

**DISSOLUTION OF AMORPHOUS AL- AND FE-PHOSPHATES: IMPLICATIONS FOR PHOSPHATE MOBILITY ON MARS.** V. Tu<sup>1</sup> and E.M. Hausrath<sup>1</sup>, <sup>1</sup>University of Nevada, Las Vegas 4505 S. Maryland Parkway, Las Vegas, NV 89154 [chavezv4@unlv.nevada.edu](mailto:chavezv4@unlv.nevada.edu).

**Introduction:**

Increasing evidence suggests the importance of amorphous phases on Mars. Amorphous weathering products, such as allophane, amorphous silica, and palagonite have been detected by orbital mid-infrared and *in-situ* mineralogical and chemical analyses [1, 2]. *In situ* measurements at Meridiani Planum outcrops indicate spectra consistent with opaline silica [3] and rocks within the Meridiani sulfate-bearing terrain contain amorphous silica [4, 5]. The CheMin instrument aboard the Mars Science Laboratory (MSL) has successfully identified amorphous phases, likely either basaltic glass, previously detected at Columbia Hills [6] or weathered basalt, similar to weathered basalts in Hawaii [7]. Under the water-limited conditions likely present on Mars, amorphous phases are likely to be important [8].

Roncal-Herrero et al. [9] report that the first phosphate-containing phases to precipitate in experiments from super-saturated acidic fluids are amorphous. Amorphous phosphate phases are also documented to persist for at least one year and up to 55 months in laboratory experiments without altering to crystalline phases [10]. The mineralogy of phosphate phases present on Mars is still not known. Previous work has indicated that P may occur in Ca-, Fe- and Al- phases on Mars based on Alpha Particle X-ray Spectrometer (APXS) and Mossbauer Spectrometer results [11]. Tosca et al. [8] indicate the presence of an Fe- phosphate phase in acidic Mars-analog experiments, and Ruff et al. [6] suggest that an Al-phosphate phase, wavellite, may be present in the Martian rock Watchtower. Sorbed phosphate phases may not be the dominant phase in Martian soils based on the lack of correlation between phosphorous and nanophase oxides in dusts encountered by the Mars Exploration rovers [12]. Due to the likely prevalence of amorphous phases on Mars due to limited water: rock interactions, and the rapid formation and persistence of amorphous phosphates on Earth, amorphous phosphate phases are likely important phosphate sources in weathering environments on Mars.

Despite their potential importance, however, few dissolution experiments have examined the dissolution rates of and phosphate release from amorphous phosphate-containing phases [13]. In this study, we measure the dissolution rates of and phosphate release from amorphous Al- and Fe- phosphates, to shed light on phosphate mobility on Mars.

**Methods:**

*Materials*

Amorphous Al- and Fe-phosphates were synthesized in batch reactors after [9], except that syntheses were performed at 50°C for 24 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 chemicals. Aqueous solutions (0.1M Al- or Fe-(NO<sub>3</sub>)<sub>3</sub>, and 0.1M KH<sub>2</sub>PO<sub>4</sub> and 0.09M KOH) were preheated to 50°C, combined while continuously stirring and immediately sealed and immersed in a 50°C shaking water bath. Batches were harvested after 24 hours, cooled to 25°C, and the slurry centrifuged at 11.5 rad for 2-10 minutes until supernatants were clear. Supernatants were decanted, and solid phases washed 3 times with 18.2 M Ω deionized water and air dried at room temperature for 2-5 days. Powders were analyzed by X-ray diffraction (XRD) using a PANalytical X'PERT Pro X-ray Diffraction Spectrometer (XRD) in the X-ray Diffraction and X-ray Fluorescence Laboratory (XXL) at UNLV, and results indicate amorphous material. Powdered samples were gold coated and observed using a JEOL JSM-6700F Field Emission Scanning Electron Microscope (FE-SEM) and Scanning Electron Microscope (SEM) (JEOL ASM-5600) in the Electron Microanalysis and Imaging Laboratory (EMIL) at UNLV. Surface areas were determined using a Micromeritics ASAP 2020 Gas Sorption Analyzer using N<sub>2</sub> and are 121.9128 ± 0.4702 (m<sup>2</sup>/g) (amorphous Fe-phosphate) and 77.155 ± 0.3943 (m<sup>2</sup>/g) (amorphous Al-phosphate).

