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In-situ XANES Spectroscopic Study on Phosphate Adsorption of Hematite

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Beamline: X19A

Introduction: Phosphate adsorption mechanisms on iron oxides are essential for understanding the bioavailability and fate of soil phosphorus. The distribution of phosphate between solid and solution phases is controlled by the compositions and structures of P associated with Fe oxides. In this study, we apply in-situ XANES spectroscopy to study the phosphate adsorption mechanism of hematite ($\alpha\text{-Fe}_2\text{O}_3$), which is one of the abundant iron oxides in soils.

Methods and Materials: An aliquot of hematite suspension containing total 300 mg solids was added into 10 mM KCl and the pH was adjusted to 4, 6 or 10. A certain amount of 10 mM KH_2PO_4 was spiked into the vigorously stirred hematite suspensions so that the concentrations of PO_4 in the suspensions range from 0 to 50 $\mu\text{mol/g}$ solids. The pH of the samples was adjusted periodically prior to equilibrium. After equilibration for 48 hours, the samples were centrifuged at 5000 rpm for 10 minutes and the sediments of the samples were collected and loaded into sample holders. The samples were then covered with 5- μm polypropylene film to preserve the moisture of the samples prior to XANES analyses at X19A.

Results: The P K-XANES spectra of phosphate adsorbed on hematite samples are shown in Figure 1, along with those of strengite and variscite. Generally, the spectra of adsorbed phosphate on hematite exhibit two peaks at -3.4 and 2.2 eV (relative energy), referred to as the pre-edge and white line peaks, respectively. No significant changes in the position, linewidth and relative intensities of the pre-edge and white line peaks were observed as pH and adsorbed phosphate concentration changed. Therefore, the corresponding structural of adsorbed phosphate configuration (as detected by XANES) was not affected by the changes in protonation and concentration of adsorbed phosphate. A single adsorbed phosphate species is predominant on hematite surface, which is consistent with our observation with in-situ ATR-FTIR spectroscopy.

Compared with the XANES spectra of strengite ($\text{FePO}_4 \cdot 2\text{H}_2\text{O}$) and variscite ($\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$), the XANES features of adsorbed phosphate on hematite are distinctive in both the region near the white line peak and the higher-energy oscillations. The energy of the pre-edge peak in the XANES spectra of adsorbed phosphate is close to that of strengite. However, the intensity of the peak for adsorbed phosphate (0.05) relative to the white line peak maximum is weaker than that of strengite (0.10). The difference between the pre-edge features of phosphate in strengite and on the surface of hematite (in normalized XANES spectra, regardless of the concentration of adsorbed phosphate) suggests that Fe-phosphate precipitate did not occur on the surface of hematite under the experimental conditions of this study. In addition, the pre-edge and white line peaks in P K-edge XANES spectra result from the electronic transition from the 1s electron of P into unoccupied p-like valence electronic state in the conduction band of phosphate. Especially, it has been shown that the intensity and energy of the pre-edge peak is sensitive to the number of 3d electrons of the cations bound to phosphate. On the contrary, a pre-edge feature does not occur in the spectrum of phosphate bound to non-transition, e.g., phosphate in variscite. Therefore, the occurrence of the pre-edge peak provides direct evidence for the formation of inner sphere phosphate complexes on the surface of hematite. Combined with the results of in-situ ATR-FTIR spectroscopy, we therefore conclude that bidentate inner-sphere complexes of phosphate occur on the surface of hematite.

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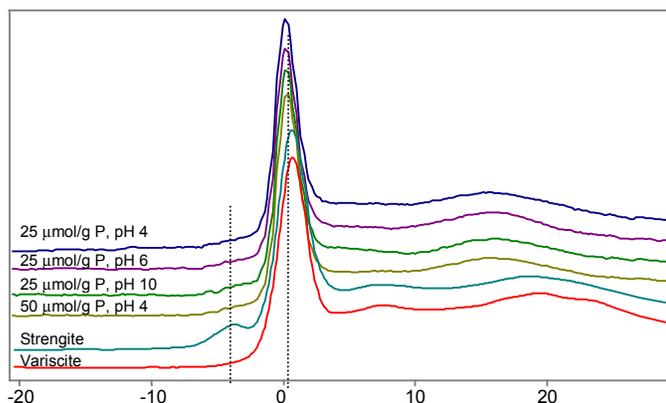


Figure 1. P K-XANES spectra of phosphates adsorbed on hematite and of strengite and variscite