

**ACID VAPOR WEATHERING OF APATITE AND IMPLICATIONS FOR MARS** E. M. Hausrath<sup>1</sup>, D. C. Golden<sup>1</sup>, R.V. Morris<sup>1</sup> and D.W. Ming<sup>1</sup> <sup>1</sup>NASA Johnson Space Center, Houston, TX 77058, USA Elisabeth.M.Hausrath@nasa.gov.

**Introduction:** Phosphorus is an essential nutrient for terrestrial life, and therefore may be important in characterizing habitability on Mars. In addition, phosphate mobility on Mars has been postulated as an indicator of early aqueous activity [1]. Rock surfaces analyzed by the Spirit Mars Exploration Rover indicate elemental concentrations consistent with the loss of a phosphate-containing mineral [2], and the highly altered Paso Robles deposit contains ~5% P<sub>2</sub>O<sub>5</sub>, modeled as 8-10 % phosphate [3]. Depending on the pH of the solution, phosphate can exist as one of four charge states, which can affect its solubility, reactivity and mobility. Phosphate may therefore prove a useful and interesting tracer of alteration conditions on Mars.

Acid vapor weathering has been previously studied as a potentially important process on Mars [4-6], and Paso Robles may have been formed by reaction of volcanic vapors with phosphate-bearing rock [3, 7]. Here we present preliminary results of acid vapor reactions in a Parr vessel [6] using fluorapatite, olivine and glass as single phases and in a mixture.

**Methods:** Sulfuric acid vapor (acid fog) experiments were performed following the methods of [6], except Teflon instead of quartz beads were used as the supporting matrix to hold the reactant minerals in the vapor zone above 2-mL of concentrated H<sub>2</sub>SO<sub>4</sub>. Mineral substrates included San Carlos forsterite, Durango fluorapatite, and basalt glass (Stapafjell Volcano, courtesy of S. Gislason, University of Iceland) [8, 9]. Samples were prepared as polished thick sections, and reacted for 6 hours, 1 day, and 3 days at ~155°C in closed Parr vessels containing sulfuric acid (see [6]). In separate experiments, samples were prepared as powdered grains (75-150µm size fraction). Powder samples (100 mg each of forsterite, apatite and glass, and a mixture of 33 mg each of forsterite, apatite, and glass) were reacted the same way in a platinum dish above the Teflon beads for 3 days at ~155°C. After each experiment, the Parr vessels were removed from the oven, cooled to room temperature, and opened to recover the sample. Powder samples were analyzed by X-Ray Diffraction (XRD) immediately after being removed from the reaction vessel and again after 72 hours storage at ~33 % humidity. The thick section reacted for 6 hours was immediately stored at ~33% humidity. The thick section reacted for 1 day was stored under ambient conditions for 48 hours and 75% humidity for 72 hours before equilibration at ~33% humidity. The thick section reacted for 3 days was stored for 72 hours at ~75% humidity before equilibration at ~33% humidity. All thick sections were stored at ~33% humidity for almost 3 weeks before carbon-coating to allow samples to equilibrate and facilitate comparison with reacted grains analyzed by XRD. No attempt was made to prevent atmos-

pheric oxidation, which is very slow under highly acidic conditions [10]. Thick sections were analyzed by Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy (EDS), and powders by XRD, SEM and EDS.

**Results:** After 6 hours reaction in acid vapor, precipitate formation on thick sections was minimal for olivine and glass (Fig. 1a and b) and significant for apatite (Fig. 1c). Olivine displayed small rod-shaped and equant Mg-sulfate precipitates (white arrows Fig. 1a). Reacted glass

