Analysis of the oxygen isotope composition of phosphate adsorbed onto Mars-analog clay minerals

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Introduction

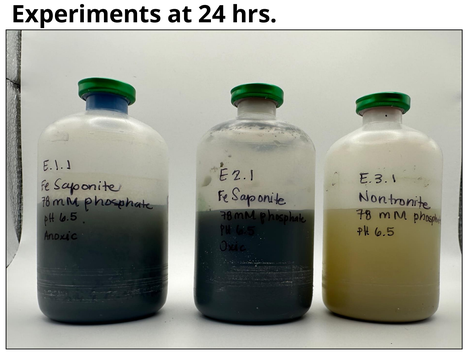
- Martian meteorites contain phosphate (PO_4^{3-}) with distinct isotope signatures[1-4]. Phosphate which is an important nutrient for life sustaining structures such as RNA/DNA, phospholipid membranes, and ATP[5].
- Mars 2020 Perseverance rover is collecting samples to be returned to Earth which are known to contain PO_4^{3-} and clay minerals. [6-7]
- PO_4^{3-} is cycled through the hydrosphere, lithosphere and biosphere. The composition of biologically cycled PO_4^{3-} contains heavier oxygen isotopes ($\delta^{18}O$) compared to PO_4^{3-} in igneous PO_4^{3-} minerals.[8-9]
- $PO_4^{3-}{}_{(aq.)}$ [10] from biotic and abiotic sources can be adsorbed onto clay minerals.
- The $\delta^{18}O$ rich PO_4^{3-} may be adsorbed at different rates compared to PO_4^{3-} containing lighter isotopes.[11]
- Adsorption experiments are being performed to understand the adsorption capacity, isotope composition, and clay mineral alteration.

Methods

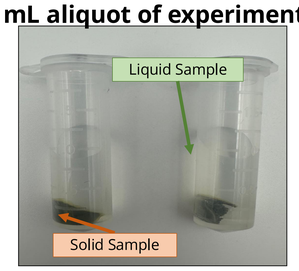
Batch Experimental Conditions

78 or 31.2 mM PO_4^{3-}, 10 g/L clay mineral, pH 6.5, 25 °C

Experiments at 24 hrs.



1 mL aliquot of experiments



pH_{pznpc} Experiments

Equilibrated with 0.01 M $NaNO_3$ for 24 hrs at a constant pH of 7. Adjusted pH of 7 to pH of 3-9 and allowed to equilibrate for 24 hrs. Increased 0.5 M $NaNO_3$ and measured Δ pH after 24 hrs.

pH_{pznpc} of allophane

Analytical Techniques

- **Phosphate Concentration**
  - Colorimetry and Ion Chromatography
- **Isotope Analysis**
  - Isotope Ratio Mass Spectrometer
- **Mineralogy**
  - X-Ray Diffraction
- **Morphology**
  - Scanning Electron Microscopy

Results

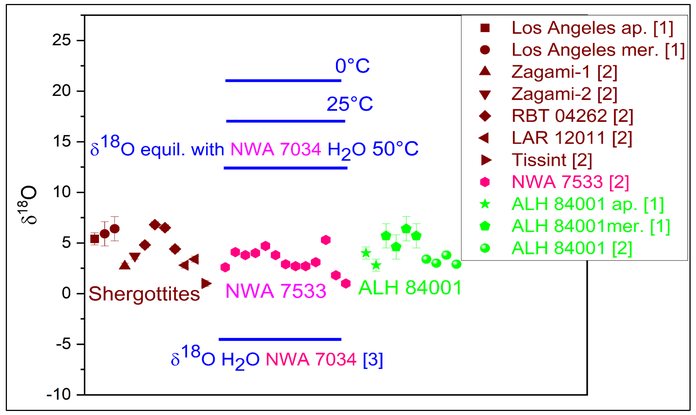


Figure 1: Oxygen isotope composition of PO_4^{3-} and water of martian meteorites and estimated temperature for water to equilibrate with PO_4^{3-}.

