CHARACTERIZING ALTERED VOLCANIC ROCKS FROM WAIMEA CANYON, KAUAI.

K. E. W. Gruendler[1,2], J. L. Bishop[1,3], A. N. Aguilera[1,4], and T. F. Bristow[3], [1]SETI Institute (Mountain View, CA; jbishop@seti.org), [2]Newark Memorial High School (Newark, CA), [3]NASA Ames Research Center (Moffett Field, CA), [4]San Jose State University (San Jose, CA).

Abstract: Characterization of altered volcanic rocks under different climates provides information on the types of minerals forming in these environments. Kauai is one of the older Hawaiian islands and receives copious rainfall, producing strong alteration of volcanic rocks even at high elevation. We used XRD, reflectance spectroscopy, bulk chemistry, and magnetic properties to characterize the samples in this study. The mineralogy of altered Kauaian lavas tends to include abundant halloysite and goethite, with additional minerals including forsterite and hematite in some locations, and can be used to constrain ancient environments on Mars when it was warm and wet.

Methods: *Samples.* Basaltic outcrops were investigated in 2009 and 2018 at Waimea Canyon State Park on the Hawaiian island of Kauai, after consultation with parks personnel. Samples were collected (**Fig. 1**) at three locations where vegetation was less apparent along the Wai'ale'ale Trail from the Kalalau Lookout towards the Pihea Trail in April 2009 at ~5000 ft elevation. Three samples were collected at the mile 9 marker along highway 550 (Koke'e Trail). Bulk fines and rocks (**Table 1**) were analyzed for this study and compared with size fractions prepared for an earlier study [1]. The bulk chemistry (**Table 2**) indicates lower Si and higher Fe abundances than most altered volcanic materials at Haleakala on Maui [2] and at Kilauea on Hawaii [3].

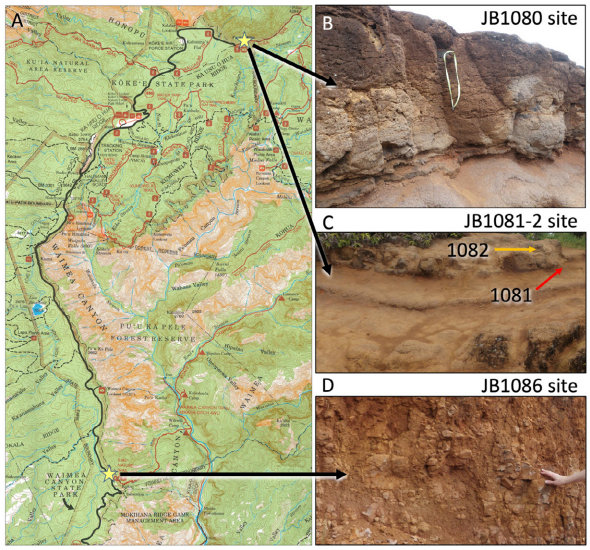

Fig. 1. *A) Map of Waimea Canyon with sampling locations. B) Stop 1, site of JB1080, C) Stop 2, site of JB1081 and JB1082, D) Stop 4, site of JB1086.*

Table 1. List of samples studied

Stop 1	JB1080	orange fines and gravel/crust
Stop 2	JB1081	red fines and gravel/crust
	JB1082	orange fines and gravel/crust
Stop 3	JB1083	red gravel/crust
Stop 4	JB1084	dark red/pink fines
	JB1085	orange soil and gravel/crust
	JB1086	fines, gravel/crust, 4-5 cm rocks

Table 2. Average bulk chemistry (as wt.% oxides)

JB#	SiO_2	Al_2O_3	Fe_2O_3	MgO	TiO_2	SO_3
1080	29.6	15.3	29.0	4.10	2.12	
1081	31.5	13.5	25.3	7.56	2.32	
1082	36.2	8.66	17.7	25.1	1.43	
1083	21.1	21.3	32.2	0.77	5.56	0.16
1084	28.7	25.3	23.0	0.49	3.60	
1085	25.7	25.4	25.6	0.23	4.37	0.09
1086	32.1	26.6	19.1	0.29	3.58	

