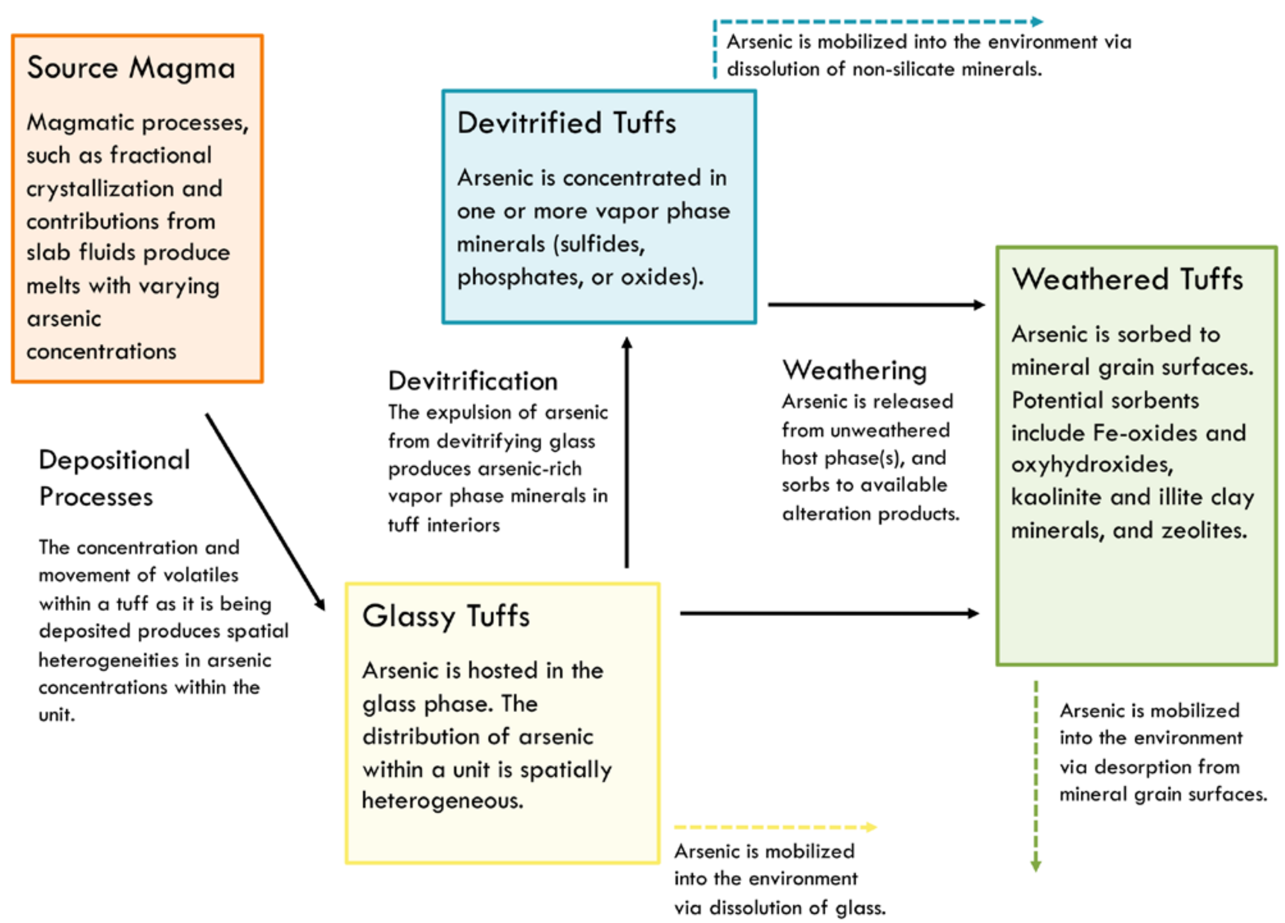

Figure 22. Conceptual model of arsenic behavior in ash-flow tuffs.

Future Work

Further identification of specific host phases should be pursued, particularly in devitrified tuffs and tuffaceous sediments. While the results of this study indicate that one or more non-silicate mineral phases are the most likely host phase of arsenic in devitrified tuffs it is still unclear what those mineral phases may be. The process of vapor phase mineralization provides a wide range of options, but identification of specific minerals would be valuable in determining what geochemical conditions present an increased risk of arsenic mobilization from devitrified tuffs. In the tuffaceous sediments investigated in this study it is still largely unclear what the host phase of arsenic may be, and how much that may be influenced by environmental conditions during the formation of these units.

Additional exploration into the role of solution chemistry in arsenic mobility should be continued as well. Investigating the leaching behavior of arsenic over a full range of pH values would provide additional insight into sorption processes in weathered tuffs, and potentially identify additional geochemical conditions that facilitate mobilization of arsenic from other categories of tuffs. Other variables that would be valuable to explore are redox state and concentration of competing anions.

Finally, further investigations into possible patterns of spatial distribution of arsenic within individual tuff units should be pursued. Spatial patterns of arsenic distribution, whether vertical patterns within the interior of the tuff, or lateral patterns varying with distance from the eruptive center, could potentially be of great use in assessing the risk of arsenic contamination at specific geographic locations. This study did not investigate possible lateral patterns of arsenic distribution, and provided inconclusive results with regard to vertical patterns of arsenic distribution.

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APPENDIX A: ANALYTICAL OPERATING CONDITIONS AND QUALITY CONTROL

Table A1. Operating conditions for ICP-OES analysis of total digests.

Condition	Value
Power (kW)	1.4
Replicate Read Time (s)	45
Instrument Stabilization Delay (s)	25
Sample Uptake Delay (s)	25
Max Rinse Time (s)	90
Number of Replicates	3
PolyBoost	On

Table A2. Operating conditions for ICP-OES analysis of partial digests.

Condition	Value
Power (kW)	1.4
Replicate Read Time (s)	45
Instrument Stabilization Delay (s)	25
Sample Uptake Delay (s)	20
Max Rinse Time (s)	30
Number of Replicates	3
PolyBoost	On

Table A3. Operating conditions for ICP-OES analysis of water extracts and pH leaching experiments.

Condition	Value
Power (kW)	1.3
Replicate Read Time (s)	45
Instrument Stabilization Delay (s)	25
Sample Uptake Delay (s)	20
Max Rinse Time (s)	60
Number of Replicates	3
PolyBoost	On

Table A4. Check standard and blank results from analytical session of 3/2/2012. QC1 contains 100 ppb, and QC2 contains 50 ppb, of all elements except Ga, P, S, and Sn.

Element and Wavelength	QC Blank a	QC1a	QC2a	Method Blank	QC1b
Al 237.312	2.40	104.84	58.71	6.41	107.33
As 188.980	ND	102.83	50.78	ND	102.23
Ba 455.403	ND	107.51	50.90	ND	109.04
Ca 317.933	ND	105.89	56.10	4.07	106.63
Cd 214.439	ND	104.19	55.09	ND	102.59
Ce 407.347	ND	105.34	4.32	ND	107.99
Co 228.615	ND	105.25	51.04	ND	105.61
Cr 267.716	1.50	105.58	63.90	1.59	105.24
Cu 327.395	1.12	106.00	44.16	1.46	106.99
Fe 238.204	ND	103.69	144.61	3.89	103.56
La 398.852	ND	105.94	0.02	ND	106.91
Mg 279.078	ND	103.90	53.01	1.49	105.00
Mn 260.568	ND	104.83	50.82	ND	103.57
Na 588.995	ND	118.04	66.08	3.66	114.47
Nd 399.467	1.86	103.99	0.29	1.37	104.57
Ni 231.604	ND	103.30	52.56	ND	102.08
P 177.434	4.41	116.39	5.95	6.24	135.93
Pb 220.353	ND	105.17	50.47	ND	104.26
S 181.972	4.03	109.39	12.37	ND	103.21
Sm 356.827	39.54	104.24	39.21	39.22	106.84
Sr 407.771	ND	106.11	51.36	ND	107.64
V 311.837	ND	103.47	43.60	ND	104.39
Zn 202.548	ND	132.89	43.31	ND	133.43

Table A5. Check standard and blank results from analytical session of 10/25/2012. QC1 contains 100 ppb, and QC2 contains 50 ppb, of all elements except P and S.

Element and Wavelength	QC Blank a	QC1a	QC2a	Method Blank	QC Blank b	QC1b	QC2b
Al 237.312	3.81	108.93	53.81	22.49	5.93	112.60	57.07
As 188.980	ND	97.51	43.66	ND	ND	98.13	45.24
Ba 455.403	ND	101.92	50.67	ND	ND	96.64	47.30
Ca 317.933	6.82	129.77	64.26	9.60	8.02	132.26	66.69
Cd 214.439	ND	102.90	49.51	ND	ND	107.28	52.63
Ce 407.347	1.57	100.21	49.79	2.23	1.58	92.64	46.66
Co 228.615	ND	101.78	49.76	ND	ND	104.93	51.68
Cr 267.716	ND	101.23	49.50	ND	ND	103.04	50.49
Cu 327.395	ND	103.22	49.60	ND	ND	100.03	47.50
Fe 238.204	ND	104.22	50.08	14.17	1.67	107.12	52.50
La 398.852	ND	104.09	52.28	ND	ND	98.90	48.31
Mg 279.078	ND	103.20	48.93	3.90	ND	108.21	52.37
Mn 260.568	ND	101.01	49.79	ND	ND	102.52	50.50
Mo 202.032	ND	96.82	45.31	ND	ND	96.12	44.83
Na 588.995	3.73	103.99	45.43	12.49	7.94	106.29	50.87
Nd 399.467	1.48	101.15	52.23	1.53	1.66	92.91	45.18
Ni 231.604	ND	101.04	49.78	ND	ND	104.27	51.61
P 177.434	3.92	1.20	1.80	3.15	2.77	ND	ND
Pb 220.353	ND	102.56	50.30	ND	ND	103.25	51.01
S 181.972	ND	3.25	-1.97	31.96	24.68	29.71	26.38
Si 185.005	ND	134.45	63.17	99.47	ND	125.17	46.87
Sm 356.827	14.73	90.94	41.71	14.73	14.68	79.93	33.29
Sr 407.771	ND	101.06	51.29	ND	ND	94.47	47.09
Ti 334.941	ND	100.51	50.10	ND	ND	96.42	47.70
V 311.837	ND	100.69	50.11	1.04	ND	99.54	48.97
Zn 202.548	ND	118.21	51.40	ND	ND	126.22	57.10

Table A6. Check standard and blank results from analytical session of 4/2/2013. QC1 contains 100 ppb, and QC2 contains 50 ppb, of all elements except P and S.

Element and Wavelength	QC Blank a	QC1a	QC2a	Method Blank 1	QC Blank b	QC1b	QC2b	Method Blank 2	Method Blank 3	QC Blank c	QC1c	QC2c
Al 237.312	2.03	106.15	51.95	6.35	3.26	109.05	55.69	2.22	8.00	ND	108.83	55.53
As 188.980	-3.48	98.17	48.19	ND	ND	98.80	45.37	ND	ND	ND	96.95	46.35
Ba 455.403	-0.01	99.67	50.09	0.01	ND	101.45	50.23	ND	ND	ND	99.79	49.54
Ca 317.933	ND	104.28	51.38	6.96	ND	106.22	51.66	2.19	2.98	ND	106.02	51.56
Cd 214.439	ND	101.08	50.45	ND	ND	103.11	50.37	ND	ND	ND	102.47	50.09
Ce 407.347	3.26	99.50	50.21	1.86	2.48	100.82	48.70	1.55	2.20	3.02	100.19	50.08
Co 228.615	ND	100.84	49.93	ND	ND	102.54	49.97	ND	ND	ND	101.01	49.78
Cr 267.716	ND	99.03	49.67	ND	ND	101.31	49.92	ND	ND	ND	100.99	49.60
Cu 327.395	ND	98.89	49.69	ND	ND	100.77	49.79	ND	ND	ND	100.25	49.67
Fe 238.204	ND	101.98	50.80	ND	ND	104.01	50.76	ND	3.91	ND	103.43	50.82
La 398.852	ND	103.51	51.99	ND	ND	105.44	51.96	ND	ND	ND	103.44	51.53
Mg 279.07	ND	100.95	50.52	ND	ND	103.70	50.38	1.27	ND	ND	102.25	49.49
Mn 260.56	ND	99.59	49.87	ND	ND	101.02	49.72	ND	ND	ND	99.89	49.26
Mo 202.03	ND	97.93	49.72	ND	ND	101.04	49.90	ND	ND	ND	99.61	49.93
Na 588.995	ND	100.02	49.52	2.95	ND	101.53	49.49	2.31	4.54	ND	98.06	49.97
Nd 399.467	1.20	100.83	50.02	1.47	1.18	102.51	49.77	2.29	ND	1.37	100.69	50.15
Ni 231.604	ND	99.73	49.79	ND	ND	100.32	49.37	ND	ND	ND	98.13	48.47
P 177.434	2.05	1.82	0.94	1.27	2.89	1.70	1.34	2.48	3.00	2.21	2.35	1.40
Pb 220.353	ND	100.87	50.81	ND	ND	101.82	49.66	ND	ND	ND	99.26	49.47
S 181.972	ND	2.97	0.74	2.41	ND	4.13	-0.78	1.25	1.55	ND	2.59	-0.52
Si 185.005	ND	154.97	79.04	129.12	156.72	313.40	216.29	192.51	287.19	293.46	431.71	461.54
Sm 356.827	ND	101.11	50.27	ND	ND	102.34	51.35	ND	ND	ND	100.87	50.12
Sr 407.771	ND	99.00	51.25	ND	ND	101.88	50.86	ND	ND	ND	100.53	49.29
Ti 334.941	ND	100.48	50.97	ND	ND	103.03	51.41	ND	ND	ND	101.85	50.75
V 311.837	ND	98.66	49.43	ND	ND	100.98	49.60	ND	ND	ND	100.11	49.19
Zn 202.548	ND	101.59	50.33	ND	ND	104.17	50.65	ND	ND	ND	103.07	50.55

