Analysis of Volcanic Ash

Conor O'Dowd

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Analysis of Volcanic Ash

Abstract
Volcanic ash begins to weather upon deposition, resulting in the in situ development of clay minerals in the glass pore spaces. Almquist (2011) established a classification scheme of weathering based on ash deposits in New Zealand using an SEM. We are examining volcanic ash collected from Mount St. Helens, New Zealand, and Cobble Cuesta of the Gabbs Valley Basin to broaden the classification scheme based on morphology and authigenic clay mineral composition. SEM and XRD analysis of the material were used to get a better understanding of the morphology and geochemistry of the weathering products. By broadening the weathering classification scheme, we can establish a useful tool for researchers to analyze weathering differences between sites and events.

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ANALYSIS OF VOLCANIC ASH

By
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Abstract

Volcanic ash begins to weather upon deposition, resulting in the in situ development of clay minerals in the glass pore spaces. Almquist (2011) established a classification scheme of weathering based on ash deposits in New Zealand using an SEM. We are examining volcanic ash collected from Mount St. Helens, New Zealand, and Cobble Cuesta of the Gabbs Valley Basin to broaden the classification scheme based on morphology and authigenic clay mineral composition. SEM and XRD analysis of the material were used to get a better understanding of the morphology and geochemistry of the weathering products. By broadening the weathering classification scheme, we can establish a useful tool for researchers to analyze weathering differences between sites and events.
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# Table of Contents

Abstract ......................................................................................................................... i
Acknowledgments ........................................................................................................... ii

1.0 Introduction .............................................................................................................. 1  
  1.1 Chemical weathering of clay minerals ................................................................. 1  
  1.2 Alteration of volcanic parent material ............................................................... 2  
  1.3 Volcanic glass ....................................................................................................... 3  
  1.4 Secondary clay formation from volcanic parent materials ............................... 4  
  1.5 Climate effect on clay mineral formation .......................................................... 7  
  1.6 Previous research ............................................................................................... 8  

2.0 Clay mineralogy ....................................................................................................... 14  
  2.1 Clay mineral structure ......................................................................................... 14  
  2.2 Short-range minerals .......................................................................................... 18  
  2.3 Polytypism ........................................................................................................... 19  
  2.4 Crystal morphology ............................................................................................ 20  
  2.5 Clay mineral formation ..................................................................................... 23  
  2.7 Clay mineral Implications .................................................................................. 24  

3.0 Methods ................................................................................................................... 26  

4.0 Results .................................................................................................................... 28  

5.0 Discussion ............................................................................................................... 45  

6.0 References .............................................................................................................. 51  

7.0 Appendix ............................................................................................................... 54
Chapter 1

1.0 Introduction

This study investigates the weathering process of volcanic material to construct a classification scheme in order to determine the level of weathering and to potentially help unravel the geologic history of a particular site. Volcanic ash deposits (tephra) begin to rapidly weather upon deposition and devitrify over time. Weathering alteration of tephra deposits result in secondary clay mineral formation which can aid in the classification of the volcanic material. Tephra deposits and ash fall obtained from Mount St. Helens, New Zealand, and Cobble Cuesta area of Nevada will be categorized based on overall grain shape and surface texture along with the geochemistry and morphology of precipitated secondary clay minerals within the grain pore spaces (authigenic). The weathering of volcanic material can be a complex process involving several factors such as climate, depth of burial, parent material composition, tephra thickness, drainage, and vegetation (Huang et al., 2012). These factors can alter the surrounding chemistry of the environment, resulting in changes in Si concentration and Al availability which ultimately determines what secondary clay minerals form. Thus, it is important to gain an understanding of the mechanisms that drive the weathering process and the resultant clay mineral formation.

1.1 Chemical weathering of clay minerals

Weathering is not only a destructive process, but can concentrate chemical species and form new mineral deposits (Formoso, 2006). Chemical weathering is characterized by the breakdown of rocks and the transformation of complex mineral structures into simpler crystal structures (e.g. tectosilicates (feldspars) to 1:1 phyllosilicates).

Hydrolysis of silicates is the dominant weathering process that produces clay minerals. It involves chemical reactions between silicate minerals and acids, leading to the breakdown of
minerals and leaching of metal cations. However, the reactions do not lead to complete
dissolution of the minerals, such as the partial leaching of $H_4SiO_4$ to form kaolinite (Boggs,
1995; Formoso, 2006). This type of incomplete dissolution is called incongruent dissolution. If
aluminum is present within the mineral undergoing incongruent dissolution, clay minerals such
as smectites, illite and kaolinite may form as a by-product (Boggs, 1995). For example, the
interaction of water with orthoclase feldspar can decompose to produce kaolinite or illite:

$$2KA1Si3O8_{orthoclase} + 2H^+ + 9H_2O \rightarrow Al_2Si2O_5(OH)_4_{kaolinite} + 4H_4SiO_4_{silicic acid} + 2K^+$$

The breakdown of albite can yield kaolinite or smectites:

$$2NaA1Si3O8_{albite} + 2H^+ + 9H_2O \rightarrow Al_2Si2O_5(OH)_4_{kaolinite} + 4H_4SiO_4_{silicic acid} + 2Na^+$$

During hydrolysis, the majority of the $H^+$ ions come from the dissociation of $H_2CO_3$ (carbonic
acid) in water. The more $CO_2$ that is dissolved in the water to form carbonic acid, the more rapid
the reactions. However, $H^+$ ions can be supplied by other means. Biological influences within the
environment can play an important role in the production of acids around the roots of living
plants and by the bacterial decomposition of plants. The interaction of these organic acids with
surrounding rocks supply $H^+$ ions that can further speed up hydrolysis reactions (Boggs, 1995;
Formoso, 2006).

1.2 Alteration of volcanic parent materials

Volcanic materials commonly contain glass (non-crystalline) that tends to rapidly
weather providing a source of Si and Al for mineral formation. The parent volcanic material may
originate from eruptions of highly fluid-like lava or explosive eruptions that eject pyroclastic
(fragmental and unconsolidated silica-rich) materials. During explosive eruptions, pyroclastic material may be distributed over large distances by wind and settle to the ground to form what is known as tephra deposits. The composition of volcanic material can be classified into three main types. This includes (1) basaltic, which consists of high amounts of Fe and Mg and typically includes mafic minerals such as amphiboles, pyroxenes, and olivines, as well as plagioclase and basaltic glass low in Si; (2) rhyolitic, which consist of Si-rich glass and includes minor amounts of mafic minerals such as biotite and feldspars; and (3) andesitic, which is intermediate in composition between basaltic and rhyolitic volcanic material (Churchman et al., 2012).

1.3 Volcanic Glass

Volcanic glass is an amorphous solid with little to no internal structure consisting of loosely linked silica tetrahedra. This lack of internal structure causes glass to weather rapidly through hydrolysis reactions. During dissolution, volcanic glass acts as a cation supplier during the rapid precipitation of secondary clay minerals from solution (Kawano et al., 1997). Dissolution of volcanic glass, determined by Oelkers and Gilason (2003), proceeds in three steps: (1) rapid removal of cations from the near-surface glass structure; (2) aluminum releasing exchange reactions between aqueous H\(^+\) and Al in the glass structure; (3) the relatively slow detachment of partially freed silica. The Si-O bonds are the most stable bonds in the crystal structure, hence glass dissolution rates increase with decreasing Si content. Fragmental and vesicular glass have high surface areas and porosity which can also increase dissolution rates (Churchman et al., 2012).
1.4 Secondary clay formation from volcanic parent materials

Allophane and halloysite are the most common secondary minerals to form within loose volcanic material or soil derived from tephra. These tephra units may comprise of pumice (silica-rich), or scoria (mafic in composition) (Churchman et al., 2012). They classify as magmatic extrusive rocks that are produced from rapidly solidifying volatile-rich molten material. Gas bubbles trapped inside the rock during rapid crystallization of the expanding froth results in very porous (vesicular) material.