XRD. Mineralogy was determined for samples JB1082 and JB1086 using a Rigaku X-ray Diffractometer at NASA Ames. JB1082 contains forsterite (Mg_2SiO_4), halloysite ($Al_2Si_2O_5(OH)_4 \bullet nH_2O$), goethite (FeOOH), and ilmenite ($(FeTi)_2O_3$), while JB1086 contains halloysite, serpentine ($Mg_3Si_2O_5(OH)_4$), goethite, and hematite (Fe_2O_3).

Reflectance spectra. VNIR reflectance spectra were measured for bulk fines, crust material, and rocks under ambient conditions using an ASD FieldSpecPro from 0.35-2.5 µm relative to Spectralon.

Results: Spectral analysis included determination of band centers and band depths for multiple features due to iron (Fe), hydroxide (OH), and water (H_2O) species in the mineral structure. The results gleaned from these analyses are providing information on how alteration occurred on Kauai, specifically the types of alteration minerals present in the Waimea samples.

The reflectance spectra of most samples exhibit vibrational features consistent with halloysite including OH doublets at 1.39/1.41 and 2.17/2.21 µm and an H_2O combination band at 1.91 µm (**Figs. 2-4**). The broader band shape near 0.92 µm could be due to ferrihydrite, which has a poorly crystalline structure and is not detected by standard XRD. The bands near 1.4, 1.9, and 2.2 µm are broadened compared to halloysite for samples JB1080-JB1083 (**Figs. 2-3**), indicating another phase is present. Ferrihydrite ($Fe_5HO_8 \bullet 4H_2O$) often forms in soils together with goethite and could be contributing to broadening of the bands near 1.4 and 1.9 µm, but not the band near 2.2 µm. Alternatively,

allophane (Al_2O_3 $(SiO_2)_{1.3\text{-}2}$ (2.5-3) H_2O), a poorly crystalline product of volcanic ash alteration, could be broadening all three of these bands. Samples JB1085 and JB1086 (**Fig. 4**) contain the least ferrihydrite or allophane because the halloysite features are the most well formed.

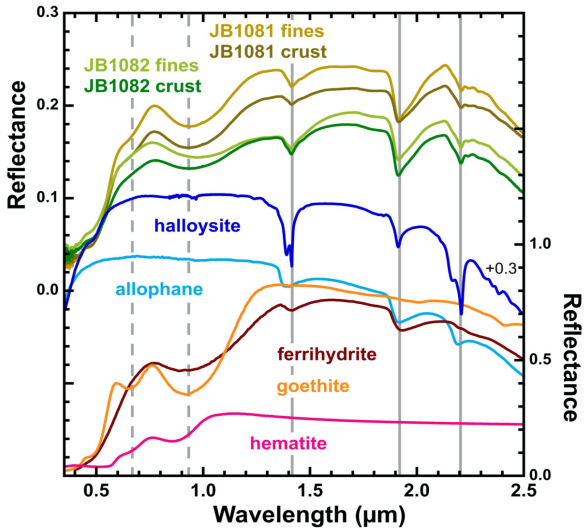

Fig. 2. *Reflectance spectra of samples JB1081 and JB1082 from Stop 2 compared with minerals.*

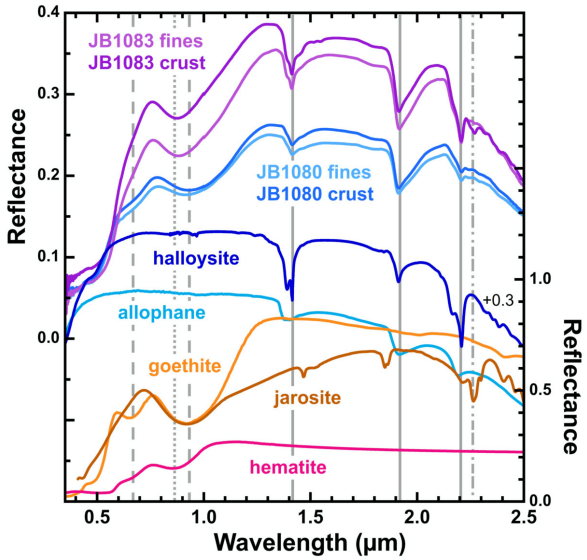

Fig. 3. *Reflectance spectra of sample JB1080 (Stop 1) and JB1083 (Stop 3) compared with minerals.*

