

# Oxygen Isotope Fractionation of Phosphate During Adsorption onto Mars-Analog Clay Minerals

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## Introduction

- Phosphate ( $\text{PO}_4^{3-}$ ) is an essential nutrient for life and is a key component in important biological structures, including nucleic acids (RNA and DNA), adenosine triphosphate (ATP), and phospholipids. It also plays a central role in the biogeochemical cycling, and its availability in natural systems is influenced by interactions between nutrient and minerals (e.g., clay minerals)<sup>[1-3]</sup>.
- Clay minerals have a high affinity for  $\text{PO}_4^{3-}$  adsorption, thereby influencing  $\text{PO}_4^{3-}$  transport and distribution in the environment. In addition to affecting  $\text{PO}_4^{3-}$  concentrations, adsorption processes may lead to isotopic fractionation based on the oxygen isotope composition of  $\text{PO}_4^{3-}$ <sup>[4,5]</sup>.
- Clay minerals and  $\text{PO}_4^{3-}$  have been detected on Mars, where  $\text{PO}_4^{3-}$  may serve as a potential biosignature through its oxygen isotope composition. Therefore, understanding how nutrient-mineral interactions influence  $\text{PO}_4^{3-}$  oxygen isotope signatures is critical in interpreting  $\text{PO}_4^{3-}$  as a biosignature<sup>[1,3,6]</sup>.
- In this work, we will determine if  $\text{PO}_4^{3-}$  adsorption onto Mars-analog clay minerals influences the oxygen isotope composition of  $\text{PO}_4^{3-}$ , with the goal of helping interpret how  $\text{PO}_4^{3-}$  can be used as a potential biosignature on future Mars returned samples.**

## Methods

### Experimental Conditions

Clay Mineral	$\text{PO}_4^{3-}$ (mM)	Clay Mineral (g)	pH
Fe-Saponite	30.0	1.00	5.00
Nontronite	30.0	1.00	5.00
Allophane	30.0	1.00	5.00
Fe-Saponite	37.5	1.25	5.00
Nontronite	37.5	1.25	5.00
Allophane	37.5	1.25	5.00
Mg-Saponite	37.5	1.25	5.00



Figure 1: Batch experiments of 37.5 mM phosphate adsorbed onto 1.25 g of clay minerals.

### Analytical Techniques and Procedures

**Phosphate Concentrations:** 0.5 mL aliquots were sampled over time, centrifuged at 9000 rpm, and the supernatant was pipetted into a new microcentrifuge tube. The phosphate in the supernatant was analyzed using Riley and Murphy (1962) colorimetric assay.

**Phosphate Oxygen Isotope Composition:**  $\text{PO}_4^{3-}$  samples collected at varying timepoints were purified through a series of precipitation and dissolution steps, including formation of an ammonium phosphomolybdate and magnesium ammonium phosphate, followed by cation exchange and a final precipitation as silver phosphate. The silver phosphate will then be analyzed using a thermal combustion-elemental analyzer coupled to a continuous flow isotope ratio mass spectrometer.

**pH Point Zero Net Proton Charge ( $\text{pH}_{\text{pznpc}}$ ):** Clay minerals were sieved to  $< 2 \mu\text{m}$  and equilibrated in 0.01 M  $\text{NaNO}_3$  at pH 7 for 24 hours to create 200 mL stock suspensions. 25 mL aliquots were then adjusted to pH 3-9, equilibrated for 24 hours, followed by the addition of  $\text{NaNO}_3$  for a final concentration of 0.5 M. After 24 hours the pH measured and the  $\Delta \text{pH}$  was calculated (Fig. 3).

**Minerology and crystallinity:** Minerology and crystallinity of the samples was conducted at the Advanced Photon Source using beamline 13 ID-E GSECARS  $\mu\text{X}$ -Ray Diffraction ( $\mu\text{XRD}$ ) microprobe.

**Specific surface area, particle size distribution, and porosity:** Characterization of clay mineral samples was determined by using  $\text{N}_2$  (g) adsorption measurements using a Micromeritics TriStar II Plus Brunauer-Emmett-Teller (BET) analyzer.