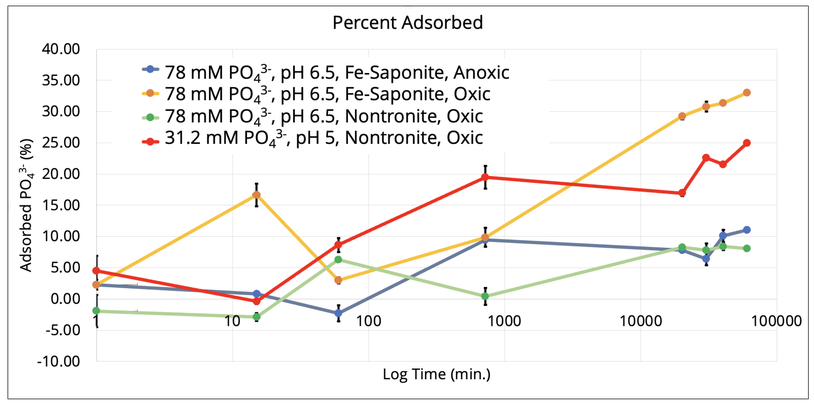


Figure 2: Percent adsorbed PO_4^{3-} in experiments containing nontronite, allophane, or Fe-saponite. Error bars are the standard deviation of the average concentration of triplicate samples.

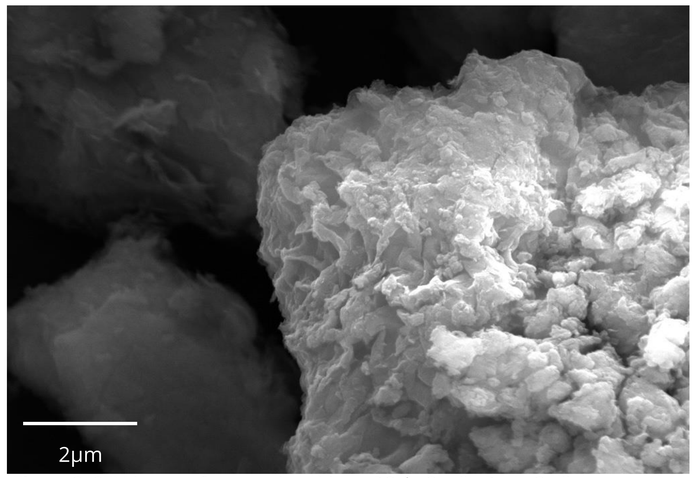


Figure 3: SEM image of nontronite without PO_4^{3-}. Credit: Dr. L. Cycil

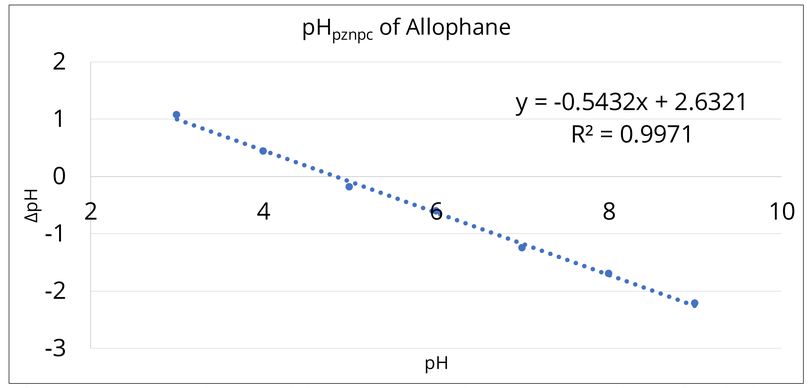


Figure 4: Experimental results of the pH_{pznpc} (point of zero net proton charge) for allophane. The surface charge of allophane is 0 at a pH of 4.85.

Conclusion/Future Work

Clay minerals are able to adsorb phosphate at a pH of 6.5. The highest adsorption of ~30 % was observed in experiments containing Fe-saponite under oxic conditions. The pH_{pznpc} for allophane was determined to be 4.85. The SEM images of our clay structure contain the sheet-like structures which is consistent with smectites.

Future work includes 1) performing phosphate adsorption experiments at an acidic to near-neutral pH based off of our pH_{pznpc} data, 2) performing isotopic analysis of our adsorbed phosphate, and 3) characterizing the morphological and mineralogical composition of our clay minerals containing phosphate through the experiments.

References

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