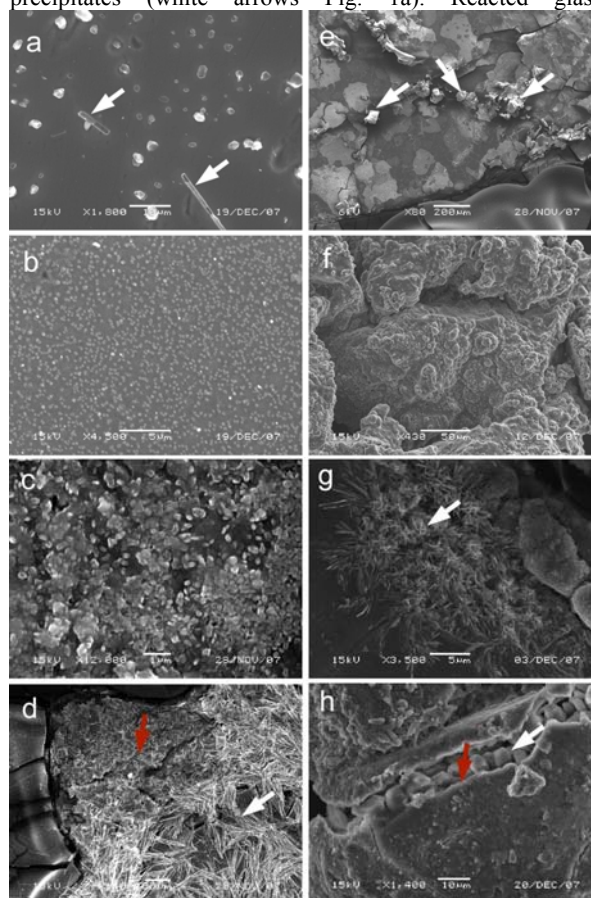


Figure 1 Precipitates on the surfaces of primary phases reacted with sulfuric acid vapor a) reacted forsterite (6 hours) showing equant and rod-shaped Mg-sulfate crystals b) reacted glass (6 hours) showing sub-micrometer-sized crystals and c) reacted fluorapatite (6 hours) showing pervasive presence of sub-micrometer-sized crystals d) thin, fibrous Al-sulfate crystals (white arrow) on the silica-rich surface (red arrow) of reacted glass (3 days) e) Mg-sulfate crystals indicated by arrows on the silica-rich surface of reacted forsterite (3 days). f) Ca-sulfate (likely anhydrite) on the surface of reacted fluorapatite (3 days) g) Ca and P-rich crystals (likely brushite) on the surface of reacted fluorapatite (1 day) h) Mg-sulfate crystals (white arrow) beneath a silica-rich crust on the surface of reacted mineral grains (red arrow) (3 days)

surfaces contained numerous submicrometer-sized crystals (Fig 1b). Apatite was pervasively altered with submicrometer-sized crystals covering much of the surface (Fig. 1c). After 24 and 72 hours reaction in acid vapor, extensive alteration was observed in all cases (Fig. 1d-h). The altered surfaces of the glass and forsterite contain Al- and Mg-sulfates respectively, as well as silica-rich leached layers. The altered apatite contained substantial Ca-sulfate (Fig. 1f).

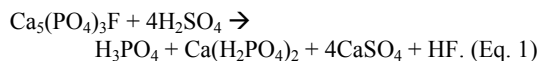
Secondary products are primarily sulfates (XRD and SEM), and amorphous silica (SEM). Small amounts of secondary phosphates were tentatively identified, including monocalcium phosphate (MCP) ( $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ ), anhydrous MCP ( $\text{Ca}(\text{H}_2\text{PO}_4)_2$ ), and strengite ( $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ ) by XRD (Table 1). Some XRD peaks remain unidentified and may be evidence of other secondary products. Ca and P-containing crystals were tentatively identified as brushite ( $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ ) based on morphology (SEM) (Fig. 1g).

Table 1. Mineralogy (XRD) of reacted powders

Sample	Unreacted phases	Immediately after acid vapor reaction	After 72 h exposure to 33% RH
Basalt glass	glass; minor forsterite	(?)	wattevilleite(?)
San Carlos forsterite	forsterite	forsterite	forsterite; hexahydrite
Durango fluorapatite	fluorapatite	fluorapatite; anhydrite; fluorite(?); MCP anhydrous(?)	fluorapatite; anhydrite; MCP; fluorite(?)
mixture	not measured	anhydrite; fluorite(?)	anhydrite; hexahydrite; strengite(?); fluorite(?)

