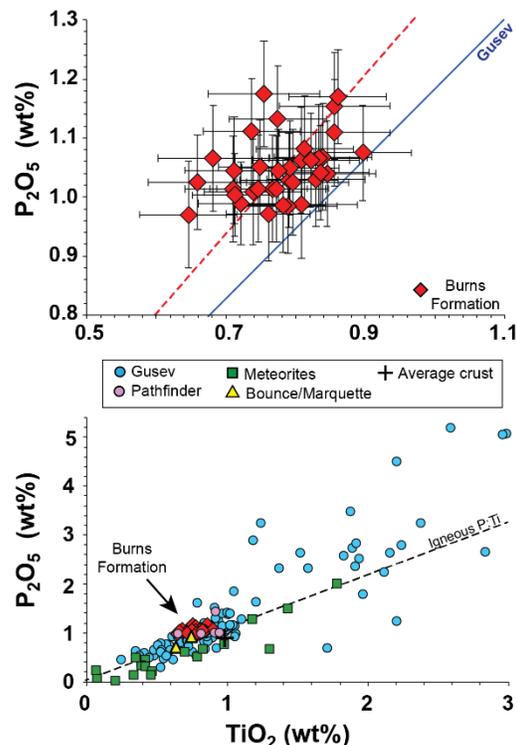


**PHOSPHOROUS WAS IMMOBILE THROUGHOUT FORMATION OF THE LAYERED-SULFATE DEPOSITS OF THE BURNS FORMATION, MERIDIANI PLANUM.** T. M. McCollom<sup>1</sup>, C. Donaldson<sup>1</sup>, and B. M. Hynek<sup>1,2</sup>, <sup>1</sup>Laboratory for Atmospheric and Space Physics and <sup>2</sup>Department of Geological Sciences, University of Colorado, Boulder, CO 80309 (mccollom@lasp.colorado.edu).

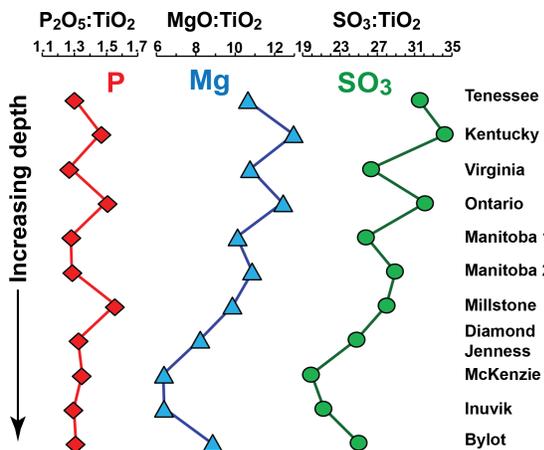
**Introduction:** Martian basalts contain elevated levels of P relative to their terrestrial counterparts, which makes it a useful element for tracking geochemical processes. In pristine martian basalts, P primarily occurs as Ca-phosphates such as apatite and merillite [1]. These minerals have high solubilities under acidic conditions, and mobilization of P by acidic fluids has been invoked to explain enrichments and depletions of this element in martian rocks and soils [e.g., 2-6]. The layered, sulfate-rich bedrocks of the Burns formation at Meridiani Planum also contain substantial amounts of P, and appear to have been exposed to acid-sulfate fluids at multiple intervals during their formation [7,8]. However, the possibility that P may have been mobilized into or out of the deposits during these episodes has never been thoroughly investigated. Accordingly, this study was undertaken to examine the mobility of P during formation of the bedrocks at Meridiani.

