ACIDIC AQUEOUS ALTERATION OF SUBSURFACE BASALTS ON HAWAII: A MINERALOGICAL AND GEOCHEMICAL ANALOG FOR MARS. P. Sheevam and W. M. Calvin, Geological Sciences, University of Nevada, Reno, Nevada, psheevam@nevada.unr.edu, wcalvin@unr.edu

Introduction: Hawaiian basalts have long been used to provide essential geologic data to extrapolate aqueous processes in early Martian history. Basaltic rock and alteration minerals such as phyllosilicates, sulfates and carbonates, have been observed on the Martian surface often within close proximity to each other [e.g. 1-2]. Landed spacecraft have similarly identified a wide range of alteration minerals [e.g. 3-6]. Varying hypotheses exist for the formation of alteration minerals, including hydrothermal systems associated with impact or volcanism, acidic weathering of volcanic ash, and authigenic alteration later in Martian history at lower water to rock ratios [1-6]. The subsurface of Hawaii provides a unique and little explored terrestrial analog for Martian alteration.

Two continuously cored holes (PTA and KMA) were drilled on the Humu'ula Saddle, HI, which lies between Mauna Kea and Mauna Loa, within 10 km of each other, to assess the groundwater and geothermal resources in the region [e.g. 7]. The PTA core comprised mostly tholeitic basalts altered to phyllosilicates and zeolites at low to mid temperature, indicating an isochemical alteration environment [8,9]. It was anticipated that the KMA survey would yield similar alteration types; however, minerals identified in our field survey indicate acidic alteration.

Methods: A visible - short wave infrared (VSWIR, 0.4 to 2.5 µm) survey of rocks recovered from KMA drilling was conducted in August 2021 using a field portable spectrometer, equipped with an internal light source and contact probe. Of the 1.5 km of recovered core, only the lower 700 m were measured based on field notes taken during active drilling that identified where alteration was pervasive. Approximately 500 spectra were collected, sorted by depth, and compiled into an image cube. The identification of spectral endmembers and their distribution were mapped using the ENVI platform and methods from [8,10]. During field collection, sections with strong mafic and alteration absorption features were identified, and twenty-six hand samples were selected for additional analysis.

The selected samples were measured from $2.5-15~\mu m$ (long wave infrared, LWIR) using an Exoscan 4100 instrument. These were crushed, sorted into fine (<125 μm) and coarse (>125 μm) grain sizes, and measured from $2.5-25~\mu m$ using a benchtop Nicolet FTIR. The long wave spectra were analyzed using a spectral unmixing model using singular value decomposition (SVD), the same model used on the PTA LWIR data [11]. The model compares pure

endmembers from USGS, JPL, JHU and other libraries to the collected spectra. The model generates a percent contribution from each end member with an associated RMSE value. The lower the RMSE indicated a better fit, although model fits were further visually inspected.

The depth sequence of KMA Mineralogy: alteration in the KMA reveals a distinct pattern of mostly unaltered "cap" units followed by altered units. Altered units either existed as oxidized, alterationfilled vugs (Fig. 1), or as red rims around olivine phenocrysts. VSWIR spectra of altered layers include jarosite, saponite, hematite, and rare cases of alunite, kaolinite, and amorphous silicates. These common alteration types were mapped with depth in the image cube (Fig. 2). Mineral abundances in the LWIR were determined using mafics common in tholeiitic basalts such as olivine, labradorite, anorthite, clinopyroxene, and alteration mineral groups found in the VSWIR survey such as sulfates, amorphous silicates, and phyllosilicates.

Discussion: Both the PTA and KMA drill core are from the same geologic setting and composed of similar parent rock - shield stage basalts. Thus, the distinct alteration assemblages reflect differing aqueous geochemistry. Sub-horizontal and subvertical variations in groundwater permeability are created based on changes in lava type and flow direction, coupled with layering of sedimentary and fall deposits, and post deposition subsurface intrusions and diking systems [e.g. 12]. Groundwater and other geophysical data suggest little to no horizontal connection between the regional aquifer found in the PTA hole and areas near the KMA hole [e.g. 12]. The distinct alteration mineralogy in each hole also supports a lack of hydrologic connection between the two wells. Furthermore, observations during drilling found temperatures over 90°C at depth in the PTA hole, where those in KMA did not reach 50°C.