APPENDIX B: DETAILS OF STATISTICAL METHODS

All statistical analysis performed in R Version 2.11.1

```
# All analysis!

rm(list = ls())

#==================================================================#
# Investigating Alk/Alumina ratios and As
#==================================================================#
load("~/Documents/Thesis/Analysis/AllData.Rdata")

# Calculate Alumina/Alkali ratios in molar percents (not wt %)
molmajors$AlkAl <- molmajors$Al/(molmajors$Na2O + molmajors$K2O)

# Look for correlations with As

cor.test(molmajors$AlkAl, totaldata$As)

# Use AllPlots.R script to plot here.


#==================================================================#
# Basic Comparisons Between Groups
#==================================================================#
rm(list = ls())
# Total fraction

# Load workspace that includes data frames of data for all three fractions (total, env.
available, and readily leachable)
load("~/Documents/Thesis/Analysis/AllData.Rdata")

# Create data frame excluding sediment samples
tuffs <- subset(totaldata, totaldata$Devitrification != "Sediment")
tuffs$Devitrification <- factor(tuffs$Devitrification)
tuffs$Weathering <- factor(tuffs$Weathering)

# Create data frame of only sediment samples
sed <- subset(totaldata, totaldata$Devitrification == "Sediment")
```

```
# Create data frame of unweathered samples only
unweathered <- subset(tuffs, Weathering == "Unweathered")

# Create data frame of weathered samples only
weathered <- subset(tuffs, Weathering == "Weathered")

# Create data frame of devitrified samples only
devit <- subset(unweathered, Devitrification == "Devitrified")

# Create data frame of glassy samples only
glassy <- subset(unweathered, Devitrification == "Glassy")

# Compare tuffs and sediments
wilcox.test(tuffs$As, sed$As)
kruskal.test(tuffs$As, sed$As)
boxplot(tuffs$As, sed$As)

# Compare weathered and unweathered samples
wilcox.test(As ~ Weathering, tuffs)
kruskal.test(As ~ Weathering, tuffs)
boxplot(As ~ Weathering, tuffs, ylab = "As (mg/kg)", main = "Total As")

# Compare glassy and devitrified samples
wilcox.test(As ~ Devitrification, unweathered)
kruskal.test(As ~ Devitrification, unweathered)
boxplot(As ~ Devitrification, unweathered, ylab = "As (mg/kg)", main = "Total As")

# Calculate mean/median/SD values for categories
mean(tuffs$As)
median(tuffs$As)
sd(tuffs$As)

mean(sed$As)
median(sed$As)
sd(sed$As)

mean(unweathered$As)
median(unweathered$As)
sd(unweathered$As)

mean(weathered$As)
median(weathered$As)
sd(weathered$As)
```

```
mean(devit$As)
median(devit$As)
sd(devit$As)

mean(glassy$As)
median(glassy$As)
sd(glassy$As)


# Environmentally available fraction

totaldatatest <- subset(totaldata, Sample != "DVC1")

# Calculate Percentage As "Environmentally Available"
envavail <- data.frame(Sample = totaldatatest$Sample,
                       Devitrification = totaldatatest$Devitrification,
                       Weathering = totaldatatest$Weathering,
                       PartialAs = partialdata$As,
                       TotalAs = totaldatatest$As,
                       percent =(partialdata$As/totaldatatest$As *100))

rm(totaldatatest)

# The partial digest method had lower detection limits than Actlabs total As limits.
# As a result some samples had percentages > 100%
# Replace values over 100% with NA values
num <- nrow(envavail)

for (i in 1: num){
  if(is.na(envavail$percent[i]) == FALSE){
    if(envavail$percent[i] >100){
      envavail$percent[i] <- NA
    }
  }
}

# Create Tuffs Only data frame
envavailtuffs <- subset(envavail, Devitrification != "Sediment")
envavailtuffs$Devitrification <- factor(envavailtuffs$Devitrification)
envavailtuffs$Weathering <- factor(envavailtuffs$Weathering)

# Create Sediments only data frame
envavailsed <- subset(envavail, Devitrification == "Sediment")
```

```
envavailsed$Devitrification <- factor(envavailsed$Devitrification)
envavailsed$Weathering <- factor(envavailsed$Weathering)

# Create data frame of unweathered samples only
envavailunw <- subset(envavailtuffs, Weathering == "Unweathered")

# Create data frame of weathered samples only
envavailw <- subset(envavailtuffs, Weathering == "Weathered")

# Create data frame of devitrified samples only
envavaildevit <- subset(envavailunw, Devitrification == "Devitrified")

# Create data frame of glassy samples only
envavailglassy <- subset(envavailunw, Devitrification == "Glassy")

# Test for normality

shapiro.test(envavailtuffs$PartialAs)
shapiro.test(envavailsed$PartialAs)
shapiro.test(envavailunw$PartialAs)
shapiro.test(envavailw$PartialAs)
shapiro.test(envavaildevit$PartialAs)
shapiro.test(envavailglassy$PartialAs)

# Compare tuffs and sediments
wilcox.test(envavailtuffs$percent, envavailsed$percent)
wilcox.test(envavailtuffs$PartialAs, envavailsed$PartialAs)


# Compare weathered and unweathered samples
wilcox.test(percent ~ Weathering, envavailtuffs)
wilcox.test(PartialAs ~ Weathering, envavailtuffs)
kruskal.test(percent ~ Weathering, envavailtuffs)
kruskal.test(PartialAs ~ Weathering, envavailtuffs)
boxplot(percent ~ Weathering, envavailtuffs,
	ylab = "As (%)", main = "Available As")
boxplot(PartialAs ~ Weathering, envavailtuffs,
	ylab = "As (mg/kg)", main = "Available As")

# Compare divitrified and glassy samples.
wilcox.test(percent ~ Devitrification, envavailunw)
wilcox.test(PartialAs ~ Devitrification, envavailunw)
kruskal.test(percent ~ Devitrification, envavailunw)
kruskal.test(PartialAs ~ Devitrification, envavailunw)
```

```
boxplot(percent ~ Devitrification, envavailunw,
        ylab = "As (%)", main = "Available As")
boxplot(PartialAs ~ Devitrification, envavailunw,
        ylab = "As (mg/kg)", main = "Available As")

# Calculate descriptive statistics
mean(envavailtuffs$PartialAs, na.rm = TRUE)
median(envavailtuffs$PartialAs, na.rm= TRUE)
sd(envavailtuffs$PartialAs, na.rm = TRUE)

mean(envavailtuffs$percent, na.rm = TRUE)
median(envavailtuffs$percent, na.rm = TRUE)
sd(envavailtuffs$percent, na.rm = TRUE)

mean(envavailsed$PartialAs, na.rm = TRUE)
median(envavailsed$PartialAs, na.rm = TRUE)
sd(envavailsed$PartialAs, na.rm = TRUE)

mean(envavailsed$percent, na.rm = TRUE)
median(envavailsed$percent, na.rm = TRUE)
sd(envavailsed$percent, na.rm = TRUE)

mean(envavailunw$PartialAs, na.rm = TRUE)
median(envavailunw$PartialAs, na.rm = TRUE)
sd(envavailunw$PartialAs, na.rm = TRUE)

mean(envavailunw$percent, na.rm = TRUE)
median(envavailunw$percent, na.rm = TRUE)
sd(envavailunw$percent, na.rm = TRUE)

mean(envavailw$PartialAs, na.rm = TRUE)
median(envavailw$PartialAs, na.rm = TRUE)
sd(envavailw$PartialAs, na.rm = TRUE)

mean(envavailw$percent, na.rm = TRUE)
median(envavailw$percent, na.rm = TRUE)
sd(envavailw$percent, na.rm = TRUE)

mean(envavaildevit$PartialAs, na.rm = TRUE)
median(envavaildevit$PartialAs, na.rm = T)
sd(envavaildevit$PartialAs, na.rm = T)

mean(envavaildevit$percent, na.rm = TRUE)
median(envavaildevit$percent, na.rm = TRUE)
```

```
sd(envavailunw$percent, na.rm = TRUE)

mean(envavailglassy$PartialAs, na.rm = T)
median(envavailglassy$PartialAs, na.rm = T)
sd(envavailglassy$PartialAs, na.rm = T)

mean(envavailglassy$percent, na.rm = TRUE)
median(envavailglassy$percent, na.rm = TRUE)
sd(envavailglassy$percent, na.rm = TRUE)


# Leachable Fraction

# Calculate Percentage As "Readily Leachable"
leachable <- data.frame(Sample = leachdata$Sample,
                Devitrification = leachdata$Devitrification,
                Weathering = leachdata$Weathering,
                LeachableAs = leachdata$As,
                TotalAs = totaldata$As,
                percent =((leachdata$As/10^3)/totaldata$As *100))

# Create tuffs only data frame
leachtuffs <- subset(leachable, Devitrification != "Sediment")
leachtuffs$Devitrification <- factor(leachtuffs$Devitrification)
leachtuffs$Weathering <- factor(leachtuffs$Weathering)

# Create sediments only data frame
leachsed <- subset(leachable, Devitrification == "Sediment")
leachsed$Devitrification <- factor(leachsed$Devitrification)
leachsed$Weathering <- factor(leachsed$Weathering)

# Create data fram of unweathered tuffs only
leachunw <- subset(leachtuffs, Weathering == "Unweathered")

# Create data frame of weathered tuffs only
leachw <- subset(leachtuffs, Weathering == "Weathered")

# Create data frame of devitrified tuffs only
leachdevit <- subset(leachunw, Devitrification == "Devitrified")

# Create data frame of glassy tuffs only
leachglassy <- subset(leachunw, Devitrification == "Glassy")

# Compare sediments and tuffs
```

```
wilcox.test(leachtuffs$percent, leachsed$percent)
wilcox.test(leachtuffs$LeachableAs, leachsed$LeachableAs)
boxplot(leachtuffs$percent, leachsed$percent)
boxplot(leachtuffs$LeachableAs, leachsed$LeachableAs)

# Compare weathered and unweathered tuffs
wilcox.test(percent ~ Weathering, leachtuffs)
wilcox.test(LeachableAs ~ Weathering, leachtuffs)
kruskal.test(percent ~ Weathering, leachtuffs)
kruskal.test(LeachableAs ~ Weathering, leachtuffs)
boxplot(percent ~ Weathering, leachtuffs)
boxplot(LeachableAs ~ Weathering, leachtuffs)

# Compare devitrified and glassy tuffs
wilcox.test(percent ~ Devitrification, leachunw)
wilcox.test(LeachableAs ~ Devitrification, leachunw)
kruskal.test(percent ~ Devitrification, leachunw)
kruskal.test(LeachableAs ~ Devitrification, leachunw)
boxplot(percent ~ Devitrification, leachunw)
boxplot(LeachableAs ~ Devitrification, leachunw)

# Calculate descriptive statistics, excluding samples that were non-detects
ND <- 51.05875

mean(leachtuffs$LeachableAs[which(leachtuffs$LeachableAs > ND)])
median(leachtuffs$LeachableAs[which(leachtuffs$LeachableAs > ND)])
sd(leachtuffs$LeachableAs[which(leachtuffs$LeachableAs > ND)])

mean(leachsed$LeachableAs[which(leachsed$LeachableAs > ND)])
median(leachsed$LeachableAs[which(leachsed$LeachableAs > ND)])
sd(leachsed$LeachableAs[which(leachsed$LeachableAs > ND)])

mean(leachunw$LeachableAs[which(leachunw$LeachableAs > ND)])
median(leachunw$LeachableAs[which(leachunw$LeachableAs > ND)])
sd(leachunw$LeachableAs[which(leachunw$LeachableAs > ND)])

mean(leachw$LeachableAs[which(leachw$LeachableAs > ND)])
median(leachw$LeachableAs[which(leachw$LeachableAs > ND)])
sd(leachw$LeachableAs[which(leachw$LeachableAs > ND)])

mean(leachdevit$LeachableAs[which(leachdevit$LeachableAs > ND)])
median(leachdevit$LeachableAs[which(leachdevit$LeachableAs > ND)])
sd(leachdevit$LeachableAs[which(leachdevit$LeachableAs > ND)])
```

```
mean(leachglassy$LeachableAs[which(leachglassy$LeachableAs > ND)])
median(leachglassy$LeachableAs[which(leachglassy$LeachableAs > ND)])
sd(leachglassy$LeachableAs[which(leachglassy$LeachableAs > ND)])


#==================================================================#
# Look for statistically significant correlations between As and other elements
#==================================================================#

# Create variable for correlation coefficent to use
cormeth = "spearman"

# Define function for doing what I want, rather than typing it over and over again

myCorrelations <- function(data, cormeth){
  numelements <- ncol(data) - 3

  cortable <- vector(mode = "numeric", length = numelements)
  ptable <- vector(mode = "numeric", length = numelements)
  elements <- vector(mode = "character", length = numelements)

  for (i in 4:(ncol(data)))
  {test <- print(cor.test(data$As,data[,i], method = cormeth))
   elements[i] <- colnames(data[i])
   cortable[i] <- test$estimate
   ptable[i] <- test$p.value}

  # Create data frame of all correlation coefficients and p values
  correlations <- data.frame(Element = elements, Correlation = cortable, pValue = ptable)
  # Find all elements with p <= 0.05
  sigcor <- subset(correlations, pValue <=0.05)
  return(sigcor)
}

# Find correlations for total fraction

tufftotalsigcor <- myCorrelations(tuffs, cormeth) # Tuffs

# Exclude extreme values
tuffs2 <- subset(tuffs, As < 25)
tuff2totalsigcor <- myCorrelations(tuffs2, cormeth)

sed2 <- subset(sed, select =  c(-Ga, -Ho, -Tm))
sedtotalsigcor <- myCorrelations(sed2, cormeth) # Sediments
```

```
weathtotalsigcor <- myCorrelations(weathered, cormeth) # Weathered
unweathtotalsigcor <- myCorrelations(unweathered, cormeth) # Unweathered
devittotalsigcor <- myCorrelations(devit, cormeth) # Devitrified
glassytotalsigcor <- myCorrelations(glassy, cormeth) # Glassy

rm(sed2)

# Correlations for the environmentally available fraction

tuffpartial <- subset(partialdata, Devitrification != "Sediment")
unweatheredpartial <- subset(partialdata, Weathering == "Unweathered")
weatheredpartial <- subset(partialdata, Weathering == "Weathered")
devitpartial <- subset(unweatheredpartial, Devitrification == "Devitrified")
glassypartial <- subset(unweatheredpartial, Devitrification == "Glassy")
sedpartial <- subset(partialdata, Weathering == "Sediment")

tuffpartialsigcor <- myCorrelations(tuffpartial, cormeth)
weathpartialsigcor <- myCorrelations(weatheredpartial, cormeth)
unweathpartialsigcor <- myCorrelations(unweatheredpartial, cormeth)
devitpartialsigcor <- myCorrelations(devitpartial, cormeth)
glassypartialsigcor <- myCorrelations(glassypartial, cormeth)
sedpartialsigcor <- myCorrelations(sedpartial, cormeth)

# Correlations for the readily leachable fraction

tuffleach <- subset(leachdata, Devitrification != "Sediment")
weatheredleach <- subset(leachdata, Weathering == "Weathered")
unweatheredleach <- subset(leachdata, Weathering == "Unweathered")
devitleach <- subset(unweatheredleach, Devitrification == "Devitrified")
glassyleach <- subset(unweatheredleach, Devitrification == "Glassy")
sedleach <- subset(leachdata, Weathering == "Sediment")

tuffleachsigcor <- myCorrelations(tuffleach, cormeth)
weathleachsigcor <- myCorrelations(weatheredleach, cormeth)
unweathleachsigcor <- myCorrelations(unweatheredleach, cormeth)
devitleachsigcor <- myCorrelations(devitleach, cormeth)
glassyleachsigcor <- myCorrelations(glassyleach, cormeth)
sedleachsigcor <- myCorrelations(sedleach, cormeth)

# Analysis of pH extractions

load("~/Documents/Thesis/Analysis/pH.Rdata")

pH9 <- subset(pHed, pH == 9)
```

```
pH11 <- subset(pHed, pH ==11)

plot(pH11$pH, pH11$As)
points(pH9$pH, pH9$As)

pHall <- c(8, 9, 11)
FD3 <- c(34, 34, 279)
FD4 <- c(143, 164, 564)
LG1 <- c(355, 181, 415)
LG2 <- c(218, 83, 154)
LG4 <- c(34, 525, 3928)

plot(pHall, LG4, type = "b", col = "dodgerblue4", pch = 15, ylim = c(0, 600))
points(pHall, FD3, type = "b", col = "gold", pch = 15)
points(pHall, FD4, type = "b", col = "gold", pch = 15)
points(pHall, LG1, type = "b", col = "gold", pch = 15)
points(pHall, LG2, type = "b", col = "dodgerblue4", pch = 15)

DC6 <- c(133, 134, 185)
DC6pH <- c(7.35, 9, 11)
MK2 <- c(103, 137, 198)
RST11 <- c(373, 85, 97)
RST11pH <- c(8.74, 9, 11)
RST13 <- c(113, 70, 91)
RST13pH <- c(8.25, 9, 11)
SR2 <- c(34, 34, 48)

devitall <- data.frame(rbind(DC6, MK2, RST11, RST13, SR2))
weatheredall <- data.frame(rbind(FD3, FD4, LG1, LG2, LG4))

stderrw <- sd(weatheredall)/sqrt(length(weatheredall))
stderrd <- sd(devitall)/sqrt(length(weatheredall))



plot(pHall, mean(weatheredall),
    type = "b",
    pch = 15,
    col = "chartreuse4",
    ylim = c(0,2000),
    ylab = expression(paste("Leachable As (",mu,"g/kg)")),
    xlab = "pH",
    xaxt = "n")
axis(1, at = c(9, 10, 11),
```

```
    labels = c("9", "10", "11"))
axis(1, at = 8, labels = "pH not\ncontrolled", cex.axis = 0.65)
errbar(pHall, mean(devitall),
      (mean(devitall)+stderrd), (mean(devitall)-stderrd),
      add = TRUE, col = "dodgerblue4", pch = 20)
errbar(pHall, mean(weatheredall),
      (mean(weatheredall)+stderrw), (mean(weatheredall)-stderrw),
      add = TRUE, col = "chartreuse4", pch = 20)
points(pHall, mean(weatheredall), pch = 15, col = "chartreuse4", cex = 1.5)
points(pHall, mean(devitall), type = "b", pch =16, col = "dodgerblue4", cex = 1.5)
points(pHall, c(34, 34, 34), type = "b", pch = 17, col = "gold", cex = 1.5)

legendtext <- c("Weathered Tuffs", "Devitrified Tuffs", "Glassy Tuffs")
legendcol <- c("chartreuse4", "dodgerblue4", "gold")
legendpch <- c(15,16,17)
legend(x = "topleft", legend = legendtext, col = legendcol, pch = legendpch, cex = 1.2,
bty = "n")



plot(DC6pH, DC6, type = "b", col = "dodgerblue4", ylim = c(0,600))
points(pH, FD3, type = "b", col = "chartreuse4")
points(pH, FD4, type = "b", col = "chartreuse4")
points(pH, LG1, type = "b", col = "chartreuse4")
points(pH, LG2, type = "b", col = "chartreuse4")
points(pH, MK2, type = "b", col = "dodgerblue4")
points(RST11pH, RST11, type = "b", col = "dodgerblue4")
points(RST13pH, RST13, type = "b", col = "dodgerblue4")
points(pH, SR2, type = "b", col = "dodgerblue4")

allpH <- c(6.36, 6.81, 8.40, 8.28, 7.35, 8.94, 8.37, 8.48,
        8.29, 8.65, 7.99, 8.05, 8.74, 6.16, 6.93,
        8.43, 8.44, 7.05, 8.65, 7.46, 8.30, 8.23, 7.90,
        8.90, 7.92, 8.64, 8.70, 8.90, 8.25, 8.19,
        6.94, 6.52, 7.03, 8.84, 8.88, 7.91, 8.01,
        8.56)
mean(allpH)


#===============================================================#
# Look at aqueous values
#===============================================================#

# Convert back to aqueous concentrations
```

```
convert <- function(x) {x/(10^3 * 0.02)}

water <- sapply(leachdata[,4:45], convert)
water <- as.data.frame(water)
water$Sample <- leachdata$Sample
water$Devitrification <- leachdata$Devitrification
water$Weathering <- leachdata$Weathering

mean(water$As)
mean(water$As[which(water$As > 0.851)])

# Remove non-detect values
water2 <- subset(water, As > 0.851)
waterunw <- subset(water2, Weathering == "Unweathered")
waterw <- subset(water2, Weathering == "Weathered")
waterdevit <- subset(waterunw, Devitrification == "Devitrified")
waterglassy <- subset(waterunw, Devitrification == "Glassy")
watersed <- subset(water2, Devitrification == "Sediment")
watertuff <- subset(water2, Devitrification != "Sediment")

mean(watertuff$As)
median(watertuff$As)
sd(watertuff$As)
max(watertuff$As)
min(watertuff$As)

mean(waterw$As)
median(waterw$As)
sd(waterw$As)
max(waterw$As)
min(waterw$As)

mean(waterunw$As)
median(waterunw$As)
sd(waterunw$As)
max(waterunw$As)
min(waterunw$As)

mean(waterdevit$As)
median(waterdevit$As)
sd(waterdevit$As)
max(waterdevit$As)
min(waterdevit$As)
```

```
mean(waterglassy$As)
median(waterglassy$As)
sd(waterglassy$As)
max(waterglassy$As)
min(waterglassy$As)


mean(watersed$As)
median(watersed$As)
sd(watersed$As)
max(watersed$As)
min(watersed$As)


#================================================================#
# Log transforming the data
#================================================================#
rm(list = ls())


# Load workspace that includes data frames of data for all three fractions (total, env.
available, and readily leachable)
load("~/Documents/Thesis/Analysis/AllData.Rdata")

# Use Grubb method to exclude outliers

grubb <- function(totaldata) {
  # Calculate g stat
  g <- abs(totaldata$As - mean(totaldata$As))
  g2 <- max(g)/sd(totaldata$As)

  # Calculate gcrit
  n <- length(totaldata$As)
  tcrit <- abs(qt(0.05/(2*n), n-2))
  gcrit <- (n - 1)/sqrt(n) * sqrt(tcrit^2/(n - 2 + tcrit^2))

  print(totaldata$Sample[which.max(g)])
  samp <- (totaldata$Sample[which.max(g)])
  print(max(g))
  print(gcrit)

  if (g2 > gcrit){
    temptot <- subset(totaldata, totaldata$Sample != samp)
```

```
    return(temptot)
    }

  if (g2 <= gcrit){
    print("No more outliers!")
    return(totaldata)
  }


}