**Overview of the Burns formation:** The layered bedrocks of the Burns formation have been described as impure sandstones, composed of a mixture of sulfate and silicate components [7-10]. Key steps in the formation of the bedrocks that influence their chemical composition include: (1) early addition of an oxidized sulfur component to siliciclastic materials from a basaltic provenance, (2) erosion of the resulting materials as sulfate-cemented siliciclastic sand grains and transport to their present location, and (3) diagenetic alteration and cementation of the sediments during one or more episodes of groundwater infiltration following emplacement [7,8,10,11]. Proposed scenarios for the early addition of the sulfur component to basalt-derived material include precipitation of Fe-, Mg-, and Ca-sulfate minerals from evaporating fluids that infiltrated into a chemically altered basaltic precursor [7,8,11] or reaction of pristine basalt with sulfuric acid solutions derived from atmospheric or volcanic sources [12-15]. In either case, these scenarios involve reaction of basalt with acid-sulfate fluids, possibly under conditions with relatively high fluid:rock ratios. Diagenetic alteration following deposition at their current location also involved interaction with acid-sulfate fluids, as suggested by the presence of jarosite [8,16]. Among the effects of this diagenetic alteration is an apparent loss of Mg-sulfates in the lower parts of the formation, as evidenced by a correlated decrease in MgO and SO<sub>3</sub> abundance with depth [8,9].



**Figure 1.** Measured abundances of P<sub>2</sub>O<sub>5</sub> and TiO<sub>2</sub> in the Burns Formation deposits at Meridiani Planum (top) and compared with measurements for representative martian basalts from other landing sites and meteorites (bottom).

**Phosphorous in Burns formation bedrocks:** The Burns formation bedrocks contain a narrow range of P contents (0.97-1.17 wt% P<sub>2</sub>O<sub>5</sub>), with abundances similar to numerous examples of relatively unaltered martian basalts (Fig. 1). In addition, the bedrocks have P<sub>2</sub>O<sub>5</sub>:TiO<sub>2</sub> ratios that cluster close to the constant ratio trend expected for martian igneous rocks [3] as well as the average ratio measured by the Spirit rover for basaltic rocks in Gusev crater (Fig. 1). Combined, these observations indicate that the sediments composing the Burns formation bedrocks maintain their original P concentrations from the basaltic precursor. This interpretation is also supported by a negative trend in P abundance with increasing SO<sub>3</sub>. Furthermore, the deposits exhibit nearly constant P<sub>2</sub>O<sub>5</sub>:TiO<sub>2</sub> with depth while MgO:TiO<sub>2</sub> and SO<sub>3</sub>:TiO<sub>2</sub> ratios decrease (Fig. 2) indicating that P was not mobilized by the acid-sulfate fluids that removed Mg-sulfates during diagenesis. Overall, the data indicate that P was not mobilized into or out of the bedrocks at any stage during their for-

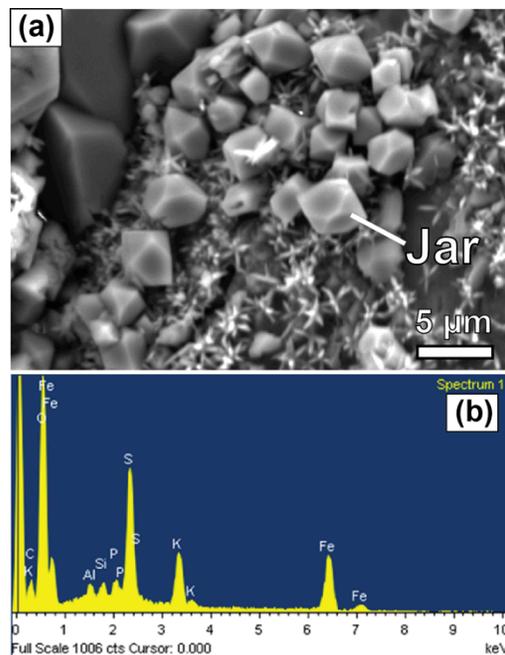


**Figure 2.** Elemental trends with depth in Burns formation bedrocks within Endurance crater showing transport and loss of Mg and  $\text{SO}_3$  by acidic fluids during diagenesis [9], but no apparent mobilization of P during this interval.

mation, including the event that initially added the sulfur component and all subsequent infiltrations by migrating groundwaters.

