CHARACTERIZATION OF THE ALTERATION OF ANTARCTIC ASH: THE PRODUCTS OF A COLD AND ICY ENVIRONMENT. S. V. Kaufman[1], J. F. Mustard[1], J. W. Head[1], [1]Brown University, Department of Earth, Environmental and Planetary Sciences, Providence, RI 02912 USA. Contact: sierra_kaufman@brown.edu

Introduction: Most primary igneous minerals are unstable and undergo breakdown, alteration, and dissolution in the presence of liquid water under the conditions at the surface of Earth and Mars [1]. This instability causes the minerals to begin to alter to secondary weathering products such as clays, oxides, and dissolved ions. Dissolution, the first step for many weathering pathways, can be studied in laboratory settings to determine rates for water-limited environments and extrapolated to conditions expected on planetary surfaces [2]. However, lab studies are limited by relatively slow reaction rates and cannot run long enough to determine final products without increasing temperature tens to hundreds of degrees above usual terrestrial/martian surface conditions. Experiments at temperatures >100°C are useful for processes such as hydrothermal or diagenetic alteration in the shallow crust; they are less applicable to surface weathering processes which can take thousands of years to occur at ambient temperatures.

There has been work to characterize weathering of basaltic rock and dolerites in a hypothermal and hyperarid environment with respect to martian analogues [3,4]. Alteration pathways in cold and dry environments with limited access to liquid water do not follow traditional terrestrial pathways [3]. It has been found that the dolerites in the Antarctic Dry Valleys (ADV) are dominated by a rind-forming alteration which is driven by an oxidation potential causing mobile divalent cations (e.g. Ca^{2+}, Mg^{2+}) to migrate to the surface and electron holes and monovalent cations (e.g. Na^{+}, K^{+}) to migrate inward as an oxidation front [3]; there is little aqueous alteration. This form of alteration in hyperarid and hypothermal environments is expected to manifest itself on both rock and particulate materials. Notably, little work has been done in these environments on volcanic ashes which have been hypothesized to be the starting material of some mineral assemblages seen on Mars [5].

The rapid nature of weathering, under conditions of high water:rock ratios with neutral to alkaline water [6] and mild to warm temperatures, erases the initial products with subsequent alteration steps. Under these conditions, volcanic ash is known to be unstable and rapidly undergo breakdown and alteration to products including aluminum phyllosilicates such as kaolinite and halloysite [7]. While this accounts for most alteration settings on Earth, they are poor analogues for the cold and dry surface environments of the ADV and Mars. The mineral formation hypotheses should be integrated with the most comprehensive Late Noachian climate models as they do not predict the abundant liquid water availability typically required to alter rock at the surface [8–10]. The study of weathering processes and products are constrained by a number of factors including time, temperature, starting mineralogy, relative humidity, and water availability and chemistry [11]. These factors need to be accounted for when determining which pathways are possible under specific climate regimes. The ADV are the closest Earth analogues to Mars as they maintain cold and dry conditions like those that exist on present day Mars and may have persisted during the Late Noachian [8,9,12].

The ADV contain three microclimate zones: the coastal thaw zone (CTZ), the inland mixed zone (IMZ), and the stable upland zone (SUZ) [13]. Due to time limits on laboratory experiments, the ADV are an ideal natural laboratory to observe the alteration of volcanic glasses while constraining a number of variables such as water availability, humidity, and temperature. To investigate the nature and extent of alteration in a cold and icy climate, samples of ash from the ADV microclimates were analyzed. The different microclimates allow the study of variation in water availability, humidity, and temperature. The SUZ has limited precipitation with some windblown snow deposits from the Polar Plateau, summertime temperatures average -10 °C, and relative humidity ~41% [13]. The IMZ has less snowfall then the CTZ but more than the SUZ; the amount of windblown snow is unknown. The temperatures average -7 °C in the summertime and ~67% relative humidity [13]. The CTZ typically receives snowfall exceeding 80 mm of water equivalent per year [14]. The summertime average is -5 °C and ~64% relative humidity [13].

Methods: To determine the alteration pathways and the first steps of alteration in a cold and icy climate, we have examined samples of ash of different ages from different microclimate zones in the Antarctic Dry Valleys. The oldest sample from each microclimate was chosen from the available sample subset. The samples were analyzed in their naturally collected condition and separated by grain size.

After using reflective microscopy to characterize the morphology of the ashes, the bulk chemistry was evaluated using flux fusion dissolution followed by inductively coupled plasma optical emission spectroscopy (ICP-OES). This technique quantifies the abundance of the major and minor rock-forming elements: Si, Al, Fe, Ca, Mg, Na, K, Ti, P, and Mn. Mineral phase composition of each sample was determined with powder x-ray

diffraction (XRD) analysis. Full near-infrared spectra were obtained using an ASD fieldspec spectroradiometer in bare fiber optic mode.