test <- grubb(totaldata)
test <- grubb(test) # Repeat until no more outliers are found.

totaldata2 <- test

# Replace missing LOI values with 100 - Total, rather than NA
MajorChemUnNorm$LOI[which(is.na(MajorChemUnNorm$LOI))] <- 100 -
MajorChemUnNorm$Total[which(is.na(MajorChemUnNorm$LOI))]

# Remove outliers from this data frame also

MajorChem <- subset(MajorChemUnNorm, Sample != "LG4")
MajorChem <- subset(MajorChem, Sample != "SR2")
MajorChem <- subset(MajorChem, Sample != "LG2")
MajorChem <- subset(MajorChem, Sample != "DS1")

# Correct for LOI values
temp <- totaldata2$As/(100 - MajorChem$LOI) * 100
totaldata2$As <- temp

temp <- totaldata$As/(100 - MajorChemUnNorm$LOI) * 100
totaldataLOI <- totaldata
totaldataLOI$As <- temp

# Log transform data
logtotaldata <- log(totaldata2[,4:36])
logtotaldata <- cbind(totaldata2[,1:3], logtotaldata)

totaldata3 <- logtotaldata

logtotaldata <- log(totaldataLOI[,4:36])
logtotaldata <- cbind(totaldataLOI[,1:3], logtotaldata)
```

```
totaldataLOI2 <- logtotaldata

# Create data frame excluding sediment samples
tuffs <- subset(totaldata3, totaldata3$Devitrification != "Sediment")
tuffs$Devitrification <- factor(tuffs$Devitrification)
tuffs$Weathering <- factor(tuffs$Weathering)

tuffsO <- subset(totaldataLOI2, totaldataLOI2$Devitrification != "Sediment")
tuffsO$Devitrification <- factor(tuffsO$Devitrification)
tuffsO$Weathering <- factor(tuffsO$Weathering)

# Create data frame of only sediment samples
sed <- subset(totaldata3, totaldata3$Devitrification == "Sediment")
sedO <- subset(totaldataLOI2, totaldataLOI2$Devitrification == "Sediment")

# Create data frame where tuff v sed is a factor

testtuff <- tuffs
testtuff$Weathering <- "Tuff"
testtuff <- rbind(testtuff, sed)
testtuff$Weathering <- factor(testtuff$Weathering)

testtuffO <- tuffsO
testtuffO$Weathering <- "Tuff"
testtuffO <- rbind(testtuffO, sedO)
testtuffO$Weathering <- factor(testtuffO$Weathering)

# Create data frame of unweathered samples only
unweathered <- subset(tuffs, Weathering == "Unweathered")
unweatheredO <- subset(tuffsO, Weathering == "Unweathered")

# Create data frame of weathered samples only
weathered <- subset(tuffs, Weathering == "Weathered")
weatheredO <- subset(tuffsO, Weathering == "Weathered")

# Create data frame of devitrified samples only
devit <- subset(unweathered, Devitrification == "Devitrified")
devitO <- subset(unweatheredO, Devitrification == "Devitrified")

# Create data frame of glassy samples only
glassy <- subset(unweathered, Devitrification == "Glassy")
glassyO <- subset(unweatheredO, Devitrification == "Glassy")

# Calculate descriptive statistics
```

```
# Geometric mean and SD
exp(mean(tuffs$As))
exp(mean(tuffsO$As))
exp(sd(tuffs$As))
exp(sd(tuffsO$As))

exp(mean(unweathered$As))
exp(mean(unweatheredO$As))
exp(mean(weathered$As))
exp(mean(weatheredO$As))
exp(sd(unweathered$As))
exp(sd(unweatheredO$As))
exp(sd(weathered$As))
exp(sd(weatheredO$As))

exp(mean(devit$As))
exp(mean(devitO$As))
exp(mean(glassy$As))
exp(mean(glassyO$As))
exp(sd(devit$As))
exp(sd(devitO$As))
exp(sd(glassy$As))
exp(sd(glassyO$As))

exp(mean(sed$As))
exp(mean(sedO$As))
exp(sd(sed$As))
exp(sd(sedO$As))

# Arithmetic Mean, Median, SD

mean(totaldataLOI$As[which(totaldataLOI$Weathering == "Weathered")])
mean(totaldata2$As[which(totaldata2$Weathering == "Weathered")])
median(totaldataLOI$As[which(totaldataLOI$Weathering == "Weathered")])
median(totaldata2$As[which(totaldata2$Weathering == "Weathered")])
sd(totaldataLOI$As[which(totaldataLOI$Weathering == "Weathered")])
sd(totaldata2$As[which(totaldata2$Weathering == "Weathered")])

mean(totaldataLOI$As[which(totaldataLOI$Weathering == "Unweathered")])
mean(totaldata2$As[which(totaldata2$Weathering == "Unweathered")])
median(totaldataLOI$As[which(totaldataLOI$Weathering == "Unweathered")])
median(totaldata2$As[which(totaldata2$Weathering == "Unweathered")])
sd(totaldataLOI$As[which(totaldataLOI$Weathering == "Unweathered")])
```

```
sd(totaldata2$As[which(totaldata2$Weathering == "Unweathered")])

mean(totaldataLOI$As[which(totaldataLOI$Devitrification == "Devitrified")])
mean(totaldata2$As[which(totaldata2$Devitrification == "Devitrified")])
median(totaldataLOI$As[which(totaldataLOI$Devitrification == "Devitrified")])
median(totaldata2$As[which(totaldata2$Devitrification == "Devitrified")])
sd(totaldataLOI$As[which(totaldataLOI$Devitrification == "Devitrified")])
sd(totaldata2$As[which(totaldata2$Devitrification == "Devitrified")])

mean(totaldataLOI$As[which(totaldataLOI$Devitrification == "Glassy")])
mean(totaldata2$As[which(totaldata2$Devitrification == "Glassy")])
median(totaldataLOI$As[which(totaldataLOI$Devitrification == "Glassy")])
median(totaldata2$As[which(totaldata2$Devitrification == "Glassy")])
sd(totaldataLOI$As[which(totaldataLOI$Devitrification == "Glassy")])
sd(totaldata2$As[which(totaldata2$Devitrification == "Glassy")])

mean(totaldataLOI$As[which(totaldataLOI$Devitrification == "Sediment")])
mean(totaldata2$As[which(totaldata2$Devitrification == "Sediment")])
median(totaldataLOI$As[which(totaldataLOI$Devitrification == "Sediment")])
median(totaldata2$As[which(totaldata2$Devitrification == "Sediment")])
sd(totaldataLOI$As[which(totaldataLOI$Devitrification == "Sediment")])
sd(totaldata2$As[which(totaldata2$Devitrification == "Sediment")])

# Test for normality
shapiro.test(tuffs$As)
shapiro.test(sed$As)
shapiro.test(weathered$As)
shapiro.test(unweathered$As)
shapiro.test(glassy$As)
shapiro.test(devit$As)


# Compare tuffs and sediments
t.test(tuffs$As, sed$As)
wilcox.test(tuffs$As, sed$As)
var.test(tuffs$As, sed$As)
levene.test(testtuff$As, testtuff$Weathering, bootstrap = FALSE)
boxplot(tuffs$As, sed$As)

# Compare weathered and unweathered samples
t.test(As ~ Weathering, tuffs)
var.test(As ~ Weathering, tuffs)
wilcox.test(As ~ Weathering, tuffs)
levene.test(tuffs$As, tuffs$Weathering)
```

```
boxplot(As ~ Weathering, tuffs, ylab = "As (mg/kg)", main = "Total As")

# Compare glassy and devitrified samples

t.test(As ~ Devitrification, unweathered)
wilcox.test(As ~ Devitrification, unweathered)
var.test(As ~ Devitrification, unweathered)
kruskal.test(As ~ Devitrification, unweathered)
levene.test( unweathered$As, unweathered$Devitrification)
boxplot(As ~ Devitrification, unweathered, ylab = "As (mg/kg)", main = "Total As")

#==================================================================#
# Log tranform and remove outliers from Env. Available Fraction
#==================================================================#

# Remove outliers
test <- grubb(partialdata)
test <- grubb(test)

partialdata2 <- test

# Log transform the data

logpartialdata <- log(partialdata2[,4:30])
logpartialdata <- cbind(partialdata2[,1:3], logpartialdata)

logpartialdataO <- log(partialdata[,4:30])
logpartialdataO <- cbind(partialdata[,1:3], logpartialdataO)

# Create data frame excluding sediment samples
tuffspartial <- subset(logpartialdata, logpartialdata$Devitrification != "Sediment")
tuffspartial$Devitrification <- factor(tuffspartial$Devitrification)
tuffspartial$Weathering <- factor(tuffspartial$Weathering)

tuffspartialO <- subset(logpartialdataO, logpartialdataO$Devitrification != "Sediment")
tuffspartialO$Devitrification <- factor(tuffspartialO$Devitrification)
tuffspartialO$Weathering <- factor(tuffspartialO$Weathering)

# Create data frame of only sediment samples
sedpartial <- subset(logpartialdata, logpartialdata$Devitrification == "Sediment")
sedpartialO <- subset(logpartialdataO, logpartialdataO$Devitrification == "Sediment")

# Create data frame where tuff v sed is a factor
```

```
testtuffpartial <- tuffspartial
testtuffpartial$Weathering <- "Tuff"
testtuffpartial <- rbind(testtuffpartial, sedpartial)
testtuffpartial$Weathering <- factor(testtuffpartial$Weathering)

testtuffpartialO <- tuffspartialO
testtuffpartialO$Weathering <- "Tuff"
testtuffpartialO <- rbind(testtuffpartialO, sedpartialO)
testtuffpartialO$Weathering <- factor(testtuffpartialO$Weathering)

# Create data frame of unweathered samples only
unweatheredpartial <- subset(tuffspartial, Weathering == "Unweathered")
unweatheredpartialO <- subset(tuffspartialO, Weathering == "Unweathered")

# Create data frame of weathered samples only
weatheredpartial <- subset(tuffspartial, Weathering == "Weathered")
weatheredpartialO <- subset(tuffspartialO, Weathering == "Weathered")

# Create data frame of devitrified samples only
devitpartial <- subset(unweatheredpartial, Devitrification == "Devitrified")
devitpartialO <- subset(unweatheredpartialO, Devitrification == "Devitrified")

# Create data frame of glassy samples only
glassypartial <- subset(unweatheredpartial, Devitrification == "Glassy")
glassypartialO <- subset(unweatheredpartialO, Devitrification == "Glassy")


# Calculate descriptive statistics

# Geometric mean and SD
exp(mean(tuffspartial$As))
exp(mean(tuffspartialO$As))
exp(sd(tuffspartial$As))
exp(sd(tuffspartialO$As))

exp(mean(unweatheredpartial$As))
exp(mean(unweatheredpartialO$As))
exp(mean(weatheredpartial$As))
exp(mean(weatheredpartialO$As))
exp(sd(unweatheredpartial$As))
exp(sd(unweatheredpartialO$As))
exp(sd(weatheredpartial$As))
exp(sd(weatheredpartialO$As))
```

```
exp(mean(devitpartial$As))
exp(mean(devitpartialO$As))
exp(mean(glassypartial$As))
exp(mean(glassypartialO$As))
exp(sd(devitpartial$As))
exp(sd(devitpartialO$As))
exp(sd(glassypartial$As))
exp(sd(glassypartialO$As))

exp(mean(sedpartial$As))
exp(mean(sedpartialO$As))
exp(sd(sedpartial$As))
exp(sd(sedpartialO$As))

# Arithmetic Mean, Median, SD

mean(partialdata$As[which(partialdata$Weathering == "Weathered")])
mean(partialdata2$As[which(partialdata2$Weathering == "Weathered")])
median(partialdata$As[which(partialdata$Weathering == "Weathered")])
median(partialdata2$As[which(partialdata2$Weathering == "Weathered")])
sd(partialdata$As[which(partialdata$Weathering == "Weathered")])
sd(partialdata2$As[which(partialdata2$Weathering == "Weathered")])

mean(partialdata$As[which(partialdata$Weathering == "Unweathered")])
mean(partialdata2$As[which(partialdata2$Weathering == "Unweathered")])
median(partialdata$As[which(partialdata$Weathering == "Unweathered")])
median(partialdata2$As[which(partialdata2$Weathering == "Unweathered")])
sd(partialdata$As[which(partialdata$Weathering == "Unweathered")])
sd(partialdata2$As[which(partialdata2$Weathering == "Unweathered")])

mean(exp(devitpartial$As))
mean(exp(devitpartialO$As))
median(exp(devitpartial$As))
median(exp(devitpartialO$As))
sd(exp(devitpartial$As))
sd(exp(devitpartialO$As))

mean(exp(glassypartial$As))
median(exp(glassypartial$As))
sd(exp(glassypartial$As))



mean(partialdata$As[which(partialdata$Devitrification == "Sediment")])
```

```
mean(partialdata2$As[which(partialdata2$Devitrification == "Sediment")])
median(partialdata$As[which(partialdata$Devitrification == "Sediment")])
median(partialdata2$As[which(partialdata2$Devitrification == "Sediment")])
sd(partialdata$As[which(partialdata$Devitrification == "Sediment")])
sd(partialdata2$As[which(partialdata2$Devitrification == "Sediment")])

mean(partialdata$As[which(partialdata$Devitrification != "Sediment")])
mean(partialdata2$As[which(partialdata2$Devitrification != "Sediment")])
median(partialdata$As[which(partialdata$Devitrification != "Sediment")])
median(partialdata2$As[which(partialdata2$Devitrification != "Sediment")])
sd(partialdata$As[which(partialdata$Devitrification != "Sediment")])
sd(partialdata2$As[which(partialdata2$Devitrification != "Sediment")])


# Test for normality
shapiro.test(tuffspartial$As)
shapiro.test(sedpartial$As)
shapiro.test(weatheredpartial$As)
shapiro.test(unweatheredpartial$As)
shapiro.test(devitpartial$As)
shapiro.test(glassypartial$As)

# Compare groups

# Compare variability

levene.test(testtuffpartial$As, testtuffpartial$Weathering)
levene.test(tuffspartial$As, tuffspartial$Weathering)
levene.test(unweatheredpartial$As, unweatheredpartial$Devitrification)

# Compare medians kinda..

wilcox.test(As ~ Weathering, testtuffpartial)
wilcox.test(As ~ Weathering, tuffspartial)
wilcox.test(As ~ Devitrification, unweatheredpartial)

# Compare weathered and unweathered devitrified and glassy

glassytest <- subset(tuffspartial, Devitrification == "Glassy")
wilcox.test(As ~ Weathering, glassytest)

devittest <- subset(tuffspartial, Devitrification == "Devitrified")
wilcox.test(As ~ Weathering, devittest)
```

```
# Check correlations with total As excluding outliers.

testcor <- subset(totaldata, Sample != "DVC1")
testcor <- data.frame(testcor$Sample,
            testcor$Devitrification,
            testcor$Weathering,
            testcor$As,
            partialdata$As)
testcor <- subset(testcor, testcor.Sample != "LG4")
testcor <- subset(testcor, testcor.Sample != "LG2")
testcor <- subset(testcor, testcor.Sample != "SR2")
testcor <- subset(testcor, testcor.Sample != "DS1")

testcorweathered <- subset(testcor, testcor.Weathering == "Weathered")
testcorun <- subset(testcor, testcor.Weathering == "Unweathered")
testcordevit <- subset(testcorun, testcor.Devitrification == "Devitrified")
testcorsed <- subset(testcor, testcor.Devitrification == "Sediment")

test <- lm(partialdata.As ~ testcor.As, testcor)
test <- lm(partialdata.As ~ testcor.As, testcorweathered)
test <- lm(partialdata.As ~ testcor.As, testcordevit)
test <- lm(partialdata.As ~ testcor.As, testcorsed)

#==============================================================#
# Log tranform and remove outliers from Readily Leachable Fraction
#===============================================================#

# Create subset of data frame that only includes As > MDL

leachdata2 <- subset(leachdata, As > 51.05875)

# Log transform the data

logleachdata <- log(leachdata2[,4:20])
logleachdata <- cbind(leachdata2[,1:3], logleachdata)

logleachdataO <- log(leachdata[,4:20])
logleachdataO <- cbind(leachdata[,1:3], logleachdataO)

# Create data frame excluding sediment samples
tuffsleach <- subset(logleachdata, logleachdata$Devitrification != "Sediment")
tuffsleach$Devitrification <- factor(tuffsleach$Devitrification)
tuffsleach$Weathering <- factor(tuffsleach$Weathering)
```

```
tuffsleachO <- subset(logleachdataO, logleachdataO$Devitrification != "Sediment")
tuffsleachO$Devitrification <- factor(tuffsleachO$Devitrification)
tuffsleachO$Weathering <- factor(tuffsleachO$Weathering)

# Create data frame of only sediment samples
sedleach <- subset(logleachdata, logleachdata$Devitrification == "Sediment")
sedleachO <- subset(logleachdataO, logleachdataO$Devitrification == "Sediment")

# Create data frame where tuff v sed is a factor

testtuffleach <- tuffsleach
testtuffleach$Weathering <- "Tuff"
testtuffleach <- rbind(testtuffleach, sedleach)
testtuffleach$Weathering <- factor(testtuffleach$Weathering)

testtuffleachO <- tuffsleachO
testtuffleachO$Weathering <- "Tuff"
testtuffleachO <- rbind(testtuffleachO, sedleachO)
testtuffleachO$Weathering <- factor(testtuffleachO$Weathering)

# Create data frame of unweathered samples only
unweatheredleach <- subset(tuffsleach, Weathering == "Unweathered")
unweatheredleachO <- subset(tuffsleachO, Weathering == "Unweathered")

# Create data frame of weathered samples only
weatheredleach <- subset(tuffsleach, Weathering == "Weathered")
weatheredleachO <- subset(tuffsleachO, Weathering == "Weathered")

# Create data frame of devitrified samples only
devitleach <- subset(unweatheredleach, Devitrification == "Devitrified")
devitleachO <- subset(unweatheredleachO, Devitrification == "Devitrified")

# Create data frame of glassy samples only
glassyleach <- subset(unweatheredleach, Devitrification == "Glassy")
glassyleachO <- subset(unweatheredleachO, Devitrification == "Glassy")


# Calculate descriptive statistics


# Geometric mean and SD
exp(mean(tuffsleach$As))
exp(mean(tuffsleachO$As))
exp(sd(tuffsleach$As))
```

```
exp(sd(tuffsleachO$As))

exp(mean(unweatheredleach$As))
exp(mean(unweatheredleachO$As))
exp(mean(weatheredleach$As))
exp(mean(weatheredleachO$As))
exp(sd(unweatheredleach$As))
exp(sd(unweatheredleachO$As))
exp(sd(weatheredleach$As))
exp(sd(weatheredleachO$As))

exp(mean(devitleach$As))
exp(mean(devitleachO$As))
exp(mean(glassyleach$As))
exp(mean(glassyleachO$As))
exp(sd(devitleach$As))
exp(sd(devitleachO$As))
exp(sd(glassyleach$As))
exp(sd(glassyleachO$As))

exp(mean(sedleach$As))
exp(mean(sedleachO$As))
exp(sd(sedleach$As))
exp(sd(sedleachO$As))

# Arithmetic Mean, Median, SD

mean(leachdata$As[which(leachdata$Weathering == "Weathered")])
mean(leachdata2$As[which(leachdata2$Weathering == "Weathered")])
median(leachdata$As[which(leachdata$Weathering == "Weathered")])
median(leachdata2$As[which(leachdata2$Weathering == "Weathered")])
sd(leachdata$As[which(leachdata$Weathering == "Weathered")])
sd(leachdata2$As[which(leachdata2$Weathering == "Weathered")])

mean(leachdata$As[which(leachdata$Weathering == "Unweathered")])
mean(leachdata2$As[which(leachdata2$Weathering == "Unweathered")])
median(leachdata$As[which(leachdata$Weathering == "Unweathered")])
median(leachdata2$As[which(leachdata2$Weathering == "Unweathered")])
sd(leachdata$As[which(leachdata$Weathering == "Unweathered")])
sd(leachdata2$As[which(leachdata2$Weathering == "Unweathered")])

mean(exp(devitleach$As))
mean(exp(devitleachO$As))
median(exp(devitleach$As))
```

```
median(exp(devitleachO$As))
sd(exp(devitleach$As))
sd(exp(devitleachO$As))


mean(leachdata$As[which(leachdata$Devitrification == "Glassy")])
mean(leachdata2$As[which(leachdata2$Devitrification == "Glassy")])
median(leachdata$As[which(leachdata$Devitrification == "Glassy")])
median(leachdata2$As[which(leachdata2$Devitrification == "Glassy")])
sd(leachdata$As[which(leachdata$Devitrification == "Glassy")])
sd(leachdata2$As[which(leachdata2$Devitrification == "Glassy")])

mean(leachdata$As[which(leachdata$Devitrification == "Sediment")])
mean(leachdata2$As[which(leachdata2$Devitrification == "Sediment")])
median(leachdata$As[which(leachdata$Devitrification == "Sediment")])
median(leachdata2$As[which(leachdata2$Devitrification == "Sediment")])
sd(leachdata$As[which(leachdata$Devitrification == "Sediment")])
sd(leachdata2$As[which(leachdata2$Devitrification == "Sediment")])

mean(leachdata$As[which(leachdata$Devitrification != "Sediment")])
mean(leachdata2$As[which(leachdata2$Devitrification != "Sediment")])
median(leachdata$As[which(leachdata$Devitrification != "Sediment")])
median(leachdata2$As[which(leachdata2$Devitrification != "Sediment")])
sd(leachdata$As[which(leachdata$Devitrification != "Sediment")])
sd(leachdata2$As[which(leachdata2$Devitrification != "Sediment")])


# Test for normality
shapiro.test(tuffsleachO$As)
shapiro.test(sedleachO$As)
shapiro.test(weatheredleachO$As)
shapiro.test(unweatheredleachO$As)
shapiro.test(devitleachO$As)
shapiro.test(glassyleachO$As)

# Compare groups

# Compare variability

levene.test(testtuffleachO$As, testtuffleachO$Weathering)
levene.test(tuffsleachO$As, tuffsleachO$Weathering)
levene.test(unweatheredleachO$As, unweatheredleachO$Devitrification)

var.test(As ~ Weathering, testtuffleachO)
```

```
var.test(As ~ Weathering, tuffsleachO)
var.test(As ~ Devitrification, unweatheredleachO)

# Compare means

t.test(As ~ Weathering, testtuffleachO, var.equal = FALSE)
t.test(As ~ Weathering, tuffsleachO, var.equal = TRUE)
t.test(As ~ Devitrification, unweatheredleachO, var.equal = FALSE)
```

