

DISSOLUTION RATES OF AMORPHOUS AL- AND FE-PHOSPHATES AND THEIR RELEVANCE TO MARS.

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Introduction: Phosphorous is a vital element for life on Earth, found in DNA, RNA, and ATP [1, 2, 3]. Therefore, if life has ever existed on Mars, it may have required phosphate. Unlike other nutrients such as C, S, O, H, and N, P does not have a gaseous phase [4], and phosphate availability is therefore directly related to mineral dissolution.

Due to its importance, multiple studies have examined phosphate on Mars. Phosphate-containing primary minerals including fluorapatite [5], chlorapatite [6], and merrillite [7] are present in Mars meteorites. Previous work [8], has indicated that P in Paso Robles soils on Mars may occur in Ca- and Fe-phosphates based on Alpha Particle X-ray Spectrometer (APXS) and Mössbauer Spectrometer results. Mössbauer results indicate the Fe-phosphate minerals ferristrunzite or strengite may be present in Paso Robles soils [9]. Acidic Mars-analogue experiments [10] indicate the formation of an Fe-phosphate phase. Enrichments in phosphates were identified by the Martian rover Opportunity within outcrops at Eagle Crater on Mars [11] and Mini-TES measurements indicate the possible identification of the secondary phosphate phase wavellite in Wishstone and Watchtower rocks [12].

Laboratory syntheses of Al- and Fe-phosphates [13] indicate that 90% of what is first precipitated from super saturated phosphate solutions is amorphous. Amorphous Al- and Fe-phosphates can persist at room temperature for greater than four years indicated by [14]. The persistence of amorphous Al- and Fe- phosphates may therefore be important in soils on Mars. Few dissolution rates, however, have been measured for amorphous Al- and Fe- phosphates. Measuring the dissolution rates of amorphous Al- and Fe-phosphates may therefore help to constrain the availability of phosphorus in weathering environments on Mars.

Materials and Methods:

Material synthesis and characterization:

Amorphous Al- and Fe-phosphates were synthesized in batch reactors after [13], except that syntheses were performed at 50°C for 24 to 48 hours, continuously shaken at 100 strokes per minute and larger volumes used to yield sufficient mass for dissolution experiments. In all cases, solutions were made with 18.2 M Ω deionized water and high purity Al(NO₃)₃, Fe(NO₃)₃, KH₂PO₄ and KOH.

After 24-48 hour agitation in the 50°C water bath, reactors were cooled to 25°C, and the slurry centrifuged at 9860 rpm for 2-10 minutes until supernatants were clear to separate synthesized phosphates. Super-

natants were decanted, and then the solid phases washed 3 times with 18.2 M Ω deionized water and air dried.

Dissolution Experiments:

Batch reactors were used to measure dissolution rates of amorphous Al- and Fe-phosphates to calculate a preliminary rate law. Acid washed 250 ml polypropylene reactors contained 0.3000 ± 0.0005g of amorphous Al- or Fe-phosphate combined with 180 ml of 0.01M KNO₃ solution adjusted to the pH of interest (pH= 3 and 5). Changes in solution chemistry with time were normalized to the BET surface area to calculate a dissolution rate, and the rate law calculated from the dissolution rates as a function of pH. The interpretation of batch reactors is complicated by the fact that solution chemistry changes with time. Therefore, in order to maintain constant solution chemistry during reaction, we are currently performing dissolution experiments using flow-through reactors based on those used by [15]. Flow-through reactors, although more difficult to run than batch dissolution reactors, are easier to interpret.

In our flow-through reactors (Figure 1), solution is pumped from a feed solution tank, using a peristaltic pump, into the reactor where the solution interacts with the mass (0.3-1.5g) of Al- or Fe-phosphate. Solution flows out of the reactor into a collection vessel, from which output solutions are collected at predetermined intervals. Solution samples are filtered through 0.45μm filters, acidified to 1% v/v, and stored at 4°C until chemical analysis. Aluminum concentrations are measured by the catechol violet colorimetric method [16], and phosphate concentrations are determined by the molybdate blue colorimetric method [17] on a Thermo Scientific Genesys 10S UV-VIS Spectrophotometer. Flame atomic absorption spectroscopy (AAS) is used to measure Fe concentrations on a Thermo Scientific iCE 3000 series AA spectrometer.

