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XAFS study of adsorbed and mineral forms of phosphate

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The solubility of inorganic phosphorus in soils is regulated by surface-adsorbed phosphate or phosphate minerals. The objective of this study was to determine whether different phosphate species of relevance to soils showed distinguishing XAFS spectral features. Phosphorus K-XANES spectra for Fe-phosphates were characterized by a unique pre-edge feature near -3 eV (relative energy) that increased in intensity with increasing mineral crystallinity and was very weak for phosphate adsorbed on goethite. Spectra of Ca-phosphates and a soil sample exhibited a distinct shoulder on the high-energy side of the absorption edge. Spectra of Al-phosphates were characterized by a weak pre-edge feature at -1 eV.

Keywords: XANES, phosphorus, speciation, soil

1. Introduction

Many agricultural soils receive excessive inputs of phosphorus from fertilizers or animal wastes (e.g., Simard et al., 1995; Mozaffari & Sims, 1994). Elevated levels of P in soils are an environmental concern because increased discharge of dissolved P from soils can potentially deteriorate the quality of surface waters (Beauchemin et al., 1996). The solubility of inorganic P in soils is usually regulated by phosphate adsorbed on mineral surfaces, or by Ca-, Fe-, or Al-phosphate minerals (Sample et al., 1980).

To develop chemical models for predicting the environmental impacts of phosphorus in soils, it is important to determine the chemical species that control P solubility. A conventional, albeit indirect, approach for determining P speciation in soils is the use of chemical extractions designed to dissolve specific forms of P. The objective of this study was to assess the feasibility of using XAFS spectroscopy for more direct identification of soil P species.

2. Materials and Methods

2.1. Phosphorus Standards

Various phosphorus standards for XANES analysis were synthesized or purchased. Iron phosphates were synthesized following the procedure of Dalas (1991). Basically, a non-

crystalline precipitate formed by mixing aqueous KH_2PO_4 and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ at ambient temperature was hydrothermally treated at 100 °C for 24 h, 3 d, or 30 d to produce non-crystalline Fe-phosphate or strengites ($\text{FePO}_4 \cdot 2\text{H}_2\text{O}$) of different crystallinities. A sample of adsorbed phosphate was prepared by reacting KH_2PO_4 with goethite ($\alpha\text{-FeOOH}$) in an aqueous suspension at pH 6, to yield an adsorbed phosphate concentration of 500 mmol/kg goethite (Oh et al., 1999). Octacalcium phosphate [$\text{Ca}_4\text{H}(\text{PO}_4)_3 \cdot 2.5\text{H}_2\text{O}$] was synthesized using the procedure of Christoffersen et al. (1989). Monetite (CaHPO_4), brushite ($\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$), and hydroxyapatite [$\text{Ca}_5(\text{PO}_4)_3\text{OH}$] were purchased from Aldrich or Sigma chemical companies. Non-crystalline Al-phosphate and variscite ($\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$) were synthesized following the procedures of Hsu and Sikora (1993), and berlinite (AlPO_4) was purchased from Aldrich Chemical Co. Phosphate adsorbed on alumina (Al_2O_3) was prepared at pH 6 and 500 mmol P/kg alumina as described above.

All mineral standards were analyzed using X-ray powder diffraction to ensure mineralogical purity or to determine differences in mineral crystallinity. Note that the strengite samples contained detectable levels of phosphosiderite (monoclinic $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$). Diffraction data were collected using unresolved Cu-K α or Co-K α radiation and equivalent scanning parameters for standards of a given chemical type.

To reduce self-absorption effects in XANES analysis, mineral samples were diluted to 800 mmol P/kg in boron nitride (BN) and pressed into disks of 1.3-cm diameter and 1-mm thickness. XANES data were collected directly on moist-paste samples containing adsorbed P.

2.2. Soil sample

The soil sample included in this study (designated pv2a) was collected from the surface (A) horizon of a Providence (series) soil in an agricultural region of Quebec, Canada. The sample contained 43 mmol P/kg and had a pH of 7.6. XANES data were collected on an air-dried subsample of the soil that was crushed and sieved to <125 μm .

2.3. XANES Spectroscopy

Phosphorus K-XANES data acquisition was done at Beamline X-19A at the National Synchrotron Light Source, Brookhaven National Laboratory. The electron beam energy was 2.5 GeV and the maximum beam current was 300 mA. Spectra were collected in fluorescence mode using a Lytle detector and a He flight path. Multiple scans were averaged, and then the data were normalized according to Sayers and Bunker (1988).

