

Title: Quantitative Speciation of Phosphate in Ternary Mineral Systems Using P K-XANES

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The goal of this research was to determine the quantitative speciation of phosphate pre- and post-organic acid promoted dissolution in model mineral systems as a function of pH abstracted from key components of well drained, phosphorus deficient, and highly fertilized acidic or alkaline soils. Although organic acid promoted phosphate dissolution is hypothesized to be the primary mechanism making mineral-soil-phosphate bioavailable, the current understanding of organic acid mediated phosphate dissolution is limited by the lack of a molecular scale characterization of its solid state speciation. Mineral systems include mixtures of sorbed and precipitated phases similar to phosphorus (P) sorbents in soils with ternary mineral systems consisting of PO₄ sorbed to ¾ of the maximum sorption capacity in 1:1 by mass ferrihydrite (FeOOH) and boehmite (γ-AlOOH) mineral-mixtures combined with hydroxyapatite [Ca₅(PO₄)₃·5H₂O] mineral. Phosphorus K-XANES spectra of P-associated with Fe, and Ca show subtle but unique spectral features in the vicinity of the white-line peak serving as spectral signatures for Fe- and Ca-associated P and, allowing for quantitative speciation of phosphorus in soils, and model systems [see Fig. 1, Hesterberg et al., (1999); Beauchemin et al., (2003); Khare et al., (2004); Khare et al., (2005); Khare et al., (2007)]. Using semi-empirical molecular orbital calculations, spectral features are attributed to the electronic transition of P 1s core electron into unoccupied molecular orbitals with the pre-edge peak attributed to transition into Fe(4p)-O(2p) molecular orbitals thus differentiating between Fe- and Al-associated P (Khare et al., 2007). Due to the low intensity of the features in the pre- and post-edge regions, quantitative speciation is challenging and requires careful data collection and excellent signal to noise ratio in the P K-XANES spectra (see Fig. 2) currently only possible at X-19 A/X-15 B at National Synchrotron Light Source (Brookhaven National Laboratory). This research has direct implications for phosphorus bioavailability and improving soil fertility; and understanding biogeochemical cycling of phosphorus, its impact on carbon sequestration, and global climate change.

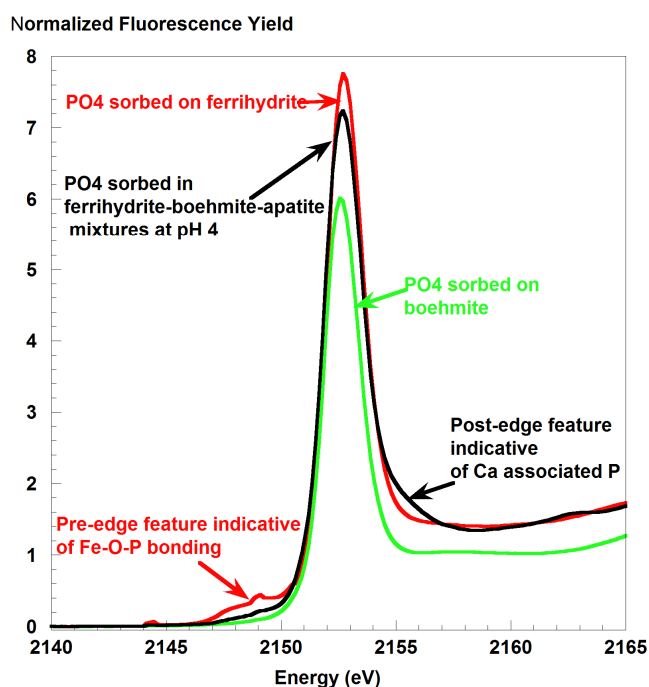


Fig. 1: Phosphorus K-XANES spectra showing pre-edge, white-line, and post-edge regions for Phosphate sorbed on ferrihydrite-boehmite-apatite mixtures at pH 4 along with average standards of phosphate sorbed on ferrihydrite (pH 4-8) and phosphate sorbed on boehmite (pH 4-8). The sorbed sample for mixtures shows a very weak post-edge feature

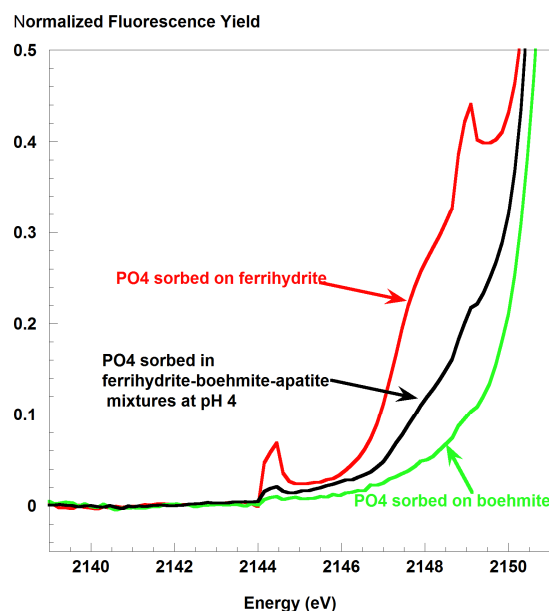


Fig. 2: Pre-edge region of P K-XANES spectra for Phosphate sorbed on ferrihydrite-boehmite-apatite mixtures at pH 4 along with average standards of phosphate sorbed on ferrihydrite (pH 4-8) and phosphate sorbed on boehmite (pH 4-8). Pre-edge peak intensity of phosphate sorbed in mineral-mixtures shows that at pH 4, more phosphate is associated with boehmite than with ferrihydrite.