

## Sorption of arsenic under oxic and anoxic conditions: Possible origins of elevated arsenic in groundwater

JÖRGEN JÖNSSON AND DAVID M. SHERMAN

Dept. of Earth Sciences, Bristol University, Bristol, UK  
 (jorgen.jonsson@bristol.ac.uk;  
 dave.sherman@bristol.ac.uk)

In Bangladesh and West Bengal, millions of people are using groundwater with elevated (> 50ppb) concentrations of arsenic. The origin of the elevated arsenic levels is still unclear. Both As(V) and As(III) are strongly sorbed to iron(III) (hydr)oxides. We have developed surface complexation models for sorption of As(III) and As(V) on goethite and ferrihydrite. These models predict that sorption should limit As concentrations to acceptable levels even when As(V) is reduced to As(III) and ferrihydrite transforms to goethite. One hypothesis for the elevated As concentrations is that sorbed As is released during bacterial reductive dissolution of Fe(III) (hydr)oxides. However, this should yield a strong correlation between dissolved Fe and As but this is not observed. The formation of secondary Fe(II) or mixed Fe(II)/Fe(III) minerals such as siderite (FeCO<sub>3</sub>), green rust (GR) and magnetite has been suggested to reduce the aqueous concentration of Fe while leaving the concentration of As high in the Bangladesh and West Bengal aquifers. To test this hypothesis we have studied the adsorption of arsenite and arsenate to siderite, carbonate GR and magnetite as a function of pH using EXAFS and batch adsorption experiments.

EXAFS spectra show that As(V) sorbs to GR, magnetite and siderite by forming bridging bidentate inner-sphere surface complexes. The adsorption is similar to that of As(V) on Fe(III) (hydr)oxides and the adsorption decreases with increasing pH. No evidence of As(V) reduction is found. Hence, reduction of iron(III) (hydr)oxides could release As(V) into solution but the formation of GR, magnetite or siderite would immediately re-adsorb the released As(V), keeping the aqueous As(V) concentration low.

EXAFS spectra show that As(III) forms strong inner-sphere surface complexes on magnetite and GR, similar to that of As(V). No evidence of As(III) oxidation is found. On siderite, however, As(III) sorbs only by forming a weak outer-sphere complex and adsorbs much less strongly than to GR, magnetite or Fe(III) (hydr)oxides.

We propose that the elevated groundwater concentrations of As in West Bengal and Bangladesh result from the reduction of iron(III) (hydr)oxides to siderite in conjunction with the reduction of As(V) to As(III).

## Magnesite dissolution in the presence of organic and inorganic ligands

G. JORDAN<sup>1</sup>, O. POKROVSKY<sup>2</sup>, X. GUICHET<sup>3</sup> AND W.W. SCHMAHL<sup>1</sup>

<sup>1</sup>Dept. f. Geo- u. Umweltwiss., LMU, München, Germany  
 (jordan@lmu.de)

<sup>2</sup>LMTG-OMP CNRS, Univ. P. Sabatier, Toulouse, France

<sup>3</sup>Division Géologie-Géophysique-Géochimie, IFP, Rueil-Malmaison, France

Quantitative and predictive modelling of CO<sub>2</sub> sequestration in deep aquifers requires precise knowledge of carbonate mineral reactivity at conditions pertinent to CO<sub>2</sub> storage. Whereas the effect of temperature, salinity, pH, and pCO<sub>2</sub> on Ca- and Mg-carbonate dissolution is extensively studied, the understanding of the influence of organic and inorganic ligands, omnipresent in deep sedimentary basins, remains very limited. Organic and inorganic molecules can exert various influences on the kinetics of growth and dissolution of crystals. The ligands can promote or inhibit growth and dissolution and can control crystal morphology.

Here, a combination of mixed-flow reactor experiments and in-situ hydrothermal atomic force microscopy experiments has been used to investigate the effect of organic (acetate, oxalate, citrate, succinate, EDTA) and inorganic (sulphate, phosphate, borate) ligands on the surface morphology of magnesite and on the molecular mechanism and kinetics of magnesite dissolution at different pH values and NaHCO<sub>3</sub> concentrations.

Since AFM enables to observe monolayer step motion on the surface as well as the step formation frequency by pit nucleation, the effect of ligands on the rate of detachment at specific surface sites can be determined. Thus, AFM data can be interpreted towards a determination of the consequences of adsorption at specific sites on the dissolution kinetics of magnesite in a molecular scale. Comparisons of these data with the dissolution rates of the (104) surfaces and with the dissolution rates of entire crystals (obtained by mixed-flow reactor experiments) allow one to link the molecular-scale effects to the macroscopic effects of ligands on magnesite dissolution.

At circum-neutral pH, the experiments showed a most pronounced effect in citrate- and EDTA-bearing solutions. For citrate, the modification of the reactivity of a distinct kink-site could be detected. More pronounced than the effect of organic ligands was the effect of 0.01 M NaHCO<sub>3</sub> (at pH around 8) which caused a general decrease in reactivity at far from equilibrium conditions. The ligands phosphate, oxalate, citrate, and EDTA were found to weaken but not to fully compensate the retardation of the reactivity generated by NaHCO<sub>3</sub>.