### Discussion and implications for Mars:

Acid vapor alteration of the primary igneous phases forsterite, basalt glass and fluorapatite forms abundant Mg, Al and Ca-sulfates respectively when reacted for sufficient lengths of time. In addition, anhydrous MCP is tentatively identified immediately following the reaction of the fluorapatite powders with sulfuric acid, consistent with the following reaction:



On Mars, chlorapatite may be more common than fluoroapatite [11], which may result in corresponding differences in secondary products.

Hydrated MCP was identified by XRD following exposure of the reacted samples to increased humidity for 72 hours as in the following equation:

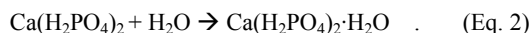
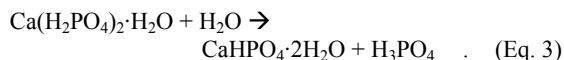


Plate-like Ca and P-rich crystals (Fig. 1g) were observed on the surfaces of reacted apatite in thick section and powder samples. We interpret these crystals as brushite. Brushite was not detected by XRD, presumably because the abundance was below detection limits. Brushite can be formed from MCP by the addition (absorption) of water as follows:



Brushite has been previously postulated to exist on Mars [2, 3], and these experiments suggest that acid vapor weathering may be a mechanism for its formation. Phosphoric acid formed during reactions 1 and 3 may also react with other minerals to form other phosphate-bearing minerals. For example, strengite may be formed due to the high availability of  $\text{Fe}^{3+}$  at low pH. Strengite and other Fe-phosphates may be present in Paso Robles [3, 12-14].

The localized formation of Paso Robles type deposits is consistent with a low water: rock process such as acid vapor weathering [3, 7]. In addition, the Ca:P ratio in Paso Robles [7] is similar to the ratio in apatite or whitlockite. This suggests that most of the Ca and P in that deposit may originate from apatite or whitlockite weathering, and that the products may not have been transported far, consistent with a low-water scenario.

Our future experiments on phosphate mobility on Mars will explore the effects of variables such as acidity, ionic strength and composition, solid: liquid ratio, parent material mineralogy, temperature, time, and oxidation state. Alteration of primary phosphates and formation of secondary products may be useful in identifying localities which could support life and yield valuable information about weathering on the surface of Mars and the conditions under which it occurs.

**References:** [1] Greenwood J.P. and Blake R.E. (2006) *Geology*, 34, 953-956. [2] Hurowitz J.A. *et al* (2006) *JGR*, 111, E02S19 [3] Ming D.W. *et al.* (2006) *JGR*, 111, E02S12 [4] Banin A. *et al.* (1997) *JGR* 102, 13341-13356 [5] Tosca N.J. *et al* (2004) *JGR*, 109, E05003 [6] Golden D.C. *et al.* (2005) *JGR*, 110, E12S07 [7] Yen A.S. *et al.* (submitted) *JGR* [8] Oelkers E.H. and Gislason S.R. (2001) *GCA*, 65, 3671-3681 [9] Gislason S.R. and Oelkers E.H. (2003) *GCA* 67, 3817-3832. [10] Burns R.G. and Fisher D.S. (1990) *JGR*, 95 14169-14173 [11] McSween H.Y. and Treiman A.H. (1998) *RIMG*, 36, 6-1 to 6-46. [12] Lane M.D. *et al* (2007) *SICM*, Abstract #3331 [13] Lane M.D. *et al.* (2007) *LPS XXXIV*, Abstract #2210 [14] Lane M.D. *et al.* (2007) *LPS XXXIV*, Abstract #2176 **Acknowledgements:** We thank S. Gislason, J. Herrin, L. Le, G. Robinson, and B. Sutter for their assistance.