EXAMINING PHOSPHATE MOBILITY IN GALE CRATER, MARS USING KINETICS AND THERMODYNAMICS.

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Introduction: Understanding phosphate mobility is crucial to understanding the history of Mars. Phosphate is a critical nutrient and present in all known terrestrial life forms as a part of DNA, RNA, ATP, and phospholipid membranes; interactions of phosphate minerals with biota and organic compounds have been previously proposed as potential biosignatures [1]; and precipitation of phosphate minerals can help preserve biosignatures [2]. Phosphate is abundant on Mars, present at about 10x the average concentrations as on Earth, and due to the quickly dissolving nature of primary phosphate minerals on Mars [3], it is likely mobilized during water-rock interactions. The formation of secondary phosphate minerals can also be an important indicator of past environmental conditions on Mars [4, 5].

However, despite the importance and abundance of phosphate on Mars, multiple questions remain. For example, in the Murray formation in Gale crater, fluorapatite and jarosite are both detected in multiple drill samples [6]. Jarosite is an indicator of low pH conditions [7], and fluorapatite dissolves rapidly under acidic conditions [3]. Multiple hypotheses have been proposed to explain this behavior, including inhibition of apatite dissolution by Fe-phosphate precipitation [8] or Zn adsorption [9]; armoring of fluorapatite by other primary minerals [10]; that acidic fluids were not present long enough to dissolve all of the fluorapatite [6]; and that fluorapatite precipitated after the acidic fluids had been neutralized [6].
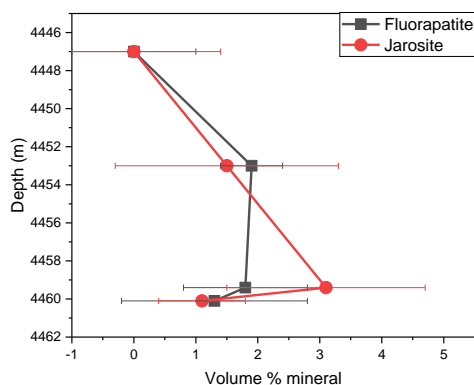

Figure 1. *CheMin measurements of jarosite and fluorapatite at Murray formation [6].*

In addition, measurements from the Murray formation also indicate that phosphate enrichment is observed both in the presence of enrichments of manganese and depletions of manganese [10, 11]. In order to interpret the behavior of phosphate in Gale crater, Mars, we performed reactive transport modeling of fluorapatite under scenarios relevant to depositional and diagenetic environments preserved by the Murray formation, and examined published dissolution rates and solubilities of Mn-phosphates.

Methods: In order to test potential conditions under which fluorapatite and jarosite are both present during water-rock interactions, we used the reactive transport code, CrunchFlow. CrunchFlow has been previously used to examine water-rock interactions in a variety of environments on Earth, including Costa Rica [12, 13], Svalbard [12], terrestrial chronosequences [14] and deep ocean sediments [15], as well as weathering of basalt [12], carbonates [16], phosphates [17], and sediments [18] on Mars. The mineralogy of the Murray formation was input into CrunchFlow as two layers of different compositions, with the top layer based on mineralogy measured by CheMin of the drill samples Buckskin and Telegraph Peak, and the bottom layer on samples Mojave and Confidence Hills [6]. The mineralogy of the layers consisted of plagioclase, pyroxene, olivine, magnetite, fluorapatite, glass, and hisingerite (both layers), cristobalite and tridymite (top layer), and nontronite (bottom layer). In addition to jarosite, the secondary phases amorphous silica, hematite, ferrihydrite, gypsum, and clinochlore were included. Fluids were modeled from top to bottom of the sedimentary stack.

Results: Modeling results indicate the persistence of fluorapatite and the formation of jarosite under conditions that were acidic, sulfate- and K-containing, and where water-rock interactions occurred for short periods of time (Figure 2). A small amount of fluorapatite also precipitated as the pH of the interacting solution increased with reaction with the minerals (Figure 2). These results are consistent with previous interpretation of the presence of both jarosite and fluorapatite in Murray formation [6], discussed above. In addition, examination of the dissolution rates of Al- and Fe-phosphates, which dissolve less rapidly than fluorapatite (Figure 3), support potential inhibition of fluorapatite dissolution by Al- and Fe-phosphate-containing phases.