Hiradate and Wada (2005) determined the weathering process of the short-ranged mineral allophane from glass using Al and Si Nuclear Magnet Resonance spectroscopy (NMR). The alteration involved the dissolution of aluminum accompanied by the transformation from its tetrahedral state to octahedral. Next, hydrolysis of aluminum in solution produces a gibbsite-like sheet followed by the dissolution of Si-O bonds to form monosilicic acid in solution. Allophane is then generated during the reaction between the gibbsite-like sheet and monosilicic acid. The crystal structure of allophane is based on that of imogolite, which is another aluminosilicate sometimes found (in small amounts) in soil derived from tephra. It consists of a defect gibbsitic Al-octahedral sheet framework. Si in each silica tetrahedron shares three of its oxygen atoms with an octahedrally coordinated Al on the gibbsitic sheet. The remaining oxygen atom acquires a hydrogen atom to form a Si-OH bond. Imogolite consists of thin hollow nanotubes and has a more defined X-ray diffraction (XRD) pattern, thus having a more long-range order than allophane. As a result of the poorly ordered nature of allophane, it is given the term “nanocrystalline”, which means it’s structured at the nanometer scale (1-100nm). The composition of allophane varies over a greater scale than imogolite, but morphologically remains as tiny hollow spherules. There are two main types of allophane: (1) Al-rich with a 2:1 of Al:Si
and are known as proto-imogolite allophanes; and (2) Si-rich with a 1:1 of Al:Si and are referred to as hallyosite-like allophanes. The Al-rich allophanes are the most common and also the most difficult to distinguish with XRD (Churchman et al., 2012).

![Diagram showing the formation of allophane](modified from Churchman et al., 2012).

**Figure 1.1** Model showing the formation of allophane (modified from Churchman et al., 2012).

Halloysite, a 1:1 phyllosilicate clay mineral, often forms by the weathering of tephra. It has the same composition as kaolinite with the difference being that it contains interlayer water. Knowing allophane is poorly ordered and a product of dissolution of glass, and halloysite being crystalline in nature, there has been debate of whether or not allophane alters to halloysite. Until the 1980s, the predominant idea was that allophane altered to halloysite over time as a result of a solid-phase transformation involving crystallization from an “amorphous” material (Churchman et al., 2012). This idea, proposed by Fieldes (1955), was based on the recognition that halloysite tends to occur at depth in many tephra-derived soil sequences, while allophane mainly occurs towards the surface. Due to the law of superposition, it was assumed that allophane formed first.
and then transformed to halloysite. At the time, Fieldes and Swindale (1954) came up with a widely accepted weathering sequence of clay minerals:

Glass and feldspar → allophane and imogolite → meta-halloysite, kaolinite and minor silica

During glass alteration, they concluded that the “amorphous” material (allophane) represented a critical stage in which silicates could not form without first passing through the “amorphous” stage. As the volcanic material rapidly weathers, it would result in the over-saturation of metastable, non-crystalline minerals, such as allophane, imogolite, opaline silica, and ferrihydrate. They determined non-crystalline materials precipitate out of solution first rather than crystalline minerals because nucleation of a soluble phase was kinetically favorable over a less soluble phase. Thus, they proposed clay minerals that derived from rhyolitic and andesitic tephras must have passed through the weathering sequence from amorphous hydrous oxides through allophane to meta-halloysite and kaolin (Fieldes and Swindale, 1954; Kanehiro and Whittig, 1961). As the non-crystalline minerals become more ordered due to warmer and dryer soils, crystalline minerals begin to form such as kaolinite, illite, smectite, and chlorite (Hallenbeck et al., 2000). However, McIntosh (1979) analyzed recent (1800 years) tephra deposits in northern New Zealand and found authigenic halloysite, which contradicted Fieldes’ idea. He established that halloysite formed due to re-silication from a Si-rich soil solution. This showed that halloysite is able to form directly from tephra materials in young soils with high Si concentrations. This lead to the alternative view that aluminosilicate secondary minerals formed due to concentrations of Si in soil solutions and the availability of Al (Parfitt et al., 1983). Stevens and Vucetich (1985) demonstrated that the formation of allophane occurred during warm, wet interglacial periods while halloysite occurred during cool, dry glacial periods. This
implies that changes in environmental conditions leads to a change in Si concentrations and thus, different clay formation.

1.5 Climate effect on clay mineral formation

Climate (the external forces acting upon alteration systems) may have a profound effect on the weathering and formation of clay minerals. Climate is controlled by two primary variables: temperature and rainfall (Velde and Meunier, 2008). The concentration of Si in solution within soils is controlled by the amount of precipitation, drainage patterns, and elevation (Churchman et al., 2012). This in turn, according to Parfitt et al.’s (1983) model, can determine the formation of secondary clay minerals. Soils that develop in younger, porous, and permeable ash deposits result in the formation of allophane due to water easily able to leach Si. Soils that develop in older, less porous and less permeable scoria and consolidated tuffs result in high concentrations of Si, allowing crystalline minerals to form, especially halloysite.

The mineralogy of soils at different altitudes can vary depending on the climate and environmental conditions. Soil from Andean Ecuador, Sierra Nevada in California, and on Kohala Mountain in Hawaii were analyzed and it was found that allophane was the dominant clay in soils at higher altitudes and halloysite was found in soils at lower altitudes (Chadwick et al., 2003; Zehetner et al., 2003; Rasmussen et al., 2007). At higher elevations, soils are more Si-poor as a result of greater precipitation and thus, strong leaching of the soils. At lower elevations, lower rates of precipitation allow for Si in solution to be higher resulting in the formation of halloysite. Intermediate elevations consist of both allophane and halloysite and soils at extreme high elevations had neither but were dominated by 2:1 silicates. These rainfall studies further support the validity of Parfitt et al.’s (1983) model in which the concentration of Si controls the
formation of secondary minerals from weathering of volcanic materials (Churchman et al., 2012).

1.6 Previous research

Previous work by Almquist (2011) studied the weathering of volcanic ash and consequent formation of clay minerals from the Waipaoa catchment in New Zealand. Pumice grains collected from the tephra layers were analyzed using a SEM for direct imaging, chemical analysis (EDS), and mineralogical analysis by FTIR and XRD. A variety of alteration textures were observed, as well as authigenic clays precipitated as by-products from weathered parent volcanic material. A weathering classification scheme was established based on the visible degree of alteration and secondary clay minerals present.

Geologic Setting of New Zealand and Sample Information

Almquist (2011) analyzed volcanic ash derived from the Taupo Hikurangi arc-trench system, located in northern New Zealand. Dominating the late Pliocene to Quaternary, volcanism occurs here due to a convergent boundary between the Pacific and Australian tectonic plates. The oceanic Pacific plate is being subducted under the Australian plate, generating the Hikurangi margin and the Taupo Volcanic Center (TVC). The TVC consists of the Taupo Volcanic Zone (TVZ), which is rhyolitic in composition and is highly active, and the Okataina Volcanic Center (OVC) which is less active. The TVC is also one of the most active rhyolitic complexes in the world and has produced at least 10,000 km$^3$ of magma. Early eruptions were more andesitic while later eruptions, starting about 0.4 million years ago, have been more explosive and volumetrically dominated by rhyolitic activity. These intense violent silicic eruptions distributed pyroclastic material over large distances and cooled to form porous grains of pumice. Eruptions
from both the TVZ and OVC deposited blankets of ash that formed several tephra deposits (Almquist, 2011).

Almquist (2011) collected volcanic ash samples from the North Island of New Zealand from various tephra layers, both terrestrial and marine. Terrestrial samples came from the Waipaoa catchment which include the Waimihia, Taupo, Waiohau, and Rerewhakaitu tephra deposits. More samples were collected from terrestrial locations along the Te Arai tributary, the central watershed near Puketarewa along Otara Road, and the Waipaoa River mouth along Wainui Road (Fig. 1.2). In addition to the terrestrial samples, marine tephra samples from cores of the Wiapaoa continental shelf were collected and include the Taupo (1,717 ± 13 years B.P., from the TVC), Waimihia (3,410 ± 40 years B.P., from the TVZ), Kaharoa (636 ± 12 years B.P., from the OVC), Waiohau (13,635 ± 165 years B.P., from the TVZ) and Rerewhakaitu (17,625 ± 425 years B.P., from the TVZ) tephra layers (ages from Lowe et al., 2008). The Waimihia tephra layer was the thickest and most pure due to the deposition of primarily ash fall. The Kaharoa and Taupo layers were the thinnest and contained impurities consisting of detrital sediment (Almquist, 2011).
Scanning Electron Microscope

Volcanic material from both settings were compared and showed distinct textural differences. The marine Taupo and Waimihia samples showed minimal to no alteration and were characterized by smooth surfaces with distinct edges. Examination of the terrestrial pumice (within the Waipaoa catchment; Te Arai, Wainui Road, Otara Rd, and Puketarewa locations) showed variable textures with a range in alteration compared to the marine pumice. The terrestrial pumice was characterized by a frosted texture with significant pitting on the surface. The edges of the grains were not as distinct and displayed more rounding. Pumice grains from the Te Arai soil profile and Otara Road displayed the most alteration and had a more weathered appearance than pumice from the Puketarewa terrace. The Waimihia pumice from the Uainui Road was the least altered of the terrestrial samples (Almquist, 2011).

Authigenic clays were observed within the pore spaces from several locations. Within the soil samples, evidence of authigenic clay formation was observed on Waiohau, Kaharoa, and Rerewhakaitu pumice grains. The majority of the authigenic clays showed a crenulated “flake-like” morphology consistent with smectites. The soil samples contained more poorly crystalline material (e.g. allophane) than the marine samples. The Waimihia marine tephra layer contained fewer authigenic clay minerals than the Taupo marine layer (Figures 1.3-1.6) (Almquist, 2011).
Figure 1.3 Scanning electron micrographs of New Zealand marine and terrestrial pumice samples. a) Taupo pumice from the continental shelf. The overall morphology of the marine pumice had smooth glass surfaces with sharp edges indicating little to no alteration. No clay mineral growth was observed; magnification = 90x. b) Taupo pumice from the watershed (terrestrial). The watershed pumice sample had a more rounded morphology with a frosted-like appearance on the surface. Clay mineral growth is evident on the surface of the grain; magnification = 80x (from Almquist, 2011).

Figure 1.4 Scanning electron micrographs of New Zealand marine and terrestrial pumice samples. a) Waimihia pumice from the continental shelf. Morphology of the pumice displays no alteration and is characterized by smooth surfaces with distinct ridges; magnification = 90-400x. b) Waimihia pumice from Wainui Road (terrestrial). Morphology shows rounded edges indicating significant alteration. Abundance of clay mineral formation is observed on the surface displaying amorphous morphologies; magnification = 100-350x. c) Waimihia pumice from Te Arai (terrestrial). Similar to figure 1.4b, the morphology is significantly rounded with amorphous clay growth on the surface and within the pores; magnification = 70-350x (from Almquist, 2011).
Figure 1.5 Scanning electron micrographs of New Zealand pumice from the Waipaoa watershed (terrestrial). a) Pumice from Kaharoa (636+/-12 years B.P.); magnification = 40-1000x. b) Pumice from Waiohau (13,635+/- 165 years B.P.); magnification = 150-1000x. c) Pumice from Rerewhakaitu (17,625+/-425 years B.P.); magnification = 80-1000x. Each of the pumice samples collected from the watershed all have similar morphologies and display very rounded surfaces with evidence of pitting indicating significant alteration. Amorphous (allophane) clay mineral growth is abundant on the surface (from Almquist, 2011).
Figure 1.7 Scanning electron micrographs from the Taupo, Waiohau, Kaharoa and Rerewhakaitu eruptions. 
a) Pumice from Taupo displayed authigenic clay formation coating the surface of the grain. The bubble-like texture and amorphous appearance may indicate allophane; magnification = 2000x.  
b) Pumice from Waiohau also shows clay mineral formation along the surface. Some of the clays looked detached and deposited within the crevasses of the pumice grain; magnification = 1000x.  
c) Pumice from Kaharoa appears to have smaller amounts of authigenic clays along the surface; magnification = 800x.  
d) Pumice from Rerewhakaitu had amorphous clay material coating the surfaces of the pumice grains and may potentially be allophane; magnification = 1500x (from Almquist, 2011).
In this thesis, additional volcanic ash samples collected from Mount St. Helens and the Cobble Cuesta of the Gabbs Valley Basin were analyzed to broaden the classification scheme previously established by Almquist (2011). Similarly, the volcanic material were visually observed using direct imaging (SEM) to identify grain texture, morphology, and authigenic clay minerals.

Chapter 2
2.1 Clay mineral structure

The atomic structure of clay minerals, a type of phyllosilicate, consist of regularly repeating layers of tetrahedrally-coordinated silica and octahedrally-coordinated cations (Ehlmann, 2012). The crystal structure of all phyllosilicates consist of two basic units, an octahedral sheet and a tetrahedral sheet. These layers are combined in different ways to produce various clay minerals. The octahedral layer consists of either divalent (e.g. Mg\textsuperscript{2+}) or trivalent (e.g. Al\textsuperscript{3+}) cations between sheets of closely packed hydroxyl ions. If a divalent cation occupies the octahedral site, then all of the sites are filled (trioctahedral). If a trivalent cation occupies the octahedral site, then only two out of the three sites are filled (dioctahedral). These vacancies are needed to balance the trivalent charge. Thus, the octahedral layer can be divided into two basic types: brucite (trioctahedral) layer and the gibbsite (dioctahedral) layer. The tetrahedral layer consists of silica tetrahedrons arranged in a sheet. Within this layer, Al\textsuperscript{3+} can substitute for Si\textsuperscript{4+} and is balanced by the addition of Na\textsuperscript{+} or K\textsuperscript{+}. The various stacking of these layers result in the main groups of clay minerals (Eby, 2004).

The simplest combination of these layers are known as 1:1 phyllosilicates and consist of one tetrahedral sheet bonded to one octahedral sheet (Fig. 2.1a). The kaolin group, comprising kaolinite, dickite, nacrite, and halloysite, consists of the 1:1 layers in which the structural unit
consist of a gibbsite layer and a tetrahedral layer (Velde and Meunier, 2008). There is limited substitution within the structure and thus, the kaolin group minerals have a low cation-exchange capacity. Weak hydrogen bonds are used between adjacent layers to link the tetrahedral sheet oxygens of one layer to the octahedral sheet OH groups of the second layer. This crystal structure explains kaolinite's susceptibility to deformation (Eby, 2004).

The second type of clays are the 2:1 phyllosilicates and consist of an octahedral sheet that is sandwiched and covalently coordinated between two tetrahedral sheets (Fig. 2.1b). Unlike the 1:1 clays, a variety of substitutions can occur in both the octahedral and tetrahedral layers. These substitutions are balanced by the addition of cations in the interlayer positions. The three major groups of 2:1 clays include illites, smectites and vermiculites (Eby, 2004).

The crystal structure of illite clays consist of a gibbsite layer and an Al$^{3+}$ tetrahedral layer. This substitution is balanced with K$^{+}$ ions within the interlayer positions. The K$^{+}$ cations produce a strong bond between sheets resulting in a low cation-exchange capacity. Illite is not an expandable clay and is very similar to muscovite (Eby, 2004).

Smectites are defined as clay minerals whose basal spacing expands to 17 angstroms when treated with ethylene glycol. The major smectite minerals include Na-montmorillonite, Ca-montmorillonite, saponite (Mg-montmorillonite), hectorite (Li-montmorillonite), and beidellite (Al-montmorillonite). A wide variety of substitutions can exist and typically involve Fe$^{3+}$, Fe$^{2+}$ and Mg$^{2+}$ for Al$^{3+}$ in the octahedral layer and Al$^{3+}$ for Si$^{4+}$ in the tetrahedral layer. These substitutions result in a net negative charge and are balanced with various cations depending on the corresponding clay mineral. The structure of montmorillonite is expandable when hydrated. These clays will expand and contract with changes in water content of the environment (Murray, 2007).
Vermiculites are comparable to 2:1 clay minerals, but have a higher net negative charge and thus, the interlayer space is no longer easily expandable by ethylene glycol. The cation-exchange capacity is similar to smectites (Eby, 2004).

Unlike illite, smectites, and vermiculite, the palygorskite-group minerals consist of 2:1 layers that are arranged in chains rather than sheets. The common minerals that make up this group, sepiolite and palygorskite, both have a brucite layer. In the octahedral layers, Al$^{3+}$ substitutes for Mg$^{2+}$ and there are some exchangeable cations. Channels exist in the octahedral layers that can accommodate water and organic molecules (Eby, 2004).

Lastly, in some phyllosilicates the 2:1 layer has a total negative charge of -1. To balance the charge, a brucite-type layer is substituted in-between the 2:1 layers instead of interlayer cations, resulting in a 2:1:1 structure. This gives rise to the chlorite group (Velde and Meunier, 2008). There is considerable substitution of Al$^{3+}$ by Fe$^{3+}$, Mg$^{2+}$ by Fe$^{2+}$, and of Si$^{4+}$ by Al$^{3+}$. Chlorite is one of the only minerals that can be identified by its distinct green color and is commonly intermixed with other clay minerals. It can also be identified by its 14 angstrom basal spacing which does not expand when treated with ethylene glycol (Murray, 2007).

![Figure 2.1](image_url)

**Figure 2.1** (a) The atomic structure of a 1:1 phyllosilicate consisting of one tetrahedral sheet on top bonded to one octahedral sheet on the bottom. (b) The atomic structure of a 2:1 phyllosilicate consisting of one octahedral layer in the middle bonded by a tetrahedral layer on top and bottom (from Velde and Meunier, 2008).
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Table 2.1 Chemical composition of the half unit cell of the principal phyllosilicates. x: Si for R\(^{3+}\) substitution in the tetrahedral sheet; R\(^{2+}\) for R\(^{3+}\) substitution in the octahedral sheet; z: number of octahedral vacancies (<>); IC: interlayer charge. Mineral types are indicated in bold (from Velde and Meunier, 2008).

### 2.2 Short-range Clay Minerals

Allophane and imogolite are clay minerals whose crystal structure is ordered over short-range distances. Allophane is nearly undeterminable using X-ray diffraction. It is currently debated whether allophane has a recognizable crystal structure or if it is amorphous. Imogolite appears to be somewhat more structured, exhibiting some broad diffraction peaks. The short range “crystalline” structure of these minerals have only been approximated (Fig. 2.2) (Cradwick et al. 1992; Wada 1989). Allophane and imogolite are commonly found in soils formed in volcanic ash/glassy rocks (andisols) in various climates. Andisols provide constant moisture to keep these minerals stable. Within dry environments, these minerals become unstable and rapidly transform into halloysite. They form complex
interactions with organic matter in humic horizons derived from volcanic ash. Imogolite is also commonly identified in spodosols (aluminum-oxide rich soils) where it forms as a result of degradation of the Al-organic matter complexes (Velde and Meunier, 2008).

<table>
<thead>
<tr>
<th></th>
<th>Allophane</th>
<th>Imogolite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Discovery</td>
<td>1816 STROMEYER</td>
<td>1962 YOSHINAGA and AOMINE</td>
</tr>
<tr>
<td>Particle morphology in soils</td>
<td>Rounded, 10–30 nm</td>
<td>Smooth and curved threadlike (µm)</td>
</tr>
<tr>
<td>Origin</td>
<td>Andisols</td>
<td>Andisols</td>
</tr>
<tr>
<td>“Crystalline” morphology</td>
<td>Spheres, diameter 35–50 Å</td>
<td>spodic horizons</td>
</tr>
<tr>
<td>Chemical composition</td>
<td>Al₃Si₂O₅·nH₂O</td>
<td>SiO₂·Al₂O₃·2.5H₂O</td>
</tr>
<tr>
<td>CEC (pH 7)</td>
<td>10–135 cmol kg⁻¹</td>
<td>17 cmol kg⁻¹</td>
</tr>
<tr>
<td>AEC (pH 4.0)</td>
<td>5–30 cmol kg⁻¹</td>
<td>40 cmolkg⁻¹</td>
</tr>
<tr>
<td>Surface area</td>
<td>700–900 m² g⁻¹</td>
<td>900–1 100 m² g⁻¹</td>
</tr>
</tbody>
</table>

Table 2.2 Characteristics of the short-range minerals allophane and imogolite (from Velde and Meunier, 2008).

2.3 Polytypism

Different polytypes of the phyllosilicates can form as a result of the specific positioning of the unit layers along the C-axis. The variability in structure can result from the style of layer-stacking defects, differences in particle size and shape, and the occurrence of minor amounts of impurities which can give rise to subtle symmetry arrangements of the atoms (Balan et al., 2014). Polymorphism of the kaolin-group minerals demonstrates the interlayer shifts within the sequence of repeated 1:1 sheets. The alteration of the stacking scheme and order can result in different crystal micro-morphologies. For example, kaolinite is described as hexagonal plates with pseudo-monoclinic symmetry. Dickite and nacrite are described as rhombohedral in shape
due to distortion of the tetrahedral layer. Hallyosite is known to be tubular or spherical in shape as a result of the slightly smaller dioctahedral layers being on the inside of the tube (Fig. 2.3) (Velde and Meunier, 2008).

![Figure 2.3](image)

**Figure 2.3** Relationship between polytype and crystal morphology for kaolin group minerals (from Velde and Meunier, 2008).

### 2.4 Crystal morphology

The geometry of clay minerals can vary depending on composition and crystallography from well-formed, sharp, and recognizable crystal faces to poorly formed and near unrecognizable shapes. Clay minerals that commonly show a euhedral morphology belong to the kaolin and illite groups. Smectites are rarely euhedral, except for beidellite or nontronite in certain circumstances. There are several factors that control the morphology of either 1:1 or 2:1 phyllosilicates. We can look at the structure and order of stacking and direction of growth of clays to get an idea of what controls morphology (Velde and Meunier, 2008).

![Figure 2.4](image)

**Figure 2.4** The pseudo-hexagonal morphology of kaolinite ("booklet" morphology) (from Velde and Meunier, 2008).
Because clay minerals from the kaolin group are classified as 1:1 phyllosilicates, they do not have interlayer cations. Stacking disorders, resulting from rotations between adjacent layers, develop the pseudo-hexagonal morphology observed in the kaolin group, especially kaolinite (Fig. 2.4) (Velde and Meunier, 2008). Halloysite, also part of the kaolin group, can occur in a variety of morphologies including tubes and microtubules, spheroids and microspheres, crumpled lamellae, crinkly films, needle-like or fiber-like forms, and prismatic forms (Churchman et al., 2012; Huang et al., 2012). Halloysite has a hydrated and dehydrated form. The hydrated form has a basal spacing of 10 angstroms and the dehydrated form has a spacing of 7.2 angstroms (Murray, 2007). The tube-like shapes develop in the 10 angstrom halloysite as a result of the substitution of the larger Fe$^{3+}$ for Al$^{3+}$ in the octahedral sheet. The impurity of Fe$^{3+}$ results in the curling in halloysite and leads to smaller particles being formed. The spheroidal forms of halloysite result from fast dissolution and recrystallization often in weathering products of volcanic ash (Bailey, 1990; Adamo et al., 2001; Singer et al., 2004). Platy halloysite forms by the interconnection of the pre-formed tubes. This form is more typical of kaolinite and is commonly unstable causing it to lead to the formation of plates of a poorly-ordered kaolinite. Overall, the morphology depends on the changing chemistry of the surrounding solutions (e.g. availability of Fe) (Churchman et al., 2012).

Illite crystals, euhedral in shape, commonly form by transformation from primary micas or by neogenesis in close proximity of feldspars (Churchman et al., 2012). They are typically smaller and have a more variable morphology than that of micas. Illite commonly exhibits either thin elongated laths or hexagonal platelets in diagenetic conditions. Even though the chemical composition between illite and the various other micas (e.g. muscovite) is nearly identical, they contrast in their structure of the interlayer ion zone. Micas have a monovalent cation (K$^+$ or Na$^+$)
that occupies each hexagonal cavity of the tetrahedral sheets (Fig. 2.5a). Thus, periodic bond chains have identical symmetry. Unlike the micas, illite (Fig. 2.5b) and beidellite (Fig. 5c) crystallites have some hexagonal cavities that are vacant. As the new chains grow, the accumulation of crystal defects results in misalignment of the crystal structure. For lath-shaped illites, the growth direction is along the (100). It is thought that beidellites grow in the similar direction but have more vacancies. The greater amount of crystal defects results in the crystallites being smaller and shapeless (Velde and Meunier, 2008).
Figure 2.5 Relationship between crystal morphology and the structure of the interlayer zone; (a) mica; (b) illite; (c) beidellite; (d) montmorillonite (modified from Velde and Meunier, 2008).

Smectites, designated as 2:1 clays, are very small in size and because of this, the XRD data is difficult to analyze. There can be considerable substitution in the octahedral sheet of Fe$^{3+}$, Fe$^{2+}$, and Mg$^{2+}$ for Al$^{3+}$, which can result in a charge deficiency of up to -0.66 per unit cell that is balanced by exchangeable cations absorbed by the unit layers. Na-montmorillonite and Ca-montmorillonite display a “cornflake, “oak leaf”, or “cellular” textures. The Na-montmorillonite is more “fluffy” or open-texted due to the Na$^{+}$ interlayer ion being more easily hydrated than Ca$^{2+}$, and thus more easily expandable (Keller et al., 1986).

