

Selenium isotope variation during oceanic anoxic events

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Selenium (Se) exhibits multiple oxidation states, including -2, 0, +4 and +6, and has six stable isotopes (atomic masses: 74, 76, 77, 78, 80 and 82). Fractionation of Se isotopes during various chemical and biological redox transformations has been experimentally verified [1]. Stable isotope signatures of Se may therefore provide potentially useful (paleo)environmental proxies.

In this study, we report Se concentrations and stable Se isotope ratios across three major ocean anoxic events: the Late Cambrian SPICE event recorded in the Alum Shale, the Lower Toarcian Posidonia Shale and the mid-Cretaceous ocean anoxic event OAE2 (ODP Leg 207, core 1258, Demerara Rise). The Se concentrations generally correlate positively with the total organic carbon contents. The Demerara Rise samples, however, are greatly enriched in Se, with concentrations up to 35 ppm, compared to 0.5-3 ppm for the two other sites.

The Se stable isotopic fractionations are fairly small: values of $\delta^{82/76}\text{Se}_{\text{NIST}}$ range from -1 to +1‰, with the largest variations in the Demerara Rise core samples. The measured $\delta^{82/76}\text{Se}_{\text{NIST}}$ variations are much smaller than would be expected for dissimilatory utilization of Se by microorganisms. We propose that the observed stable isotope signatures primarily reflect assimilatory Se uptake by phytoplankton in the water column, which only causes small fractionation effects ($\epsilon^{82/76}\text{Se}_{\text{NIST}}$ between 1.5 and 3.9‰ [2]). The Se is subsequently buried with organic matter without further isotopic fractionation.

[1] Johnson (2004) *Chem. Geol.* **204**, 201–214. [2] Clark (2007) *PhD Thesis*, Univ. Illinois, 80.

Antimony(V) incorporation into synthetic and natural Fe hydroxides

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Antimony (Sb) is the ninth most mined metal for industrial uses and one of toxic elements. Elevated concentrations of Sb in soils have been detected around mining and smelter areas, at shooting ranges, and along roadsides. However, geochemical and environmental behaviors of Sb in aquatic systems are still unknown. The oxidation states of Sb most frequently observed in the environment are Sb (III) and Sb (V). Recent studies have shown that Sb (V) is the stable species over a wide redox range in soil and that the Sb (V) is strongly associated with Fe (III) hydroxides in oxic soils and sediments [1-2]. Although several studies have investigated the Sb (V) adsorption mechanism on Fe (III) hydroxides, influences of surface coverage and pH on the surface complex species are still unclear. Moreover, another process, coprecipitation into the Fe (III) hydroxides, has not been investigated at all.

In this study, we investigated the local structures of Sb species in synthetic Sb (V)-coprecipitated and -adsorbed ferrihydrite and goethite, which are common Fe (III) hydroxides, at various Sb/Fe molar ratios using *in situ* speciation method, extended X-ray absorption fine structure (EXAFS).

The EXAFS analyses showed that Sb (V) is adsorbed on ferrihydrite and goethite by formation of inner-sphere complex around neutral pH. In the EXAFS spectra of the coprecipitated ferrihydrite and goethite, some features of the spectra significantly differed from those in the adsorbed samples. The EXAFS simulation indicated that the difference is due to the larger coordination number of Fe to Sb atom in the coprecipitation samples, indicating the structural incorporation of Sb (V) into the ferrihydrite and goethite. The incorporation of Sb (V) was also confirmed in natural Fe (III) hydroxides in contaminated soil near an Sb mine tailing using μ -EXAFS.

Our new findings are important for understanding the fate of Sb in the aquatic environment, since the behavior of elements incorporated into solids is not greatly influenced by aquatic factors such as pH and ionic strength because of isolation of the incorporated metal ions from the aqueous phase.

[1] Mitsunobu *et al.* (2006) *Environ. Sci. Technol.* **40**, 7270.

[2] Mitsunobu *et al.* (2010) *Environ. Sci. Technol.* **44**, 1281.