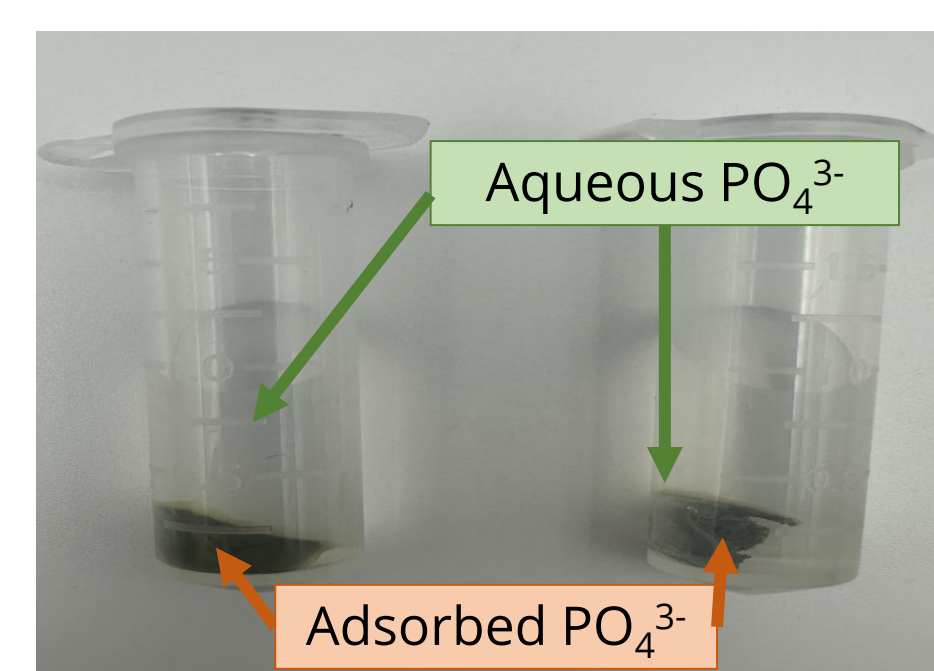


Figure 2: Sample after centrifuge to separate aqueous  $\text{PO}_4^{3-}$  and adsorbed  $\text{PO}_4^{3-}$ .

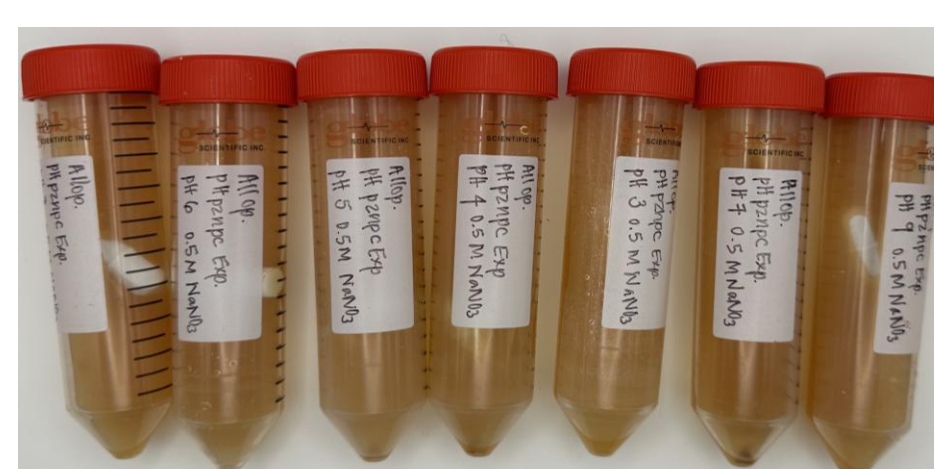


Figure 3:  $\text{pH}_{\text{pznpc}}$  of allophane in 0.5 M  $\text{NaNO}_3$ .

