Preferential Phosphate Sorption and Al Substitution on Goethite

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Abstract

Iron (hydr)oxides, which are ubiquitously distributed in the environment, often contain impurities such as Al. Aluminum-substituted goethite (AlG) is a typical assemblage of Al and Fe (hydr)oxides. In this study, the molecular-level mechanisms of PO_4 sorption in relation to structural changes in AlG with Al/(Al+Fe) molar ratios up to 17.4% and the PO_4 distribution between Al and Fe were determined. While the XRD results showed that Al preferred to substitute for Fe on relatively low-index planes of goethite, the Fe-XAS and XPS data indicated the particular Al substitution in edge-shared FeO_6 octahedral linkages and a tendency of Al segregation near the surface of AlG, respectively. The maximum PO_4 sorption capacity increased from 135 to 584 mmol kg^{-1} as Al/(Al+Fe) mol% increased from 0 to 17.4%. Phosphorus-XANES data of PO_4 sorbed on AlG showed either preferential PO_4 bonding for Al or no preference for Al or Fe. Compared to goethite with adsorbed PO_4, the density functional theory (DFT) result of AlG containing 12.5 Al mol% showed outwardly relaxed Al atoms relative to topmost atomic layers of the supercell upon the PO_4 adsorption, a smaller Al-O-P angle than the corresponding Fe-O-P angle, and the relatively stable PO_4 complex formed on the AlG surface. New insights into the PO_4 sorption mechanisms and related structural changes in Al/Fe assemblages could improve the assessment of P dynamics and mass balance in agricultural and PO_4-induced-eutrophication systems.

Keywords – goethite, phosphate sorption, X-ray absorption, density functional theory