

Phosphate interactions with schwertmannite

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PO₄ interaction with Fe-(hydr)oxide minerals such as hematite, goethite and ferrihydrite is well studied due to its implications for PO₄ removal from the environment [e.g., 1] and the use of O-isotopes in PO₄ as biomarkers [2]. In this study we explore the interaction of PO₄ with Fe(III)-sulphate minerals that are found in acidic conditions. Schwertmannite (Fe₈O₈(OH)₆(SO₄)_nH₂O) precipitation experiments were conducted at pH 2 in the presence of 0.3, 0.5, 1 or 2 mM PO₄ as well as experiments of phosphate adsorption to PO₄-free schwertmannite between pH 2 and 5. Both K₂HPO₄ and Na₂HPO₄ were tested as phosphate sources.

The co-precipitation experiments show that increased PO₄ concentrations extend the time required for nucleation. Raman spectroscopy, diffuse reflectance infra-red fourier transform spectroscopy (DRIFTS) and X-ray diffraction (XRD) also showed that both jarosite and schwertmannite were produced in experiments with K₂HPO₄ in solution. Whereas, only schwertmannite was present in the analyses of precipitates from the Na₂HPO₄ solutions. Significant PO₄ was removed from the solution in both sets of experiments and spectroscopic analysis indicates that PO₄ may be incorporated into the solid structure. Negligible PO₄ oxygen isotopic fractionation between aqueous-phase and solid-phase PO₄ was observed. The adsorption experiments demonstrated that schwertmannite readily adsorbs PO₄ within 24 hours throughout the pH range tested. Attenuated total reflectance fourier transform infra-red (ATR-FTIR) spectroscopy analysis of the adsorption modes show a similar mode of binding for the PO₄ to that observed previously on goethite [3] and hematite [4] at these pHs. The findings of this study have implications for PO₄ removal from sulphate-rich solutions and PO₄ related biosignatures in sulphate-rich, acidic environments, such as the Martian surface.

[1] Rhoton & Bigham (2004) J. Environ. Qual., 34, 890-896.

[2] Blake et al. (2010) Nature, 464, 1029-1032.

[3] Luengo et al. (2006) J. Colloid Interface Sci., 300, 511-518.

[4] Elzinga et al. (2007) J. Colloid Interface Sci., 308, 53-70.