PHOSPHATE RECORDS ENVIRONMENTAL CONDITIONS IMPORTANT TO HABITABILITY IN SOILS AND ROCKS ON MARS  
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Introduction: Phosphate is a crucial nutrient, used by life for ATP, DNA, RNA and phospholipid membranes [1]. In long-term ecosystems on Earth, P is generally considered to be a limiting nutrient [2, 3], with inputs due to dust an important P source [4]. Phosphate contributions from dust may therefore also be important in characterizing the habitability of soils on Mars.

A number of measurements from the Mars Pathfinder and Mars Exploration Rovers suggest that soils on Mars may be enriched in P relative to the rock [5-7]. Measurements of the composition of dust collected on the magnets of the Mars Exploration Rovers also indicate that the dust may be enriched in P relative to soil [8]. Previous observations have documented variation in P content in martian soils and rocks attributed to aqueous alteration [9]. Rock classes Watchtower, Wishstone, and Independence are enriched in P relative to the P: Ti ratio consistent with igneous fractionation, suggesting enrichment in P through aqueous processes. In contrast, the rock class Fuzzy Smith is depleted in P relative to this P: Ti ratio, suggesting leaching of P through aqueous processes [9]. Phosphorus contents in different subclasses of the Laguna Soil Class also vary, with the Liberty subclass and Doubloon subclass enriched in P [9]. This variation suggests that P addition and loss may be important processes affecting the most common soil class present in Gusev Crater.

Phosphate behaves differently under different conditions of pH, water: rock ratio, time and oxidation state. Under different conditions, phosphate adsorbs onto mineral surfaces, substitutes as a trace element into other mineral phases, forms amorphous precipitates, and forms secondary crystalline phases. Phosphate may therefore be important in recording environmental conditions important to habitability in soils and rocks on Mars. Here we use reactive transport modeling to test the effect of environmental conditions on phosphate behavior which may be preserved in rocks and soils on Mars, and compare these results to observations from Mars.

Methods: Reactive transport modeling of chemical weathering was performed using CrunchFlow, written by Carl Steefel at Lawrence Berkeley National Laboratory [10]. Weathering was conceptualized as occurring within a 1-m thick layer of soil or sediment consisting of a mixture of olivine, apatite and basalt [9, 11]. To constrain the modeling, weathering is considered similar to previous column dissolution experiments of a mixture of apatite, olivine and basalt, leached under acidic conditions [12], and reactive transport modeling of those experiments [13]. The reacting solution at the surface was conceptualized as dust dissolved in solution, with the chemical composition constrained by chemical measurements of martian dust [8], the solubility of primary minerals, and dust settling rates on Mars measured by the Mars Pathfinder [14, 15]. Solution infiltration rates were varied, but were always less than flow rates from carbonate-forming desert environments on Earth corrected for evaporation [16]. Dissolution rates for basalt, olivine, and fluorapatite were from the literature [17]. Secondary minerals allowed to precipitate included strengite, variscite, vivianite, brushite, amorphous silica and hydroxylapatite. Work is ongoing to add more amorphous phases, likely important in weathering environments on Mars [18] and a broader range of Mars relevant primary phosphate minerals [19]. Models were run under a variety of environmental parameters important to habitability to test for distinct signatures of those conditions in the behavior of phosphate within the weathering environment.

Results and discussion: When phosphate-rich parent material is reacted with pure, acidic solutions, the minerals are heavily leached, which may be similar to rocks on Mars such as Fuzzy Smith. When input solutions are more concentrated, reflecting the presence of significant dissolved dust in reacting solutions, secondary phosphates precipitate (Figure 1). Analyses from Meridiani Planum indicate enrichment in phosphate, consistent with the addition of dissolved phosphate [7]. Enrichment of P due to phosphate precipitation from dissolved dust is also consistent with the variability in P content in different subclasses of the Laguna Class soils, and may help explain the enrichment observed in Watchtower, Wishstone, and Independence [9]. The relative proportion of water: dust inputs is therefore likely preserved in phosphates on Mars, with abundant water causing heavily leached rocks and soils, less water leading to dissolution and reprecipitation of phosphate minerals in the soils, and very minimal water causing primarily physical deposition of dust.

In our model results, solution pH is also preserved in secondary phosphates. Under acidic conditions
(pH = 3), only strengite precipitated (Figure 1A). Under more alkaline conditions (pH = 8.3), both strengite and hydroxylapatite precipitated (Figure 1B).

Conclusions: Reactive transport modeling results indicate that the water: dust ratio is preserved in the phosphate content of weathered rocks and soils, with dilute solutions causing leaching, and more concentrated solutions, resulting from a higher concentration of dust relative to water, causing precipitation of secondary phosphates. Analysis of phosphates within weathering environments may therefore yield information about the total water that has interacted with the rocks and soils. The pH of the reacting solution is also preserved within the phosphates, with strengite precipitating under acidic conditions, and predominantly hydroxylapatite (with strengite) under alkaline conditions. Modeling is ongoing to test the effect of additional environmental conditions important to habitability. Future analyses of phosphates on Mars may yield important information about constraints on habitability in environments containing this important nutrient.

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References: