

ALUMINUM PHOSPHATE-SULFATE MINERALS: THE FATE OF MOBILE PHOSPHORUS IN SULFUR-RICH, MARS-RELEVANT SYSTEMS. J. A. Berger¹, D. W. Ming¹, R. V. Morris¹, P. L. King², M. E. Schmidt³, V. M. Tu¹. ¹NASA Johnson Space Center, Houston, USA; ²Australian National University, Canberra, AUS; ³Brock University, St. Catharines, CAN.

Introduction: Phosphorus mobility on the martian surface is fundamental to habitability because the element is essential for biochemical reactions and biological structures. The *Spirit*, *Opportunity*, and *Curiosity* rovers have discovered a range of P concentrations on the martian surface suggesting pervasive mobility of the element [e.g., 1, 2, 3]. A key pathway for P mobilization is via dissolution of primary phosphates (apatite, merrillite) [4, 5] and reprecipitation of P-rich phases in soils, veins, alteration haloes, localized features and/or rock matrix. The secondary P-bearing phases are not fully characterized by rover observations; where primary apatite is not apparent, P is variably associated with Ca, Fe, Al, and Mn with no detectable affinity with any single cation [e.g., 1, 2, 3].

In Mars analogue samples from the summit of Maunakea, Hawai'i, we have identified an association of P with S in secondary aluminum-phosphate-sulfate (APS) minerals. Here, we describe the occurrence of APS minerals in analogue samples and propose a similar fate for P in S-rich martian systems.

Samples and Methods: Two Maunakea summit samples representative of acid-sulfate alteration processes were investigated: (1) a tephra fragment with an unaltered interior and an ~1-cm-thick alteration rind (HWMK953) and (2) breccia containing highly altered lithic fragments cemented by sulfates, phyllosilicates, and amorphous silica-rich material (HWMK959). The average unaltered parent composition of the summit tephra is hawaiite. A field-emission SEM was used to acquire an EDS element map of the breccia and spot EDS analyses on polished thin sections of both samples. Bulk chemistry and mineralogy of the breccia sample was obtained with powder X-ray diffraction (XRD) and X-ray fluorescence (XRF).

Results: Unaltered tephra: The least-altered zone of the tephra (HWMK953) is typical for unaltered hawaiitic/mugearitic volcanics capping Maunakea, which have bulk P_2O_5 ~1 wt% [6, 7]. Phosphorus is contained within apatite, which occurs as 1-100 μm hexagonal and acicular grains (mostly skeletal) in the glass matrix and as inclusions in olivine. F, Cl, and OH were not analyzed with EDS and S was below detection limits.

Altered lithic material: The altered rock fabric largely maintains its primary trachytic texture, albeit with silica pseudomorphs after feldspar, pyroxene, and olivine, and Ti-oxide pseudomorphs after Fe-Ti-oxide. No residual primary apatite grains were found.

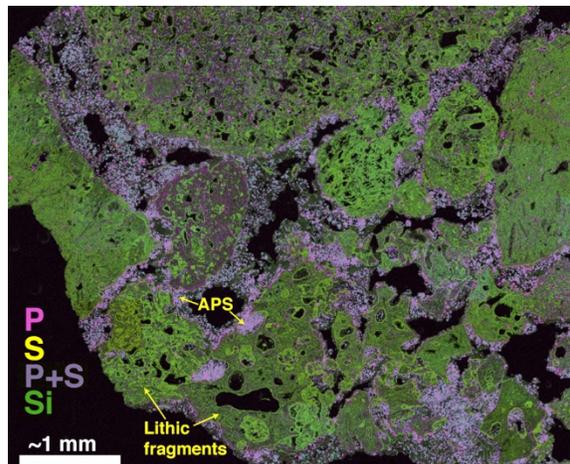


Figure 1: Element maps of P, S, and Si in acid-sulfate altered breccia (HWMK959). Si indicates altered lithic fragments (green) cemented together by P- and S-rich secondary materials (magenta and light violet).

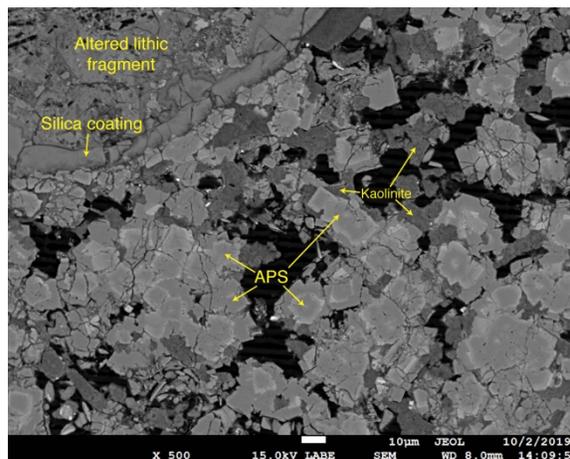


Figure 2: BSE image showing zoned P+S phases interpreted to be APS (HWMK959).

P- and S-bearing secondary phases: P- and S-rich material is found on the surfaces of lithic fragments and within vesicles, fractures, and voids where primary material was leached out. P and S element maps have a strong correlation (Fig. 1). The maps further indicate that minor amounts of P occur without S, whereas S does not occur without P. Al and K also correlate with the P+S phase. BSE imaging shows the P+S phase is a collection of equigranular, subcubic grains (Fig. 2). Most of the grains are zoned with Ca+P enriched cores and rims. EDS spot analyses reflect the zoning in the correlation of P, S, and Ca (Fig. 3). The XRD pattern

best fits alunite, followed by crandallite and woodhouseite (S-scores 80, 60, & 50, respectively). The other major crystalline phase is kaolinite.