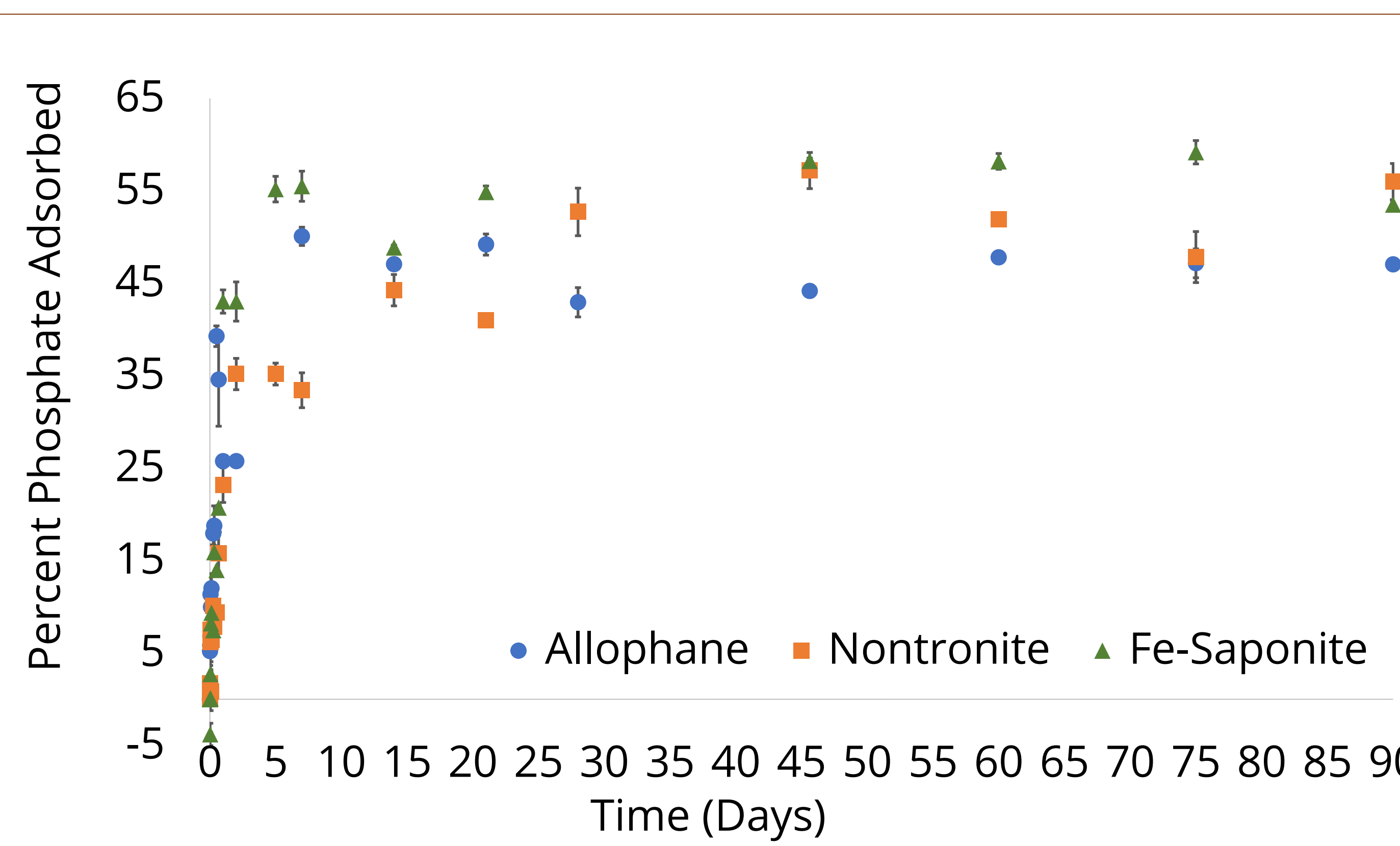


Figure 4: Percent adsorbed phosphate over 3 months in experiments containing 30 mM  $\text{PO}_4^{3-}$  and 1.0 g of either allophane, nontronite, or Fe-Saponite at pH 5.0. Error bars are the standard deviation from triplicate samples from 1 experiment.