In addition to the importance of Fe- and Al-phosphates to phosphate mobility in terrestrial environments [19], previous work has also indicated that

manganese phosphates may be important in terrestrial soils [20]. For example, measurements of multiple soils indicate that solutions in most of the soils studied were oversaturated with respect to $MnPO_4·1.5H_2O$, and $Mn_3(PO_4)_2·3H_2O$ and $MnPO_4·1.5H_2O$ have been shown to be thermodynamically favored to precipitate under relatively low concentrations of phosphate [20]. On phosphate-rich Mars, therefore, manganese phosphate may be present and important in aqueous systems.
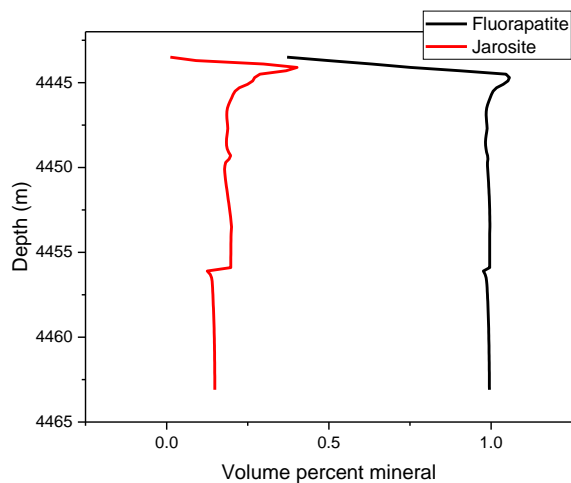

Figure 2. Reactive transport modeling results showing the precipitation of jarosite and persistence and small amounts of precipitation of fluorapatite under acidic (pH =2), sulfate- and K-containing, and short duration conditions.
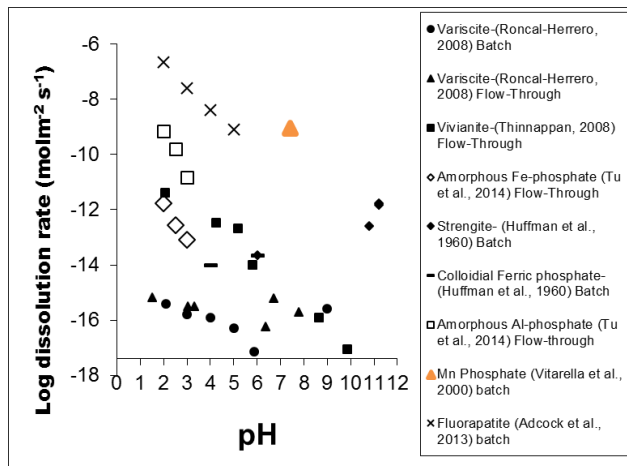

Figure 3. Dissolution rates of fluorapatite and Fe, Al, and Mn phosphates show that fluorapatite dissolves more rapidly than Fe- and Al-phosphates. Few data are available for Mn-phosphate dissolution. Figure modified after [21] with data from [19](variscite), [22] (vivianite), [21] (amorphous Al- and Fe-phosphates), [23] (strengite and colloidal ferric phosphates), [3] (fluorapatite), and [24] ($Mn_5(PO_4)_2(PO_3(OH)_2·4H_2O$).

However, very limited data are available measuring the dissolution rates of Mn phosphates (Figure 3). Mn phosphates may dissolve rapidly relative to other phosphates, but much more work is needed to examine the behavior of Mn phosphates.

Conclusions: Understanding phosphate mobility is critically important to interpreting the aqueous alteration history of Mars because phosphate is essential for life, potentially important for biosignatures, and because the dissolution and precipitation of phosphate minerals can provide a record of past aqueous conditions on Mars. Reactive transport modeling indicates precipitation of jarosite, and both preservation as well as small amounts of precipitation of fluorapatite under short-term, acidic, K- and sulfate-containing water-rock interactions, consistent with previous observations [6]. Slower dissolution rates of Fe- and Al-phosphate minerals relative to fluorapatite are consistent with their potential inhibition of fluorapatite dissolution (Figure 3). Enhanced phosphate concentrations in the presence of manganese may be consistent with the presence of manganese phosphates, which are thermodynamically favored in terrestrial soils [20], and may be mobile in martian soils (Figure 3). More work is needed to understand phosphate cycling on Mars.

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