A SONG OF ICE AND FIRE: WEATHERING OF ANTARCTIC ASH AND IMPLICATIONS FOR ALTERATION ON A COLD AND ICY EARLY MARS. S. V. Kaufman[1], J. F. Mustard[1], J. W. Head[1], [1]Brown University, Department of Earth, Environmental and Planetary Science. Contact: sierra_kaufman@brown.edu

Introduction: Many processes have been proposed to account for the alteration products seen both on and below the surface of Mars. These include hydrothermal alteration [1,2], impact-driven alteration [3,4], and aqueous alteration/leaching [1,5–7]. However, the formation conditions of these minerals have not been completely constrained [1,4,8].

The ambient Noachian climate may have been characterized by mean annual temperatures well below the melting point of water [9–11], but peak summertime conditions [12] and/or short term influence of punctuated warming events such as impacts [13], volcanic outgassing [14], and variations in obliquity [15] and eccentricity [12] may have produced short term climates, permitting incipient or complete alteration. While warmer and wetter than Mars, the Antarctic Dry Valleys (ADV) are Earth's closest analogue to the Noachian climate, as they maintain cold and dry conditions year round [9–11,16]. This area has had a relatively stable climate for the past ~20 Myr [17] making it ideal to observe the results of long term reactions.

The ADV contain three microclimate zones, varying in water availability, temperature, and relative humidity (RH): the coastal thaw zone (CTZ), the inland mix zone (IMZ), and the stable upland zone (SUZ) [18]. The SUZ has limited precipitation with some windblown snow deposits from the Polar Plateau, summertime temperatures average -10 °C, and RH is ~41% [18]. The IMZ has less snowfall than the CTZ but more than the SUZ. The temperatures average -7 °C in the summertime and ~67% RH [18]. The CTZ typically receives snowfall >80 mm of water equivalent per year [19]. The summertime average is -5 °C and RH is ~64% [18].

While weathering of basaltic rock and dolerites in hypothermal and hyperarid environments has been characterized [20,21], little has been done on Mars-relevant particulate samples, e.g. volcanic ash, hypothesized to be the parent material of some martian assemblages [7]. Under conditions with high water:rock ratios, neutral to alkaline water [22], and mild to warm temperatures, the initial kinetically stable products are erased with subsequent alteration steps. Under these conditions on Earth, volcanic ash (glassy and particulate) is known to be unstable and rapidly breaks down and alters to products including aluminum phyllosilicates such as kaolinite and halloysite [23]. On Mars, a large component (27-54 wt% [24]) of the regolith and sedimentary rock is composed of poorly crystalline or amorphous phases. This is suggested to indicate alteration of volcanic ash in an environment where water was sporadic and rapidly depleted, never progressing past the initial kinetic products [7].

Methods: To determine the first steps and pathways of alteration in a cold and icy climate, we examined samples of ash of different ages from different microclimate zones in the ADV. The time the ash had been exposed to the surface was incorporated as the timescale over which alteration had occurred. Samples from each microclimate, spanning ages of 4.0 Ma to 16.96 Ma, as $^{40}Ar/^{39}Ar$ dated by [25], have been used as chronosequences in each. The samples were analyzed in their naturally collected condition and separated by grain size using the ranges: 500-250 µm, 250-125 µm, 125-75 µm, 75-25 µm, and <25 µm.

Samples were evaluated using flux fusion dissolution followed by inductively coupled plasma optical emission spectroscopy (FF/ICP-OES) to quantify the abundance of the major and minor rock-forming elements: Si, Al, Fe, Ca, Mg, Na, K, Ti, P, and Mn.

Mineral phases were identified using powder x-ray diffraction (XRD) to show potentiality of conversion of primary mineralogy and glass to secondary alteration minerals or poorly crystalline components.

Full near-infrared spectra were obtained using an ASD fieldspec spectroradiometer. The samples were then analyzed using mid-infrared FTIR spectroscopy, which can also aid in determining the percentage of amorphous components.