**Potential reservoirs for P in the Burns formation:** The apparent immobility of P suggests that it is present in a relatively insoluble secondary phase. One possibility is that P is sequestered in Fe- or Al-phosphates, such as the giniite that formed during experimental acid-sulfate alteration of P-enriched basalt [4,17]. Although Fe-phosphates have not been identified in the Mössbauer results from Meridiani, the low abundance and overlap with other phases might make such detections difficult. Another possibility is that P may be sequestered in jarosite or other members of the alunite group. Minerals in this group can contain substantial amounts of P through  $\text{PO}_4$ -for- $\text{SO}_4$  substitutions (e.g., Fig. 3). Other potential reservoirs for P include volcanic glass or adsorption on surfaces of minerals such as Fe-oxides/oxyhydroxides, although it appears unlikely that either of these possibilities could account for the amount of P found in the rocks.

**Implications for formation scenarios:** The sedimentary-evaporite scenario that has been proposed as one possible origin of the Burns formation deposits invokes multiple episodes of interaction of the materials with acid-sulfate fluids as well as extensive transport of divalent cations (Fe, Mg, Ca) and  $\text{SO}_3$  both into and out of the materials at various stages [7,8,9,11]. Yet, the apparent immobility of P would require that mobilization of these other elements occurred without simultaneously mobilizing P into or out of the deposits. Perhaps these seemingly incongruent trends can be reconciled if P was sequestered into a highly immobile phase at a very early stage in the scenario, although this remains to be tested with rigorous geochemical models. Alternate scenarios that



**Figure 3.** (a) SEM image of  $\text{PO}_4$ -rich jarosite in a sandstone from the Aztec formation, southeast Nevada. (b) EDS analysis of jarosite showing  $\text{PO}_4$  and Al enrichment.

propose  $\text{SO}_3$  was initially added to pristine basalt from atmospheric or volcanic sources [12-15] suggest that this addition took place without mobilization of other elements into or out of the deposits, which would be consistent with the apparent immobility of P and maintenance of igneous  $\text{P}_2\text{O}_5:\text{TiO}_2$  ratios. Even in this case, however, it would require that P remained immobile during diagenesis, including during the loss of Mg and  $\text{SO}_3$  (Fig. 2). This may require either that P is sequestered in a phase with low solubility or that the infiltrating fluids during diagenesis were already saturated with respect to P-bearing mineral phases and thus did not transport P into or out of the deposits.

**References:** [1] McSween, H. and Treiman, A. H. (1998) *Rev. Mineral. Geochem.*, 36, F1-F53. [2] Hurowitz J. A. et al. (2006) *JGR* 111, E02S19. [3] Ming D. W. et al. (2008) *JGR* 113, E12S39. [4] Hausrath E. M. et al. (2013) *JGR* 118, 1-13. [5] Greenwood J. P. & Blake R. E. (2006) *Geology* 34, 953-956. [6] Yen A. S. et al. (2008) *JGR* 113, E06S10. [7] Squyres S. W. et al. (2004) *Science* 306, 1709-1714. [8] McLennan S. M. et al. (2005) *EPSL* 240, 95-121. [9] Clark B. C. et al. (2005) *EPSL* 240, 73-94. [10] Grotzinger J. P. et al. *EPSL* 240, 11-72. [11] Squyres S. W. et al. (2006) *Science* 313, 1403-1407. [12] McCollom T. M. and Hynke B. M. (2005) *Nature* 438, 1129-1131. [13] Berger et al., (2009) *Am. Min.* 94, 1279-1282. [14] Tréguier, E., et al. (2008) *JGR* 113, E12S34. [15] Niles P. B. & Michalski J. (2009) *Nat. Geosci.*, 2, 215-220. [16] Klingelhöfer G. et al. (2004) *Science*, 306, 1740-1745. [17] McCollom T.M. & Donaldson, C. (2016) *LPSC XLVII*, abs. #1690.