

CHEMICAL AND MINERALOGICAL CHARACTERIZATION OF ACID-SULFATE ALTERATION OF BASALTIC MATERIAL ON MAUNA KEA VOLCANO, HAWAII: JAROSITE AND HYDRATED HALLOYSITE.

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Introduction: Sulfates have been identified on the martian surface during robotic surface exploration and by orbital remote sensing. Measurements at Meridiani Planum (MP) by the Alpha-Particle X-ray Spectrometer (APXS) and Mössbauer (MB) instruments on the Mars Exploration Rover Opportunity document the presence of a ubiquitous sulfate-rich outcrop (20-40% SO₃) that has jarosite as an anhydrous Fe³⁺-sulfate [1-3]. The presence of jarosite implies a highly acidic (pH <3) formation environment [4]. Jarosite and other sulfate minerals, including kieserite, gypsum, and alunite have also been identified in several locations in orbital remote sensing data from the MEx OMEGA and MRO CRISM instruments [e.g. 5-8].

Acid sulfate weathering of basaltic materials is an obvious pathway for formation of sulfate-bearing phases on Mars [e.g. 4, 9, 10]. In order to constrain acid-sulfate pathways on Mars, we are studying the mineralogical and chemical manifestations of acid-sulfate alteration of basaltic compositions in terrestrial environments. We have previously shown that acid-sulfate alteration of tephra under hydrothermal conditions on the Puu Poliahu cone (summit region of Mauna Kea volcano, Hawaii) resulted in jarosite and alunite as sulfate-bearing alteration products [11-14]. Other, more soluble, sulfates may have formed, but were leached away by rain and melting snow. Acid-sulfate processes on Puu Poliahu also formed hematite spherules similar (except in size) to the hematite spherules observed at MP as an alteration product [14]. Phyllosilicates, usually smectite ± minor kaolinite are also present as alteration products [13].

We discuss here an occurrence of acid-sulfate alteration on Mauna Kea Volcano (Hawaii). We report VNIR spectra (0.35-2.5 μm, ASD spectrometer), Mössbauer spectra (MER-like ESPI backscatter spectrometer), powder XRD (PANalytical), and major element chemical compositions (XRF with LOI and Fe redox) for comparison to similar data acquired or to be acquired by MRO-CRISM and MEx OMEGA, MER-MB, MSL-CheMin, and MER and MSL APXS, respectively.

Samples: The rock (HWMK418 and HWMK421) and soil (HWMK420) samples are representative of a small (~30 m) alteration zone exposed at the termination and beneath a massive basaltic lava flow ~5 m thick. The local is E of the VLBA telescope on the SE flank of the Mauna Kea Volcano at an elevation of

~11,000 feet. The area maps within the Laupahoe Volcanics Member and just outside of the summit region covered by the Makaanaka Glacial Till Member [15]. Weathered remnants of this altered material stretch for ~900 m downslope.

Rocks HWMK418 and HWMK421 (Fig. 1) are hydrothermal breccias composed of unsorted 2-30 mm clasts of scoria to more massive basaltic material within a fine-grained yellow-colored matrix. HWMK418 has white material filling numerous vugs. HWMK420 is a representative soil sample from this region, consisting of basaltic sand size particles.



Fig. 1a. HWMK418 saw-cut surface. 1-cm cube for scale.



Fig. 1b: Microscopic depth composition image of HWMK418 displaying jarosite-containing (yellow) matrix material, basaltic clasts, and white vug fill material. Blue scale bar in lower right = 1000 μm.

Results and Discussion: Table 1 lists the major element compositions for the two breccias and soil. The breccias are volatile rich (LOI = 20-22 wt.% with SO₃T = 5-7 wt.%) and oxidized. XRD powder patterns for the breccias are dominated by a broad peak centered at 1.0 nm that is consistent with hydrated halloysite. Also present are sharp peaks from natrojarosite and feldspar. A diffraction peak at 1.5 nm that would indicate smectite was not present.

Table 1: Major element composition.