2.5 Clay Mineral Formation

Clay minerals form near the Earth’s surface or subsurface in several different environments. Clays commonly form in soils, continental hydrothermal systems, weathered rocks, sedimentary layers or diagenetic series. Aqueous solutions present within particular environments interact with rocks and play an important role in the formation and/or transformation of clay minerals. Depending on the local environmental conditions in which they form, clays adjust their chemical composition and crystal structure. Since pressure has a negligible effect on the formation of clay minerals, temperature, chemical composition, and time are the predominant influential factors. The leading mechanism to the formation of clay minerals involves alteration processes or the direct precipitation from solutions (nucleation and crystal growth). During clay formation, the composition and quantity of reacting fluids, the chemistry of the parent rock, temperature of the reaction, and the distance of transport of fluids determines the composition and petrology of clay minerals (Velde and Meunier, 2008).
During crystal growth, atoms are added onto the surface to form a crystalline lattice. The construction and addition of new layers can be thought of as "building blocks" (Velde and Meunier, 2008). The transition from solution to solid (crystal structure) results from the free energy of the initial solution phase being greater than the sum of the free energy of the crystalline phase plus the final solution phase (Gibbs 1876, 1878). Thus, incipient crystals begin to grow due to the progressive reduction in free energy with increasing crystal size (Wilkinson, 2015). The shape of the crystal depends on the ordering of interlayer cations. For example, beidellite, vermiculite and illite tend to be euhedral due to interlayer cations being more ordered within the crystal structure. As the interlayer occupancy becomes more dense, then hexagonal shaped crystals develop. However, if the interlayer cations are placed randomly, the crystals become smaller and shapeless (e.g. montmorillonite). Ion transport and surface processes (absorption, surface nucleation, surface diffusion, ion dehydration, and cation exchange) can also affect the growth rate, which in turn, can change the crystal shape (Velde and Meunier, 2008).

2.7 Clay Mineral Implications

The physical and chemical properties of clays allow them to be used for a variety of purposes. Clay minerals are often utilized in the process industries, in agriculture applications, in engineering and construction applications, in environmental re-mediations, and as geologic indicators (Murray, 2007).

Kaolin minerals are one of the more useful group of clays that are characterized by low surface charge, low surface area, low ion exchange, and tend to be chemically inert. Kaolin is often used in coatings, fillings, and paints due to the fine particle size and platy shape of kaolinite. Ceramics, rubber, and plastics also include a wide range of products in which kaolin minerals are utilized (Murray, 2007).
Bentonite, derived primarily from the weathering of volcanic ash, is comprised predominantly of smectite, specifically montmorillonite. Montmorillonite, known as an expandable clay, occur as extremely fine particles of the order of 0.5 um or less. It can expand or contract its layers in response to changes in environmental factors (e.g. dry and wet conditions, temperature) and have high absorption and swelling capacities (Murray, 2007). The hydration or dehydration of these minerals can result in changes in thickness of a single clay particle by almost a 100 percent. For example, a 10 angstrom thick clay mineral can expand to 19.5 angstroms in water (Velde, 2008). This useful property allows bentonite to be a major constituent of drilling mud. As bentonite becomes hydrated, it becomes significantly more viscous due to its high gel strength and forms a thick impervious layer along the edge of the bore hole. This helps prevent drilling fluid from penetrating porous formations, aids in keeping the drill bit lubricated, and removes cuttings from the drill hole (Murray, 2007). Bentonite deposits can also pose a threat to infrastructure. Houses, buildings, and roads built on soils containing expandable clays may be subject to structural damage caused by seasonal swelling (Velde, 1995). Thus, it is important from an engineering stand point to understand and recognize the geology of a particular site before construction proceeds.

Another important and useful characteristic of clay minerals are their ability to exchange ions. Various ions can be attracted to the surface of clays or become incorporated within the crystal structure (Murray, 2007). This allows clay minerals to absorb and transport potentially harmful metals, and thus can be beneficial for industrial use. The high cation exchange capacity of bentonite (89.0 meq/100g) and the high specific surface area of sepiolite (272 m²/g) can serve as great absorbents of heavy metals present in industrial wastewater (Eby, 2004).
Clay minerals also have several geologic implications. They can serve as reliable indicators of provenance and depositional environments of sedimentation. Clay mineral assemblages can help establish the geologic context of a particular area and can serve as a tool for reconstructing the burial history of sedimentary basins (Chaudhri, 2012). Clays are also indicative of paleoclimate changes as well as tectonic activity (Bristow et al., 2015). Geologists can study the type of primary mineral and abundance in a particular environment by analyzing the detrital inheritance, transformation and neoformation of clays. Looking at the variation in abundance of clay minerals can determine the source rock, changes in weathering patterns, distance of transport of sediments, and post depositional alterations of clay minerals (Chaudhri, 2012). Clay minerals are also prevalent in weathered volcanic ash and can be used to determine the degree of alteration of ash deposits as well as the soil chemistry within particular environments.

Chapter 3
Methods
Scanning Electron Microscope (SEM)

Scanning electron microscopes can provide a substantial amount of information about clay minerals through direct visual observations and using secondary electrons to acquire topological data. The SEMs in this study were used to analyze the surface and 3-dimensional features of the clay minerals, such as the morphology and texture.

The volcanic ash fall sample from Mount St. Helens, collected the day after the eruption, was acquired from Dr. Stephen Kissin at Lakehead University. The sample was pristine enough that separation and density fractionation procedures were not necessary. The clay sized grains were uniform and did not need to be filtered to remove impurities. The ash sample was directly
prepared and mounted to be observed under the scanning electron microscope. This was done by placing the ash onto carbon tape and lightly shaking off any excess material to produce a fine layer for examination. The ash sample was sputter-coated with gold in a vacuum evaporator to prevent static build-up. The sample was analyzed at Eastern Michigan University using a Amray 1820 SEM with magnification range between 464x-5500x, with an 8 KeV accelerating voltage, and a working distance was between 12mm-17mm.

Tephra deposits from the Cobble Cuesta of the Gabbs Valley Basin, Nevada were acquired from the USGS Tephrochronology Project. Ten samples were prepared for the SEM in a similar fashion. Larger samples were lightly crushed in a mortar and pestle. They were placed onto carbon adhesive and sputter-coated with 20nm of gold. The samples were analyzed at Miami University using a Zeiss SUPRS 35VP SEM with magnification range of 118x-371.10kx, an 8 KeV accelerating voltage, and a working distance between 7.5mm-9.2mm.

X-ray Diffraction

X-ray diffraction (XRD) is a technique used for the identification and quantification of all minerals present in a particular sample. XRD can easily distinguish long-range crystal structures (e.g. smectites, illite, kaolinite and chlorite). However, it becomes more difficult to recognize and identify poorly-structured short-ranged minerals (e.g. allophane and imogolite). XRD uses basal reflection to distinguish the various clay minerals. During XRD, the clay minerals produce peaks at characteristic wavelengths, measured in degrees 2θ. Using Bragg’s Law (Eqn. 1), the angles can be used to calculate the d-spacing of the crystal structure in angstroms to determine the clay mineral (Almquist, 2011).
\[ n\lambda = 2d\sin\theta \]

\textbf{Eqn. 1} where \( n \) is 1, \( \lambda \) is the wavelength, \( d \) is the d-spacing between the mineral planes and \( \theta \) is the angle of incidence.

Ten samples from the Cobble Cuesta area were analyzed by XRD using the Scintag X1 Powder Diffractometer at Miami University. Jade 7 software was used for phase identification. Prior to analysis, the larger samples were lightly crushed in a mortar and pestle. Approximately 1-3 grams of material was used and was prepped using a smear mount with ethanol to induce a preferred orientation on (001) on glass slides. The samples were run in the XRD instrument from 5-40° 2\( \theta \) using a step scan mode with a step-size of 0.01° and a 0.5 second dwell time.

\textbf{Chapter 4}

\textbf{RESULTS}

\textbf{Geologic settings and Sample Information}

\textit{Mount St. Helens}

Mount Saint Helens, located in southwestern Washington, is the most active and most explosive volcano in the Cascade Range of the Pacific Northwest. Its formation results from the subduction of the Juan de Fuca plate beneath the North American Plate. For over 40,000 years, Mount St. Helens has been erupting, depositing over 100 distinct tephra deposits. These tephra layers are produced from the settlement of wind-blown pyroclastic material and can be traced to specific eruptions. The eruptive history of Mount St. Helens has mainly consisted of silica-rich volcanic material. On May 18, 1980, Mount St. Helens had its most recent explosive eruption, resulting in massive amounts of pyroclastic material released into the atmosphere. The majority of the silica-rich ash material settled to the ground. For this project, rather than tephra, direct ash-fall collected the day after the eruption was analyzed.
Cobble Cuesta of the Gabbs Valley Basin, Nevada

Tephra samples were collected from Miocene strata that was exposed in the Cobble Cuesta of the Gabbs Valley Basin, Nye County, Nevada (Fig. 4.1). Based on tephrochronological studies, the strata range in age from 12.96 to 9.79 Ma. The tephra layers along the outcrop range from individual airfall tuff a few centimeters thick to subunits as thick as about 20 meters that contain several airfall tuffs. Nine major tephra layers, or subunits, were mapped and consist, from bottom to top, of tephra A, C-3, B, C-1, C, D, EL, EU, and E+1 (Table 4.1; Fig. 4.2). Ten samples were analyzed from tephra layers A, B, C, D and EU (Stewart et al., 1999).

