

# SULFATE-OPAL-PHYLLOSILICATE ASSEMBLAGES AT KILAUEA CALDERA AS AN ANALOG FOR SURFACE ALTERATION ON MARS

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**FIGURE 1. KILAUEA STUDY SITE LOCATION**  
a) View of Kilauea indicated on a map of the Big Island of Hawaii, and b) View of Kilauea with the altered ash bank marked by a red arrow.

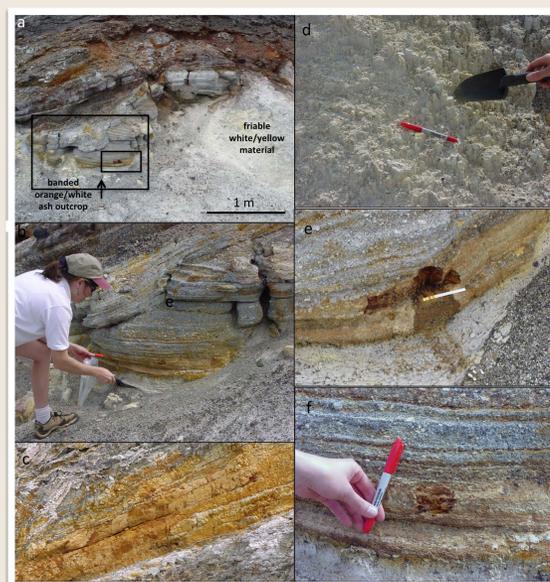


**FIGURE 2. VIEWS OF KILAUEA ASH BANK REGION**  
Top: Aerial view of ash bank with respect to lava flows from 2006. Center: Ground views of altered ash bank below basaltic rock. Bottom: View of region taken from vista across Halema'uma'u crater taken in 2021, showing collapse of the previously exposed altered ash bank region and a significantly more widespread solfatara region below the surface than previously realized.

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## SUMMARY

Many outcrops of complex phyllosilicate-sulfate assemblages have been observed on Mars 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 Keanakako'i ash was deposited (Figure 1). Unfortunately, this site was disturbed during the recent eruptions (Figure 2). Bands of orange and light-toned material are present where iron oxides, jarosite and gypsum are observed in a silica/clay matrix (Figure 3). 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. Using multiple lab techniques (Figures 4-9) 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 at Mars.



**FIGURE 3. SAMPLE COLLECTION IN THE FIELD**  
a) View of banded orange/white ash units and friable white/yellow material, b) JB collecting samples of orange and white layers, c) Banded orange material from nearby outcrop, d) Fluffy morphology of white/yellow silica-rich material, e) pH indicator stick in fresh hole below the surface of the banded orange material showing pH ~3-4, and f) Close-up view of orange and white banded units. (Samples collected during 2004 & 2006 field work).

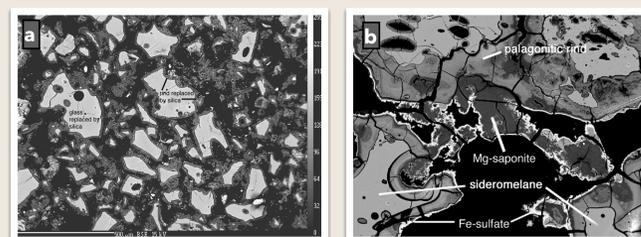
**FIGURE 4. SCANNING ELECTRON MICROSCOPY**  
Back-scattered electron images showing altered phases a) Light-toned material, and b) Orange layers.

## RESULTS

Mineralogical analyses show the presence of opal, saponite, gypsum, jarosite, and ferric oxides/hydroxides in the ash as well as remnants of the original basaltic components and volcanic glass. The alternating bands of light-toned gypsum-bearing material and orange-colored bands of Fe-bearing material mark changes in the alteration environment (Figure 3). SEM reveals Fe sulfate, Mg smectite, and palagonitic rinds surrounding sideromelane and pyroxene crystals (Figure 4). Bulk chemical analyses and BSE imaging indicate basaltic components in addition to the opal, sulfates, and saponite.