APPENDIX C: ADDITIONAL CHEMICAL DATA

Table C1. Log transformed total elemental concentrations used in statistical analysis.

Sample	Devitrification	Weathering	Al2O3	As	Ba	Be	CaO	Cr	Cu	FeO	K2O	MgO
BC1	Glassy	Weathered	2.48	1.83	6.71	0.00	1.31	2.20	2.40	2.25	-0.02	0.82
BC2	Sediment	Sediment	1.03	-1.29	3.22	-0.69	-0.69	0.00	2.20	0.57	-2.12	-0.60
BC3	Sediment	Sediment	2.71	1.81	6.54	1.10	0.69	2.89	2.48	1.89	-0.63	0.55
DC1	Glassy	Unweathered	2.47	1.66	7.21	0.87	-0.56	1.10	0.00	0.56	1.76	-2.04
DC4	Glassy	Unweathered	2.47	1.64	7.11	1.10	-0.63	0.00	1.79	0.87	1.76	-2.21
DC5	Devitrified	Unweathered	2.50	-1.37	7.05	1.10	-1.17	0.00	1.61	0.63	1.34	-2.04
DC6	Devitrified	Unweathered	2.44	1.93	6.86	1.10	-1.27	0.00	1.79	0.94	1.26	-2.21
DC7	Devitrified	Unweathered	2.37	1.35	6.91	1.10	-1.20	0.00	1.79	0.79	1.17	-2.41
DC8	Glassy	Weathered	2.55	1.01	6.84	1.10	0.10	0.00	1.61	1.12	1.24	0.46
DC9	Devitrified	Unweathered	2.53	-1.38	7.08	1.10	-1.51	0.00	1.10	-0.25	1.34	-3.22
DS2	Sediment	Sediment	1.51	1.72	5.52	0.00	1.04	1.95	2.40	0.65	-2.41	-0.15
DS3	Sediment	Sediment	0.51	-1.32	4.70	0.00	-0.76	2.40	1.79	-0.65	-1.66	-1.56
DT1	Glassy	Unweathered	2.51	1.34	6.44	0.71	-0.03	2.56	2.77	0.55	1.38	-1.83
DT2	Glassy	Unweathered	2.51	1.67	6.42	0.78	-0.48	1.79	2.08	-0.01	1.70	-2.53
DT3	Devitrified	Unweathered	2.52	1.59	6.40	1.10	-0.71	1.10	1.39	0.33	1.53	-1.05
DVC1	Devitrified	Unweathered	2.46	1.28	5.14	1.21	-1.43	2.20	2.48	1.04	1.50	-1.77
DVC2	Devitrified	Weathered	2.56	0.42	5.57	0.91	-0.29	2.30	1.95	0.97	1.32	-0.20
DVC4	Glassy	Unweathered	2.37	2.18	3.22	2.08	-1.56	2.83	1.95	1.14	1.66	-3.00
FD1	Glassy	Weathered	2.52	1.80	6.29	0.50	1.29	1.79	2.30	1.38	0.26	-0.46
FD2	Glassy	Weathered	2.52	1.83	6.22	0.41	1.29	1.79	2.08	1.16	0.25	-1.08

Sample	Devitrification	Weathering	Al2O3	As	Ba	Be	CaO	Cr	Cu	FeO	K2O	MgO
FD3	Glassy	Weathered	2.49	2.33	6.14	0.50	1.30	1.39	1.95	1.11	-0.27	-0.84
FD4	Glassy	Weathered	2.53	2.68	6.57	0.53	1.03	1.39	2.30	1.40	0.85	-0.11
LB1	Glassy	Weathered	2.60	1.80	6.60	-1.14	-0.92	1.79	1.61	0.60	1.47	-1.77
LG1	Glassy	Weathered	2.44	2.46	7.00	1.61	0.54	0.00	1.10	0.94	0.91	-5.30
LG3	Devitrified	Weathered	2.16	1.02	5.94	1.10	0.17	0.00	1.10	0.60	1.36	-2.30
LST1	Glassy	Weathered	2.35	2.03	6.18	0.81	1.31	1.39	2.40	0.72	1.11	-1.02
MA1	Devitrified	Weathered	2.51	2.14	7.17	1.02	0.73	2.30	3.00	1.08	0.57	-0.42
MK1	Devitrified	Weathered	2.64	1.57	6.00	0.11	0.87	3.00	3.00	0.99	0.48	-1.39
MK2	Devitrified	Weathered	2.68	2.25	6.04	0.19	0.72	1.10	1.95	0.85	0.46	-1.14
MTA1	Glassy	Weathered	2.73	1.21	6.32	0.16	1.30	3.18	2.93	1.62	0.78	0.50
PG1	Devitrified	Weathered	2.17	1.51	6.46	0.64	0.43	1.39	1.95	0.92	1.56	-2.30
PG2	Devitrified	Unweathered	2.57	-1.37	7.15	1.10	-0.73	0.00	1.79	0.58	1.34	-2.30
PG3	Glassy	Unweathered	2.49	2.33	6.58	1.61	-0.08	2.77	2.08	0.91	1.69	-0.46
RST1	Glassy	Unweathered	2.48	1.10	6.41	1.06	-1.14	1.61	1.06	0.29	1.56	-3.00
RST10	Glassy	Unweathered	2.46	1.85	5.99	1.39	-1.51	0.00	1.61	0.48	1.71	-2.66
RST11	Devitrified	Unweathered	2.34	1.75	6.40	1.39	-1.43	0.00	2.08	0.50	1.34	-2.30
RST13	Devitrified	Unweathered	2.48	2.03	6.98	1.39	-1.05	2.56	1.95	0.69	1.46	-1.66
RST2	Glassy	Unweathered	2.46	1.23	6.58	1.00	-1.14	1.79	0.69	0.29	1.62	-3.51
RST4	Devitrified	Unweathered	2.49	1.37	6.61	0.91	-1.20	1.61	1.39	0.44	1.48	-3.00
RST5	Devitrified	Unweathered	2.47	1.73	6.17	1.10	-2.53	2.30	1.95	0.60	1.59	-3.51
RST6	Glassy	Unweathered	2.48	2.00	6.33	1.39	-0.62	3.09	2.20	0.71	1.56	-1.56
RST7	Devitrified	Unweathered	2.51	1.47	6.27	1.39	-0.89	0.00	3.64	0.79	1.46	-1.66
RST8	Glassy	Unweathered	2.49	1.20	5.91	1.39	-1.43	0.00	1.61	0.40	1.78	-2.66
RST9	Glassy	Unweathered	2.54	0.84	5.67	1.39	-1.47	0.00	1.39	0.49	1.70	-2.53
RU1	Glassy	Weathered	2.48	1.41	6.31	0.03	0.88	1.61	2.08	0.91	0.11	-0.39

Sample	Devitrification	Weathering	Al2O3	As	Ba	Be	CaO	Cr	Cu	FeO	K2O	MgO
SLNM	Devitrified	Weathered	2.61	1.02	6.65	1.32	0.73	2.20	2.48	0.82	1.45	-0.25
SLRC	Glassy	Weathered	2.74	0.84	7.51	0.62	0.76	1.39	3.04	0.89	1.46	0.36
SR1	Glassy	Weathered	2.44	2.03	6.35	1.38	0.91	1.39	2.30	0.36	0.73	-0.40
TS1	Sediment	Sediment	2.30	2.77	3.22	0.69	-0.02	3.47	3.26	1.19	-1.27	0.01
TS3	Sediment	Sediment	1.90	1.72	3.22	-0.69	-0.60	3.40	3.04	0.99	-1.47	-0.46
TS4	Sediment	Sediment	2.68	1.97	3.22	1.61	-0.69	0.00	1.61	1.12	1.14	0.21
TSD1	Sediment	Sediment	2.77	1.07	6.78	-0.69	1.98	5.10	4.17	2.21	-0.27	1.06
TSD2	Sediment	Sediment	2.79	-1.32	6.40	0.00	1.88	4.93	4.19	2.06	0.29	1.07
TW1	Devitrified	Weathered	2.71	1.65	5.86	0.22	1.02	1.95	3.26	1.14	0.64	-1.56
TW2	Sediment	Sediment	2.67	-0.44	5.04	-0.86	1.86	2.77	5.08	2.40	-1.43	1.21
WU1	Devitrified	Weathered	2.70	1.45	6.77	0.68	0.28	2.40	2.77	1.31	1.03	-0.84

Table C2. Log transformed total elemental concentrations used in statistical analysis (continued).