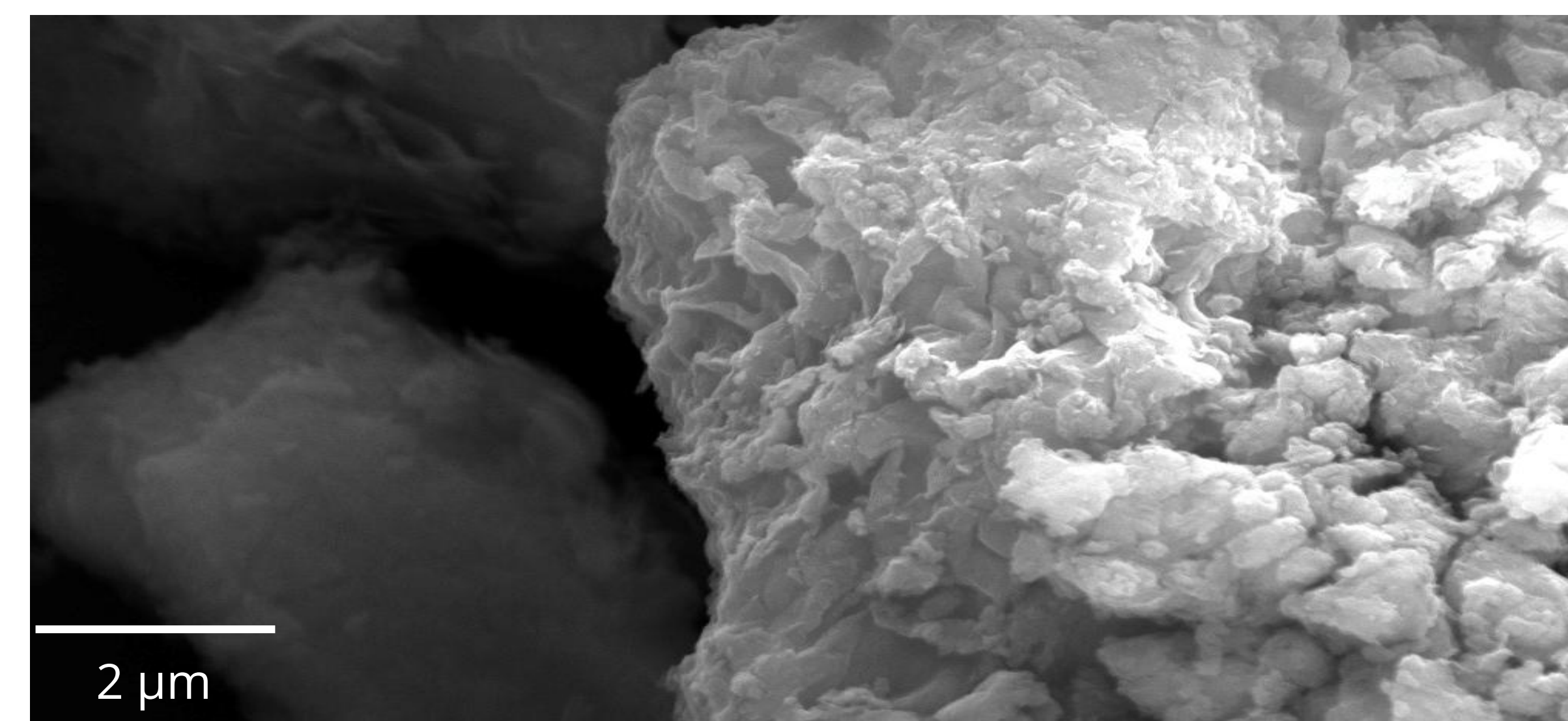


Figure 6: SEM image of nontronite without  $\text{PO}_4^{3-}$ . Credit: Dr. L. Cyclic

