

A geochemical model of arsenic sorption on clay mineral functional sites

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The Method

The mobility of arsenic species in the environment is largely controlled by solid phase sorption reactions. Quantitative evaluations of the solid phase/water partitioning of many toxic metals, including arsenic, are best accomplished by a surface complexation approach. Equilibrium-based thermodynamic modelling is currently one of the most appropriate methods to evaluate the competitive geochemical processes that affect the transport and toxicity of arsenic, including predictions regarding arsenic persistence and mobility in the environment.

Computation

The USGS numerical computer code PHREEQC version 1.6 was used for all simulations. The code was used to simulate arsenic surface complexation from a small watershed with naturally high levels of arsenic on clay mineral components (kaolinite and montmorillonite) of a stream sediment. Surface complexation mass-action coefficients were obtained from the literature in the generalized two-layer model form, or from linear free energy relationships. The WATEQ4F thermodynamic database formed the core to which surface complexation parameters were added. The code was used for the calculation of saturation indices, sensitivity analysis of parameters such as Eh, pH and temperature, modelling the mixing of stream water of different compositions. The surface complexation routine was used in the generalized two-layer model and competition between arsenic and other ions for sorbing phases for a finite number of sites was allowed. Both mineral assemblages were allowed to come to equilibrium by simulating the flushing of many pore volumes through the sediment-mineral surface assemblage.

The model output was evaluated using the ratio "R" of modeled vs. expected arsenic concentrations. Small differences in the conceptual model and data acquisition techniques can have a large effect on the simulation error. The error of neglecting competition by common compounds such as bicarbonate or silicic acid can equal or exceed the bias resulting from inappropriate choice of mineral phases.

References

Sadiq M., (1997), *Water, Air and Soil Pollution*, **93**, 117-136.
Wilkie J.A. and Hering, J., (1998), *Env.Sci.Tech.*, **32**, 657-666.

Controls on schwertmannite transformation rates and products

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The formation and transformation of schwertmannite is of geochemical significance in acid mine drainage (AMD) polluted surface waters. Sediments dominated by schwertmannite typically adjust to a pH around 3, as the mineral slowly transforms into more stable phases and thereby releases protons. At such low pH and only short supply of electron donors due to the low productivity of AMD polluted lakes, the sediments are characterized by an iron reducing regime. Sulfate reduction would be desirable to reverse pyrite weathering and sequester acidity, but was found to take place at significant extent only at a pH higher than 5, though. The impact of environmental factors such as dissolved organic carbon (DOC), high sulfate concentrations, pH or temperature on schwertmannite transformation is thus of particular interest when studying the biogeochemistry of AMD affected lake sediments.

To evaluate the effect of geochemical conditions on the fate of schwertmannite in AMD polluted sediments, we varied pH, concentrations of sulphate and DOC, and temperature in batch experiments. We quantified schwertmannite transformation by titration of released acidity and investigated the product with FTIR, XRD, SEM/EDX, and chemical extraction with 1N HCl. Transformation rates ranged from 0.0002 d⁻¹ to 0.13 d⁻¹ (transformed fraction / incubation time). Raising pH from 3 to 5 increased transformation by a factor of 5.8 (±2.1) and temperature from 10 to 20° C by a factor 3.8 (±1.6). Sulphate (20 mmol L⁻¹) and DOC (20 mg L⁻¹) lowered transformation by a factor of 2.5 (±0.4) and 2.4 (±0.5). The newly formed iron phase was less dissolvable in 1N HCl but goethite was not detected by XRD. The morphology did hardly change, even in sulphate-poor iron phases and no goethite-typical needle structures could be observed. Thus we concluded that an amorphous, sulphate depleted iron phase had formed. Most of the sulphate released from the schwertmannite structure remained bound to the solid phase. We interpreted changes in IR bands at 1108 cm⁻¹ (ν₃) and 984 cm⁻¹ (ν₁) as a relocation of sulphate.

The study documents the high potential of schwertmannite to buffer pH increase in sediments, particularly at low sulphate concentrations, and high temperatures. This coincides with the finding that strongly acidic sediments dominated by schwertmannite remain in an iron reducing state for a long time.

In contrast to other studies conducted in deionized water we could not identify goethite to be the transformation product under the conditions chosen.