Surface Complexation Modeling of P_i-Goethite Adsorption Behavior: Integrating Adsorption Edge and Surface Charging Data

Christopher J. Tadanier (ctadanie@vt.edu)[1], **Matthew J. Eick** (eick@vt.edu)[2] &
Michael F. Hochella (hochella@vt.edu)[1]

[1] Department of Geological Sciences, Virginia Polytechnic Institute and State University, Blacksburg, VA 24060, USA
[2] Department of Crop and Soil Environmental Sciences, Virginia Polytechnic Institute and State University, Blacksburg, VA 24060, USA

Sorptive interactions between oxyanions and mineral surfaces have received considerable attention due to their important nutrient and contaminant roles and the ubiquitous distribution of minerals in aquatic, sedimentary, and terrestrial environments. Mineral surfaces, particularly metal (hydr)oxides, concentrate oxyanions through both specific and non-specific complexation mechanisms. Specifically adsorbed oxyanions are strongly surface-associated through covalent bonds formed by ligand exchange with surface hydroxyl groups (inner-sphere complexed), whereas non-specifically absorbed oxyanions are weakly surface-associated due to electrostatic interaction through an intervening water molecule (outer-sphere complexed). Because goethite (α-FeOOH) is one of the most widespread minerals in the earth's near-surface environment, and is by far the most abundant iron (hydr)oxide in soils world-wide (Cornell and Schwertmann, 1996), it is thought to play a major role in the retention and cycling of geochemically and environmentally important oxyanions.

Of the common inorganic and organic oxyanions, orthophosphate (P_i) is one of the more strongly adsorbed by goethite surfaces (McBride, 1994). Based on experimental evidence from a variety of direct and indirect methods, a consensus exists supporting inner-sphere complexation of phosphate on goethite. Because of its high affinity for mineral surfaces and lack of volatile forms, phosphorous is often the least available of the biologically essential elements. Both micro-organisms and plants generally take-up phosphorus as soluble P_i from solution (Frossard et al., 1995), making knowledge of the distribution between adsorbed and solution phases essential to elucidating the processes involved in P_i bio-availability. However, due to sorption on oxide minerals and continuous scavenging by micro-organisms and plants, solution phase P_i concentration is often so low that direct quantification is difficult. It is therefore often necessary to estimate the distribution of P_i between sorbed and solution phases using surface complexation modeling. A number of surface complexation models including the Constant Capacitance (CC), Diffuse Double-layer (DD), Basic Stern (BS), Triple Layer (TL), and CD-Music (CD-M) models have been extensively used to model the sorptive behavior of oxyanions on oxide mineral surfaces (Goldberg, 1992; Hiemstra and Van Riemsdijk, 1999). These models have generally been used to describe the adsorption edge behavior (pH dependence) of oxyanions at moderate to high surface loadings. However, little work has been done to compare these models with respect to their adequacy of fit to adsorption edge data or their ability to describe other adsorption phenomena such as surface charging behavior.

We have recently conducted a comprehensive experimental and computational study of P_i-goethite adsorption behavior, which focused on comparing the ability of various surface complexation models to adequately describe adsorption edge and surface charging phenomena. Colloidal goethite with an N_2 BET surface area of 64.4 m^2/g and characteristically acicular euhedral crystals with dimensions of ~ 750 nm by 75 nm was synthesized by oxidation of $FeSO_4$. Adsorption edges at 8 environmentally relevant total P_i loadings (0 to 1000 μM) were generated by titrating suspensions with 0.5 g/L goethite in 0.01 M $NaClO_4$ from pH 12 to pH 3 with HCl. Prior to collecting each sample for residual soluble P_i analysis, each suspension was equilibrated for 8h at constant pH with continuous N_2 sparging. Surface charging data in the form of ζ-potential was also collected for each adsorption edge.

Adsorption edge data were modeled using the CC, BS, TL, and CD-M surface complexation models at each total P_i loading , using the FITEQL v. 4.0 computer program (Herbelin and Westall, 1999) as the computational engine. Outer-sphere complexation of Na^+ and ClO_4^- electrolyte ions was included in all models. Each model adequately described P_i-goethite adsorption edge behavior at total P_i loadings up to 100 μM; however, the BS and TL models did not converge at higher total P_i concentrations. The CC, BS, and TL models all required relatively large intrinsic equilibrium constants ($K_{int}^{+,-}$) for electrolyte-goethite interaction, whereas the CD-M model used more realistic $K_{int}^{+,-}$ values. Furthermore, the CD-M model was the only model examined which adequately described ζ-potential charging data. The CD-M model thus appears to be the most appropriate model for describing P_i adsorption behavior on goethite, but further work is needed to confirm this finding for other oxyanion-mineral systems.

Cornell RM & Schwertmann U, *The Iron Oxides: Structure, Properties, Reactions, Occurrence and Uses. VCH, Weinheim*, 395-432, (1996).

Frossard E, Brossard M, Hedley MJ & Mertherell A, *Phosphorus in the Global Environment: Transfers, Cycles, and Management. John Wiley & Sons, Chichester*, 107-137, (1995).

Goldberg S, *Advances in Agronomy. Academic Press, San Diego*, **47**, 233-329, (1992).

Herbelin A & Westall JC, *FITEQL ver 4.0. Department of Chemistry, Oregon State University*, (1999).

Hiemstra T & Van Riemsdijk WH, *J. Colloid Interface Sci.*, **210**, 182-193, (1999).

McBride MB, *Environmental Chemistry of Soils. Oxford University Press, New York*, 121-168, (1994).