Tephra layer A (sample 13384-7J) is 4.8m thick and consists of very-light to medium-light-gray vitric-ash tuff with 1 to 2mm shards. It is indistinctly laminated to thinly bedded. About 1.5 km west of stratigraphic section 3, it consists of a meter-thick layer of vitric-ash and is overlain by 5m of tuffaceous siltstone (Stewart et al., 1999).

Figure 4.1 Index map showing location of Cobble Cuesta, west-central Nevada near Middlegate Station (modified from Stewart et al., 1999).

Tephra layer B (samples 13384-8J and 2379-14J) is 4.3m thick and consists of white tuff composed of fine ash to coarse ash and lapilli (up to 5mm). It is very thinly bedded and contains minor small-scale soft-sediment folds. At stratigraphic section 4, it is 5.5m thick and composed of very-light-gray, fine-ash tuff containing distinct shards (Stewart et al., 1999).
Tephra layer C (samples 13384-9J and 2379-19J) is 4m thick and is composed of yellow-gray, coarse ash to lapilli tuff. It contains irregular lenses and layers of black vitrophyre produced in an airfall tuff (Stewart et al., 1999).

Tephra layer D is a 14.9m thick unit composed of three separate tuffs; a basal tuff (sample JS-92-62) 24cm-thick composed of fine ash, a 30cm-thick fine-ash tuff (sample JS-92-63) about 4m above the basal unit, and a fine, vitric-ash tuff (sample JS-92-64) in the top 4.6m of the unit (Stewart et al., 1999).

Tephra layer EU (samples 2379-12J and 2-96-46J) is a 0.3m thick, white, reworked, fine ash containing 20% grains of quartz and possible feldspar. At stratigraphic section 2, it is 0.3m thick with shard structure. At stratigraphic section 3, the tephra layer is 2.4m thick composed of white tuff with fine vitric ash (Stewart et al., 1999).
Samples (listed in stratigraphic position on field mapping)

Age (Ma) based on tephrochronology

<table>
<thead>
<tr>
<th>Age (Ma)</th>
<th>Samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.24</td>
<td>2-96-47J, local tephra layer (probably lower than JS-92-67, but not certain)</td>
</tr>
<tr>
<td>9.79</td>
<td>JS-92-66, 2379-12J, and 2-96-46J, tephra layer EU</td>
</tr>
<tr>
<td>10.54</td>
<td>2-96-38J, local tephra layer, about half way between tephra layer D and E</td>
</tr>
<tr>
<td>10.83-10.94</td>
<td>JS-92-64, tuff within tephra layer D</td>
</tr>
<tr>
<td>11.0</td>
<td>JS-92-63, middle tuff in tephra layer D</td>
</tr>
<tr>
<td>11.51</td>
<td>2-57-22JB, local tephra layer, half way between tephra layer C and D</td>
</tr>
<tr>
<td>10.83-11.1</td>
<td>2-57-22JA, local tuff, half way between tephra layer C and unit D, in basal 2 cm of 0.6 m tuff that contains 2-57-22JB in upper part</td>
</tr>
<tr>
<td>11.66</td>
<td>2-96-43J, local tephra layer 22.3 m above tephra layer B</td>
</tr>
<tr>
<td>11.78</td>
<td>2-57-16J, local tephra layer, 61.0 m below tephra layer B, could be close to position of tephra layer C-3, or same as tephra layer C-3</td>
</tr>
<tr>
<td>11.81</td>
<td>2379-17JB, tephra layer C-3</td>
</tr>
<tr>
<td>12.96</td>
<td>13384-77J, tephra layer A</td>
</tr>
</tbody>
</table>

Table 4.1 Stratigraphic column showing location of tephra samples underlined in red (modified from Stewart et al., 1999).
Figure 4.2 Stratigraphic diagram of Miocene strata in Cobble Cuesta area (from Stewart et al., 1999).

Scanning Electron Microscope

The samples shown under the SEM in this study were selected from several secondary electron micrographs at different magnifications and orientations. The particular magnification settings shown were those that best depict the distinctive texture of the volcanic material and authigenic clay minerals. Samples observed under the SEM showed variable surface textures and evidence of alteration.
**Morphology of Mount St. Helens Sample**

The light gray ash is very fine grained and irregular in shape. Figure 4.4 illustrates the morphologies of pristine, unaltered volcanic glass with polished smooth-surface textures. The volcanic material has sharp distinct edges and conchoidal fractures, representative of glass shards. There was little to no observed pitting within the samples and is characterized by its angular and blocky appearance. The majority of the Mount St. Helen grains were tiny pieces of glass rather than grains of pumice. The few pumice grains that were identified displayed a vesicular texture and had a “sponge-like” appearance. In terms of authigenic clay mineral precipitation, little to none was observed within the pore spaces of the pumice or on the surface of the glass shards.

![Figure 4.3 Scanning electron micrograph of Mount St. Helens volcanic ash. a) Overall grain morphology displays a micro-vesicular texture with sharp distinct edges. Minor amounts of detached amorphous or soil material appear to be laying within the pore spaces; magnification = 468x. b) Close up on figure 4.3a shows the detailed pore spaces of the grain; magnification = 1240x.](image)
Figure 4.4 Scanning electron micrograph of Mount St. Helens volcanic ash. a) Overall grain morphology show angular characteristics with distinct edges and conchoidal fractures, representative of glass shards; magnification = 800x. b) Close-up showing the distinct conchoidal fractures along the surface with small amounts of detached particles laying in the fractured grooves; magnification = 2300x. c) Continuation of angular grains indicative of pristine glass with minimal to no evidence of alteration; magnification = 500x.
d) Close-up on glass shard showing no authigenic clays. Several prominent edges can be seen with an overall irregular shape; magnification = 1240x. e) Elongate glass shard with a smooth surface indicating no weathering alteration; magnification = 1000x. f) Close-up on the edge of the glass to show the distinct conchoidal fracture along with minor amounts of detached glass material laying on the surface; magnification = 5500x.

**Morphology of Cobble Cuesta of the Gabbs Valley Basin, Nevada samples**

Tephra deposits from Nevada, analyzed on the SEM, show distinct alteration and authigenic clay formation. The volcanic material ranges from glass shards to pumice-like grains with micro-vesicular textures. Overall, the morphology of the tephra samples show more evidence of weathering alteration compared to the Mount St. Helens samples (Figures 4.5-4.14). A few of the grains show conchoidal fractures indicating that some of that material has a glassy texture. Most of the volcanic ash is covered by authigenic clay mineral overgrowth.
Figure 4.5 Scanning electron micrographs of sample 2-96-46J from the EU horizon of the Miocene strata in Nevada. a) Sample shows rounded edges with clear indication of clay mineral growth on the surface; magnification = 436x. b) On the right of the image, the sample displays the growth of needle-like to fibrous-like clays indicating halloysite growth; magnification = 1720x. c) Continuation of the needle-like clays and also showing a splinter-like appearance within the crevasses of the ash grain; magnification = 9470x. d) Sample shows a clear web-like texture growing on the surface of the grain, possibly indicating smectite growth. Towards the center, more needle-like clays appear along with less developed amorphous material; magnification = 12160x.