Sample	Devit.	Weathering	MnO	Mo	Na2O	Ni	P2O5	Pb	Rb	S	Sb	SiO2	Sr	TiO2	V	Zn
BC1	Glassy	Weathered	-2.55	-0.69	0.48	2.20	-1.71	1.61	2.01	5.70	-0.22	3.97	5.33	0.16	4.36	4.85
BC2	Sediment	Sediment	-4.34	-0.69	-2.53	1.10	-4.61	0.41	2.01	3.91	-0.51	4.43	3.43	-1.51	3.99	3.91
BC3	Sediment	Sediment	-3.30	-0.69	-0.63	2.08	-2.53	2.56	2.01	5.30	-0.11	3.92	5.04	0.22	3.76	4.97
DC1	Glassy	Unweathered	-3.22	1.66	0.86	-Inf	-3.91	2.83	4.47	NA	0.21	4.27	3.37	-1.77	1.10	4.96
DC4	Glassy	Unweathered	-2.88	1.95	1.02	1.79	-3.91	2.56	4.33	4.61	0.10	4.29	3.30	-1.77	1.39	5.32
DC5	Devitrified	Unweathered	-5.30	-0.69	1.43	0.69	-3.51	2.08	2.01	3.91	-0.22	4.32	3.56	-1.77	1.61	5.22
DC6	Devitrified	Unweathered	-4.42	0.00	1.41	0.69	-2.53	2.30	2.01	3.91	0.00	4.33	3.40	-1.83	3.18	4.90
DC7	Devitrified	Unweathered	-3.12	0.69	1.37	1.10	-3.91	1.79	4.01	3.91	-0.11	4.35	3.53	-1.90	2.48	4.62
DC8	Glassy	Weathered	-2.16	1.39	0.78	0.69	-3.51	2.64	3.85	3.91	-0.36	4.18	3.91	-1.71	2.56	5.48
DC9	Devitrified	Unweathered	-5.30	0.00	1.55	-0.69	-3.51	2.56	5.08	3.91	0.00	4.34	3.40	-1.77	1.79	4.86
DS2	Sediment	Sediment	-5.30	-0.69	-2.04	1.61	-3.91	0.41	2.01	5.70	1.03	4.36	4.26	-1.31	4.30	4.06
DS3	Sediment	Sediment	-5.30	-0.69	-2.81	-0.69	-4.61	0.41	2.01	3.91	-0.69	4.49	3.50	-2.30	3.53	2.30
DT1	Glassy	Unweathered	-3.58	0.97	0.96	1.61	-3.44	2.77	4.45	NA	0.13	4.27	4.52	-1.53	2.89	3.56
DT2	Glassy	Unweathered	-3.96	1.26	0.72	0.69	-4.02	2.77	4.81	NA	-0.10	4.30	3.64	-2.51	0.69	3.47
DT3	Devitrified	Unweathered	-4.51	0.00	1.11	0.69	-3.91	2.77	4.64	3.91	-0.11	4.32	3.43	-2.53	1.79	3.14
DVC1	Devitrified	Unweathered	-3.32	0.59	1.40	1.61	-3.02	3.18	4.44	NA	0.36	4.31	3.14	-1.22	2.71	5.07
DVC2	Devitrified	Weathered	-2.70	0.39	1.00	1.39	-3.44	2.71	3.76	NA	0.03	4.23	3.95	-1.24	2.71	4.85
DVC4	Glassy	Unweathered	-2.78	1.95	1.31	1.10	-4.61	3.33	5.22	3.91	0.47	4.30	1.39	-1.71	1.10	5.65
FD1	Glassy	Weathered	-3.02	-2.43	0.51	0.69	-2.53	2.20	3.26	NA	1.15	4.16	5.25	-0.79	3.37	4.62
FD2	Glassy	Weathered	-2.81	-0.60	0.78	0.00	-2.85	2.30	3.66	NA	0.22	4.16	4.88	-1.02	3.14	4.62
FD3	Glassy	Weathered	-2.73	-2.43	0.71	0.00	-2.94	2.40	3.37	NA	0.41	4.16	5.02	-1.19	2.71	4.63
FD4	Glassy	Weathered	-3.04	-1.40	0.38	1.10	-2.88	2.20	4.33	NA	0.26	4.16	6.66	-0.86	3.37	4.61
LB1	Glassy	Weathered	-4.07	-0.36	-0.08	1.39	-4.51	2.48	4.64	NA	0.38	4.29	3.50	-1.75	2.48	3.56
LG1	Glassy	Weathered	-5.30	-0.69	1.32	-0.69	-4.61	2.71	4.80	6.40	-0.51	4.16	3.30	-1.43	0.00	5.13

Sample	Devit.	Weathering	MnO	Mo	Na2O	Ni	P2O5	Pb	Rb	S	Sb	SiO2	Sr	TiO2	V	Zn
LG3	Devitrified	Weathered	-5.30	-0.69	0.45	0.00	-3.91	2.64	4.17	5.99	-0.11	4.32	1.95	-1.77	0.69	4.84
LST1	Glassy	Weathered	-0.25	0.00	0.57	0.69	-3.51	2.77	4.14	NA	0.60	4.16	5.80	-1.35	2.83	4.71
MA1	Devitrified	Weathered	-2.04	-0.34	1.11	1.61	-2.12	2.89	3.99	NA	0.66	4.23	5.17	-0.76	3.50	4.86
MK1	Devitrified	Weathered	-3.19	-0.08	1.46	2.08	-2.42	1.79	3.56	NA	-0.56	4.26	5.21	-0.99	3.18	4.14
MK2	Devitrified	Weathered	-4.96	-0.79	1.40	1.10	-4.07	1.79	3.43	NA	0.52	4.25	5.18	-0.96	3.18	3.30
MTA1	Glassy	Weathered	-2.12	0.48	1.08	2.08	-1.52	2.56	3.85	NA	1.07	4.10	5.74	-0.28	4.20	4.32
PG1	Devitrified	Weathered	-3.41	-1.38	0.82	0.69	-2.85	2.40	4.88	NA	0.40	4.35	3.30	-1.83	2.30	4.88
PG2	Devitrified	Unweathered	-4.61	-0.69	1.47	0.00	-3.91	2.40	2.01	3.91	-0.11	4.31	3.76	-1.56	2.40	4.99
PG3	Glassy	Unweathered	-3.12	1.61	0.82	0.69	-3.51	1.95	4.49	4.61	0.34	4.26	3.89	-1.51	2.20	5.15
RST1	Glassy	Unweathered	-2.47	1.39	1.28	1.10	-4.71	2.94	4.50	NA	0.84	4.30	2.30	-1.92	1.79	4.68
RST10	Glassy	Unweathered	-2.60	1.61	1.18	1.39	-3.22	2.64	4.37	3.91	0.34	4.31	1.79	-2.04	1.39	4.88
RST11	Devitrified	Unweathered	-2.40	1.10	1.26	1.61	-3.91	2.40	4.94	3.91	0.69	4.37	2.83	-2.04	2.48	4.62
RST13	Devitrified	Unweathered	-2.19	0.00	1.43	1.79	-2.81	2.40	4.70	5.30	0.47	4.33	3.53	-1.71	2.48	4.88
RST2	Glassy	Unweathered	-2.66	1.30	1.20	0.69	-4.20	2.94	4.44	NA	0.26	4.30	2.40	-1.93	1.61	4.79
RST4	Devitrified	Unweathered	-2.59	0.32	1.44	1.39	-3.35	2.64	4.48	NA	0.61	4.33	2.77	-1.78	1.79	4.56
RST5	Devitrified	Unweathered	-2.47	0.69	1.37	0.69	-3.51	2.77	4.96	3.91	0.10	4.35	1.61	-2.12	2.30	4.84
RST6	Glassy	Unweathered	-2.33	1.61	1.25	1.39	-3.00	2.48	4.67	3.91	0.53	4.29	3.22	-1.61	2.40	4.82
RST7	Devitrified	Unweathered	-2.51	0.69	1.42	2.40	-3.00	2.48	2.01	3.91	0.59	4.32	3.30	-1.56	2.94	4.67
RST8	Glassy	Unweathered	-2.59	1.61	1.02	0.00	-1.90	2.77	4.60	3.91	0.47	4.29	2.56	-2.04	1.39	4.93
RST9	Glassy	Unweathered	-2.40	1.79	1.13	1.10	-3.91	2.83	2.01	3.91	0.34	4.29	2.20	-1.97	1.39	4.93
RU1	Glassy	Weathered	-3.00	-2.43	1.25	-Inf	-0.69	2.30	3.00	NA	-0.46	4.17	5.04	-1.24	2.71	4.29
SLNM	Devitrified	Weathered	-1.97	0.70	1.24	0.69	-0.63	3.33	5.06	NA	-0.41	4.24	5.58	-1.12	3.74	4.58
SLRC	Glassy	Weathered	-2.19	0.40	1.01	1.39	-2.32	3.04	4.66	NA	-0.81	4.15	6.09	-0.78	3.00	4.25
SR1	Glassy	Weathered	-3.19	-0.53	0.07	0.00	-3.32	2.94	4.52	NA	0.31	4.23	4.57	-1.92	2.20	5.10
TS1	Sediment	Sediment	-5.30	0.69	0.16	2.77	-3.51	1.10	2.89	8.16	-0.92	4.25	4.30	-0.58	5.02	4.47

Sample	Devit.	Weathering	MnO	Mo	Na2O	Ni	P2O5	Pb	Rb	S	Sb	SiO2	Sr	TiO2	V	Zn
TS3	Sediment	Sediment	-5.30	0.69	-0.84	1.79	-3.91	0.41	2.01	7.24	-1.61	4.33	3.66	-1.27	4.23	3.58
TS4	Sediment	Sediment	-2.43	1.10	1.20	1.79	-3.22	3.00	2.01	7.78	-0.11	4.19	4.03	-1.77	3.00	5.19
TSD1	Sediment	Sediment	-1.55	-0.69	0.60	4.39	-0.87	0.41	2.01	5.99	-3.00	3.91	5.41	0.14	4.85	4.25
TSD2	Sediment	Sediment	-1.94	-0.69	0.79	4.37	-1.51	1.79	2.01	5.99	-0.92	4.02	5.25	0.09	4.61	4.34
TW1	Devitrified	Weathered	-2.34	-0.45	1.51	1.10	-1.57	2.08	3.50	NA	0.03	4.22	5.38	-0.18	3.76	3.89
TW2	Sediment	Sediment	-1.67	-2.43	1.27	2.71	-1.82	1.10	1.61	NA	0.92	3.95	5.61	0.51	5.67	4.70
WU1	Devitrified	Weathered	-2.07	0.19	1.71	2.20	-2.22	2.64	3.97	NA	0.55	4.22	4.91	-0.62	3.71	4.44

Table C3. Environmentally available elements present in tuff samples prepared via EPA Method 3051a, and analyzed via ICP-OES. All values reported in mg/kg.

Sample	Devitrification	Weathering	Al	As	Ba	Ca	Cd	Ce	Co	Cr	Cu
BC1	Glassy	Weathered	26032	0.66	332.71	8848	0.85	16.29	15.58	5.33	9.01
BC2	Sediment	Sediment	11633	ND	39.68	2440	0.22	11.82	4.01	3.38	7.68
BC3	Sediment	Sediment	50795	2.32	299.44	9914	1.14	52.35	12.56	8.97	10.68
DC1	Glassy	Unweathered	3042	ND	11.99	691	0.07	4.03	0.65	0.59	1.37
DC4	Glassy	Unweathered	1790	ND	24.02	420	0.04	5.26	0.51	1.37	1.78
DC5	Devitrified	Unweathered	6565	1.49	63.26	1221	0.12	54.54	1.43	0.99	2.23
DC6	Devitrified	Unweathered	3642	5.51	34.91	837	0.22	158.38	2.04	2.37	60.24
DC7	Devitrified	Unweathered	3055	2.35	70.96	752	0.23	81.89	1.66	1.58	11.74
DC8	Glassy	Weathered	20261	2.27	52.32	4353	0.57	49.79	2.06	0.51	2.75
DC9	Devitrified	Unweathered	2346	1.30	28.03	319	0.09	84.69	0.78	1.33	55.62
DS1	Sediment	Sediment	21293	9.66	60.47	9552	0.54	20.06	3.61	6.68	9.52
DS2	Sediment	Sediment	19653	2.74	189.82	14628	0.33	19.38	3.08	5.20	47.59
DS3	Sediment	Sediment	5468	0.43	89.65	2294	0.16	9.97	0.75	2.48	4.17
DT1	Glassy	Unweathered	16263	0.71	95.77	1262	0.17	15.40	3.77	15.17	6.53
DT2	Glassy	Unweathered	5001	ND	31.89	995	0.09	5.35	0.89	7.42	2.55
DT3	Devitrified	Unweathered	5584	0.43	26.98	1012	0.10	8.70	1.35	16.68	3.00
DVC2	Devitrified	Weathered	23354	4.54	115.88	4162	0.40	189.02	4.22	6.64	7.37
DVC4	Glassy	Unweathered	797	ND	9.63	229	0.03	9.85	0.20	1.02	3.88
FD1	Glassy	Weathered	33215	3.05	322.48	18266	0.41	56.32	5.52	4.39	74.81
FD2	Glassy	Weathered	34183	2.53	322.27	18196	0.49	55.02	4.03	4.80	101.70
FD3	Glassy	Weathered	35974	5.10	304.16	18718	0.38	58.93	3.50	2.14	6.61
FD4	Glassy	Weathered	29175	8.16	486.05	14402	0.27	57.36	3.95	2.83	9.43
LB1	Glassy	Weathered	11005	2.49	83.03	1655	0.11	17.33	2.36	1.20	2.51
LG1	Glassy	Weathered	28029	4.24	518.44	8767	0.32	112.39	1.61	0.55	2.93
LG2	Devitrified	Weathered	7582	9.09	25.54	5351	0.56	138.79	0.92	0.38	14.75
LG3	Devitrified	Weathered	6832	2.40	40.71	5858	0.43	93.58	1.92	0.58	9.32
LG4	Devitrified	Weathered	4891	64.51	8.58	2345	0.47	93.72	2.43	0.67	4.42

