MOBILITY OF PHOSPHORUS IN ACID-SULFATE ENVIRONMENTS ON EARTH AND MARS. T. M. McCollom and C. Donaldson, Laboratory for Atmospheric and Space Physics, University of Colorado, Boulder, CO 80309 (mccollom@lasp.colorado.edu).

Introduction: Most martian rocks have phosphorous concentrations that are significantly higher than their terrestrial counterparts, making this element a potentially useful tracer of conditions during alteration. A number of studies have used the abundance of P to infer chemical conditions and processes involved in alteration of martian rocks [e.g., refs. 1-3]. Phosphorous is often thought to be particularly mobile in acidic conditions, owing in large part to the rapid dissolution of apatite at low pH. In order to place additional constraints on the behavior of P in acidic environments for use as a geochemical tracer, we are examining the mobility of this element in acid-sulfate environments using a combination of approaches that includes study of terrestrial analogs, analysis of geochemical trends in Mars rover data, and laboratory experiments.

P mobility during acid-sulfate alteration in a terrestrial fumarolic environments: As part of a study to examine the effects of acid-sulfate alteration on basaltic cinders in fumaroles at Cerro Negro volcano, Nicaragua [4,5], we have measured the chemical compositions of more than 50 samples representing a range in extent of alteration. The results indicate that, as alteration proceeds, the deposits are progressively depleted in nearly all of the major rock-forming elements other than Si, P, and K (Fig. 1). Phosphorous is depleted in only the most extensively altered samples that consist of little more than amorphous silica. Additionally, in most samples, P retains constant molar ra-

![Figure 1](image1.png)

Figure 1. Enrichment (>1) or depletion (<1) of elements in a selected subsample of acid-sulfate altered basaltic cinders at Cerro Negro relative to pristine basalt [5].

![Figure 2](image2.png)

Figure 2. Measured abundance of P$_2$O$_5$ in the Burns Formation deposits at Meridiani Planum. The dashed red line represents the expected trend for dilution of P abundance by addition of SO$_3$ to an end-member S-free basalt with P immobile. Mobilization of P into the deposits along with SO$_3$ would be expected to result in a positive enrichment trend.

P mobility at Meridiani Planum: The layered sulfate deposits of the Burns Formation at Meridiani Planum contain an average of 1.05 wt% P$_2$O$_5$, higher than the majority of martian rocks other than a few basalts from Gusev Crater. Geochemical models for Meridiani propose that this unit formed by addition of sulfate to a basaltic precursor [6-8]. The measured abundance of P$_2$O$_5$ in the deposits conform to a decreasing linear trend as a function of SO$_3$ that is consistent with dilution of an immobile element during addition of the sulfur component (Fig. 2). The scatter of measured P$_2$O$_5$ can largely be accounted for by secondary (post-depositional) mobilization of Mg-, Fe, and Ca-sulfate minerals. If P had been transported into the rocks along with the sulfate, it would be expected to conform to a positive linear trend, but this is not observed. Consequently, the data suggest that elevated P contents were already present in the precursor, and it was not mobilized into or out of the deposits during addition of the sulfur component.

The layered sulfate deposits of the Burns Formation also have a depletion of Mg and SO$_3$ with
depth, which has been attributed to transport of Mg-sulfate salts out of the lower parts of the formation by acidic fluids [9]. In this same cross-section, mass balance calculations indicate that P levels remained unchanged, and P:Ti ratios are essentially constant in those samples that have lost Mg and SO₃ (Fig. 3). These observations indicate that the fluids that removed the Mg-sulfates did not mobilize P, indicating that the fluids were already saturated with respect to P-bearing phases when they entered the formation or that the phases have very low solubility.

**Experimental acid-sulfate alteration of basalt:**
To further study the behavior of P in acid-sulfate environments, we are also conducting laboratory experiments reacting pristine basalt cinders and phospoate minerals with sulfuric acid solutions. The experiments are similar to those performed previously [5], but with the addition of apatite to reach a bulk P₂O₅ abundance in the solids of 1 wt%, similar to the Meridiani deposits. In experiments performed at 150 °C, apatite dissolves rapidly and the PO₄³⁻ released then precipitates as giniite. This phase occurs as football-shaped crystals distributed along with amorphous silica, anhydrite, and natroalunite on the surfaces of the altered cinders (Fig. 4). EDS analysis indicates the giniite contains significant amounts of Al and S along with Fe and P. In agreement with previous work [10,11], these results suggest that giniite or other Fe-bearing phosphates may be key reservoirs for P in martian rocks. Experiments are currently underway to determine whether giniite or other Fe-phosphate are produced during alteration at lower temperatures.

**Conclusions:** Contrary to the general perception that P is mobilized in acidic, sulfur-rich environments, the evidence suggests that in many such environments it may be highly immobile. Iron-phosphate minerals may be key phases that sequester the P in these environments and prevent it from being mobilized.

**References:**