**Experimental Set-up**

Dissolution experiments of amorphous Al- and Fe-phosphates at varying pH values were conducted using flow-through reactors based on those used by [14] (Figure 1A and B). Samples were sieved to a particle size of 75-150µm before dissolution. A sample size of 1.000g to 3.000g ± 0.004 was placed on a 0.45µm acrylic membrane filter held in place with an acrylic sleeve within the reactor, with the reactor already filled with solution to prevent the formation of bubbles. The input solution consisted of a 0.01M KNO<sub>3</sub> solution adjusted to the pH of the experiment (2, 2.5, or 3) with high purity 1 N HCl or 1 N KOH. Solution was pumped up through the filter using an ultra low flow peristaltic feed pump, and the reactor was continuously agitated on a shaker plate at 150 rpm. The outlet solution was filtered through a 0.45µm filter before entering the collection vessel, and concentrations were

measured until steady state was obtained, defined as 4 consecutive samples of similar concentration, pH values and flow rates.

### Analyses

#### Sampling

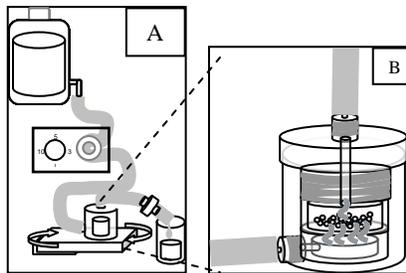
Samples of outlet solution were collected at predetermined intervals based on preliminary experiments, weighed for flow rate determination, and measured for pH using a SevenEasy Mettler Toledo AG pH probe. Separate solution samples were re-filtered through 0.45  $\mu\text{m}$  filters, acidified below pH 2 for preservation using 1 N high purity HCl, and stored at 4°C until chemical analysis. Aluminum concentrations were measured by the catechol violet colorimetric method [15] at a wavelength of 585 nm, and phosphate concentrations were determined by the molybdate blue colorimetric method [16] at a wavelength of 882 nm on a Thermo Scientific Genesys 10S Uv-vis Spectrophotometer. Flame atomic absorption spectroscopy (AAS) was used to measure Fe concentrations on a Thermo Scientific iCE 3000 series AA spectrometer.

#### Dissolution rate calculation

Dissolution rates were calculated from steady state Al, Fe and  $\text{PO}_4$  concentrations, and flow rates normalized to the BET surface area after [17]

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

where  $C_{out}$  is the measured steady state output concentration (M),  $C_{in}$  is the input concentration (M),  $Q$  is the flow rate (L/s),  $A$  is the specific surface area ( $\text{cm}^2/\text{g}$ ), and  $m$  is the mass (g).

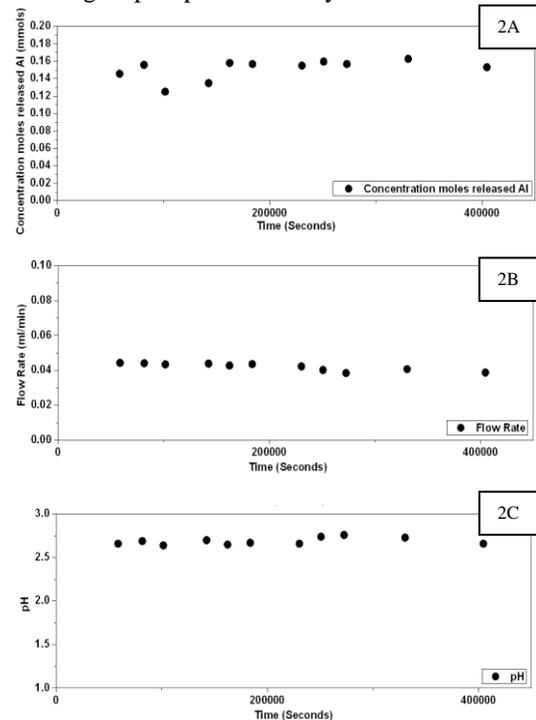


**Figure 1A and 1B.** (1A) Schematic image of flow-through reactor (based on [14]) illustrating solution input pumped through a peristaltic pump, to a reactor on a shaking plate. Effluent flows through a 0.45  $\mu\text{m}$  filter before entering a collection vessel. (1B) Enlarged schematic image of reactor showing solution flowing up through sample located on a 0.45  $\mu\text{m}$  filter.

### Results and Conclusions

Release rates are being calculated from steady state concentrations and flow rates. Rates will be used to

investigate phosphate mobility on Mars.



**Figure 2.** Solution chemistry and flow rates versus time for dissolution of amorphous Al-phosphate at pH=2, Figure 2A Al concentrations, 2B flow rate, 2C solution pH

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