

Copper speciation in variably toxic sediments: Ely Copper Mine Superfund Site, Vermont

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Near the Ely Copper Mine, a Superfund site in Vermont, both surface water and sediment quality are impacted by acid rock drainage and elevated metal concentrations, with Cu being the dominant metal and contaminant of concern [1]. Chronic water-quality criteria for Cu are exceeded in the section of Ely Brook that drains mine waste. In this same section, however, stream bed sediment toxicity, as measured by detritus-feeding invertebrates called amphipods, varies. At an upstream sample location where surface and *in situ* pore water pHs are near 7, stream bed sediments display high toxicity (6% survival), but at a downstream sample location where surface and *in situ* pore water pHs are near 3, stream bed sediments have lower toxicity (91% survival) [1]. Because Cu concentrations in Ely Brook stream bed sediments are high throughout the study area (0.33 – 0.93 wt.%), the toxicity results suggest that Cu in upstream sediments is more bioavailable than Cu in downstream sediments. In sediment samples examined using bulk X-ray diffraction, no Cu minerals were detected above detection limits, so we hypothesize that the variable Cu toxicity is due to differences in the identity, relative abundance, and/or distribution of solid-phase Cu species, where Cu is a trace to minor component.

In an effort to characterize Cu speciation in these distinct toxicity environments, we collected six stream bed sediment samples along the toxicity gradient and conducted meso-scale (50-100 µm beam size) X-ray fluorescence microscopy (XRF) on sediment thin sections, and X-ray absorbance spectroscopy (XAS) on bulk dried sediment powders and representative model compounds. Both datasets were collected under ambient conditions.

Preliminary XRF results indicate that Cu in the relatively toxic upstream sample correlates with Mn, and generally coats mineral grain surfaces. In less toxic downstream samples, Cu correlates strongly with S and Zn, and weakly with Fe. Preliminary analysis of calibrated and normalized X-ray absorption near edge spectra (XANES) shows clear evidence of the presence of a Cu-sulfide phase in downstream, low-toxicity sediments. The upstream, high-toxicity sample displays an overall XANES spectrum similar to spectra for Cu-sorbed Fe- and Mn-(hydr)oxides. The relative abundance of dominant Cu species is being determined by linear-combination, least-squares fitting. Preliminary results indicate that downstream sediment spectra are fit 80-90% by chalcopyrite and 10-20% by Cu-jarosite. The upstream sediment spectrum is fit nearly 100% by Cu-sorbed MnO₂. The spectroscopic findings are consistent with the toxicity results given the lower solubility of Cu sulfides relative to Cu sorbed phases under relevant environmental conditions.

[1] Seal, R.R. II *et al.* (2010) *US Geological Survey Scientific Investigations Report* 2010-5084.

Sulphate inhibition of magnesite dissolution: An in-situ AFM study

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Magnesite is the expected product phase of CO₂ sequestration in strategies involving Mg-silicates. Its formation and stability in these environments will be controlled by the ions present in rock pore fluids, e.g. NaCl and sulphates, as well as temperature and pH. The effect of different ligands on magnesite stability has been studied at aquifer conditions, i.e. low concentrations, in *ex-situ* flow-through experiments where sulphate was shown to enhance the dissolution [1]. To test whether this effect is also prominent at higher sulphate concentrations we have conducted *in-situ* dissolution experiments of the {10¹4} magnesite surface using atomic force microscopy (AFM) at room temperature with Na₂SO₄ concentrations between 0.01 and 0.1 M. Solutions were acidified to pH 2 because magnesite dissolution under ambient conditions is slow. However, rather than observing an increase in dissolution under our experimental conditions, sulphate dramatically reduced the magnesite dissolution rate. To determine whether this effect was a consequence of the mixed electrolytes used in the experiments of Pokrovsky *et al.* [1] magnesite dissolution in solutions of 0.1 M NaCl and 0, 0.01, 0.03 or 0.1 M Na₂SO₄ was tested. Experiments at approximately 40 °C were also conducted to study the role of temperature on the sulphate effect.

Increased dissolution was observed with 0.1 M NaCl without sulphate in comparison to dissolution in 0.1 M Na₂SO₄. The effect of sulphate was not diminished by the concomitant presence of chloride even when the concentration of the different anions was equal. Increasing the solution temperature also did not change the effect of sulphate on magnesite dissolution. Formation of Mg-sulphate interactions are expected to be facilitated by the presence of NaCl in solution due to its effect on ion hydration [2]. Similarly, higher temperatures have been shown to increase the number of contact ion pairs between Mg and sulphate in solution [3]. Both of these effects are possibly a consequence of changes in the ion hydration. Therefore, it would be expected that the presence of sulphate in higher ionic strength solutions or higher temperatures would also retard magnesite dissolution. A precipitate was observed on the surface during the experiments despite the undersaturation of the input solution with respect to Mg-carbonate phases and the inhibition of magnesite dissolution in the presence of sulphate. This indicates that in our experiments the fluid boundary layer present at the mineral surface plays a crucial role in the reaction. Thus, sulphate in this boundary layer, which could be present in nature but was minimized in previous *ex-situ* flow-through experiments, plays a critical role in magnesite reactivity.

[1] Pokrovsky *et al.* (2009) *Chemical Geology* **265**, 33-43.

[2] Ruiz-Agudo *et al.* (2011) *Chemical Geology* **281** 364-371.

[3] Rudolph *et al.* (2003) *Physical Chemistry Chemical Physics* **5**, 5253-5261.