Figure 4.6 Scanning electron micrographs of sample 2379-12J from the EU horizon of the Miocene strata in Nevada. a) Overall grain texture shows distinct edges with a platy grain morphology. Rounding of some of the grains can also be observed with clay mineral overgrowth on the surfaces; magnification = 634x. b) Flaky/fluffy clays may indicate smectite formation on the surface; magnification = 20870x. c) Grain shows sharp edges with conchoidal fractures. Abundance of fluffy clays and amorphous material is present; magnification = 11190x. d) Zoomed in image of 4.6c, small unusual-looking bumps observed along the glass surface may indicate the growth of authigenic clay on the glass shard; magnification = 34380x.
Figure 4.7 Scanning electron micrographs of sample JS-92-64 from the D horizon of the Miocene strata in Nevada. a) The grains are bladed with clear edges and sharp corners. The shards of glass have minor amounts of clay mineral growth on the surface; magnification = 767x. b) Zoom-in on the bladed appearance with small amounts of amorphous material growing on the surface; magnification = 2460x. c) Elsewhere the sample shows more rounded characteristics rather than a bladed morphology. Clay mineral growth is present on the surface indicating possible smectites and/or aggregates of allophane particles; magnification = 5420x. d) Increasing the magnification of figure 4.7c, the fluffy-like texture of smectite becomes more apparent; magnification = 33780x.
Figure 4.8 Scanning electron micrographs of sample JS-92-63 from the D horizon of the Miocene strata in Nevada. a) Overall morphology of the grains looks irregular in shape, displaying rounded edges and have a similar appearance to oatmeal; magnification = 8090x. b) Sample shows web-like clay textures indicating possible smectites along with more rounded amorphous material; magnification = 27010x. c) A more rounded texture is prominent with clay minerals that have a flakier morphology coating the surface of the grains; magnification = 48360x. d) Close-up on figure 4.8c shows the overgrowth of the amorphous clays obscuring the primary minerals/grain shape; magnification = 90240x.
Figure 4.9 Scanning electron micrographs of sample JS-92-62 from the D horizon of the Miocene strata in Nevada. a) Distinct accumulation of spheroidal shapes were observed along the surface of the grains; magnification = 41590x. b) Increased magnification of figure 4.9a shows the distinct bubble-like aggregate of potentially growing clay material; magnification = 71410x. c) A micro-vesicular texture is observed within the grain giving it a pumice-like appearance. Towards the right of the image, a platy mineral may be present along with small amounts of authigenic growth on the surface; magnification = 4050x. d) Flared flakes of smectites are observed with some of the edges scalloped into sharp points; magnification = 22290x.
Figure 4.10 Scanning electron micrographs of sample 13384-9J from the C horizon of the Miocene strata in Nevada. a) Overall grain morphology shows a range between rounded and angular, displaying areas with conchoidal fractures. Clay minerals are observed coating the surfaces and within the pore spaces of the grains; magnification = 389x. b) A micro-vesicular texture is observed within the grain with possible allophane particles coating the pore spaces; magnification = 2900x. c) Distinct conchoidal fracture near the top of the image with a bubble-like coating of amorphous material, possibly allophane; magnification = 4990x. d) Close-up on figure 4.10c shows the amorphous coating on the curved glass along with flaky-like plates typical of illite near the right of the image; magnification = 7880x.
Figure 4.11 Scanning electron micrographs of sample 2379-19J from the C horizon of the Miocene strata in Nevada. a) Overall grain morphology show pumice-like textures with rounded edges indicating alteration. Variable clay mineral formation is present within the pore spaces; magnification $\approx 394x$. b) Various clay minerals are observed coating the surface of the crystal face, some of which appear to be detached; magnification $\approx 1520x$. c) A close-up on figure 4.11b shows the elongate structure of possible clay minerals which appear clumped together. The fine bubble-like coating near the elongated clay material may potentially be allophane; magnification $\approx 10720x$. d) The web-like texture of smectite is present along with irregular to spheroidal clays which may indicate the clumping together of clay material. The material has a pebble-like appearance and may be detrital in origin; magnification $\approx 18870x$. 

41
Figure 4.12 Scanning electron micrographs of sample 2379-14J from the B horizon of the Miocene strata in Nevada. a) Overall grain morphology is rounded and spherical with distinct clay mineral overgrowth; magnification = 118x. b) The curled web-like clay morphology indicates the formation of smectite clearly observed on the edges of the grain; magnification = 1580x. c) More overgrowth of the web-like smectite dominates the grain surface; magnification = 2260x. d) Close-up on figure 4.12c shows the continuation of the dominate smectite growth; magnification = 10990x.
Figure 4.13 Scanning electron micrographs of sample 13384-8J from the B horizon of the Miocene strata in Nevada. a) Overall grain morphology displays angular edges with conchoidal fractures indicative of glass shards. The micro-vesicular texture can also be seen with minor amounts of clay minerals deposited within the pore spaces; magnification = 10110x. b) Individual spheroidal clay particles can be seen growing on the surface of the glass; magnification = 28600x. c) and d) Increased magnification on the spheroidal clay particles, some of which have combined together; magnification = 63000-77600x.
Figure 4.14 Scanning electron micrographs of sample 13384-7J from the A horizon of the Miocene strata in Nevada. a) Overall morphology of the grains are angular and bladed with distinct edges and conchoidal fractures; magnification = 506x. b) Well developed clay minerals coat the surface of the glass and are characterized by the distinct web-like texture with scalloped edges typical of smectite; magnification = 4780x. c) Close-up on figure 4.14b shows the detailed structure of the smectite clay mineral growth; magnification = 22290x. d) Continuation of smectite growth on the bladed glass; magnification = 3580x.

X-ray Diffraction

After running XRD on each of the 10 samples from Cobble Cuesta, the majority of the patterns were poorly resolved and did not display distinct peaks (Appendix). In terms of amorphous material, the results support the large quantity of glass as observed using the SEM. However, the clays observed with the SEM were not resolved with the XRD. Overall, the XRD results were inconclusive, and due to the size constraints of the material, it was difficult to get an
accurate analysis to be able to confidently identify the authigenic clay minerals from the XRD patterns. Therefore, morphology was mainly used to identify potential clay minerals.

Electron-Microprobe Analysis

Electron-microprobe analysis of the ten samples from Cobble Cuesta show an increase in Si content with age/depth, with layer EU having the lowest percent SiO₂ and layer A having the highest percent SiO₂ (Table 4.2) (Stewart et al., 1999). Higher concentrations of Si may lead to the formation of more crystalline minerals (e.g. halloysite, smectite, and illite).

Table 4.2 Chemical composition of volcanic glass shards in tephra layers of the Cobble Cuesta area, Nevada, as determined by electron-microprobe analysis. Samples are listed in stratigraphic order from youngest to oldest. Analyses by Charles E. Meyer, U.S Geological Survey, Menlo Park, Calif., using the JEOL 8900 instrument (modified from Stewart et al., 1999).

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>MgO</th>
<th>MnO</th>
<th>CaO</th>
<th>TiO₂</th>
<th>Na₂O</th>
<th>K₂O</th>
<th>Total</th>
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<tr>
<td>2379-12J</td>
<td>74.54</td>
<td>12.68</td>
<td>2.51</td>
<td>0.15</td>
<td>0.03</td>
<td>0.95</td>
<td>0.38</td>
<td>3.17</td>
<td>5.59</td>
<td>100.00</td>
</tr>
<tr>
<td>2-96-46J</td>
<td>75.20</td>
<td>12.56</td>
<td>2.55</td>
<td>0.13</td>
<td>0.04</td>
<td>0.90</td>
<td>0.33</td>
<td>3.20</td>
<td>5.34</td>
<td>100.25</td>
</tr>
<tr>
<td>JS-92-64</td>
<td>76.08</td>
<td>12.24</td>
<td>2.15</td>
<td>0.04</td>
<td>0.02</td>
<td>0.69</td>
<td>0.23</td>
<td>2.38</td>
<td>6.17</td>
<td>100.00</td>
</tr>
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<td>12.84</td>
<td>0.75</td>
<td>0.08</td>
<td>0.06</td>
<td>0.59</td>
<td>0.09</td>
<td>3.11</td>
<td>5.58</td>
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<td>0.12</td>
<td>1.12</td>
<td>0.10</td>
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<td>0.50</td>
<td>0.80</td>
<td>2.39</td>
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<tr>
<td>2379-19J</td>
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<td>12.27</td>
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<td>0.07</td>
<td>0.07</td>
<td>0.52</td>
<td>0.08</td>
<td>2.71</td>
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</tr>
<tr>
<td>2379-14J</td>
<td>77.21</td>
<td>12.60</td>
<td>0.53</td>
<td>0.06</td>
<td>0.06</td>
<td>0.36</td>
<td>0.09</td>
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<tr>
<td>13384-8J</td>
<td>78.05</td>
<td>12.16</td>
<td>0.52</td>
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<td>0.06</td>
<td>0.37</td>
<td>0.08</td>
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<td>6.30</td>
<td>100.00</td>
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<tr>
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<td>1.73</td>
<td>0.05</td>
<td>0.03</td>
<td>0.58</td>
<td>0.18</td>
<td>2.26</td>
<td>6.01</td>
<td>99.98</td>
</tr>
</tbody>
</table>

Chapter 5

Discussion

The sample from Mount St. Helens, being the youngest ash analyzed (37 years, and collected the day after the eruption), showed the least weathering as expected. Since the dacitic ash fall is pristine volcanic ash, it was not subjected to potential weathering agents within the soil (e.g. water and/or biological influences). Thus, as a result of its pristine glassy nature, the Mount
St. Helens ash sample serves as the initial weathering stage displaying the least alteration with no authigenic clay precipitation within the pore spaces.