XANES spectra were not corrected for self absorption. However, we calculated the reduction in fluorescence signal caused by self absorption at the energy of the white line peak (2150 eV), based on known matrix composition and density, an infinitely thick sample relative to beam penetration, and our sample geometry of 45° for both the glancing angle of

incident X-rays and the angle of detected fluorescence radiation (see Tröger et al., 1992 - Eqn. 7). Self absorption decreased the fluorescence signal by 7% to 8% for the mineral standards in BN and by 1% to 2% for the adsorbed P standards, which would not change our data interpretation. Self absorption should be negligible for the soil sample, because of its lower concentration of P (Tröger et al., 1992).

3. Results and Discussion

Phosphorus K-XANES spectra for non-crystalline Fe-phosphate and strengite exhibited a characteristic pre-edge feature between -5 and -2 eV (Fig. 1), which increased in intensity with increasing mineral crystallinity. X-ray diffraction patterns (not shown) showed no discernible peaks for the non-crystalline Fe-phosphate. Characteristic diffraction peaks for strengite increased in intensity and sharpness when the hydrothermal treatment (during synthesis) was increased from 3 to 30 days. For example, the widths at half height measured on the most intense peak at 4.38 Å (002, 201 peak) were 4.47 mrad for the sample treated for 30-d and 5.41 mrad for the sample treated for 3 d. Also, several minor diffraction peaks were only distinguishable in the sample treated for 30 d. In contrast to Fe-phosphate minerals, the pre-edge feature was very weak in the K-XANES spectrum for phosphate adsorbed on goethite (Fig. 1). The spectrum for adsorbed phosphate did exhibit a stronger white-line peak than those of the Fe-phosphate minerals, and the oscillation near 17 eV was more intense.

Fluorescent X-ray Intensity (normalized)

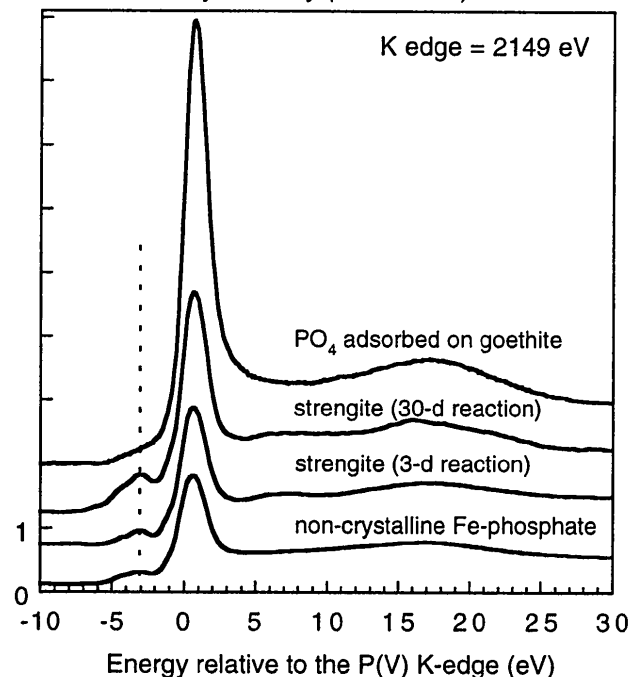


Figure 1
Stacked phosphorus K-XANES spectra for non-crystalline iron phosphate, adsorbed phosphate, and strengite of varying crystallinity as induced by hydrothermal treatment time.

Phosphorus K-XANES spectra for Ca-phosphate minerals exhibited a unique post-edge shoulder between 2 and 6 eV (Fig. 2). The structure of this shoulder varied between the different Ca-phosphate minerals, and was more well-defined for hydroxyapatite and octacalcium phosphate. A shoulder in the XANES spectrum for the soil sample (Fig. 2) was similar in structure to those of the Ca-phosphate minerals, particularly monetite and brushite, indicating that the soil sample contained some form of Ca-phosphate. Note that the soil sample spectrum showed no pre-edge feature, indicating that Fe-phosphate was not present in detectable quantities.

