KINETIC STUDIES OF PHOSPHATE CONTAINING MINERALS AND IMPLICATIONS FOR MARS.

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Introduction: Water is a required environmental component for life as we currently understand it. As such, understanding the role of water in the environments of planets other than Earth gives us greater insight into the possibility of life, extant or extinct, on those planets. Though Mars is relatively dry today, it is an ideal target of study, as it shows abundant evidence of once having water in the liquid state at the surface and near surface [1]. Geomorphic evidence suggests that multiple bodies of water could be discrete, such as isolated springs or lakes [1]. The pH of these discrete water bodies could have been highly variable and evidence of both acidic and basic environments has been noted for Mars [2, 3]. Residence times, solution chemistry, and temperature may also have been highly variable. This variability in pH, chemistry, and presence of water from location to location has broad implications for large region hydrologic Martian modeling, as well as for the possible development of life. Knowing where water bodies existed, when, and of what chemical character, will greatly improve our understanding of past hydrologic conditions on Mars and the implications for life.

A comprehensive understanding of dissolution rates of minerals and their alteration products, and surface or near surface concentrations derived from orbital remote sensing, Mars landers, future sample return, or meteorites, can yield info about the presence, duration, and pH of past surface and near surface waters. The presence of one mineral and absence or alteration product of another, for example, can be an indicator of contact time with a solution, the solution pH, and temperature [4,5]. Such contact times can be calculated as mineral lifetimes using laboratory dissolution rates (e.g. [6]) by the expression

$$t = \frac{d}{2V_m r} \qquad \textbf{(Eq. 1)}$$

where d is grain diameter, V_m is molar volume, and r is the dissolution rate [7]. Dissolution rates for olivine, fluorapatite, and basalt glass at 298 K are shown in Figure 1. Figure 2 depicts the corresponding mineral lifetimes with d=1mm (similar to [8]).

Mineral lifetimes for Mars conditions have been calculated for minerals such as olivine [8] and the sulfate bearing mineral jarosite [9]. Such lifetimes for phosphate bearing minerals are of interest concerning Mars. Phosphate mobility, which is tied to mineral dissolution, has been suggested as an indicator of Martian aqueous activity [10] and surface rock analyses from the Mars Exploration Rover (MER) Spirit indicate the loss of a phosphate bearing mineral [11].

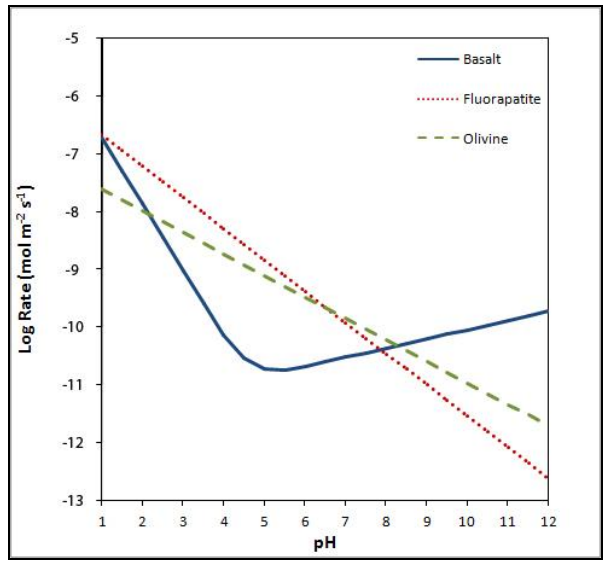

Figure 1. Dissolution rates of basalt glass, olivine, and fluorapatite. Rate laws from [6] versus pH.

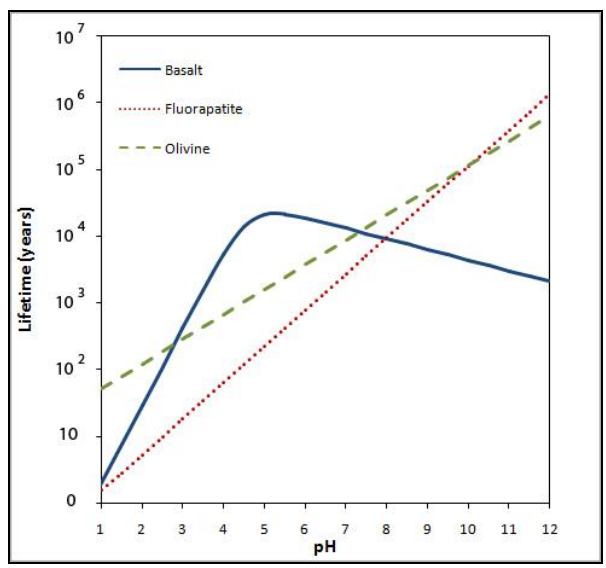

Figure 2. Mineral lifetimes of basalt glass, olivine, and fluorapatite. Calculated from kinetic rate laws [6] and the disappearing sphere model (Eq. 1).

Multiple studies have examined the dissolution rates of the phosphate mineral fluorapatite [12,13,14]. However chlorapatite and merrillite are more common

phosphate bearing minerals on Mars [15] and are not as well studied. Therefore, we are focusing our research on chlorapatite and merrillite dissolution behavior in order to calculate dissolution rates (similar to Figure 1) and mineral lifetimes (similar to figure 2) for these Mars relevant minerals.

Methods: Natural chlorapatite from Kragero, Norway, has been obtained from Minerals Unlimited. Whitlockite from Palermo #1 mine in New Hampshire has been obtained as a terrestrial substitute for merrillite. Natural minerals are used, rather than synthetic, as a better analog to minerals that may be found on Mars. Additionally, fluorapatite from Durango, Mexico, a well characterized mineral [16], has been obtained from Minerals Unlimited. Since there are a number of dissolution studies of fluorapatite, dissolution rates of the mineral will be studied under the same conditions as the chlorapatite and whitlockite, and compared to the results of previous studies for correlation.

All samples are now in the process of being reduced in particle size using a steel impact pestle and platen, picked to purify where needed, followed by grinding in an automated agate mortar and pestle to obtain a 75-150um size fraction. The resulting 75-150um target size fraction will then be washed to remove any statically adhered fine particles. Batches of the washed material will be agitated in solutions of variable pH and temperature. Solution will be extracted from the experiments at predetermined intervals and analyzed for chemistry that has been leached from the original sample. The resulting analyses will be compiled to form dissolution rate curves at variable temperature and pH conditions, similar to Figure 1. In addition, mineral lifetimes, similar to Figure 2, will be calculated for the more Mars relevant minerals chlorapatite and whitlockite.

Expected Conclusions: We expect dissolution rates and mineral lifetimes to help constrain time intervals associated with phosphate mobility on Mars, such as that observed in MER Spirit rock surface data [11]. We further expect this research to indicate whether dissolution rates of chlorapatite and whitlockite are significantly different from fluorapatite, and what the implications are for water contact times and phosphate mobility from these Mars relevant minerals.

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