The tephra deposits from the Miocene strata in the Cobble Cuesta area were significantly older (12.96 to 9.79 Ma) than New Zealand and Mount St. Helens. Morphologies of the tephra units had variable alteration textures but overall the degree of weathering was much greater compared to the younger tephra samples. Authigenic clay minerals were clearly prominent and were more easily identifiable by their morphology compared to the New Zealand tephra. Based on morphology, the potential clay minerals that were identified included smectite, illite, halloysite, and allophane/imogolite. The majority of the grains contained smectites growing on the surfaces and coated the glass shards. Other authigenic clays may have been observed growing on the surface and within the pore spaces of the volcanic material but were morphologically unidentifiable. Some of the clays showed a platy form, possibly indicating a more crystalline clay mineral. However, the majority of the unidentifiable clays showed little to no structure and were amorphous in appearance. Soil or detrital material also may have been stuck on the surface or packed within the pore spaces.

The youngest samples (2-96-46J and 2379-12J; Figures 4.5-4.6) from the EU tephra layer consisted of what appeared to be halloysite and smectite growing on the surface with small amounts of allophane within the crevasses of the vitric ash material. The abundance of more crystalline minerals in these ash samples may indicate higher concentrations of Si according to Parfitt et al. (1983). This may have resulted from more indurated tuff material which would have lowered the porosity and permeability of the soil, in turn, minimizing the leaching of cations, causing increased concentrations of Si to aid in the formation of halloysite and smectite. Lower rates of precipitation may also elevate Si in solution. Since the Cobble Cuesta area is within the
Great Basin formed from the Sierra Nevada and Cascade Mountains, the sustained rain shadow in the area may have reduced the annual precipitation resulting in higher concentrations of Si in the soil. Looking at the previous research done in New Zealand, an opposite trend was observed in which more poorly crystalline clay minerals were present in the majority of the terrestrial samples. This suggests that increased interaction of water within the soil due headwaters of the Waipaoa River and higher rates of precipitation would result in the elevated leaching of Si. In this case, a low Si environment would favor the precipitation of more amorphous material such as allophane. New Zealand’s climate is relatively humid compared to Nevada allowing the soil to have a higher moisture content. Therefore, more short-ranged clays remain stable in the soil.

Tuff within tephra layer D (samples JS-92-64, JS-92-63, JS-92-62; Figures 4.7-4.9) showed variable morphology and authigenic clay mineral formation. Layer D, composed mostly of fine ash tuff, consisted of bladed and glassy shards with micro-vesicular and conchoidal textures. However, some of the tuff material within the middle of the tephra layer displayed more of a rounded morphology. There was a mix of clay formation within each section of the layer. The top section of layer D consisted of more smectite with allophane potentially coating some of the glass shards. The middle section consisted of more amorphous material indicating possible allophane/imogolite, with flakier and potentially more crystalline material. The bottom section consisted of well-crystallized smectite with platy minerals, possibly illite. It also contained distinct spheroidal clay material that could potentially be allophane or halloysite. The majority of the authigenic clays in layer D appear to be more crystalline. Thus, the more rounded grains and amorphous material within the middle section may have been detrital in origin and were later mixed in with the more fine vitric tuff material. The detrital grains may have been more extensively weathered before being transported and deposited into the Gabbs Valley Basin. The
more weathered middle section of layer D may have also resulted from a period of higher precipitation causing greater levels of alteration as observed.

The next tephra unit (samples 13384-9J, 2379-19J; Figures 4.10 and 4.11), layer C, consisted of coarse ash that had a rounded to angular morphology with micro-vesicular textures and conchoidal fractures. Again, the majority of the authigenic clay mineral formation had a more crystalline appearance, displaying platy clays possibly indicating illite along with smectite growth. Elongated clay minerals were observed along the surface of the ash grains and could potentially be a form of halloysite or the clumping of clay material. Similar to tephra layer EU, the formation of halloysite may indicate higher concentrations of Si within the soil. The increased Si would also explain the abundant smectite overgrowth along the grain surfaces.

Within the oldest tephra unit (sample 13384-7J; Figure 4.14), layer A, smectite growth is the dominant authigenic clay and covers nearly all of the glass shards. The significant abundance of smectite within this layer may have been controlled by its relative concentration of Si due to its depth and age compared to the other tephra layers. At a depth of approximately 700m, limited drainage may have resulted in higher concentrations of Si, allowing for well-developed smectite to form. Layer A was the oldest tephra deposit, thus more time had passed for authigenic clay mineral precipitation to have occurred.

Comparing tephra and ash fall from Mount St. Helens, New Zealand, and Nevada, age might be a potential factor when determining the level of alteration. Almquist (2011) suggested age did not appear to explain the differences in the amounts of alteration experienced by volcanic ash within New Zealand tephra. However, the age gap between samples may not have been large enough to observe a significant difference in alteration. After placing the New Zealand tephra along a longer time scale between pristine to 12.96 Ma, it becomes more apparent that age may
indeed influence weathering of the volcanic material. The Mount St. Helens ash displayed no authigenic clays growing on the surface while older tephra that had more time to interact with the environment from New Zealand showed significant amounts of amorphous material (allophane). Looking at tephra that was significantly older (Miocene) from the Cobble Cuesta area, the tephra showed contrasting characteristics. The Miocene tephra consisted of more well-developed authigenic clay minerals that were easily identifiable by their characteristic morphology (e.g. smectite, halloysite, and allophane). It was also observed that the overall grain shape (e.g. rounded or bladed) did not always indicate the level of authigenic clay formation. Tephra within some of the Nevada samples had well-developed clay growth, but also showed a more glassy appearance. This may be due to minimal weathering by water or organic material. Thus, age is not the only controlling factor in the level of alteration. As previously stated, soil conditions and composition (concentration of Si and availability of Al), whether water played a role in the weathering processes, and climate may also control the formation of authigenic minerals and overall grain morphology.

Identifying morphology of tephra deposits and potential authigenic clay minerals within pore spaces may serve as an aid in depositional environment interpretation and weathering history. The degree of alteration may indicate environmental conditions involving soil chemistry and paleoclimate. Various micrographs were selected from the three regions studied to construct a weathering classification scheme. The samples selected were categorized based on overall alteration and authigenic clay formation. The tephra classification scheme is scaled from 0-7, 0 representing the initial stage with no weathering alteration and 7 representing the most weathered consisting of well-developed authigenic clays.
<table>
<thead>
<tr>
<th>Ranking and description</th>
<th>Example</th>
<th>Ranking and description</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>0: Pristine glass characterized by distinct edges and smooth surfaces with conchoidal fractures. No authigenic clay formation (pre-deposition).</td>
<td>![Image]</td>
<td>4: Edges are slightly rounded. Surface is rough with amorphous authigenic clays within pore spaces.</td>
<td>![Image]</td>
</tr>
<tr>
<td>1: Smooth surfaces and distinct edges. Little to no evidence of alteration.</td>
<td>![Image]</td>
<td>5: Edges are more rounded with increased formation of authigenic clays. Development of more crystalline clays (needle-like morphology).</td>
<td>![Image]</td>
</tr>
<tr>
<td>2: Majority of the edges are sharp with some indication of rounding along ridges. Detached material on the surface.</td>
<td>![Image]</td>
<td>6: Surface is concealed by either an oxide or clay coating resulting from surface alteration.</td>
<td>![Image]</td>
</tr>
<tr>
<td>3: Majority of the edges are sharp, but show evidence of authigenic clay growth coating the surface of the glass. Bubble-like spheroidal shape indicates short-order clays.</td>
<td>![Image]</td>
<td>7: Surface is coated in well-developed crystalline authigenic clays (smectites).</td>
<td>![Image]</td>
</tr>
</tbody>
</table>

Figure 5.1 Tephra weathering class descriptions and example SEM micrographs developed in this study, weathering classification is modified and extended from the initial classification developed by Almquist (2011).
References


Appendix

X-ray Diffraction results of Cobble Cuesta area

Sample 2-96-46J

Sample 2379-12J
Sample JS-92-62

Sample 13384.9J