The PTA exhibits alteration mineralogy indicative of a subsurface environment with moderate temperatures at neutral pH. The alteration is a product of a horizontally confined regional aquifer that exhibits some degree of permeability, where fresh meteoric water is stored for several thousands of years. The source of heat is inferred to come from later intrusive volcanic activity. Whereas the KMA mineralogy suggests an acidic environment of formation. It is possible that the system was open to the surface then subsequently covered by later flows. There is also the possibility of sulfur and oxygen being introduced in the groundwater system.

Acidic alteration is common in volcanic surface environments, and usually associated with fumarole or steam vent activity where vapor rich in SO₂ and H₂S leaches surrounding rock and can condense sulfur and sulfates [e.g. 13.14]. However, it should be noted that the KMA alteration seems to be in a pattern suggesting a series of confined aquifers. Jarosite and iron oxides, the most common alteration products found in the KMA core, are also known to be products of acid alteration of sulfides in oxidative reactions of mine wastes [15], and precipitates from saline lakes [16], but their precipitation from ground water is not well studied [17]. There are instances in which oxidation and acid-sulfate alteration may be attributed to a collapsed steam-heated zone, in which acidic fluids are forced to flow back down a vein or fracture causing the reddish staining and formation of sulfides [e.g. 18]. Further study will examine whether the local abundance of sulfides and other sulfur species in the parent rock contributes to the marked difference in alteration style at these two locations, or if open system conditions contribute to the dominance of sulfates and iron oxides as alteration products in the KMA core.

Relevance to Mars: The differences between two drill cores in close proximity to each other have exciting implications for a more localized geochemistry in the Martian subsurface. They demonstrate that it is plausible for a subsurface basalt to exist in a distinct geochemical environment, based on small scale geophysical constraints. These results support the idea that subsurface reservoirs on Mars were locally constrained by volcanism that generated subsurface stresses, strains, and fracturing, and possibly dike impounded water systems generating unique local geochemistry. This can contribute to the diversity of altered outcrops observed on the Martian surface.

References: [1] Bibring, et al. (2006) Science, 312. [2] Ehlmann, et al. (2011) Nature, 479. [3] Arvidson, et al. (2008) JGR, https://doi.org/10.1029/ 2008JE003183. [4] Squyres, et al. (2006) JGR, https://doi.org/10.1029/2006JE002771.[5]McLennan, et al. (2014) Sci, 343, 1244734. [6] Rampe, et al. (2020) ChEG, 80, 125605. [7] Jerram et al. (2019) Sci Drill, 25, 15. [8] Calvin et al. (2020) Am Min, 105, 1297. [9] Rasmussen et al. (2020) Am Min, 105, 1306. [10] Calvin and Pace (2016) Geothermics, 61, 12. [11] Sheevam and Calvin (2020) IGARSS 2020, doi: 10.1109/IGARSS39084.2020.9323121. [12] Thomas, D. (2017) GSA Cordilleran 113th Meeting doi: 10.1130/abs/2017CD-292772 [13] Henley and Ellis (1983) Earth Sci Rev, 1. [14] Yant et al. (2018) Am Min 103, 11. [15] Bigham and Nordstrom (2000) in Rev Min v 40, 351. [16] Bennison and Bowen (2013) Chem Geol, 154. [17] Herbert, (1997) Clays Clay Min, 45, 261. [18] Schranz, (2021) *UNR Masters Thesis*. **Figures:**



Figure 1: Example of KMA hand sample. Here, alteration is present in vugs.

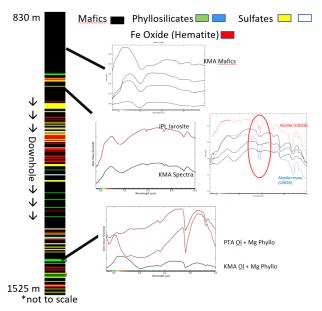


Figure 2: Distribution of common endmembers along with example spectra from select layers. Black = mafics, yellow = sulfates, red = hematite/FeOxide, white= alunite mixture, green=phyllosilicates.