

**SYNTHESIS OF PHOSPHATE MINERALS FOR USE IN DISSOLUTION EXPERIMENTS.** C. T. Adcock, A. C. Simon, E. M. Hausrath University of Nevada Las Vegas, Department of Geoscience 4505 S. Maryland Pkwy, Las Vegas, NV 89154. Adcockc2@unlv.nevada.edu.

**Introduction:** A comprehensive understanding of dissolution rates of minerals combined with Mars mission data or data from Martian meteorites can yield information regarding aqueous activity including elemental mobility and cycling, and the presence, duration, and chemical characteristics of past surface and near surface Martian waters [1-4]. Such information is vital to our understanding of past hydrologic conditions on Mars and has implication for the possibility of extant or extinct life on the planet.

Of particular interest to Martian mineral dissolution studies are the phosphate minerals. Phosphate is an essential nutrient for life as we know it and has broad implications to biologic studies of Mars. Mars is about ten times richer in phosphorus than Earth [5] and phosphates have been found in Martian meteorites [6]. Analyses from the Mars Exploration Rover Spirit indicate the loss of a phosphate-bearing mineral in rock surfaces [7, 8] which implies phosphate mobility and mineral dissolution. Laboratory dissolution data exist for the phosphate mineral fluorapatite, but other Mars relevant phosphates such as chlorapatite and merrillite found in Mars meteorites have not been well studied and dissolution rate laws are lacking. In order to interpret the rates of release of phosphate from these minerals on Mars, dissolution experiments to develop a rate law are required.

Mineral dissolution experiments require well-characterized mineral material. Here we report syntheses of chlorapatite and whitlockite, which we will use in dissolution experiments similar to those we are currently performing with fluorapatite [9].

#### Methods:

##### *Chlorapatite*

We used modified methods based on those of Prener [10, 11]. Modified versions of Prener's methods have been used by a number of researchers to synthesize small amounts of chlorapatite [12-15]. A mixture of  $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$  was thoroughly mixed with  $\text{CaCl}_2$  in a ratio of 3:4 respectively, by weight. Pt tubes of 5mm diameter and ~25mm length were annealed and welded on one end. Approximately 0.2g of the mixture was packed into the Pt vessels and the filled, open top, vessels were desiccated under vacuum overnight at 100-110°C. Immediately upon removing the tubes from vacuum, the open ends were tightly crimped and the tubes placed in a 1080-1100°C box furnace for 24 hours. At 24 hours, the Pt tubes were removed from the furnace and cooled in air.

##### *Whitlockite*

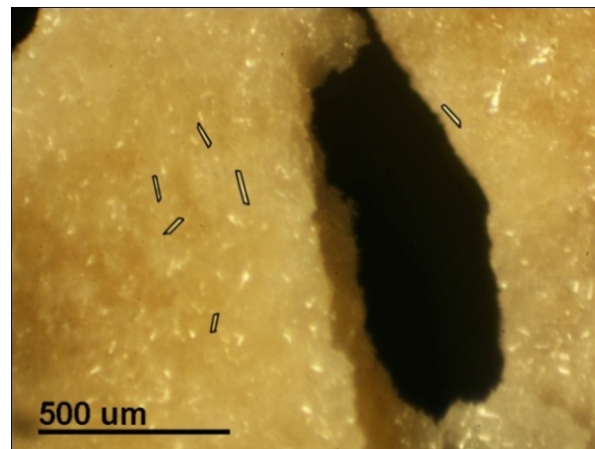
Hughes et al. 2008 [16] document the inadvertent synthesis of small quantities of whitlockite at 240°C in

sealed reaction vessels. We replicated the Hughes et al. procedure, but intentionally provided the Mg in the form of  $\text{Mg}(\text{NO}_3)_2 \cdot 6(\text{H}_2\text{O})$ . A dry mixture of 4 parts  $\text{Mg}(\text{NO}_3)_2 \cdot 6(\text{H}_2\text{O})$  and 13 parts  $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$  was loaded into 23 ml PTFE lined acid reaction vessels (Parr #4749). The amount of mixture loaded into the vessel was varied from 0.066g to 0.945g. Approximately 12 ml of 18MΩ de-ionized water was added to the vessel and gently stirred. The pH of the solution was then adjusted to <2.8 with phosphoric acid as per Hughes et al [15]. The vessels were sealed and placed in a 240 (+/- 3) °C oven for times varied from 5 to 14 days.

*Characterization and Identification of products.* Products of synthesis experiments were dried (where required) and imaged in a Barska binocular scope with a mounted camera at 90x magnification. Particle measurements were made using the acquired images and a photo analysis tool (Adobe PhotoShop). The synthesis products were then analyzed in a PANalytical X'Pert Pro X-ray Diffractometer. Identifications were made using X'Pert Highscore Plus software.

#### Results:

*Chlorapatite results.* Figure 1 is an image of synthesized crystals in an aggregate mass identified by XRD as chlorapatite. A few individual crystals are outlined for clarity. Crystals in the mass are acicular, 50-100um long, and 10-20um wide.



**Figure 1. Synthetic acicular chlorapatite crystals. Black outlines define individual crystals.**

*Whitlockite results.* Figure 2 is an image of synthesized material identified by XRD as whitlockite from a batch containing 0.066g of mixture and run for 5 days. Figure 3 is a large crystal from a similar batch of 0.066g run for 10 days. Generally, longer run times

result in a wider size distributions and larger overall crystal sizes. Although most runs produced pure whitlockite, at higher concentrations monetite was formed. Monetite is a calcium phosphate which may also be present on Mars [17].

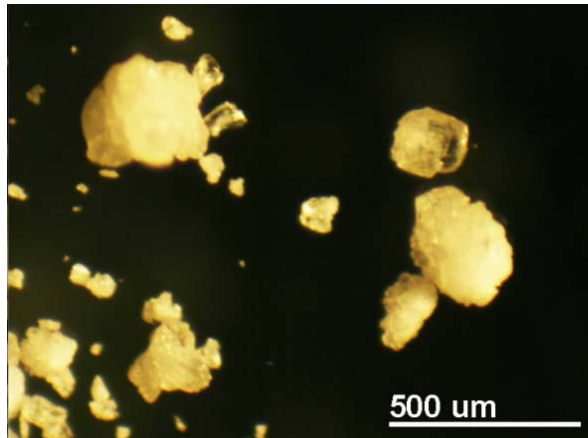


Figure 2. Synthetic whitlockite from a 5 day run.



Figure 3. Large (>1mm) synthetic whitlockite crystal produced in a 10 day run.

**Conclusions and Future Work:** We have successfully synthesized single phase products of the phosphate minerals chlorapatite and whitlockite. We will synthesize merrillite, a non-terrestrial mineral, from whitlockite after [16] and use these synthesized minerals in dissolution experiments similar to those we are currently performing to develop rate laws for interpretation of phosphate mobility on Mars.

**Acknowledgements:** This work was supported by a Nevada Space Grant Graduate Fellowship and the Mars Fundamental Research Program. We would also like to thank Dr. Christopher Tacker of the North Carolina Museum of Natural Sciences for assistance with synthesis methods.

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