DISTINGUISHING BETWEEN ORGANIC AND INORGANIC PHOSPHATE COMPOUNDS ON POORLY CRYSTALLINE FERRIC OXIDES

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Introduction: Phosphate from both inorganic and organic sources is of interest to the Mars scientific community, as it can broaden our understanding of ancient and modern aqueous alteration processes and the potential for ancient life [1]. As an important element required for metabolic function in organisms on Earth, phosphate is often a limiting nutrient in terrestrial settings, regulating primary productivity [2]. Detection of organic phosphate sources can be an indication of previous microbial activity in a past soil environment [3]. Mars is a comparatively phosphorous-rich environment where secondary hydrated P-bearing minerals may be in abundance, as supported by recent data from Gale Crater, Gusev Crater, and Meridiani Planum [1, 4]. Previous and ongoing research investigates potential bioavailability of P from minerals of igneous origin, and associated secondary phases Elevated P and Fe availability may have provided conditions necessary for past microbial activity on Mars.

In terrestrial systems, phosphate is often readily adsorbed onto oxides and other clay-sized minerals [5]. Given ferrihydrite’s high mineral surface area, it often forms inner-sphere complexes with PO$_4^{3-}$ ion groups and/or leads to the precipitation of ferric iron phosphates crystals [6]. Previous research by our research group found that ferrihydrite preservation during reaction with aqueous solutions is more likely to occur in near saturated sulfate, chloride, and perchlorate brines in Martian environments as opposed to more diluted concentrations [7]. This geochemical behavior may in part explain how ferrihydrite manages to persist in abundance in Mars soil, despite its poor crystallinity and metastable nature. Therefore, ferrihydrite is a likely phosphorous sink that may preserve evidence of past biotic activity in modern Mars environments.

Previous analyses of phosphate-bearing brines also found that dissolved phosphate phases produce extremely strong Raman signals, allowing even small concentrations to be detected as well as differentiating different species of phosphate present in the solution [8, 9]. Therefore, we hypothesize that 1) phosphate species adsorbed to ferrihydrite may be detectable with via Raman analyses and 2) adsorbed inorganic and organic phosphate phases may be discernable based on the Raman spectra of the absorbed phases.

Materials and Methods: For this experiment, we based our procedures on previous experiments.

Figure 1: Raman spectra for ferrihydrite + A- 0 mg PO$_4$/L (green), B- 10 g inorganic PO$_4$/L (brown), C- 1 g inorganic PO$_4$/L (yellow), D- 10 g organic PO$_4$/L (dark orange), and E- 1 g organic PO$_4$/L (light orange).
investigating the rate of phosphate adsorption [2, 10, 11]. We selected phytic acid (C8H18O2P4O) as a source for organic phosphate and KH2PO4 as a source for inorganic phosphate. We created 30 mL solutions of 1 and 10 g PO4/L in 50 mL plastic centrifuge tubes, which were purged with N2—and adjusted to pH 4.5 ± 0.1 with 0.1 mol/L KOH and 0.1 mol/L HCl, as well as a blank control sample of ultra-pure water (UPW).

We then added 50 mg of synthesized 2-line ferrihydrite to each solution and mixed them at 200 rpm for 3 hours. The ferrihydrite slurries were then vacuum filtered with 0.2 μm filter paper and set out to air dry.

Once the solid ferrihydrite was filtered from solution, we analyzed the material using Renishaw Raman spectrometer with a 532 nm laser at 1% power to avoid thermally altering the ferrihydrite to hematite. We collected spectra for 450s via 15 30s accumulations. The Raman spectra collected were compared with a spectra of 2-line ferrihydrite without added phosphate to identify peak shifts and appearance of orthophosphate (PO4^3-, HPO4^2-, H2PO4^- ) peaks alongside Fe-O peaks.

Results and Discussion: In the blank control sample, 2-line ferrihydrite Raman spectrum exhibits three broad, noisy peaks at 360-370, 510, and a primary peak at 710 cm^-1 (as shown in Figure 1a). The spectra for ferrihydrite mixed with organic and inorganic phosphate solutions showed the same peak positions for ferrihydrite. Raman spectra for phosphate groups is expected to appear at 990.5 (PO4^3-), 990.5 (HPO4^2-), and 880/1080 cm^-1 (H2PO4^-). Spectra collected from the organic and inorganic 1 and 10 g PO4/L samples did not exhibit peaks from these phosphate groups as expected. Ferrihydrite samples from the organic 1 g PO4/L and inorganic 10 g PO4/L solutions exhibited an additional peak at 1043 and 1049 cm^-1 respectively, which are in close range for phosphate symmetric stretching [12]. However, no other additional peaks could be preserved in the 800-1200 cm^-1 range. As such, we are unable to definitively distinguish between sorbed organic and inorganic phosphate with confidence.

The lack of clear PO4 group peaks in the inorganic phosphate experiments may be a result of 1) lack of adsorption of phosphate to the ferrihydrite surface or 2) high detection limits needed to discern adsorbed phosphate on ferrihydrite. Phosphate may not have adsorbed to the mineral surface due to relatively short mixing times and/or pH conditions that were not ideal for adsorption [13]. Therefore, pH changes may also account for the difficulty in observing phosphate peaks. Maintaining a constant acidic pH of 4.5 is therefore necessary for conducting proper observations of phosphate adsorption on ferrihydrite, as adsorption tends to decrease with increasing pH [13].

Upcoming Research: In order to verify phosphate adsorption onto the ferrihydrite, we intend to also measure phosphate concentrations in solution using a UV spectrophotometry colorimetric method [14]. We will also vary the initial concentration of phosphate in solution to determine the adsorption isotherms for of both organic and inorganic phosphate compounds, including lower concentrations in the 1-50 mg/L range over a 24-hour mixing period.

We also intend to investigate the effect of salinity on phosphate adsorption and detection. As ferrihydrite is detected alongside sulfate and chloride salt deposits on the Martian surface, hypersaline conditions could impact detection of PO4 adsorption on ferrihydrite surfaces. The same concentrations of organic and inorganic phosphate compounds will be synthesized in a matrix of varying salt solutions. Such investigations will more closely resemble conditions observed in Mars surface environments and hopefully yield more accurate results.

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