SULFATE-OPAL-PHYLLOSILICATE ASSEMBLAGES AT KILAUEA CALDERA AS AN ANALOG FOR SURFACE ALTERATION ON MARS. J.L. Bishop[1], P. Schiffman[2], L. Gruendler[1], E. Murad[3], M.D. Dyar[4], M.D. Lane[5], and R.J. Southard[2], [1]SETI Institute (Mountain View, CA 94043; jbishop@seti.org), [2]University of California, (Davis, CA 95616), [3]formerly at Bavarian Environmental Agency (Marktredwitz, Germany), [4]Mount Holyoke College (South Hadley, MA 01075), [5]Fibernetics LLC (Lititz, PA 17543).

Introduction: Many outcrops of complex phyllosilicate-sulfate assemblages have been observed on Mars [e.g. 1] and understanding formation of these on Earth can provide constraints on the geochemical environment of Mars. This study considers solfataric alteration as a potential formation mechanism for rocks containing opal, sulfate and phyllosilicates on Mars. Alteration via fumaroles in the Kilauea caldera, HI, has created a light-toned solfataric bank on the south wall of the caldera where Keanakakoi ash was deposited. Bands of orange and light-toned material are present where iron oxides, jarosite and gypsum are observed in a silica/clay matrix (**Fig. 1**). Friable patches of white/yellow material has also formed from solfataric alteration of the ash. An orange-brown soil below the basaltic lava contains nontronite, iron oxides, and jarosite.

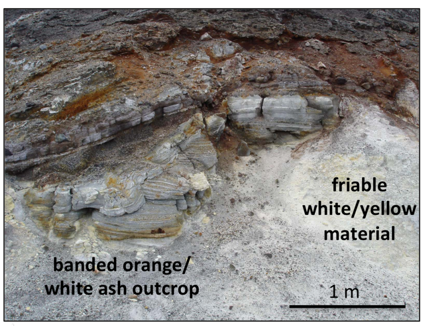

Fig. 1. View of field site. Solfatarically altered ash deposit at Kilauea showing banded units and friable material.

Methods: VNIR reflectance spectra were measured *in situ* at Kilauea and of rocks in the lab at the SETI Institute using an ASD FieldSpecPro. VNIR and mid-IR reflectance spectra of particulate samples were measured at RELAB as in [2]. TIR spectra were collected at ASU's Mars Space Flight Facility as in [3]. Mössbauer spectra were acquired at Mount Holyoke College as in [4], and XRD, SEM and BSE imaging were conducted at UC Davis as in [5].

Results: Mineralogical analyses show the presence of opal-A, saponite, gypsum, jarosite and ferric oxides/hydroxides in the ash as well as remnants of the original basaltic components and volcanic glass. Silica and sulfates were also observed in another study of altered ash in this region [6]. The alternating bands of light-toned gypsum-bearing material and orange-colored bands of Fe-bearing layers in our study mark changes in the alteration environment.

SEM reveals Fe sulfate, Mg smectite and palagonitic rinds surrounding sideromelane and pyroxene crystals. Mössbauer spectra indicate the presence of ferric oxide-bearing species in addition to jarosite. The VNIR spectra show changes in the Fe bands for the light and orange bands in the outcrop. The VNIR spectra also include features consistent with hydrated silica, gypsum, jarosite and saponite (**Fig. 2**). Mid-IR reflectance and emissivity spectra are consistent with these sulfates and silica. XRD shows that opal-A is prevalent over opal-CT. Bulk chemical analyses and BSE imaging indicate basaltic components in addition to the opal, sulfates and saponite. The brown soil below the basaltic flow but above the layered unit contains nontronite and increased iron oxide/hydroxide components.

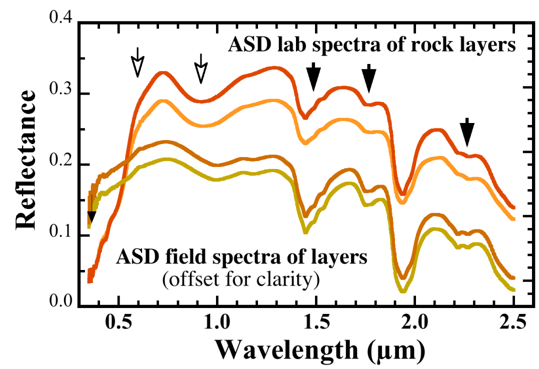

Fig. 2. VNIR field and lab spectra of orange layers. Features due to ferric iron (open arrows) and the sulfates gypsum and jarosite (filled arrows) are observed near 1.45-1.53, 1.75, 1.94, 2.22, and 2.27 µm.

Implications for Mars: Using multiple lab techniques to characterize the alteration products of solfataric alteration at Kilauea, we hope to enable improved interpretation of orbital and *in situ* data of complex assemblages of phyllosilicates, sulfates, and poorly crystalline phases on Mars.

Acknowledgments: Support to JLB from NASA's NAI and MDAP are much appreciated.

References: [1] Murchie S.L. et al. (2019) Chapter 23 in *Remote Compositional Analysis …*, Cambridge Univ. Press, 453-483, [2] Bishop J.L. & E. Murad (2005) The visible and infrared spectral properties of jarosite and alunite, *Amer.Miner., 90,* 1100-1107, [3] Lane M.D. (2007) Mid-IR emission spectroscopy of sulfate and sulfate-bearing minerals, *Amer.Miner., 92,* 1-18, [4] Dyar M.D. et al. (2013) Mössbauer parameters of iron in sulfate minerals, *Amer.Miner., 98,* 1943-1965, [5] Schiffman P. et al. (2006) Acid fog deposition at Kilauea Volcano: A possible mechanism for the formation of siliceous-sulfate rock coatings on Mars, *Geology, 34,* 921-924, [6] Yant M. et al. (2017) Visible, Near-Infrared and Mid-Infrared Spectral Characterization of Hawaiian Fumarolic Alteration …, *Amer.Miner.*, 103, 11-25.