REACTIVE TRANSPORT MODELING OF PHOSPHATE MINERAL DISSOLUTION IN HIGH-P MARTIAN ROCKS.

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Introduction: Phosphate is among the nutrients considered critical for all known life [1-4]. The ion is a component in ATP, DNA, RNA, phospholipid cell membranes and required in numerous fundamental biochemical reactions [5]. Phosphorus, either as phosphate or a more reduced species such as phosphite, is also considered crucial in pre-biotic reactions that may have led to the origin of life on Earth [5-7]. A determining factor for the potential of Mars to develop and maintain life may therefore be the availability of phosphorus.

Though Mars is rich in phosphate (5-10x Earth) [8-11], the presence of phosphate alone is not equivalent to phosphate availability. Unlike other bioessential nutrients, phosphate has no significant volatile phase and remains locked in phosphate-bearing minerals within rocks until rock/water interactions release it into the environment [12].

On Earth, the most common primary phosphate mineral is fluorapatite ($Ca_5(PO_4)_3F$). The dissolution of fluorapatite in igneous rocks is a major source of inorganic phosphate available for biological reactions. In contrast, meteorite evidence suggests the most abundant primary phosphate minerals on Mars are Cl-rich apatite ($Ca_5(PO_4)_3Cl$) and the extraterrestrial mineral merrillite ($Ca_9(Na,Fe,Mg)(PO_4)_7$) [13]. The dissolution and release of phosphate from these primary phosphate minerals is likely the main source of phosphate in Martian environments, and therefore important in investigating the potential for the origin and persistence of life on Mars. In previous studies we have synthesized chlorapatite and merrillite (Figures 1 and 2) [14, 15] and measured the dissolution rates and solubilities of these more Mars-relevant primary minerals [11, 16]. In addition, we have also examined phosphate mobility in basalts of a Mars-analog environment, Craters of the Moon National Monument in Idaho [17]. Here we use results of these previous studies and reactive transport modeling to investigate the dissolution and release of phosphate from phosphate-rich martian rocks (e.g. Wishstone) during rock/water interactions, to gain insight into past and present martian phosphate availability, aqueous interactions, and the implications for life, past, present, or future on Mars.

Methods: Modeling is being carried out using the reactive transport code CrunchFlow. CrunchFlow is a computer model written by Carl Steefel [18] for simulating multicomponent, multi-dimensional, reactive transport in porous media. The program reads required thermodynamic and kinetic data from an included user modifiable database and allows mineral dissolution and precipitation reactions to be modeled. The code has been used in previous studies including those applied to Mars [19-23]. In our current modeling a Wishstone class rock is conceptualized as a column of 100 cells of 50 μm depth representing the rock surface to the interior. Rock mineralogy is based on a CIPW normative of major minerals using MER Spirit APXS and Mössbauer data [24]. Because the exact primary phosphate mineral in Wishstone class rocks is unknown, we run separate models for a merrillite, and a chlorapatite bearing Wishstone rock. For comparison we also model mineral dissolution in a fluorapatite containing Wishstone rock. Thermodynamic and kinetic data for the Ca-phosphate minerals are derived from our previous work [11]. For the remaining minerals we use previously published values [25-27]. Parameters such as porosity, tortuosity, and mineral surface area are based on typical basalt values [28-30] and our observations from basalts of Craters of the Moon National Monument [17]. In our current modeling, rock/water interaction is modeled with a low ionic strength water of variable pH at 1°C and under martian atmospheric conditions. During modeling, mineral volumes, surface areas, porosity, and other parameters are updated within CrunchFlow after each time iteration. Models are run for up to 100,000 years of water-rock interaction.
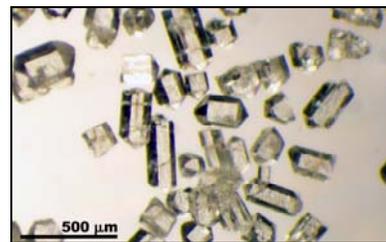

Figure 1. Synthetic chlorapatite produced in previous work by the authors [11, 15] and used to derive dissolution and solubility data used in this research [11].
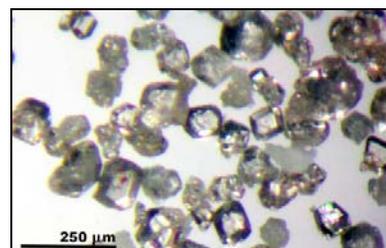

Figure 2. A sample of merrillite produced in previous work by the authors (here, a Fe-bearing version)[15]. The authors also produced Mg-bearing species and derived the kinetic and thermodynamic data used in this study from them [11].
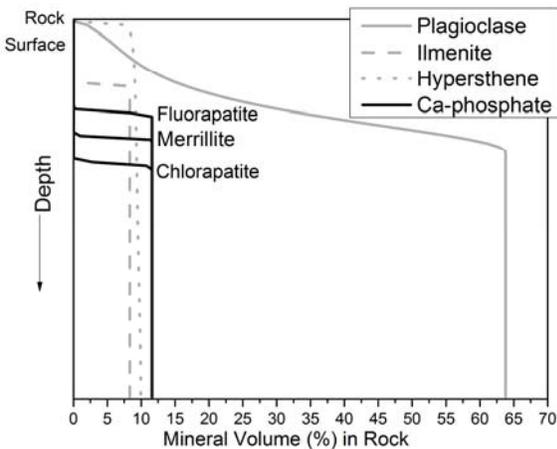
Figure 3. Dissolution profiles from three model runs with the three different Ca-phosphate minerals (fluorapatite, merrillite, and chlorapatite) modeled for 10,000 years of aqueous interaction at pH 5.

Results and Discussion: In Figure 3 dissolution profiles from three models run with the three different Ca-phosphate minerals have been overlain (model time 10,000 years with pH 5 interaction waters). Dissolution depths of the non-phosphate minerals do not significantly change between models, and therefore the minerals are only shown from the chlorapatite model. However, the faster dissolution rates and higher solubilities of the more Mars-relevant phosphate minerals result in deeper dissolution of those minerals relative to fluorapatite. Chlorapatite and merrillite dissolution are among the deepest of all the modeled minerals in the rock, broadly consistent with Spirit APSX observations indicating the weathering of only a calcium and phosphate mineral from Wishstone class rocks [31]. It is also of note that this model was run with interaction waters having an initial pH value of 5. Previous research has suggested the unique phosphate mineral weathering profiles of Wishstone class rocks are the result of highly acidic weathering [32]. These modeling results suggest such weathering profiles might occur under more neutral conditions. Brushite is a Ca-phosphate mineral also suggested as plausible within Wishstone class rocks, although it is a secondary mineral usually formed by precipitation [31]. Initial modeling using brushite as the phosphate bearing mineral in a conceptualized Wishstone rock shows trends similar to the other Ca-phosphate modeling, with brushite having the deepest dissolution profile into the rock, even greater than that of merrillite or chlorapatite under similar conditions. Our results combined with the overall higher abundance of phosphate on Mars in general, suggest phosphate release during aqueous interactions on Mars may be greater than that of Earth. Thus, in otherwise habitable environments on Mars, phosphate availability for potential prebiotic and biotic reactions should be comparatively higher than for Earth, a positive implication for the potential of past or present martian life.

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