Sample	Devitrification	Weathering	Al	As	Ba	Ca	Cd	Ce	Co	Cr	Cu
LST1	Glassy	Weathered	28020	3.69	297.98	47000	0.35	55.48	3.78	2.72	11.99
MA1	Devitrified	Weathered	9978	0.89	252.14	4757	0.25	34.38	4.37	3.33	14.08
MK1	Devitrified	Weathered	6694	3.28	23.11	2742	0.35	29.45	6.18	2.63	18.16
MK2	Devitrified	Weathered	11585	5.60	26.32	2033	0.21	19.73	2.68	3.41	8.62
MTA1	Glassy	Weathered	16747	0.87	114.52	5809	0.25	7.00	7.25	5.73	12.92
PG1	Devitrified	Weathered	2544	3.74	30.94	8330	1.16	87.32	1.48	14.53	3.56
PG2	Devitrified	Unweathered	5457	1.42	72.49	901	0.16	73.94	2.29	8.14	3.92
PG3	Glassy	Unweathered	7014	ND	26.68	2454	0.05	24.05	1.36	2.97	3.39
RST1	Glassy	Unweathered	4812	ND	43.30	303	0.08	5.96	0.61	1.89	2.54
RST10	Glassy	Unweathered	1187	ND	15.58	160	0.05	5.35	0.38	1.38	1.73
RST11	Devitrified	Unweathered	1458	3.60	72.88	477	0.15	52.73	1.14	2.42	85.33
RST13	Devitrified	Unweathered	1589	3.64	286.26	937	0.34	64.78	1.78	1.95	4.28
RST2	Glassy	Unweathered	3752	ND	57.07	454	0.11	8.00	0.78	2.37	4.13
RST4	Devitrified	Unweathered	2479	1.76	46.29	933	0.16	70.50	1.53	7.26	3.77
RST5	Devitrified	Unweathered	1056	2.00	18.03	180	0.09	89.31	0.84	0.47	2.38
RST6	Glassy	Unweathered	2842	ND	50.84	775	0.11	5.06	1.71	2.48	4.18
RST7	Devitrified	Unweathered	2917	1.77	75.72	786	0.29	54.98	3.31	5.16	14.18
RST8	Glassy	Unweathered	4319	ND	12.24	253	ND	5.34	0.34	0.61	1.13
RST9	Glassy	Unweathered	8010	ND	35.31	209	0.07	10.40	0.52	1.22	13.12
RU1	Glassy	Weathered	9570	1.83	171.12	9924	0.28	39.26	3.12	1.84	9.48
SLNM	Devitrified	Weathered	4538	ND	315.04	3450	0.35	21.66	3.04	3.84	9.23
SLRC	Glassy	Weathered	10271	1.04	303.49	3959	0.13	38.50	3.17	0.75	9.81
SR1	Glassy	Weathered	27242	5.09	331.21	13902	0.65	116.16	1.44	4.46	43.73
SR2	Devitrified	Unweathered	3308	28.13	34.51	471	0.65	128.32	6.60	241.55	15.86
TS1	Sediment	Sediment	35235	7.13	33.17	4862	0.30	28.00	5.60	17.90	20.19
TS3	Sediment	Sediment	20817	1.49	33.52	2638	0.13	12.47	3.21	11.33	13.52
TS4	Sediment	Sediment	23658	1.35	29.43	1700	0.64	48.78	3.18	0.58	2.57
TSD1	Sediment	Sediment	33670	1.03	369.63	14532	0.48	9.78	24.94	60.54	38.18
TSD2	Sediment	Sediment	23473	ND	149.38	8857	0.22	4.91	16.91	40.68	22.91

Sample	Devitrification	Weathering	Al	As	Ba	Ca	Cd	Ce	Co	Cr	Cu
TW1	Devitrified	Weathered	6972	2.91	26.23	2955	0.40	43.84	5.31	6.37	24.82
TW2	Sediment	Sediment	30175	ND	103.98	21135	0.97	13.12	31.29	9.90	541.48
WU1	Devitrified	Weathered	9527	1.24	95.21	2675	0.43	38.50	8.38	21.72	13.64

Table C4. Environmentally available elements present in tuff samples prepared via EPA Method 3051a, and analyzed via ICP-OES. All values reported in mg/kg (continued).

Sample	Devitrification	Weathering	Fe	La	Mg	Mn	Mo	Na	Nd	Ni
BC1	Glassy	Weathered	17852	10.62	7318	202.10	0.41	1644	10.14	4.23
BC2	Sediment	Sediment	8020	9.36	2656	66.59	ND	213	8.01	2.07
BC3	Sediment	Sediment	17677	28.91	8484	230.16	1.08	502	23.04	5.26
DC1	Glassy	Unweathered	2599	ND	631	11.37	NA	1579	ND	0.21
DC4	Glassy	Unweathered	2803	3.66	246	73.05	0.20	3791	2.62	2.36
DC5	Devitrified	Unweathered	7568	28.32	614	23.74	0.08	3538	22.82	1.10
DC6	Devitrified	Unweathered	9447	59.04	487	60.31	0.36	790	53.72	5.93
DC7	Devitrified	Unweathered	8434	32.79	376	328.76	0.52	936	28.97	2.64
DC8	Glassy	Weathered	6906	39.75	7217	468.51	ND	1252	29.82	1.43
DC9	Devitrified	Unweathered	1652	26.35	106	13.60	ND	765	25.10	14.01
DS1	Sediment	Sediment	10473	ND	5249	45.63	0.18	2032	9.50	4.44
DS2	Sediment	Sediment	8401	ND	4204	18.98	0.09	956	9.26	4.52
DS3	Sediment	Sediment	2202	5.65	863	8.12	ND	204	4.76	0.82
DT1	Glassy	Unweathered	8673	8.56	820	82.03	NA	4637	5.93	5.44
DT2	Glassy	Unweathered	4287	4.18	397	25.42	NA	5298	ND	0.98
DT3	Devitrified	Unweathered	6508	4.87	1171	56.67	0.33	567	3.72	1.89
DVC2	Devitrified	Weathered	12610	91.65	4830	396.39	NA	1474	54.97	3.07
DVC4	Glassy	Unweathered	1234	5.24	125	59.73	0.11	1569	3.18	1.70
FD1	Glassy	Weathered	16107	27.36	3268	285.73	NA	5422	21.43	10.45
FD2	Glassy	Weathered	13595	25.26	1676	369.64	NA	6931	20.67	5.25
FD3	Glassy	Weathered	12666	27.68	2065	389.28	NA	6992	22.02	0.94
FD4	Glassy	Weathered	13698	37.73	3439	225.28	NA	3890	28.45	1.14
LB1	Glassy	Weathered	8236	7.53	719	68.92	NA	233	4.72	0.27
LG1	Glassy	Weathered	8168	59.36	257	39.97	0.53	8177	43.01	0.84
LG2	Devitrified	Weathered	2558	60.73	88	30.37	ND	6276	47.83	1.63
LG3	Devitrified	Weathered	8068	44.39	351	51.06	ND	6604	32.60	1.50
LG4	Devitrified	Weathered	10123	54.41	712	216.48	0.46	1753	39.81	0.48
LST1	Glassy	Weathered	11053	26.48	1894	1781.68	NA	9346	22.07	0.87
MA1	Devitrified	Weathered	7888	ND	2005	536.18	NA	4332	ND	2.11

Sample	Devitrification	Weathering	Fe	La	Mg	Mn	Mo	Na	Nd	Ni
MK1	Devitrified	Weathered	11927	ND	1429	293.96	NA	1159	ND	1.66
MK2	Devitrified	Weathered	9616	ND	1514	35.39	NA	1026	7.43	0.83
MTA1	Glassy	Weathered	12569	5.33	2438	280.47	NA	2298	5.60	6.13
PG1	Devitrified	Weathered	6776	38.96	367	128.60	NA	1507	30.33	1.15
PG2	Devitrified	Unweathered	7795	31.00	473	57.90	0.17	1013	26.15	1.40
PG3	Glassy	Unweathered	4777	ND	3207	68.99	ND	2911	9.22	1.26
RST1	Glassy	Unweathered	1296	2.91	163	34.93	NA	4956	2.57	0.72
RST10	Glassy	Unweathered	2142	2.50	95	71.61	0.19	4462	ND	2.17
RST11	Devitrified	Unweathered	4677	20.39	320	469.88	0.76	511	ND	11.23
RST13	Devitrified	Unweathered	6552	22.11	898	615.54	0.41	941	20.67	3.23
RST2	Glassy	Unweathered	2110	4.75	182	64.14	NA	4333	4.24	1.28
RST4	Devitrified	Unweathered	5733	28.55	334	351.21	NA	1969	26.87	1.57
RST5	Devitrified	Unweathered	4196	31.01	111	434.48	0.44	399	28.92	1.10
RST6	Glassy	Unweathered	4138	3.74	624	229.92	0.08	2456	3.45	2.83
RST7	Devitrified	Unweathered	7733	23.57	800	465.33	1.04	779	22.68	6.79
RST8	Glassy	Unweathered	1532	2.73	105	68.18	0.09	929	2.65	0.68
RST9	Glassy	Unweathered	2605	3.72	201	184.63	ND	1579	3.22	1.61
RU1	Glassy	Weathered	7918	ND	1703	233.65	NA	11172	ND	0.70
SLNM	Devitrified	Weathered	6168	ND	1771	416.29	NA	1326	8.79	1.91
SLRC	Glassy	Weathered	5065	ND	4734	308.54	NA	1243	ND	0.74
SR1	Glassy	Weathered	6812	59.65	3145	226.83	NA	5734	50.88	1.38
SR2	Devitrified	Unweathered	22411	91.81	205	478.88	NA	1319	81.58	14.26
TS1	Sediment	Sediment	10577	ND	4471	38.65	ND	4154	ND	9.06
TS3	Sediment	Sediment	9042	6.59	2593	11.61	0.45	1499	5.67	3.99
TS4	Sediment	Sediment	8030	20.53	4097	167.94	ND	5595	ND	2.35
TSD1	Sediment	Sediment	16020	6.86	5328	901.52	ND	2241	7.26	54.18
TSD2	Sediment	Sediment	11246	3.54	3423	341.42	ND	2043	3.90	46.62
TW1	Devitrified	Weathered	14434	ND	1081	695.29	NA	1218	20.57	2.08
TW2	Sediment	Sediment	25190	7.15	13548	977.90	NA	5060	9.52	24.70
WU1	Devitrified	Weathered	15192	ND	1970	665.56	NA	3116	ND	6.76

Table C5. Environmentally available elements present in tuff samples prepared via EPA Method 3051a, and analyzed via ICP-OES. All values reported in mg/kg (continued).

Sample	Devitrification	Weathering	P	Pb	S	Si	Sm	Sr	Ti	V	Zn
BC1	Glassy	Weathered	180.04	3.18	81.89	609.07	2.92	72.95	692.25	66.41	81.57
BC2	Sediment	Sediment	13.94	1.43	7.26	783.37	ND	16.00	155.41	25.15	39.94
BC3	Sediment	Sediment	82.44	10.62	27.87	701.38	5.70	74.14	374.02	48.92	125.78
DC1	Glassy	Unweathered	42.30	ND	81.41	NA	6.37	2.97	NA	2.85	15.49
DC4	Glassy	Unweathered	19.88	0.75	5.53	149.78	ND	3.08	90.14	ND	36.92
DC5	Devitrified	Unweathered	89.77	4.85	17.21	108.30	6.31	9.47	167.79	ND	118.05
DC6	Devitrified	Unweathered	302.04	6.84	81.69	384.95	ND	6.78	94.81	ND	123.21
DC7	Devitrified	Unweathered	77.10	3.19	8.44	365.74	7.57	5.30	135.57	9.18	76.05
DC8	Glassy	Weathered	97.30	6.28	23.71	417.21	8.38	24.37	222.66	7.02	101.05
DC9	Devitrified	Unweathered	79.05	9.19	6.65	198.49	6.49	2.59	82.82	3.64	129.70
DS1	Sediment	Sediment	107.90	3.96	2297.62	514.28	ND	44.72	290.17	59.46	30.32
DS2	Sediment	Sediment	40.88	3.99	114.72	562.26	ND	44.02	95.43	34.38	68.72
DS3	Sediment	Sediment	12.04	1.12	30.00	438.94	ND	17.56	87.82	21.73	7.03
DT1	Glassy	Unweathered	83.07	2.69	30.35	NA	3.92	13.99	NA	ND	24.65
DT2	Glassy	Unweathered	24.34	1.39	10.52	NA	3.95	8.15	NA	ND	14.76
DT3	Devitrified	Unweathered	23.03	1.77	7.27	319.43	ND	4.49	21.25	4.03	18.80
DVC2	Devitrified	Weathered	157.18	10.13	11.92	NA	9.65	36.86	NA	ND	80.63
DVC4	Glassy	Unweathered	17.11	ND	3.72	149.00	ND	1.56	47.09	ND	8.53
FD1	Glassy	Weathered	268.69	9.72	13.40	NA	5.19	117.44	NA	ND	107.58
FD2	Glassy	Weathered	155.17	10.99	31.52	NA	5.32	76.60	NA	ND	121.27
FD3	Glassy	Weathered	161.68	7.09	12.48	NA	5.53	95.21	NA	6.34	74.28
FD4	Glassy	Weathered	171.78	5.46	13.23	NA	8.17	560.11	NA	8.59	60.54
LB1	Glassy	Weathered	27.55	3.14	19.96	NA	6.26	9.46	NA	4.87	20.68
LG1	Glassy	Weathered	16.86	14.16	492.25	390.19	ND	15.05	289.73	ND	126.89
LG2	Devitrified	Weathered	6.08	8.81	12.43	480.39	ND	1.36	335.98	ND	68.25
LG3	Devitrified	Weathered	18.55	13.80	342.47	513.40	8.35	2.91	490.09	ND	116.48
LG4	Devitrified	Weathered	38.14	12.47	38.07	203.53	9.13	9.58	623.31	ND	114.30
LST1	Glassy	Weathered	62.16	10.95	109.72	NA	6.64	205.89	NA	7.11	70.24
MA1	Devitrified	Weathered	357.63	4.43	22.16	NA	6.39	35.91	NA	ND	41.53

Sample	Devitrification	Weathering	P	Pb	S	Si	Sm	Sr	Ti	V	Zn
MK1	Devitrified	Weathered	413.44	1.21	9.46	NA	3.97	17.08	NA	ND	53.12
MK2	Devitrified	Weathered	59.99	1.06	9.59	NA	3.91	22.46	NA	ND	30.41
MTA1	Glassy	Weathered	537.38	4.98	376.39	NA	6.27	61.88	NA	23.82	20.85
PG1	Devitrified	Weathered	219.68	3.27	48.82	NA	8.54	6.30	NA	3.06	48.24
PG2	Devitrified	Unweathered	71.68	3.66	9.45	178.17	6.44	7.26	231.60	6.50	106.31
PG3	Glassy	Unweathered	71.71	1.79	45.83	198.93	ND	9.47	191.35	5.65	44.63
RST1	Glassy	Unweathered	16.53	1.35	5.78	NA	3.94	5.23	NA	3.33	11.12
RST10	Glassy	Unweathered	148.66	0.67	20.85	42.41	ND	1.20	59.50	ND	20.19
RST11	Devitrified	Unweathered	70.42	8.76	18.66	62.46	5.58	4.16	141.74	7.08	100.84
RST13	Devitrified	Unweathered	190.49	2.97	132.46	67.29	6.04	12.76	158.83	7.57	75.41
RST2	Glassy	Unweathered	41.58	1.96	15.32	NA	3.90	3.82	NA	ND	23.72
RST4	Devitrified	Unweathered	130.87	2.84	12.88	NA	7.73	4.26	NA	3.66	48.62
RST5	Devitrified	Unweathered	90.38	9.25	8.01	62.83	8.37	1.43	197.61	6.09	71.71
RST6	Glassy	Unweathered	131.17	1.80	22.58	118.00	ND	5.39	207.82	5.38	23.61
RST7	Devitrified	Unweathered	189.26	3.85	55.20	126.72	6.08	5.99	461.10	ND	71.41
RST8	Glassy	Unweathered	598.90	1.17	9.82	265.93	ND	6.79	54.20	ND	11.45
RST9	Glassy	Unweathered	27.94	2.47	9.90	369.62	ND	3.77	108.35	ND	31.24
RU1	Glassy	Weathered	197.17	8.64	15.20	NA	6.86	114.58	NA	25.46	37.30
SLNM	Devitrified	Weathered	2437.44	5.23	347.67	NA	6.24	51.46	NA	ND	47.22
SLRC	Glassy	Weathered	396.99	4.01	19.04	NA	6.27	33.96	NA	4.49	20.72
SR1	Glassy	Weathered	112.62	18.06	33.32	NA	ND	79.84	NA	6.62	128.13
SR2	Devitrified	Unweathered	336.62	9.35	45.77	NA	25.94	3.91	NA	24.30	58.27
TS1	Sediment	Sediment	85.62	5.04	2831.05	400.07	2.69	35.48	185.32	71.13	58.44
TS3	Sediment	Sediment	49.83	2.53	1143.82	291.79	ND	19.09	184.00	29.86	21.51
TS4	Sediment	Sediment	117.26	7.33	2051.26	241.39	6.08	35.57	21.58	6.18	62.41
TSD1	Sediment	Sediment	1029.20	1.75	38.64	544.27	ND	95.33	1039.47	60.42	37.09
TSD2	Sediment	Sediment	144.15	1.53	44.32	371.71	ND	54.42	403.21	44.56	26.07
TW1	Devitrified	Weathered	965.19	1.76	14.25	NA	6.07	15.94	NA	31.82	37.01
TW2	Sediment	Sediment	412.50	19.08	7.50	NA	4.22	138.89	NA	84.62	244.22
WU1	Devitrified	Weathered	490.71	4.96	40.90	NA	3.98	21.82	NA	31.34	61.28

Table C6. Log transformed environmentally available elemental concentrations used in statistical analysis.

