

Anion adsorption and post-adsorption behavior of metastable iron hydroxides

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Pollution by dissolved anions has been a pertinent environmental concern in many areas around the world. For example, acid mine drainage from abandoned mines and contaminated waters resulting from the Fukushima nuclear power plant accident emphasize the importance of predicting the behavior of the dissolved trace elements on Earth's surface environments. Iron minerals may play a potentially important role in the control of dissolved trace elements in the environment. In particular, poorly crystalline iron minerals exhibit excellent adsorption capacities for toxic anions due to their high specific surface areas and reactivity. In order to evaluate the potential of poorly crystalline iron minerals as stable sinks of dissolved hazardous ions, it is necessary to investigate the adsorption mechanism on these minerals and their post-adsorption behaviors.

Adsorption experiments using arsenate, phosphate, chromate, sulfate, selenate, fluoride, and chloride were performed to investigate the selectivity of Schwertmannite and Ferrihydrite for various anions. Adsorption selectivity decreases in the following order: $\text{H}_2\text{AsO}_4^- > \text{H}_2\text{PO}_4^- > \text{HCrO}_4^- > \text{SeO}_4^{2-} \approx \text{SO}_4^{2-} \gg \text{F}^- \approx \text{Cl}^-$. Schwertmannite and Ferrihydrite didn't have an ability to adsorb F^- and Cl^- . The adsorption mechanism of these anions was investigated using zeta potential measurements. The results indicated that H_2AsO_4^- , H_2PO_4^- and HCrO_4^- formed inner-sphere complexes while SeO_4^{2-} and SO_4^{2-} formed outer-sphere complexes. The adsorption mechanism of these anions to both Schwertmannite and Ferrihydrite is generally similar, except in the case of HCrO_4^- .

Accelerated alteration experiments were performed to observe post-adsorption behaviors of Schwertmannite and Ferrihydrite. Oriented specimens loaded with varying amounts of adsorbed anions were aged under saturated water vapor pressure conditions at 50 °C for 30 days and analyzed by XRD. Results show that larger amounts of adsorbed anions delay the transformation of Schwertmannite and Ferrihydrite into more stable phases, indicating that adsorption of anions, particularly as inner-sphere complexes, stabilizes poorly crystalline iron minerals.

These results show that poorly crystalline iron minerals are capable of taking up a range of toxic anions from contaminated waters and that the stability of these minerals will be affected by the amount of anions sorbed on the surface. These suggest that poorly crystalline iron minerals may serve as stable, long-term sinks for toxic anions.