## Results

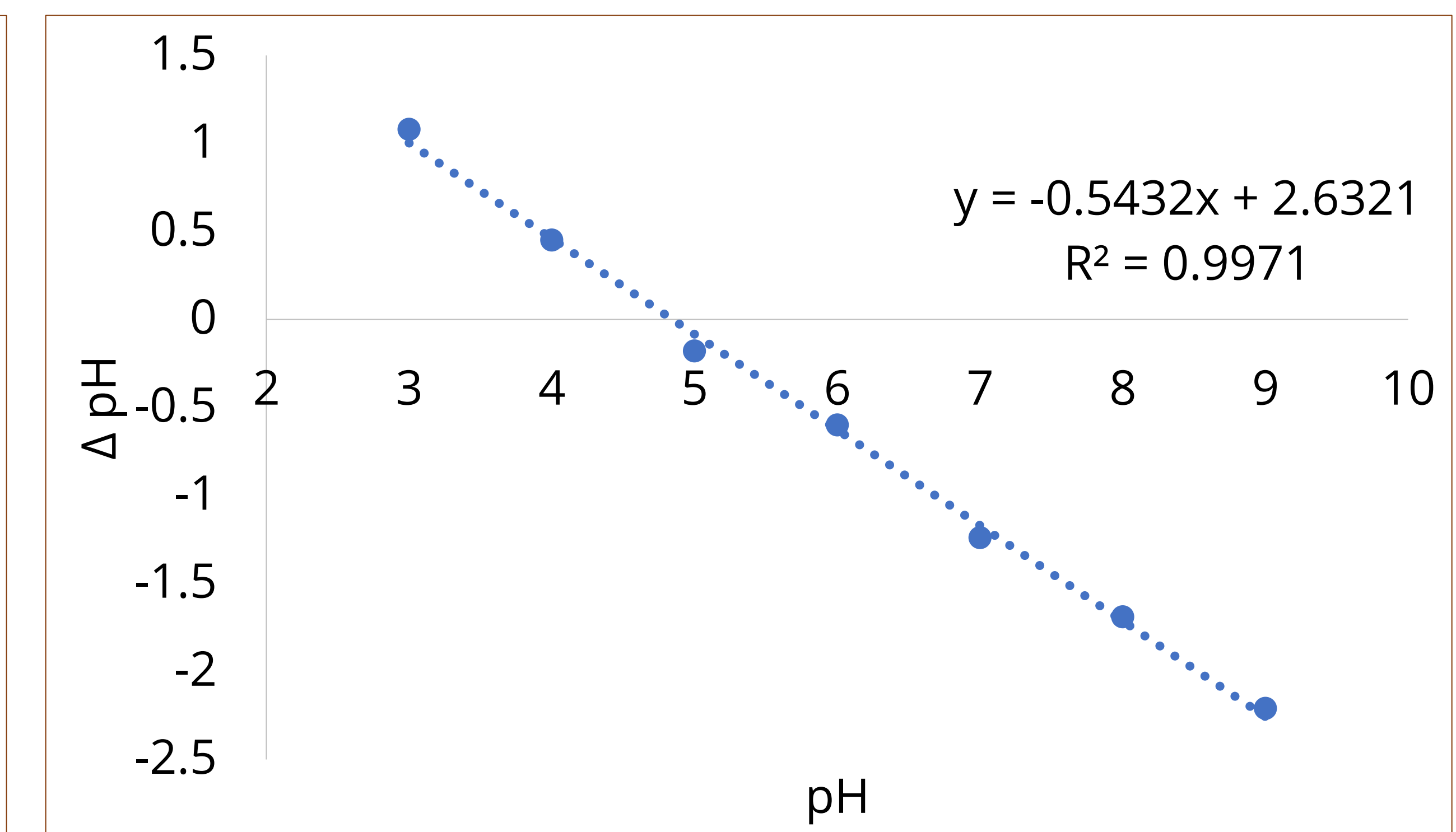


Figure 5: Experimental results of the  $\text{pH}_{\text{pznpc}}$  of allophane.

Table 1: Experimental  $\text{pH}_{\text{pznpc}}$  of clay minerals.

Clay mineral	$\text{pH}_{\text{pznpc}}$
Nontronite	4.41
Fe-Saponite	4.65
Allophane	4.85
Mg-Saponite	7.92

## Conclusion and Ongoing Work

Clay minerals adsorb phosphate at a pH 5.00, with adsorption varying by mineral type. In experiments with 30 mM phosphate and 1.00 g of clay mineral, maximum adsorption reached 50.08 %, 59.18 %, and 57.20 % for nontronite, Fe-saponite, and allophane, respectively (Figure 4). The  $\text{pH}_{\text{pznpc}}$  results indicate that below pH of 5.00, iron-rich clay minerals are positively charged, favoring phosphate adsorption (Table 1). The SEM image confirms the sheet-like structure of our nontronite clay mineral.

Ongoing work includes extracting the phosphate and converting it to  $\text{Ag}_3\text{PO}_4$  for oxygen isotope analysis, determining remaining phosphate concentrations, and processing  $\mu\text{XRD}$  data.

## References

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