

A continuum of oxyanion adsorption mechanisms on metal oxides: results from *in situ* spectroscopies

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Many different oxyanions are found in the soil environment, and the chemistry of these oxyanions is quite varied. Oxyanions are studied for both agronomic and environmental reasons by soil chemists. Some oxyanions such as phosphate and sulfate are essential nutrients for plant growth and are found in relatively high concentrations in soils. Other oxyanions such as borate are micronutrients. They are essential for plant growth at low concentrations but become toxic at higher concentrations. The range between deficiency symptoms and toxicity is usually quite narrow. A third group of oxyanions, such as arsenate, arsenite, selenate, selenite, and chromate are frequently studied because they have little agronomic use and are instead detrimental to human health. Understanding the mechanisms by which these oxyanions react with mineral surfaces is vital for predicting their bioavailability, toxicity, and transport in natural systems.

Our research group has conducted many *in situ* spectroscopic studies to determine the mechanism by which many different oxyanions sorb to an array of soil components. Several types of X-Ray Absorption Spectroscopy (XAS) have been utilized to study arsenate, arsenite, selenate, sulfate, and phosphate sorption on iron and aluminum oxides. Attenuated Total Reflectance (ATR) FTIR spectroscopy was employed to study sulfate, phosphate, and borate adsorption on iron oxides. Additionally, Nuclear Magnetic Resonance (NMR) spectroscopy was utilized to study phosphate sorption on aluminum oxides. While the mechanisms of adsorption are unique to both the sorbate and sorbent being studied, there is also a recurring theme in all studies that is of great importance.

In many cases, more than one adsorption mechanism can be seen to occur simultaneously. In systems where only adsorption is occurring, then both outer-sphere and inner-sphere complexation are often seen at the same time. This distribution of outer-sphere and inner-sphere surface complexes has been seen with sulfate, selenate, and borate on iron oxides, and for arsenite on both aluminum and iron oxides. In systems where precipitation is occurring, then adsorption complexes are still present. This has been determined for phosphate sorption on both aluminum and iron oxides. Reaction conditions such as pH, ionic strength, and reactant concentration have all been shown to influence the relative distribution of the simultaneously occurring sorption complexes. Therefore it is necessary to conduct spectroscopic studies at a wide range of reaction conditions to truly understand the reactivity of oxyanions. It is also important to account for outer-sphere complexation of oxyanions when attempting to describe their adsorption with surface complexation models.

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