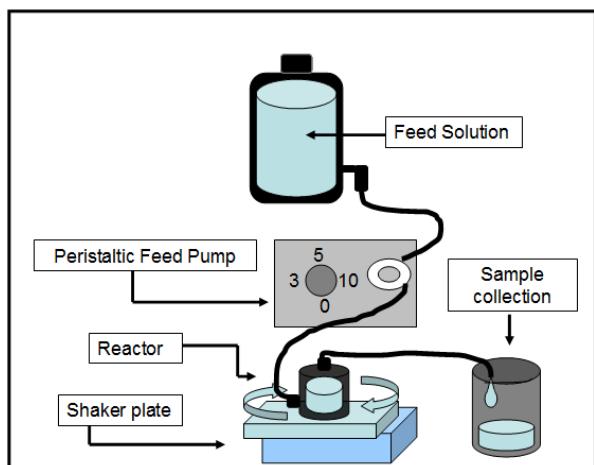


Figure 1- Schematic image of our flow-through reactor.

Dissolution Rate Calculation:

Dissolution rates are calculated from steady state Al, Fe and PO₄ concentrations, and flow rates normalized to BET surface area (equation 1):

$$R = \frac{(C_{out} - C_{in})Q}{A \cdot m} \quad (\text{Eq. 1})$$

where C_{out} is the measured steady state output concentration, C_{in} is the input concentration, Q is the flow rate, A is the specific surface area, and m is the mass. Preliminary rates calculated in this manner suggest that the amorphous Fe-phosphate phase dissolves faster than its crystalline counterpart.

Conclusion: Amorphous Fe- and Al-phosphates have been synthesized and dissolved in batch and flow-through reactors, and a preliminary rate law measured. Rates will be used to constrain possible P concentrations in Martian environments.

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References: [1] Wald, G. (1964), *GSA*, 52, 595-611. [2] Redfield, A.C. (1934), *In James Johnstone Memorial Vol.* (ed. R.J. Daniel) 177-192. [3] Madigan, M.T., J.M., Martinko, and J. Parker, (2000) *Brock Biology of Microorganisms*, 991. [4] Filippelli, G. (2008) Elements, 4, 89-95. [5] McCubbin, F.M. and Nekvasil, H., (2008) *Am. Min.* 93(4): 676-684. [6] Bridges, J.C.

and Grady, M.M., (2000) *Earth and Planetary Science Letters*. 176(3-4): p. 267-279. [7] Greenwood, J.P., Blake, R.E., Coath, C.D. (2003) *Geo. Chim. Acta*, 67, 12, 2289-2298. [8] Ming, D.W., Mittlefehldt, D.W., Morris, R.V., Golden, D.C., Geller, R., Yen, A., Clark, B.C., Squyres, S.W., Farrand, W.H., Ruff, S.W., Arvidson, R.E., Klingelhoefer, G., McSween, H.Y., Rodionov, D.S., Schroder, C., de Souza Jr., P.A., and Wang, A., (2006) *JGR*, 111, 1-23. [9] Lane, M. D., Bishop, J. L., Dyar, M. D., King, M. P., and Hyde B. C., (2008) *Am. Min.*, 93, 728-739. [10] Tosca, N. J., S. M. McLennan, D. H. Lindsley, and M. A. A. Schoonen (2004) *JGR*, 109. [11] Rieder, R., Gellert, R., Anderson, R.C., Bruckner, J., Clark, B.C., Dreibus, G., Economou, T., Klingelhoefer, G., Lugmair, G., Ming, D.W., Squyres, S.W., d'Uston, C., Wanke, H., Yen, A., and Zipfel, J. (2004) *Science*, 306, 1746-1749. [12] Ruff, S. W., et al. (2006) *JGR*, 111. [13] Roncal-Herre, T., Rodriguez-Blanco, J. D., Benning, L. G., and Oelkers, E. H. (2009) *Crystal Growth and Design Article*, 9, 5197-5205. [14] Hsu, P. H. (1982) *Soil Sci.*, 133, 305. [15] Rimstidt, D. J., and Weissbart, E. J. (2000) *Geo. Chim. Acta*, 64, 23, 4007-4016. [16] Dougan, W. K., and Wilson, A. L. (1974) *Analyst*, 99, 413-430. [17] Murphy, J., and Riley, J. P. (1962) *Anal. Chim. Acta*, 27, 31-36.