Sample	Devit.	Weathering	Al	As	Ba	Ca	Cd	Ce	Co	Cr	Cu	Fe	Ga	La	Mg	Mn
BC1	Glassy	Weathered	10.17	-0.41	5.81	9.09	-0.16	2.79	2.75	1.67	2.20	9.79	2.48	2.36	8.90	5.31
BC2	Sediment	Sediment	9.36	-1.59	3.68	7.80	-1.51	2.47	1.39	1.22	2.04	8.99	1.62	2.24	7.88	4.20
BC3	Sediment	Sediment	10.84	0.84	5.70	9.20	0.13	3.96	2.53	2.19	2.37	9.78	3.02	3.36	9.05	5.44
DC1	Glassy	Unweathered	8.02	-1.59	2.48	6.54	-2.64	1.39	-0.43	-0.53	0.32	7.86	0.18	0.18	6.45	2.43
DC4	Glassy	Unweathered	7.49	-1.59	3.18	6.04	-3.28	1.66	-0.67	0.31	0.58	7.94	0.18	1.30	5.51	4.29
DC5	Devitrified	Unweathered	8.79	0.40	4.15	7.11	-2.10	4.00	0.36	-0.01	0.80	8.93	1.31	3.34	6.42	3.17
DC6	Devitrified	Unweathered	8.20	1.71	3.55	6.73	-1.51	5.07	0.71	0.86	4.10	9.15	1.16	4.08	6.19	4.10
DC7	Devitrified	Unweathered	8.02	0.85	4.26	6.62	-1.49	4.41	0.51	0.46	2.46	9.04	0.88	3.49	5.93	5.80
DC8	Glassy	Weathered	9.92	0.82	3.96	8.38	-0.56	3.91	0.72	-0.67	1.01	8.84	2.01	3.68	8.88	6.15
DC9	Devitrified	Unweathered	7.76	0.26	3.33	5.76	-2.43	4.44	-0.24	0.29	4.02	7.41	0.18	3.27	4.67	2.61
DS1	Sediment	Sediment	9.97	2.27	4.10	9.16	-0.62	3.00	1.28	1.90	2.25	9.26	2.09	2.32	8.57	3.82
DS2	Sediment	Sediment	9.89	1.01	5.25	9.59	-1.11	2.96	1.13	1.65	3.86	9.04	2.04	2.35	8.34	2.94
DS3	Sediment	Sediment	8.61	-0.85	4.50	7.74	-1.84	2.30	-0.29	0.91	1.43	7.70	0.89	1.73	6.76	2.09
DT1	Glassy	Unweathered	9.70	-0.35	4.56	7.14	-1.79	2.73	1.33	2.72	1.88	9.07	1.84	2.15	6.71	4.41
DT2	Glassy	Unweathered	8.52	-1.59	3.46	6.90	-2.44	1.68	-0.11	2.00	0.94	8.36	0.18	1.43	5.98	3.24
DT3	Devitrified	Unweathered	8.63	-0.83	3.29	6.92	-2.31	2.16	0.30	2.81	1.10	8.78	1.24	1.58	7.07	4.04
DVC2	Devitrified	Weathered	10.06	1.51	4.75	8.33	-0.90	5.24	1.44	1.89	2.00	9.44	2.55	4.52	8.48	5.98
DVC4	Glassy	Unweathered	6.68	-1.59	2.27	5.43	-3.50	2.29	-1.61	0.02	1.36	7.12	0.18	1.66	4.83	4.09
FD1	Glassy	Weathered	10.41	1.11	5.78	9.81	-0.88	4.03	1.71	1.48	4.31	9.69	2.78	3.31	8.09	5.66
FD2	Glassy	Weathered	10.44	0.93	5.78	9.81	-0.71	4.01	1.39	1.57	4.62	9.52	2.68	3.23	7.42	5.91
FD3	Glassy	Weathered	10.49	1.63	5.72	9.84	-0.96	4.08	1.25	0.76	1.89	9.45	2.69	3.32	7.63	5.96
FD4	Glassy	Weathered	10.28	2.10	6.19	9.58	-1.31	4.05	1.37	1.04	2.24	9.53	2.33	3.63	8.14	5.42
LB1	Glassy	Weathered	9.31	0.91	4.42	7.41	-2.21	2.85	0.86	0.18	0.92	9.02	1.56	2.02	6.58	4.23
LG1	Glassy	Weathered	10.24	1.45	6.25	9.08	-1.13	4.72	0.47	-0.59	1.08	9.01	2.83	4.08	5.55	3.69
LG2	Devitrified	Weathered	8.93	2.21	3.24	8.58	-0.58	4.93	-0.08	-0.98	2.69	7.85	2.31	4.11	4.48	3.41
LG3	Devitrified	Weathered	8.83	0.88	3.71	8.68	-0.83	4.54	0.65	-0.54	2.23	9.00	2.25	3.79	5.86	3.93
LST1	Glassy	Weathered	10.24	1.30	5.70	10.76	-1.04	4.02	1.33	1.00	2.48	9.31	2.61	3.28	7.55	7.49
MA1	Devitrified	Weathered	9.21	-0.11	5.53	8.47	-1.38	3.54	1.47	1.20	2.64	8.97	1.63	2.63	7.60	6.28
MK1	Devitrified	Weathered	8.81	1.19	3.14	7.92	-1.06	3.38	1.82	0.97	2.90	9.39	1.33	2.50	7.26	5.68
MK2	Devitrified	Weathered	9.36	1.72	3.27	7.62	-1.55	2.98	0.99	1.23	2.15	9.17	1.42	2.31	7.32	3.57

Sample	Devit.	Weathering	Al	As	Ba	Ca	Cd	Ce	Co	Cr	Cu	Fe	Ga	La	Mg	Mn
MTA1	Glassy	Weathered	9.73	-0.14	4.74	8.67	-1.37	1.95	1.98	1.75	2.56	9.44	1.68	1.67	7.80	5.64
PG1	Devitrified	Weathered	7.84	1.32	3.43	9.03	0.15	4.47	0.39	2.68	1.27	8.82	1.14	3.66	5.91	4.86
PG2	Devitrified	Unweathered	8.60	0.35	4.28	6.80	-1.85	4.30	0.83	2.10	1.37	8.96	1.19	3.43	6.16	4.06
PG3	Glassy	Unweathered	8.86	-1.59	3.28	7.81	-2.97	3.18	0.31	1.09	1.22	8.47	1.26	2.43	8.07	4.23
RST1	Glassy	Unweathered	8.48	-1.59	3.77	5.71	-2.58	1.79	-0.50	0.63	0.93	7.17	0.18	1.07	5.09	3.55
RST10	Glassy	Unweathered	7.08	-1.59	2.75	5.07	-3.03	1.68	-0.96	0.32	0.55	7.67	0.18	0.92	4.55	4.27
RST11	Devitrified	Unweathered	7.28	1.28	4.29	6.17	-1.87	3.97	0.13	0.88	4.45	8.45	0.18	3.01	5.77	6.15
RST13	Devitrified	Unweathered	7.37	1.29	5.66	6.84	-1.08	4.17	0.58	0.67	1.45	8.79	0.18	3.10	6.80	6.42
RST2	Glassy	Unweathered	8.23	-1.59	4.04	6.12	-2.24	2.08	-0.25	0.86	1.42	7.65	0.18	1.56	5.20	4.16
RST4	Devitrified	Unweathered	7.82	0.57	3.83	6.84	-1.85	4.26	0.42	1.98	1.33	8.65	0.18	3.35	5.81	5.86
RST5	Devitrified	Unweathered	6.96	0.69	2.89	5.19	-2.45	4.49	-0.17	-0.77	0.87	8.34	0.18	3.43	4.71	6.07
RST6	Glassy	Unweathered	7.95	-1.59	3.93	6.65	-2.19	1.62	0.54	0.91	1.43	8.33	0.18	1.32	6.44	5.44
RST7	Devitrified	Unweathered	7.98	0.57	4.33	6.67	-1.25	4.01	1.20	1.64	2.65	8.95	0.90	3.16	6.69	6.14
RST8	Glassy	Unweathered	8.37	-1.59	2.50	5.53	-4.90	1.68	-1.09	-0.49	0.12	7.33	0.18	1.00	4.65	4.22
RST9	Glassy	Unweathered	8.99	-1.59	3.56	5.34	-2.65	2.34	-0.66	0.20	2.57	7.87	1.02	1.31	5.31	5.22
RU1	Glassy	Weathered	9.17	0.60	5.14	9.20	-1.27	3.67	1.14	0.61	2.25	8.98	1.53	2.94	7.44	5.45
SLNM	Devitrified	Weathered	8.42	-1.59	5.75	8.15	-1.06	3.08	1.11	1.34	2.22	8.73	1.00	2.43	7.48	6.03
SLRC	Glassy	Weathered	9.24	0.04	5.72	8.28	-2.07	3.65	1.15	-0.29	2.28	8.53	1.17	2.93	8.46	5.73
SR1	Glassy	Weathered	10.21	1.63	5.80	9.54	-0.44	4.75	0.37	1.49	3.78	8.83	2.82	4.09	8.05	5.42
TS1	Sediment	Sediment	10.47	1.96	3.50	8.49	-1.22	3.33	1.72	2.88	3.01	9.27	2.41	2.67	8.41	3.65
TS3	Sediment	Sediment	9.94	0.40	3.51	7.88	-2.05	2.52	1.17	2.43	2.60	9.11	1.85	1.89	7.86	2.45
TS4	Sediment	Sediment	10.07	0.30	3.38	7.44	-0.44	3.89	1.16	-0.54	0.94	8.99	2.02	3.02	8.32	5.12
TSD1	Sediment	Sediment	10.42	0.03	5.91	9.58	-0.73	2.28	3.22	4.10	3.64	9.68	2.26	1.92	8.58	6.80
TSD2	Sediment	Sediment	10.06	-1.59	5.01	9.09	-1.53	1.59	2.83	3.71	3.13	9.33	1.85	1.26	8.14	5.83
TW1	Devitrified	Weathered	8.85	1.07	3.27	7.99	-0.93	3.78	1.67	1.85	3.21	9.58	1.56	2.72	6.99	6.54
TW2	Sediment	Sediment	10.31	-1.59	4.64	9.96	-0.03	2.57	3.44	2.29	6.29	10.13	2.87	1.97	9.51	6.89
WU1	Devitrified	Weathered	9.16	0.22	4.56	7.89	-0.84	3.65	2.13	3.08	2.61	9.63	1.68	2.70	7.59	6.50

Table C7. Log transformed environmentally available elemental concentrations used in statistical analysis (continued).

Sample	Devitrification	Weathering	Mo	Na	Ni	P	Pb	S	Si	Sm	Sr	Ti	V	Zn
BC1	Glassy	Weathered	-0.88	7.40	1.44	5.19	1.16	4.41	6.41	1.07	4.29	6.54	4.20	4.40
BC2	Sediment	Sediment	-3.68	5.36	0.73	2.63	0.36	1.98	6.66	0.18	2.77	5.05	3.22	3.69
BC3	Sediment	Sediment	0.08	6.22	1.66	4.41	2.36	3.33	6.55	1.74	4.31	5.92	3.89	4.83
DC1	Glassy	Unweathered	NA	7.36	-1.55	3.74	-1.28	4.40	NA	1.85	1.09	NA	1.05	2.74
DC4	Glassy	Unweathered	-1.59	8.24	0.86	2.99	-0.29	1.71	5.01	0.18	1.12	4.50	0.18	3.61
DC5	Devitrified	Unweathered	-2.47	8.17	0.10	4.50	1.58	2.85	4.68	1.84	2.25	5.12	0.18	4.77
DC6	Devitrified	Unweathered	-1.02	6.67	1.78	5.71	1.92	4.40	5.95	2.73	1.91	4.55	2.93	4.81
DC7	Devitrified	Unweathered	-0.65	6.84	0.97	4.35	1.16	2.13	5.90	2.02	1.67	4.91	2.22	4.33
DC8	Glassy	Weathered	-3.68	7.13	0.35	4.58	1.84	3.17	6.03	2.13	3.19	5.41	1.95	4.62
DC9	Devitrified	Unweathered	-3.68	6.64	2.64	4.37	2.22	1.89	5.29	1.87	0.95	4.42	1.29	4.87
DS1	Sediment	Sediment	-1.70	7.62	1.49	4.68	1.38	7.74	6.24	0.18	3.80	5.67	4.09	3.41
DS2	Sediment	Sediment	-2.40	6.86	1.51	3.71	1.38	4.74	6.33	0.18	3.78	4.56	3.54	4.23
DS3	Sediment	Sediment	-3.68	5.32	-0.20	2.49	0.11	3.40	6.08	0.18	2.87	4.48	3.08	1.95
DT1	Glassy	Unweathered	NA	8.44	1.69	4.42	0.99	3.41	NA	1.37	2.64	NA	2.52	3.20
DT2	Glassy	Unweathered	NA	8.58	-0.02	3.19	0.33	2.35	NA	1.37	2.10	NA	0.18	2.69
DT3	Devitrified	Unweathered	-1.09	6.34	0.63	3.14	0.57	1.98	5.77	0.18	1.50	3.06	1.39	2.93
DVC2	Devitrified	Weathered	NA	7.30	1.12	5.06	2.32	2.48	NA	2.27	3.61	NA	2.38	4.39
DVC4	Glassy	Unweathered	-2.18	7.36	0.53	2.84	-1.28	1.31	5.00	0.18	0.45	3.85	0.18	2.14
FD1	Glassy	Weathered	NA	8.60	2.35	5.59	2.27	2.60	NA	1.65	4.77	NA	2.75	4.68
FD2	Glassy	Weathered	NA	8.84	1.66	5.04	2.40	3.45	NA	1.67	4.34	NA	2.31	4.80
FD3	Glassy	Weathered	NA	8.85	-0.07	5.09	1.96	2.52	NA	1.71	4.56	NA	1.85	4.31
FD4	Glassy	Weathered	NA	8.27	0.13	5.15	1.70	2.58	NA	2.10	6.33	NA	2.15	4.10
LB1	Glassy	Weathered	NA	5.45	-1.29	3.32	1.14	2.99	NA	1.83	2.25	NA	1.58	3.03
LG1	Glassy	Weathered	-0.64	9.01	-0.18	2.82	2.65	6.20	5.97	2.52	2.71	5.67	0.18	4.84
LG2	Devitrified	Weathered	-3.68	8.74	0.49	1.81	2.18	2.52	6.17	2.63	0.31	5.82	0.18	4.22
LG3	Devitrified	Weathered	-3.68	8.80	0.40	2.92	2.62	5.84	6.24	2.12	1.07	6.19	0.18	4.76
LST1	Glassy	Weathered	NA	9.14	-0.14	4.13	2.39	4.70	NA	1.89	5.33	NA	1.96	4.25
MA1	Devitrified	Weathered	NA	8.37	0.75	5.88	1.49	3.10	NA	1.85	3.58	NA	2.39	3.73
MK1	Devitrified	Weathered	NA	7.06	0.51	6.02	0.19	2.25	NA	1.38	2.84	NA	2.90	3.97
MK2	Devitrified	Weathered	NA	6.93	-0.18	4.09	0.06	2.26	NA	1.36	3.11	NA	2.74	3.41