Fe excitation bands due to goethite are observed near 0.67 and 0.92 μm in most samples, but are shifted towards longer wavelengths for sample JB1082 (**Fig. 2**) due to forsterite and towards shorter wavelength for sample JB1083 (**Fig. 3**) due to hematite.

The bulk elemental analyses indicate significantly elevated wt.% MgO for sample JB1082, which is consistent with a higher forsterite abundance. Sample JB1083 crust has a vibrational band at 2.26 μm that is typically due to jarosite and this sample also contains S. It appears that the jarosite is concentrated in the crust rather than the fines because this band is not observed in the fines and the S may not be as well represented in the bulk chemistry if the jarosite is concentrated in the crust material.

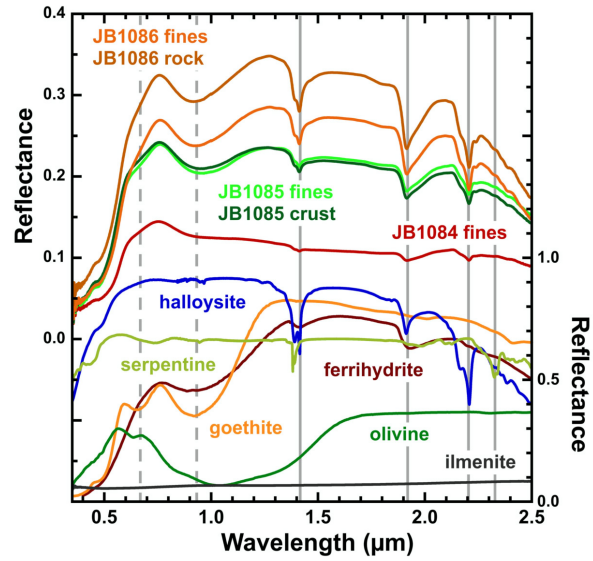

Fig. 4. *Reflectance spectra of samples JB1084, JB1085, and JB1086 from Stop 4 compared with minerals.*

Implications for Mars: The spectral data generated here for altered volcanic material from Kauai will contribute towards understanding the minerals observed on Mars by comparison with orbital spectra collected by NASA's CRISM instrument. Mawrth Vallis [4] and Nilli Fossae [5] are two regions on Mars containing halloysite (or kaolinite) in the ancient clay-rich rocks and these could be indicators for environments where long-term liquid water was present on Mars in the past.

Acknowledgments: The authors are grateful to the NASA EPOESS program for support of ANA, to the NASA postdoctoral program for support of TFB, and to NASA's Mars Fundamental Research Program for support of JLB.

References: [1] Aguilera A. N. et al. (2012) Characterization of Mars Analog Rocks on Kauai, *NCUR Proceedings.* [2] Bishop J. L. et al. (2007) Characterization of Alteration Products in Tephra from Haleakala, Maui, *CCM, 55,* 1-17. [3] Schiffman P. et al. (2000) Controls on palagonitization versus pedogenic weathering of basaltic tephra, *Geochem. Geophys. Geosys., 1,* 2000GC000068. [4] Bishop J. L. et al. (2008) Phyllosilicate diversity and past aqueous activity revealed at Mawrth Vallis, Mars, *Science, 321,* 830-833. [5] Ehlmann B. L. et al. (2009) Identification of hydrated silicate minerals on Mars using MRO-CRISM: Geologic context near Nili Fossae and implications for aqueous alteration, *JGR, 114,* 2009JE003339.