Results and Implications: We analyzed 8 SUZ, 3 IMZ, and 1 CTZ samples using the above techniques to find any discrepancies in their mineralogy, spectroscopy, and chemistry as a function of age and climate zone. While all the SUZ show evidence of hydration, there is no clear trend with age in the amount of alteration. The IMZ shows differential alteration in samples of varying ages. The IMZ is a spatial mixture of the SUZ and CTZ; highly arid areas exist just meters from gulleys with seasonally flowing liquid water. It is possible that the difference in the degree of alteration in similarly aged samples is due to this spatial difference in water availability.

Samples of the oldest ashes from each microclimate all show evidence of hydration in their ASD spectra while the CTZ shows features consistent with more advanced weathering than the samples from the IMZ or SUZ. This is interpreted from the absorption at ~2200 nm having a shape consistent with an Al-OH stretch in

aluminum phyllosilicates while the same absorption in the SUZ and IMZ have broader shapes consistent with Si-OH stretch in hydrated silica.

The XRD results support the ASD measurements and show primary igneous mineralogy (quartz and anorthoclase) in the SUZ with little to no indication of alteration products. The IMZ shows halite, primary mineralogy (quartz, anorthoclase, pyroxene), as well as the largest amorphous component, consistent with a progression of weathering through the kinetic stage, but not yet reaching thermodynamic stability [26]. The CTZ shows both primary mineralogy (quartz and anorthoclase) and evidence of kaolinite, dickite and a swelling smectite. This follows a typical terrestrial weathering sequence and produces final alteration products comparable to the martian surface.
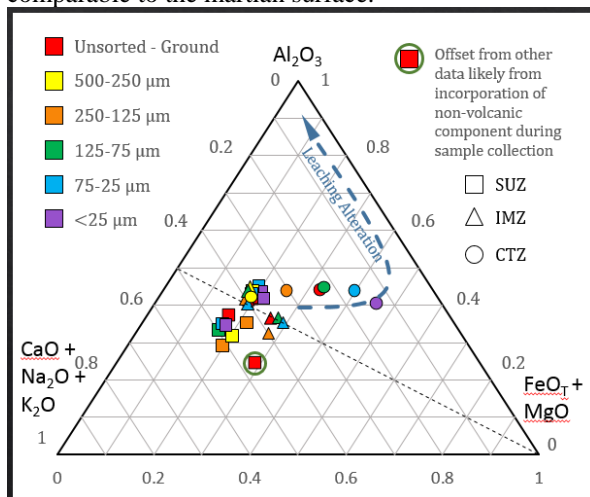
Figure 1. *FM/A/CNK diagram with varied grain sizes from each microclimate. CTZ is denoted by circles, SUZ by squares, and IMZ by triangles. Traditional leaching alteration pathway shown by dashed arrow.*

Bulk chemistry plotted on a FM/A/CNK ternary diagram (**Figure 1**) is useful to determine if the ashes have undergone weathering concordant with typical terrestrial alteration pathways [27,28]. Weathering products such as thin rinds may not exhibit major changes in bulk chemistry. Therefore, absence of a distinct trend does not preclude instances of alteration [20]. The FF/ICP-OES results do not show a perceptible trend in bulk chemistry change corresponding to the microclimates, ergo with increasing water availability and temperature. This may be indicative of a closed system transformation of the primary mineralogy with no loss or change in bulk chemistry even with a mineralogical change. The CTZ sample shows a loss of alkali elements and an increase in Fe and Mg with decreasing grain size.

Conclusions/Further Work: As water availability and temperature increases from the SUZ to the CTZ,

more advanced alteration products were observed, forming a weathering sequence in the oldest samples from each microclimate. The SUZ samples show no signs of alteration, yet display hydration signatures. The IMZ samples show an increased amorphous abundance and spatially variable amounts of alteration not correlating with age. The CTZ samples (MAT still <0 Celsius) have secondary alteration products such as kaolins and smectites. The SUZ and IMZ alteration seems to be retentive of bulk chemistry, indicative of an in situ transformation of the minerals without ion removal. The CTZ sample shows a traditional terrestrial leaching pattern with proportionally less alkali and more Fe/Mg with lower grain sizes. Thus, we conclude Mars-like alteration can occur in a cold and icy climate akin to the CTZ in less than 17 Myr, implying a sustained warm and wet climate may be unnecessary to produce the alteration suite observed on Mars.

Additional samples, including 2 CTZ, 1 IMZ, and 7 SUZ, will expand the chronosequences.

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