The fate of mobile phosphorus in sulfur-rich, Mars-relevant systems

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Phosphorus mobility is fundamental to the habitability of Mars, and the *Spirit*, *Opportunity*, and *Curiosity* rovers have discovered evidence of pervasive P mobilization on the ancient martian surface [e.g., 1]. A key pathway for P mobilization is via dissolution of primary phosphates (apatite, merrilite) and reprecipitation of P-rich phases in soils, rock matrix, and localized features. However, the secondary P-bearing phases are not fully characterized by the rovers, so we turn to terrestrial analogues to constrain martian processes.

In Mars analogue samples from the summit of Maunakea, Hawai'i, we have identified an association of P with S in secondary aluminum phosphate-sulfates (APS). Hawaiitic tephra altered in an acid-sulfate regime was investigated with XRF, XRD, and SEM-EDS. In unaltered tephra, P occurs in apatite (bulk P ~0.5 wt%). Altered tephra consists of Si- and Ti-rich residual rock fabric with secondary kaolinite, amorphous silica, Fe^{3+}-oxides, and alunite. Apatite was not found in the residue. P and S occur together in subcubic, equigranular sulfate with P + Ca zoning. All of the sulfate contains P (molar S:P ~1-15). The (P + S)-rich material in the Maunakea samples is consistent with the isostructural APS alunite-woodhouseite-crandallite solid solution series, which has the coupled substitution of (Ca^{2+} + PO_4^{3-}) for (K^+, Na^+ + SO_4^{2-}) [2]. This reflects the dissolution of apatite and release of Al, Ca, Na, and K from glass and feldspar in sulfate-rich fluids that react to form APS.

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 [2] suggests that similar processes occurred on Mars. In natural terrestrial settings, APS minerals form in low pH conditions, but can also persist in circumneutral fluids due to low solubility [3]. APS minerals thus have the potential to sequester P, limiting availability for biochemical reactions. We therefore encourage consideration of APS with respect to Mars because they may be key for understanding P mobility on the martian surface.

References: [1] Ming et al. (2006) *JGR, 111, E2*. [2] Dill (2001) *Earth-Sci Rev, 53, 1*. [3] Borruel-Abadía (2016) *Chem Geology, 429*.