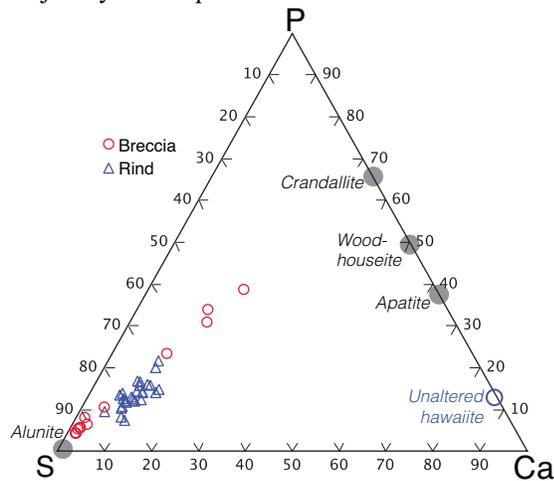


Figure 3: Ternary plot of molar P, S, and Ca in spot EDS analyses of S-rich secondary phases in Maunakea breccia and alteration rind. Variation is attributed primarily to zoning in individual APS grains, not to variation between grains. Endmembers are denoted.

Discussion: The FE-SEM and XRD observations indicate that the (P + S)-rich material in the Maunakea samples fits into the APS alunite-woodhouseite-crandallite solid solution series (Fig. 3) [8]. Woodhouseite $\text{CaAl}_3(\text{PO}_4/\text{SO}_4)(\text{OH})_6$ and crandallite $\text{CaAl}_3(\text{PO}_4/\text{SO}_4)(\text{PO}_3\text{OH})(\text{OH})_6$ are APS minerals isostructural with alunite group minerals, with a solid solution coupled substitution of $(\text{Ca}^{2+} + \text{PO}_4^{3-})$ for $(\text{K}^+, \text{Na}^+ + \text{SO}_4^{2-})$.

Lesser amounts of secondary P occurs in the Maunakea samples without corresponding S (Fig. 1). We attribute this P to Fe- and Al-phosphates (amorphous and/or crystalline), which have been discussed as likely secondary P-bearing phases in Mars-relevant systems where low-pH fluids dissolve apatite [9, 10].

The occurrence of secondary P in the Maunakea samples is interpreted to be a mixture of APS minerals and minor Al-phosphate. This reflects the dissolution of apatite and release of Al, Ca, Na, and K from glass and feldspar in sulfate-rich fluids, as described by the generalized reaction [8]:



The relative activities of PO_4^{3-} and SO_4^{2-} are important for the fate of P: the S-free P phases we observe indicate locally high P/S activity ratios such that Al-phosphate precipitated separately from sulfate. This may be due to changing P/S in the fluid. Note that we don't have information on the Cl- and F-bearing phases, but these are known to be present in apatite, melt, basaltic gases, and hydrothermal fluids.

Implications for Mars exploration: The martian surface is enriched in P and S, and the fact that phosphate is incorporated into sulfates in a wide range of terrestrial settings [8] suggests that similar processes occurred on Mars. We encourage consideration of aluminum phosphate-sulfate (APS) minerals with respect to Mars because there are several implications for understanding P mobility on the martian surface:

(1) APS compositions can be used to infer geochemical conditions of formation, and they have a relatively good preservation potential [8, 11]. Micrometer-scale analyses of zoning in APS minerals are very sensitive to small changes in fluid conditions, particularly when common APS elements are detectable (e.g., Sr, REE, Ba, Pb). APS-bearing samples may therefore be fruitful targets for Mars sample return.

(2) In natural terrestrial settings, APS minerals form in low pH environments, but can also persist in circum-neutral fluids due to low solubility [11]. APS minerals thus have the potential to sequester P, limiting availability for biochemical reactions. The solubility of APS minerals may be a significant determining factor for phosphate availability, and are thus important for assessing habitability.

(3) APS minerals in terrestrial samples are often overlooked because they usually occur with abundant alunite [8], and this oversight may apply to Mars exploration. We predict that the phosphate ion can also be incorporated into alunite group minerals containing Fe^{3+} such as jarosite, which has been detected in situ by martian rovers. We also suggest that phosphate/sulfate substitution is plausible in Mg- and Fe-sulfates, which are common on the martian surface. If phosphate is incorporated into sulfates in martian samples, and if the substitution is not detected by in situ rover analyses, then the geochemical characteristics and history of P-bearing phases may be poorly constrained.

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References: [1] Ming et al. (2006) *JGR*, 111, E2. [2] Rieder et al. (2004) *Science*, 306, 5702. [3] Berger et al. (2019) *9th Intl Conf on Mars*, #6336. [4] Adcock et al. (2013) *Nature Geosci*, 6, 10. [5] Adcock and Hausrath (2015) *Astrobiology*, 15, 12. [6] Morris et al. (2000) *JGR*, 105, E1. [7] Berger (2017) *Western Univ*, #4674. [8] Dill (2001) *Earth-Sci Rev*, 53, 1. [9] Tu et al. (2014) *Am Mineralogist*, 99, 7. [10] Berger et al. (2016) *47th LPSC #1652*. [11] Borruel-Abadía (2016) *Chem Geology*, 429.