

## Non-skeletal carbonate precipitates: Indicators of Molybdenum isotopic seawater composition?

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Studies on black shales and oxic manganese crusts indicate that the Mo isotopic signature is a suitable proxy for the detection and interpretation of changes in past ocean redox conditions (Siebert *et al.*, 2003, Arnold *et al.*, 2004, Barling *et al.*, 2001). Carbonate rocks are a reservoir not yet investigated with respect to their Mo isotopic composition. Due to their occurrence during most of Earth's history and in a wide variety of geological settings, their Mo isotopic signature has the potential to provide a continuous record of ocean redox chemistry.

We present Mo isotopic data obtained from modern ooid sands from the Bahamas and the Persian Gulf. Their isotopic composition approximates modern seawater signature, while modern skeletal material has a significantly lighter value. Also, our data from chemically precipitated marine cements from the Carboniferous of Spain and China exhibit a heavy isotopic composition similar to today's ocean water and a distinct offset from their surrounding isotopically lighter sediment material. This has led us to hypothesize that the Mo budget of non-skeletal marine carbonates is controlled by seawater and may serve as an archive of ocean water Mo isotopic composition. As a pilot study we analyzed a transgressive carbonate sequence of Mid-Cambrian age. The already well defined Mo isotopic seawater composition of the early Cambrian (Lehmann *et al.*, 2007) serves us as a reference for the interpretation of the isotopic signal of the section. Our results indicate that Mid-Cambrian non-skeletal carbonates differ from their Carboniferous counterparts, which indicates that Early Paleozoic oxygen levels had not yet risen to Late Paleozoic and present-day concentrations.

### References

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## Colloid formation in aerated Fe(II) and As(III) containing water: Effect of phosphate, silicate and Ca on local coordination by XAFS spectroscopy

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Colloid formation due to iron oxidation and hydrolysis affects the cycling of nutrients and contaminants in environmental and technical systems. The extent of As oxidation and uptake by colloids and the composition and colloidal stability of the resulting colloids are major factors controlling the removal of As from As-rich anoxic drinking water. We investigated Fe(III)-colloid formation and concomitant As(III) oxidation and removal in synthetic carbonate-buffered groundwater (pH 7, 2-30 mg/L Fe(II), 0.5 mg/L As(III)) as influenced by phosphate (2-20 mg/L P), silicate (2-20 mg/L Si), and Ca (2.5 mM Ca- and 1.5 mM Mg- versus 8 mM Na-bicarbonate). The oxidation state of As and the local coordination of As, Fe, P, Si, and Ca in colloids collected after 4 hours of oxidation were investigated by X-ray absorption fine structure (XAFS) spectroscopy.

The removal of As from solution by uptake into settling colloids depends on a range of coupled processes such as the enhanced As(III) oxidation in presence of Fe(II), the competition of phosphate, silicate, and As for sorption sites on Fe(III)-colloids, and the effect of phosphate, silicate and Ca on molecular-scale colloid structure and colloid aggregation. While higher Fe(II) concentrations promote As(III) oxidation in solution, the associated increase of sorption sites on Fe(III)-colloids reduces anion competition, resulting in a higher fraction of colloidal As(III) (relative to total colloidal As). Increasing P/Fe ratios promote the formation of basic Fe-phosphates and increasing Si/Fe ratios the formation of ferrihydrite at the expense of lepidocrocite (which forms in the absence of P and Si). In the presence of P and Si, the P/Fe and Si/Fe ratios determine the extent to which basic Fe(III)-phosphate- and ferrihydrite-type colloids form. In the absence of Ca, colloids formed at low Fe concentration and high P/Fe ratio are colloidal stable, resulting in reduced As removal from solution. The presence of Ca promotes colloid coagulation by diminishing electrostatic colloid repulsion. Especially at high P/Fe ratios, we find that Ca is also directly incorporated into the colloid structure, suggesting the formation of mixed basic Ca-Fe(III)-phosphates. Spectroscopic data further suggest that also As(V) may be incorporated into these phosphates.