THE DISSOLUTION RATE OF WHITLOCKITE AND IMPLICATIONS FOR THE HABITABILITY OF EARLY MARS.
C. T. Adcock[1] and E. M. Hausrath[1], [1]Department of Geoscience, University of Nevada Las Vegas 4505 S. Maryland Parkway, Las Vegas, NV 89154, adcockc2@unlv.nevada.edu

Introduction: Phosphate is an essential element for life as we understand it. The phosphate anion is a component of ATP which provides the energy required for cellular operations [1,2]. Phosphate is also a structural component of RNA and DNA [3] and has been suggested to have played multiple prebiotic roles on Earth [2,4] including the formation of prebiotic RNA [5]. If life ever arose on Mars, it would likely be significantly influenced by phosphate availability.

Mars is generally phosphate rich as evidenced through SNC meteorites [6], and both primary and secondary phosphate minerals have been observed in Martian meteorites [7]. Surface rock analyses from MER Spirit show the loss of a phosphate mineral, possibly merrillite, from Wishstone and Watchtower class rocks at Gusev Crater [8-10]. This indicates phosphate mineral dissolution and past aqueous activity. A strong understanding of dissolution of Mars relevant phosphate minerals under Martian conditions can yield insights into the bioavailability of Martian phosphate for prebiotic chemistry and possible life.

On Earth, fluorapatite is the most common primary phosphate mineral [11] and previous studies have measured dissolution rates of fluorapatite [12-14]. Fluorapatite is also found in Martian meteorites [15] and thus presumably exists on Mars. However, chlorapatite and merrillite (an extraterrestrial end-member of whitlockite) [16,17] have been identified as well [7,18,19], and are more common phosphate minerals in Martian meteorites, with merrillite being the predominant mineral [7]. Few dissolution data exist for these Mars relevant minerals.

Whitlockite and merrillite are structurally and chemically similar, and differ only by structural adjustments that result from the accommodation of hydrogen in whitlockite [16]. Therefore the two minerals likely exhibit similar dissolution behaviors. Here we report dissolution rate results for the mineral whitlockite as part of a broader research study to establish rate laws for Mars-relevant phosphate minerals. Additionally, we report measured dissolution rate data for Durango fluorapatite acquired using the same methods. Durango fluorapatite dissolution is well studied [12-14] and we compared our results with those in the literature as a method check.

Methods: Whitlockite (Figure 1) was synthesized hydrothermally using a method based on Hughes et al., 2008 [16]. Durango fluorapatite was obtained from Minerals Unlimited of Ridgecrest, California. Mineral phases were confirmed by XRD prior to dissolution experiments.

Minerals were reduced in size using an agate mortar and pestle and sieved to obtain 38-75µm and 75-150µm size fractions for whitlockite and fluorapatite respectively. Resulting powders were cleaned by agitating and sonicating in ethanol repeatedly until the supernatant was clear. Dissolution rates were measured by the batch initial rate method [see 20,21]. This method uses early chemical changes that occur in far from equilibrium closed batch experiments to determine dissolution rates and has been demonstrated to yield comparable results to other experimental methods [20]. Batch dissolution experiments were run from pH values of 2 to 5 to determine a dissolution rate law as a function of pH.

Figure 1. Reflected light microscope image of synthetic whitlockite crystal grown as part of this study.

Each batch experiment consisted of a 0.01 molar KNO_3 solution adjusted to a required pH with HNO_3. LDPE reaction vessels were filled with 180ml of the solution and 0.150g or 0.300g of mineral powder for whitlockite or fluorapatite experiments respectively. The vessels were sealed and placed in a 25˚C agitated water bath. At intervals determined through preliminary experiments, 10ml samples were taken from each batch and analyzed for Ca by flame AA. Dissolution rates were calculated from the rate of change of elemental concentration in solution as a function of time, and normalized to the mineral surface area as determined by BET.

Results: Whitlockite dissolution experiments were run in duplicate at pH values of 2, 3, 4, and 5 and are plotted in Figure 2 (circles). The fitted line (solid) represents a whitlockite rate law based on these data. Figure 2 also includes fluorapatite dissolution rates measured in this study (triangles) and a fluorapatite rate law based on these data (dashed). The fluorapatite rate law from this study falls within half an order of magnitude of that based on a compilation of studies [12-14,22] and we are confident our method is producing results comparable to those in the literature.

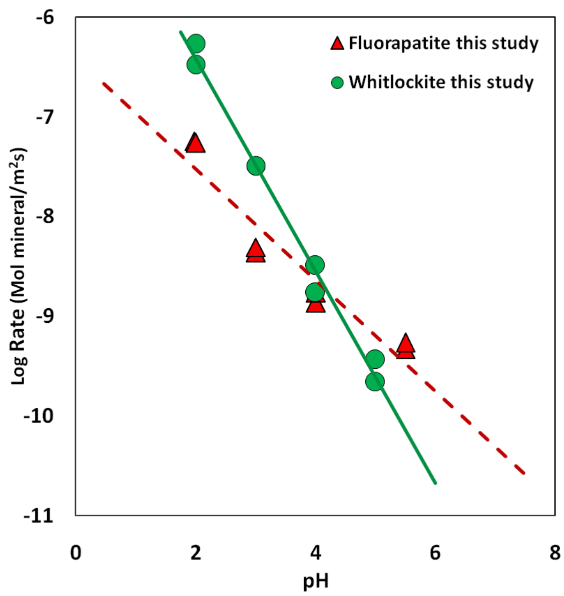

Figure 2. Results of whitlockite (green circles) and fluorapatite dissolution (red triangles) with rate laws (lines) determined from those data.

Discussion: The rate law for whitlockite derived in this study indicates that whitlockite dissolution proceeds at a faster rate than fluorapatite at pH values of <4. This has implications for Mars. Acidic waters on Mars are possible as evidenced by the identification of the secondary mineral jarosite at Meridiani Planum which typically forms under acidic aqueous conditions [23,24]. The combination of merrillite, a mineral very similar to whitlockite, as the predominant phosphate mineral on Mars, and past acidic aqueous conditions, could mean that phosphate dissolution on Mars has occurred at a significantly greater rate than on Earth. Past and present Martian phosphate availability may therefore be significantly higher than that of Earth, thus mitigating phosphate availability as a limiting factor for life on Mars.

Future Work: We are currently finalizing a whitlockite rate law. Rate laws for chlorapatite and merrillite are also to be determined. These data will be used in future reactive transport modeling to better characterize and quantify Martian phosphate mineral dissolution.

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