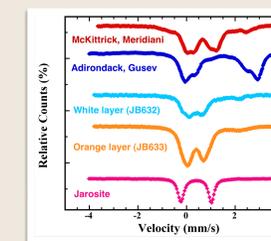
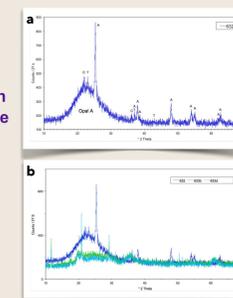
Microprobe analyses of Mg-saponite indicate 50.4% SiO<sub>2</sub>, 17.3% Al<sub>2</sub>O<sub>3</sub>, 14.4% MgO, 4.5% Fe<sub>2</sub>O<sub>3</sub> (as Fe<sup>3+</sup> and/or Fe<sup>2+</sup>), 0.1% CaO, 0.9% MnO, 0.7% P<sub>2</sub>O<sub>5</sub> and <0.1% of other oxides. The chemistry of Fe-sulfate grains in these samples is ~55-60% Fe<sub>2</sub>O<sub>3</sub>, ~7-12% Al<sub>2</sub>O<sub>3</sub>, ~12-13% SO<sub>3</sub> and ~3% P<sub>2</sub>O<sub>5</sub>.

XRD analyses of a sample from the white layer indicate it is primarily opal-A, whereas the orange layer has multiple components (Figure 5). Mössbauer spectra indicate the presence of ferric oxide-bearing species in addition to jarosite (Figure 6). The VNIR spectra show changes in the Fe bands for the light and orange bands in the outcrop (Figure 7). The VNIR spectra also include features consistent with hydrated silica, gypsum, jarosite and saponite. Mid-IR reflectance and emissivity spectra are consistent with sulfate and silica (Figure 8). Using multiple lab techniques to characterize the alteration products of hydrothermal and solfataric alteration at Kilauea, we hope to enable improved interpretation of orbital and *in situ* data of Mars.



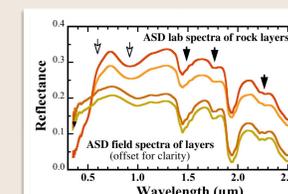
## FIGURE 5. X-RAY DIFFRACTION

a) XRD analyses of the <125 μm fraction of the light-toned sample JB632 indicate this sample is primarily opal-A. b) XRD analyses of the orange sample JB633 are more complex indicating the presence of less opal and additional components.



## FIGURE 6. MÖSSBAUER SPECTRA

Mössbauer spectra of samples of both the white and orange layers contain ferric oxides and jarosite. These minerals, plus Fe-silicates are observed in Mössbauer spectra of rocks from Gusev and Meridiani.

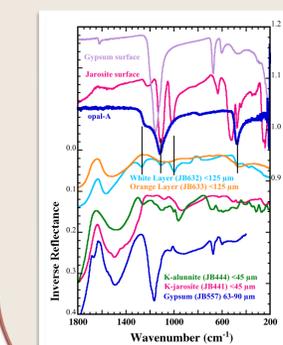
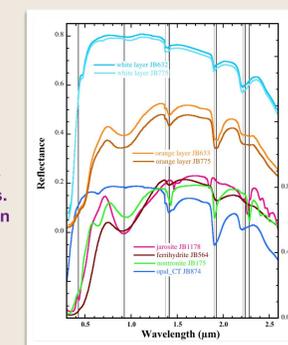


## FIGURE 7. VNIR SPECTRA

VNIR reflectance spectra of rocks taken with an ASD spectrometer in the field and in the lab illustrate features due to gypsum, jarosite, and iron oxides/hydroxides.

## FIGURE 8. VNIR SPECTRA

VNIR reflectance spectra of sample subsections indicate that opal dominates the white layers, while ferrihydrite dominates the orange layers. Some jarosite and nontronite are also present in the orange layers. Other light-toned material (not shown here) have bands consistent with spinel and gypsum.



## FIGURE 9. MID-IR SPECTRA

Mid-IR region reflectance and emittance spectra indicate that the white layer is consistent with opal-A plus some additional sulfate and phyllosilicate components. The spectrum of the orange layer contains broad Si-O features that are most consistent with amorphous or fine-grained components.