Results and Discussion: The first sample (*DMS-91-22)*, from an ash within a sand wedge deposit in Nibelungen Valley in the SUZ, is 15.15±0.02 million years old [15]. The second sample (*DMS-88-610)* is a mafic ash from central Taylor Valley in the IMZ dated at ~10.39±0.78 million years old [15]. The final sample (*DMS-94-004)* is from the CTZ near a wet-based ice till deposit and is 16.959±0.169 million years old [15].

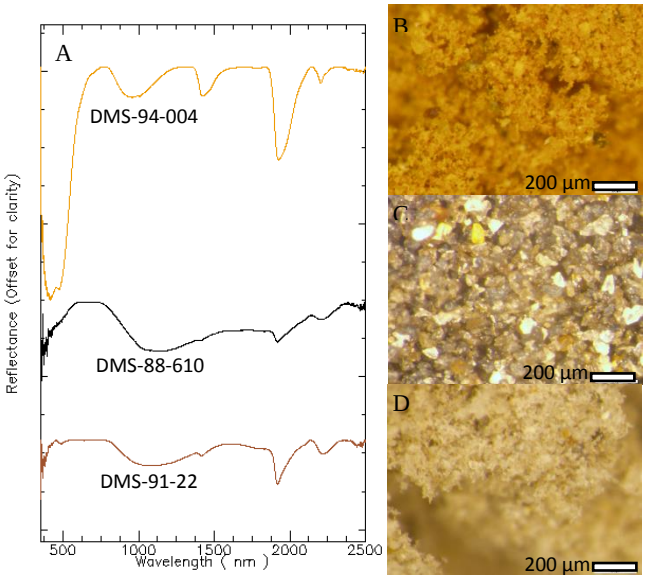

Fig 1. A) Continuum removed reflectance spectra from ASD measurements of each sample's 25-75 micron component. Orange spectra (top) is *DMS-94-004* of the CTZ. Black spectra (middle) is *DMS-88-610* of the IMZ. Brown spectra (bottom) is *DMS-91-22* from the SUZ. **B)** 25-75 micron component from *DMS-94-004*. **C)** 25-75 micron component from *DMS-88-610*. **D)** 25-75 micron component from *DMS-91-22*.

The microscope images (**Fig. 1 B-D**) show a variation in the texture and color of the samples. The cohesive strength of the samples from the CTZ and SUZ behave like powders while the sample from the IMZ behaves more like beach sand. The ASD reflectance spectra of *DMS-94-004* (**Fig. 1 A**) shows very strong hydration bands associated with water at ~1400 and ~1900 nm. The absorption at ~2200 nm has a shape consistent with an Al-OH stretch in aluminum phyllosilicates. There are also strong absorptions around 425-500 nm which is associated with iron oxide absorptions. The spectra from the IMZ and SUZ (**Fig. 1 A**) have weaker band depths at ~1400 and ~1900 nm but stronger ferrous absorptions from 900-1400 nm. The weaker hydrous absorptions suggest less aqueous alteration and the strong ferrous absorptions more unaltered glass. The weak absorption at ~2200 nm in both samples has a broader shape than in *DMS-91-22* that is consistent with hydrated silica Si-OH stretch [16].

The spectra show a possible progression in ash weathering from the SUZ sample that shows no ferric and weak aqueous absorptions to the CTZ sample that shows strong ferric absorptions, absent ferrous absorptions, strong water bands and an incipient alumino-phyllosilicate absorption.

Conclusions: All samples showed evidence of hydration. In terms of preliminary weathering, the CTZ shows the furthest progression as opposed to the IMZ and SUZ. Based on the spectroscopic measurements and microscope observations, the ashes have begun to weather along typical terrestrial weathering pathways such as those seen in the more humid areas on Earth. This will be further investigated with the XRD and FF/ICP-OES analysis. Based on these results, given a cold and icy background climate with mean annual temperatures and average summertime temperatures below zero Celsius, it is possible to aqueously alter particulate samples. This is due to variations in temperature and water availability in the microclimates.

This preliminary work implies that there is a possibility of hydrous surface alteration on early Mars in a cold and icy background climate predicted by the current 3D climate models [8-10]. While these ashes have not been completely altered to thick deposits of phyllosilicates like those seen on early Mars, short periods of warming brought on by punctuated events such as impacts [17], volcanic outgassing [18], and variations in obliquity [19] and eccentricity [20] may be able to close the gap required to cause larger-scale alteration. Further work will expand these techniques to a wider range of ash ages in each microclimate to determine the timescale necessary for this alteration to occur.

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