Sample	Devitrification	Weathering	Mo	Na	Ni	P	Pb	S	Si	Sm	Sr	Ti	V	Zn
MTA1	Glassy	Weathered	NA	7.74	1.81	6.29	1.61	5.93	NA	1.84	4.13	NA	3.17	3.04
PG1	Devitrified	Weathered	NA	7.32	0.14	5.39	1.18	3.89	NA	2.14	1.84	NA	1.12	3.88
PG2	Devitrified	Unweathered	-1.78	6.92	0.34	4.27	1.30	2.25	5.18	1.86	1.98	5.44	1.87	4.67
PG3	Glassy	Unweathered	-3.68	7.98	0.23	4.27	0.58	3.82	5.29	0.18	2.25	5.25	1.73	3.80
RST1	Glassy	Unweathered	NA	8.51	-0.33	2.81	0.30	1.75	NA	1.37	1.65	NA	1.20	2.41
RST10	Glassy	Unweathered	-1.68	8.40	0.77	5.00	-0.40	3.04	3.75	0.18	0.18	4.09	0.18	3.01
RST11	Devitrified	Unweathered	-0.28	6.24	2.42	4.25	2.17	2.93	4.13	1.72	1.43	4.95	1.96	4.61
RST13	Devitrified	Unweathered	-0.89	6.85	1.17	5.25	1.09	4.89	4.21	1.80	2.55	5.07	2.02	4.32
RST2	Glassy	Unweathered	NA	8.37	0.24	3.73	0.67	2.73	NA	1.36	1.34	NA	0.18	3.17
RST4	Devitrified	Unweathered	NA	7.59	0.45	4.87	1.04	2.56	NA	2.04	1.45	NA	1.30	3.88
RST5	Devitrified	Unweathered	-0.83	5.99	0.09	4.50	2.23	2.08	4.14	2.12	0.36	5.29	1.81	4.27
RST6	Glassy	Unweathered	-2.47	7.81	1.04	4.88	0.59	3.12	4.77	0.18	1.69	5.34	1.68	3.16
RST7	Devitrified	Unweathered	0.04	6.66	1.92	5.24	1.35	4.01	4.84	1.81	1.79	6.13	2.53	4.27
RST8	Glassy	Unweathered	-2.46	6.83	-0.38	6.40	0.16	2.28	5.58	0.18	1.92	3.99	0.18	2.44
RST9	Glassy	Unweathered	-3.68	7.36	0.48	3.33	0.91	2.29	5.91	0.18	1.33	4.69	0.18	3.44
RU1	Glassy	Weathered	NA	9.32	-0.35	5.28	2.16	2.72	NA	1.93	4.74	NA	3.24	3.62
SLNM	Devitrified	Weathered	NA	7.19	0.65	7.80	1.65	5.85	NA	1.83	3.94	NA	2.95	3.85
SLRC	Glassy	Weathered	NA	7.13	-0.30	5.98	1.39	2.95	NA	1.84	3.53	NA	1.50	3.03
SR1	Glassy	Weathered	NA	8.65	0.32	4.72	2.89	3.51	NA	2.81	4.38	NA	1.89	4.85
TS1	Sediment	Sediment	-3.68	8.33	2.20	4.45	1.62	7.95	5.99	0.99	3.57	5.22	4.26	4.07
TS3	Sediment	Sediment	-0.80	7.31	1.38	3.91	0.93	7.04	5.68	0.18	2.95	5.21	3.40	3.07
TS4	Sediment	Sediment	-3.68	8.63	0.85	4.76	1.99	7.63	5.49	1.81	3.57	3.07	1.82	4.13
TSD1	Sediment	Sediment	-3.68	7.71	3.99	6.94	0.56	3.65	6.30	0.18	4.56	6.95	4.10	3.61
TSD2	Sediment	Sediment	-3.68	7.62	3.84	4.97	0.42	3.79	5.92	0.18	4.00	6.00	3.80	3.26
TW1	Devitrified	Weathered	NA	7.11	0.73	6.87	0.57	2.66	NA	1.80	2.77	NA	3.46	3.61
TW2	Sediment	Sediment	NA	8.53	3.21	6.02	2.95	2.02	NA	1.44	4.93	NA	4.44	5.50
WU1	Devitrified	Weathered	NA	8.04	1.91	6.20	1.60	3.71	NA	1.38	3.08	NA	3.44	4.12

Table C8. Readily leachable elements present in tuff samples prepared via water leaching experiments, and analyzed via ICP-OES. All values reported in ug/kg.

Sample	Devitrification	Weathering	Al	As	Ba	Ca	Co	Cu	Fe	Mg	Mn
BC1	Glassy	Weathered	16722	ND	3078	142200	11.69	71.38	30140	161327	ND
BC2	Sediment	Sediment	244218	ND	4310	293440	79.13	131.29	245270	136664	ND
BC3	Sediment	Sediment	398179	123.62	5977	476183	162.13	210.81	324780	206829	ND
DC1	Glassy	Unweathered	45642	ND	449	113109	ND	96.36	44962	62044	ND
DC4	Glassy	Unweathered	74536	ND	1008	24673	6.74	ND	68586	10316	ND
DC5	Devitrified	Unweathered	285379	ND	4365	96014	38.44	91.26	265150	41774	ND
DC6	Devitrified	Unweathered	234035	99.12	3843	468364	140.22	ND	456480	262019	7342.58
DC7	Devitrified	Unweathered	259351	364.22	4520	61357	53.81	1358.71	463810	30970	9216.71
DC8	Glassy	Weathered	46385	ND	346	51900	ND	8.24	24914	33462	ND
DC9	Devitrified	Unweathered	191398	61.36	2523	74654	77.10	8251.80	133100	14337	ND
DS1	Sediment	Sediment	ND	1627.53	1884	135370	ND	274.91	ND	73196	ND
DS2	Sediment	Sediment	ND	3436.80	41347	1139997	136.22	4346.50	347520	546669	ND
DS3	Sediment	Sediment	ND	191.64	6524	423093	9.27	877.11	32351	66177	ND
DT1	Glassy	Unweathered	ND	ND	334	4427	ND	41.88	11230	2608	ND
DT2	Glassy	Unweathered	ND	ND	102	2921	ND	ND	9598	1380	ND
DT3	Devitrified	Unweathered	ND	ND	2377	117750	29.30	43.35	254460	81564	ND
DVC1	Devitrified	Unweathered	8243	ND	132	4198	ND	36.15	58716	2902	ND
DVC2	Devitrified	Weathered	ND	ND	365	19195	ND	ND	29669	12314	ND
DVC4	Glassy	Unweathered	ND	ND	715	20728	8.93	185.64	53811	7490	ND
FD1	Glassy	Weathered	ND	ND	290	35702	ND	ND	65556	8016	ND
FD2	Glassy	Weathered	99648	ND	421	38021	ND	ND	74323	4130	ND
FD3	Glassy	Weathered	ND	ND	276	33508	ND	27.80	68105	4543	ND
FD4	Glassy	Weathered	ND	143.91	729	33513	ND	59.89	53274	11589	ND
LB1	Glassy	Weathered	ND	ND	350	22865	ND	18.84	5840	1955	ND
LG1	Glassy	Weathered	ND	355.62	1680	27974	5.30	58.49	186674	1775	ND
LG2	Devitrified	Weathered	ND	218.84	778	32339	12.14	590.43	109565	6213	ND
LG3	Devitrified	Weathered	ND	39.38	264	41363	ND	195.53	84242	6679	ND
LG4	Devitrified	Weathered	ND	ND	139	142287	ND	17.78	1795	346430	ND
LST1	Glassy	Weathered	ND	481.65	1164	140141	122.70	532.05	526460	67332	ND

Sample	Devitrification	Weathering	Al	As	Ba	Ca	Co	Cu	Fe	Mg	Mn
MA1	Devitrified	Weathered	ND	42.29	624	57933	5.90	90.60	36999	9096	ND
MK1	Devitrified	Unweathered	ND	34.65	135	50963	ND	42.96	23097	30056	ND
MK2	Devitrified	Unweathered	ND	132.45	232	17701	ND	42.44	35387	7411	ND
MTA1	Glassy	Weathered	ND	ND	1347	137698	37.26	219.54	69718	111144	ND
PG1	Devitrified	Weathered	ND	56.12	218	95570	ND	35.91	32797	4509	ND
PG2	Devitrified	Unweathered	ND	ND	11326	120005	123.10	477.65	610540	39410	ND
PG3	Glassy	Unweathered	ND	ND	1465	1117111	48.16	984.54	75442	446300	ND
RST1	Glassy	Unweathered	ND	ND	139	971	ND	6.35	3134	ND	ND
RST10	Glassy	Unweathered	7513	ND	126	2282	ND	ND	7497	773	ND
RST11	Devitrified	Unweathered	ND	373.22	2987	26704	15.10	2969.10	100921	ND	ND
RST13	Devitrified	Unweathered	ND	111.48	40115	692426	272.87	1863.68	100989	ND	ND
RST2	Glassy	Unweathered	ND	ND	219	1399	ND	23.67	6770	ND	ND
RST4	Devitrified	Unweathered	8352	ND	156	1554	ND	45.65	4136	ND	ND
RST5	Devitrified	Unweathered	ND	47.28	263	1532	ND	41.29	16615	ND	ND
RST6	Glassy	Unweathered	ND	ND	467	7619	ND	34.56	21978	ND	932.13
RST7	Devitrified	Unweathered	ND	50.39	580	18702	ND	386.65	32381	ND	ND
RST8	Glassy	Unweathered	ND	ND	243	15997	ND	59.52	8915	ND	ND
RST9	Glassy	Unweathered	ND	ND	286	1720	ND	85.53	4675	ND	ND
RU1	Glassy	Weathered	ND	211.58	409	134570	82.68	ND	313460	67864	ND
SLNM	Devitrified	Weathered	ND	ND	1618	137823	ND	ND	5442	64322	ND
SLRC	Glassy	Weathered	ND	ND	1058	50847	ND	40.18	8682	ND	984.05
SR1	Glassy	Weathered	ND	ND	296	22336	ND	ND	22882	9674	ND
SR2	Devitrified	Unweathered	9261	77.07	76	614	ND	19.18	11616	ND	ND
TS1	Sediment	Sediment	ND	2766.90	1306	1102057	227.74	1903.09	1601	ND	ND
TS3	Sediment	Sediment	ND	3030.30	2369	1146764	1346.82	9262.20	79093	ND	ND
TS4	Sediment	Sediment	ND	2173.70	1460	163630	62.50	296.64	109512	ND	ND
TSD1	Sediment	Sediment	ND	ND	7396	580886	371.19	582.58	374370	ND	8660.73
TSD2	Sediment	Sediment	ND	ND	5008	1095931	307.60	849.70	238485	705047	ND
TW1	Devitrified	Unweathered	ND	ND	285	19587	ND	49.17	31962	6043	ND
TW2	Sediment	Sediment	ND	ND	41	39730	39.75	655.65	107155	ND	ND
WU1	Devitrified	Unweathered	ND	ND	302	4265	ND	142.67	26426	ND	ND

Table C9. Readily leachable elements present in tuff samples prepared via water leaching experiments, and analyzed via ICP-OES. All values reported in ug/kg (continued).

Sample	Devitrification	Weathering	Mo	P	S	Si	Sr	Ti	V	Zn
BC1	Glassy	Weathered	21.52	3037	59729	1402178	3411.8	1543.0	729.97	64.4
BC2	Sediment	Sediment	ND	2189	15545	9124540	2145.7	8802.6	3813.99	918.2
BC3	Sediment	Sediment	ND	9534	72749	13056210	3396.2	13450.5	9655.55	1054.5
DC1	Glassy	Unweathered	33.69	2348	86580	448821	409.1	1094.7	ND	445.1
DC4	Glassy	Unweathered	ND	9162	14902	1810935	184.5	1221.3	ND	697.4
DC5	Devitrified	Unweathered	ND	155134	49970	5132010	709.0	3528.8	ND	2965.5
DC6	Devitrified	Unweathered	129.88	123411	727436	4081800	2613.2	2294.8	ND	8938.9
DC7	Devitrified	Unweathered	403.92	38333	28962	7738600	409.6	4282.8	ND	4035.3
DC8	Glassy	Weathered	16.11	2567	19930	1100316	307.7	754.4	ND	253.1
DC9	Devitrified	Unweathered	ND	83033	27725	1792738	433.2	5721.5	ND	11536.4
DS1	Sediment	Sediment	ND	1047	2264930	1031016	10124.5	ND	8504.10	248.2
DS2	Sediment	Sediment	ND	18608	558514	13182200	18427.3	8488.8	ND	4256.9
DS3	Sediment	Sediment	ND	19955	154705	10482280	2525.5	ND	ND	82.3
DT1	Glassy	Unweathered	35.46	2636	16066	323681	43.5	ND	ND	55.9
DT2	Glassy	Unweathered	ND	804	2008	173231	19.1	ND	ND	113.9
DT3	Devitrified	Unweathered	ND	2036	35724	3674000	526.8	ND	ND	738.3
DVC1	Devitrified	Unweathered	32.86	5589	67704	258759	34.8	ND	ND	346.3
DVC2	Devitrified	Weathered	ND	1242	3480	847964	165.3	ND	83.00	238.0
DVC4	Glassy	Unweathered	ND	8208	21218	1532573	137.6	ND	ND	417.7
FD1	Glassy	Weathered	ND	3752	2478	525495	97.6	ND	87.20	219.4
FD2	Glassy	Weathered	28.50	6008	6559	654734	82.5	ND	ND	397.7
FD3	Glassy	Weathered	ND	3805	3156	544549	74.8	950.8	ND	365.3
FD4	Glassy	Weathered	ND	4815	2539	561298	868.4	767.0	ND	223.7
LB1	Glassy	Weathered	ND	ND	15536	116999	141.2	91.0	ND	22.2
LG1	Glassy	Weathered	25.99	1925	544479	1136816	35.0	ND	ND	2677.1
LG2	Devitrified	Weathered	ND	3074	3281	1296727	19.0	ND	9.09	4299.2
LG3	Devitrified	Weathered	13.40	2562	366899	611712	32.4	ND	ND	876.2
LG4	Devitrified	Weathered	22.33	ND	36710	155305	4874.0	ND	ND	ND
LST1	Glassy	Weathered	220.86	7837	83579	2738310	783.0	ND	ND	ND

Sample	Devitrification	Weathering	Mo	P	S	Si	Sr	Ti	V	Zn
MA1	Devitrified	Weathered	ND	3030	8326	682070	359.3	ND	650.79	91.8
MK1	Devitrified	Unweathered	ND	2233	1508	324412	394.5	ND	ND	ND
MK2	Devitrified	Unweathered	ND	5474	3163	397828	212.9	ND	ND	ND
MTA1	Glassy	Weathered	ND	1213	298682	621098	2096.8	ND	ND	ND
PG1	Devitrified	Weathered	13.66	3158	6895	776802	112.3	ND	ND	ND
PG2	Devitrified	Unweathered	ND	12788	33922	4755290	941.8	7612.3	877.60	7173.8
PG3	Glassy	Unweathered	ND	25802	363410	6338740	4515.6	ND	ND	ND
RST1	Glassy	Unweathered	ND	1518	1390	119467	17.7	ND	ND	ND
RST10	Glassy	Unweathered	15.32	46125	15467	123058	14.4	ND	ND	ND
RST11	Devitrified	Unweathered	716.36	27800	65761	2705560	239.9	ND	ND	ND
RST13	Devitrified	Unweathered	241.49	30187	691899	2941260	8496.6	ND	ND	ND
RST2	Glassy	Unweathered	4.48	4926	4037	138314	13.4	ND	68.61	78.9
RST4	Devitrified	Unweathered	61.75	7599	4875	150852	11.9	ND	ND	ND
RST5	Devitrified	Unweathered	57.79	14140	1538	187233	15.2	ND	ND	ND
RST6	Glassy	Unweathered	6.99	17719	3662	342697	59.7	ND	90.00	98.8
RST7	Devitrified	Unweathered	75.64	19430	8665	410759	118.6	ND	ND	ND
RST8	Glassy	Unweathered	42.23	107566	3524	169047	229.9	603.3	ND	ND
RST9	Glassy	Unweathered	6.59	11597	6199	239173	34.8	ND	ND	ND
RU1	Glassy	Weathered	2.11	33611	6701	1892137	230.2	ND	ND	ND
SLNM	Devitrified	Weathered	20.86	241710	168647	185742	1572.8	ND	67.09	ND
SLRC	Glassy	Weathered	8.22	1339	2217	489439	424.4	ND	ND	ND
SR1	Glassy	Weathered	66.87	2155	8727	434278	60.0	ND	ND	ND
SR2	Devitrified	Unweathered	8.59	2696	3508	122108	ND	70.0	62.14	ND
TS1	Sediment	Sediment	2360.10	ND	14599210	5202830	ND	80.9	6019.06	75.5
TS3	Sediment	Sediment	4004.17	ND	7461630	5834720	ND	ND	ND	ND
TS4	Sediment	Sediment	1972.64	ND	14888500	8790260	ND	ND	9183.44	984.3
TSD1	Sediment	Sediment	ND	5740	75741	7209030	ND	ND	ND	ND
TSD2	Sediment	Sediment	ND	3845	203739	8410310	ND	ND	ND	ND
TW1	Devitrified	Unweathered	ND	10804	2123	410928	ND	ND	ND	ND
TW2	Sediment	Sediment	ND	4272	1245	387117	ND	ND	925.60	ND
WU1	Devitrified	Unweathered	52.70	9342	9837	253232	ND	ND	ND	94.8