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Cu and Zn isotope fractionation during sorption experiments

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Introduction

Chemistry occurring at mineral/fluid interfaces is fundamental in the natural cycling of many chemical species. Such processes control the concentration of trace metals in solution, with major impact in environments such as rivers, estuaries and the drainage from acid mines. Despite recent advances in understanding of such sorption processes, little is known about the relationship between sorption and isotope fractionation. Such fractionation will, however, play a fundamental role in setting the isotope composition of metals in natural solutions, and may provide new ways to study the mechanisms of surface sorption that occur in the natural environment.

Li isotopes are known to fractionate during sorption onto gibbsite but not during sorption onto smectite [1]. Interpretation of these observations in terms of the chemical bonding involved is difficult because sorption processes are poorly known for Li because its low atomic mass precludes the use of relevant spectroscopic methods. In this study we therefore focus on understanding the isotope fractionation associated with the surface chemistry of Cu and Zn for which sorption mechanisms are well constrained [2].

Results

Sorption experiments were performed at various pH and ionic strengths onto montmorillonite, kaolinite, goethite and gibbsite. Cu and Zn remaining in solution were then separated from the electrolyte by ion-exchange and analysed by MC-ICP-MS. Preliminary results exhibit a slight Cu-isotope fractionation during sorption onto gibbsite while no fractionation occurs onto smectite. At the low ionic strengths investigated, this result suggests that inner-sphere sorption generates fractionation of transition metal isotopes while outer-sphere sorption does not. Present work is testing this model by repeat experiments at higher ionic strength where inner-sphere sorption of copper onto smectite is known to occur. This and other laboratory experiments will lead to quantitative understanding of the way that sorption processes generate isotope fractionation, and therefore control the isotope composition of natural waters and minerals.

References

- [1] Pistiner J.S. and Henderson G.M. (2003) *EPSL* **214**, 327-339.
- [2] Brown G.E. and Parks G.A. (2001) *Int. Geol. Rev.* **43**, 963-1073.

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Fe isotope fractionation during redox cycling of Fe in lake water

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Elucidating Fe isotope fractionation in redox cycles in natural environments is important in order to use Fe isotopes as a signature of biogeochemical conditions in the past. An optimum approach to investigate Fe isotope fractionation mechanisms during redox cycling of Fe in natural waters is high resolution sampling of seasonally anoxic lake water from the ice.

The sampling of suspended particulate matter (SPM) and filtered water was performed across the oxic-anoxic interface in lake water. Fe isotope compositions were determined by high-resolution multiple-collector ICP-MS (Neptune, Thermo-Finnigan MAT, Bremen, Germany). Prior to analysis, Fe was extracted from the samples using anion-exchange chromatography. Instrument mass discrimination was corrected with a Ni "element spike". External precision (1 σ) on $\delta^{56}\text{Fe}$ was better than $\pm 0.05\%$.

$\delta^{56}\text{Fe}$ values for SPM sampled incrementally from anoxic to oxygenated water display statistically significant negative shifts, relative to IRMM-014 isotopic standard. $\delta^{56}\text{Fe}$ values for SPM in the water column change from $0.01 \pm 0.03\%$ in anoxic water to $-0.83 \pm 0.04\%$ in oxygenated water within 0.8 m of the vertical profile. Dissolved Fe (II) species in the anoxic water show $\delta^{56}\text{Fe}$ value equal to $-1.05 \pm 0.03\%$. Fe isotopic composition of dissolved Fe (III) species in the oxygenated water was not possible to measure due to low concentration. However, using the concentration data and $\delta^{56}\text{Fe}$ values for SPM and dissolved Fe (II) species at the oxic-anoxic interface the estimation was made that dissolved Fe (III) species might have very light Fe isotopic composition. The observed distribution of $\delta^{56}\text{Fe}$ values during redox cycling of Fe is consistent with the model of equilibrium Fe isotope fractionation between co-existing aqueous Fe (II) species, such as $\text{Fe}(\text{OH})^+$, prior to oxidation as earlier proposed by Bullen et al. [1].

References

- [1] Bullen T.D., White A.F., Childs C.W., Vivit D.V., and Schulz M.S. (2001) *Geology* **29**, 699-702.