Fluorescent X-ray Intensity (normalized)

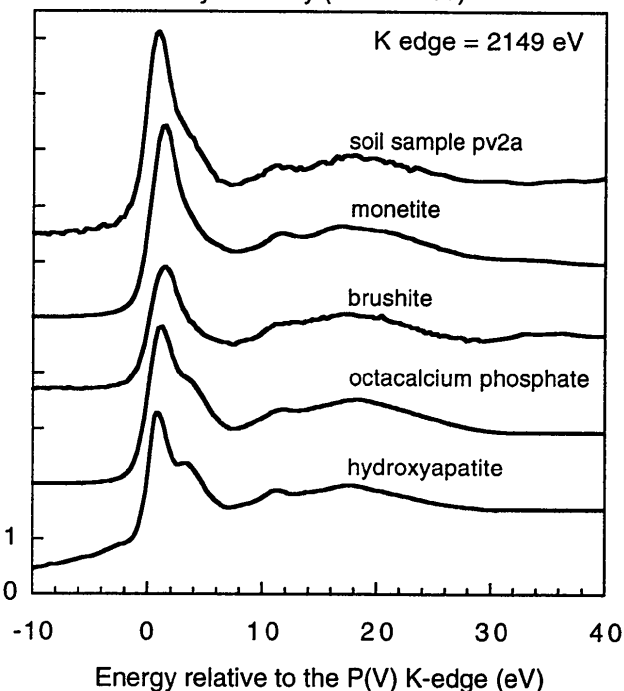


Figure 2
Stacked phosphorus K-XANES spectra for selected calcium phosphate minerals and a soil sample.

The P K-XANES spectra for selected Al-phosphate minerals exhibited a weak pre-edge inflection at about -1 eV (Fig. 3). Analogous to Fe-phosphates (Fig. 1), the pre-edge feature was more distinct in the spectra for crystalline forms of Al-phosphate (variscite and berlinite) and was not evident for the sample of adsorbed phosphate. The inflection was more easily distinguished from first-derivative spectra (not shown). It is noteworthy that we observed a similar inflection in the K-XANES spectrum from a sample of adenosine triphosphate (ATP), but not from inositol hexaphosphate (data not shown). The spectrum for phosphate adsorbed on alumina also exhibited a stronger white-line peak than the crystalline Al-phosphates. The combination of an inflection at -1 eV and differences in post-edge oscillations between Al-phosphates and ATP (not

shown) should be useful for identifying the presence of Al-phosphate minerals in soils.

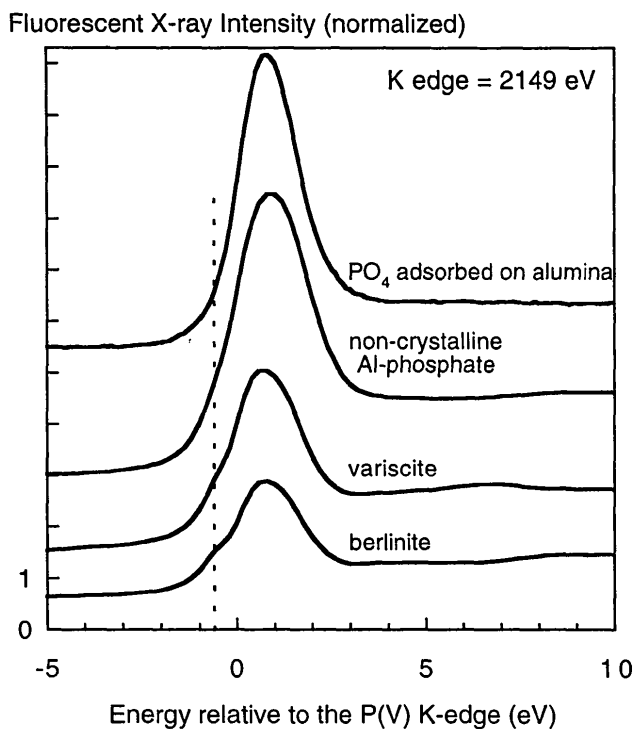


Figure 3

Stacked phosphorus K-XANES spectra for selected aluminum phosphate minerals and phosphate adsorbed on alumina.

4. Conclusions

Phosphorus K-XANES spectra of different phosphorus species contained unique spectral features that should be useful for distinguishing different forms of phosphate in soils. Spectra for Fe- and Al-phosphate minerals exhibited unique pre-edge features, while those for Ca-phosphates exhibited a post-edge shoulder on the main white-line peak. The principle was illustrated in the K-XANES spectrum for a soil sample, which indicated the presence of Ca-phosphate.

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