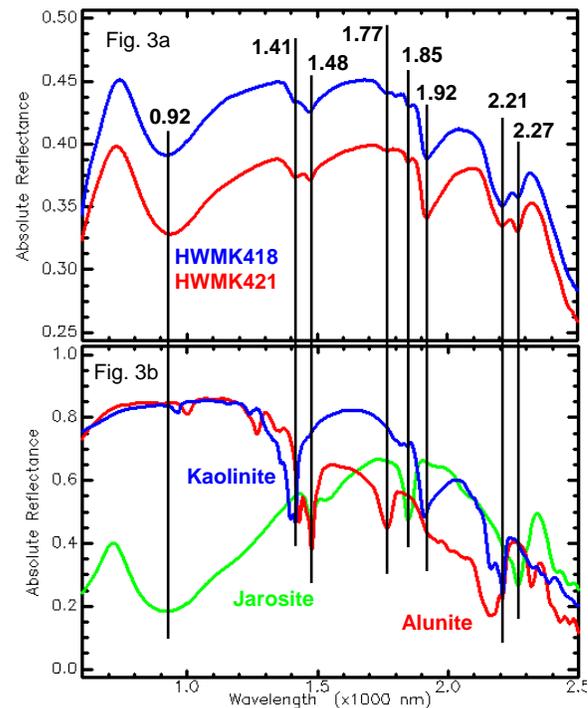
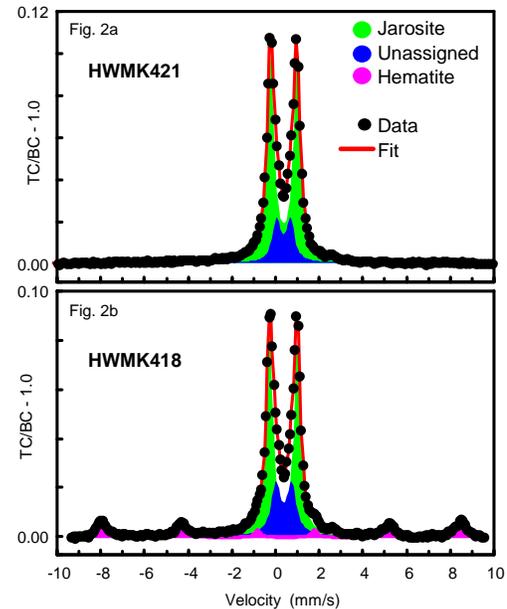
	HWMK418	HWMK421	HWMK420
	Breccia	Breccia	Soil
SiO ₂	44.65	48.94	43.84
TiO ₂	2.51	2.11	3.24
Al ₂ O ₃	21.16	25.15	20.38
Fe ₂ O ₃ T	17.47	9.57	15.22
MnO	0.10	0.08	0.26
MgO	0.66	0.38	4.89
CaO	2.80	2.49	5.60
Na ₂ O	5.00	5.17	3.57
K ₂ O	2.21	2.56	1.09
P ₂ O ₅	1.41	1.27	0.99
SO ₃	1.39	1.54	0.09
Total	99.36	99.26	99.19
LOI	20.08	21.86	6.46
FeO	0.47	0.43	6.75
Fe ₂ O ₃	16.95	9.09	7.72
SO ₃ T	5.22	7.22	0.29

Major elements measured on LOI residue. LOI, FeO, Fe₂O₃, and SO₃T measured on bulk sample

The Mössbauer spectrum for HWMK421 (yellow matrix separate) shows that the matrix has jarosite (CS= 0.37 mm/s and QS = 1.20 mm/s) and an unassigned Fe³⁺ phase (CS= 0.37 mm/s and QS = 0.63 mm/s) as the primary Fe-bearing phases (Fig. 2a). The spectrum for HWMK418 (bulk powder) shows hematite (CS = 0.37mm/s, QS = -0.20 mm/s, and B_{hf} = 51.0 T) is also present and probably corresponds to the scattered black areas in Fig. 1b. The MB spectrum of HWMK418 is very similar to the MB spectra of the sulfate-rich outcrop at MP.

Visible and near-IR spectra (Fig. 3) for HWMK418 and HWMK421 breccias are characterized by a jarosite spectral signature (Fe³⁺ feature at 0.92 μm and Fe-OH features at 1.48, 1.85, and 2.27 μm). We attribute the features near 1.41, 1.92, and 2.21 μm (consistent with XRD data) to hydrated halloysite, by comparing with the spectrally similar kaolinite (except for the broad 1.92 μm H₂O feature). Minor alunite is also indicated by the spectral feature at 1.77 μm.

Conclusion and Application: The presence of both jarosite and hydrated halloysite in the Mauna Kea breccias indicates that phyllosilicates can form at low pH conditions, so that the phases can occur together on Mars in acid sulfate weathering environments (e.g., MP). The basaltic bulk composition of the jarosite-bearing breccias implies hydrothermal alteration without significant leaching (low water to rock ratios). As a corollary, alteration mineralogy is an indicator of formation pathway but not reliable as an indicator of bulk composition. The S- and Cl-free bulk composition of the MP sediments is also basaltic, again suggesting that they were altered without significant leaching.



- References:** [1] Rieder et al. (2004) *Science*, 306, 1746. [2] Moore (2004) *Nature*, 428, 711. [3] Klingelhöfer et al. (2004) *Science*, 306, 1740. [4] Golden et al. (2005) *JGR*, 110, E12S07. [5] Gendrin et al. (2005) *Science*, 307, 1587. [6] Wray et al. (2009) *GRL*, 36, L21201. [7] Wendt et al. (2011) *Icarus*, 213, 86. [8] Swayze et al. (2008) *AGU*, P44A-04. [9] Morris et al. (2000) *LPSC 31*, 2014. [10] Morris et al. (2008) *LPSC 39*, 2208. [11] Morris et al. (1996) *Mineral Spectroscopy, Spec. Publ. Geochem. Soc.*, 5, 327. [12] Morris et al. (2000) *JGR*, 105, 1757. [13] Hamilton et al. (2008) *JGR*, 113, E12S43. [14] Morris et al. (2005) *EPSL*, 240, 168. [15] Wolfe and Morris (1996) USGS Series Map I-2524-A.