

Redox fractionation of copper isotopes in sedimentary conditions

DAN ASAEEL^{1,2}, ALAN MATTHEWS¹, MIRYAM BAR-MATTHEWS², LUDWIK HALICZ², SARA EHRLICH²
AND NATALIYA TEPLYAKOV²

¹Institute of Earth Sciences, Hebrew University of Jerusalem, Israel (barvaz@pob.huji.ac.il; alan@vms.huji.ac.il)

²Geological Survey of Israel, 95501 Jerusalem, Israel (matthews@gsi.gov.il; ludwik@gsi.gov.il)

Experimental study (Ehrlich et al., 2004) has shown that a relatively large negative copper isotope (⁶⁵Cu/⁶³Cu) fractionation (~3‰) occurs during the precipitation of Cu(I)S (covellite) from Cu(II) solution. Biogenic processes may similarly lead to heavy-isotope depletion (1-1.7‰) in bacteria (Zhu et al., 2002). This research presents a copper isotope fractionation study of sedimentary copper minerals in the Cambrian and Lower Cretaceous sedimentary sequences of the Timna Valley area, southern Israel. These rocks are emplaced on top of Precambrian igneous basement, whose weathering provided the solution source from which the copper minerals precipitated. Several cycles of copper mobilization occur within the sediments including: (1) diagenetic deposition of copper sulphides [djurleite (Cu_{1.93}S) and covellite (CuS)] within Cambrian dolomites and their in-situ oxidation to give copper (II) minerals [malachite (Cu₂(OH)₂CO₃); paratacamite (Cu₂OH₃Cl); (2) epigenetic remobilization in Cambrian sandstones and shales giving veins of malachite, paratacamite and copper silicates; (3) biogenic formation of copper sulphide concretions in Lower Cretaceous sandstones and their oxidation. Isotopic measurements were made on a Nu Instruments MC-ICP-MS with nickel internal standard and ion exchange separation.

^{δ65}Cu (SRM 976) values of copper sulphides range from ~ -4 to -1 ‰, whereas oxidized copper minerals range from -2 to +2 ‰. Fractionation factors (Δ_{Cu(II)-CuS}) for copper oxide minerals replacing copper sulphides vary from ~ 1 to 3 ‰, with most values being around 2 ‰. Thus, there is a clearly defined positive fractionation accompanying the supergene oxidation of copper sulphides. Since the igneous source for the copper (quartz-porphyr) probably had ^{δ65}Cu values of about 0.0 ± 0.5 ‰ (published literature and our own analyses), it is also clear that a large negative isotopic fractionation is associated with the formation of copper sulphides. Thus, redox cycling of copper leads to significant isotopic fractionation, as predicted in experiments. Whereas the oxidation processes are clearly abiogenic, it appears that fractionation processes involving the formation of low ^{δ65}Cu copper sulphides are biogenic in origin.

References

- Ehrlich et al. (2004) *Chem. Geol.* **209** 259-269.
Zhu et al. (2002) *Earth Planet. Sci. Lett.* **200** 47-62.

Isotopic effects during Cu sorption onto goethite

R.E. CLAYTON, K.A. HUDSON-EDWARDS AND
S.L. HOUGHTON

Research School of Earth Sciences at UCL-Birkbeck, Gower Street, London, WC1E 6BT, UK (r.clayton@ucl.ac.uk)

Of the many particles found in the environment, Fe (oxy)hydroxides are among the most common and reactive in terms of contaminant uptake. Isotopic effects during the sorption process have not been widely studied but may hold application in quantifying contaminant retardation. Preliminary sorption experiments were conducted using synthetic goethite and Cu^{II} solutions according to Parkman et al. (1999). Each batch was checked for purity by XRD. The Cu^{II} solution and Cu-sorbed goethite particulate were then separated by centrifuge prior to sub-sampling, digestion (goethite) and purification by ion exchange. Isotopic measurements (Micromass *IsoProbe* (GV Instruments)) were conducted using simultaneous standard-sample bracketing and Zn doping methods to enable alternative correction algorithms to be applied for mass discrimination effects. The external reproducibility on the standard was typically <150ppm.

Two out of three of our triplicates showed slight ⁶⁵Cu enrichment in the goethite relative to the Cu^{II} solution, whilst the third showed no change outside the propagated analytical error (±0.1‰ 2σ). For the experiments that showed a difference the respective ^{δ65}Cu were 1.08 ± 0.10‰, 1.07 ± 0.09‰, and 0.71 ± 0.09‰, 0.73 ± 0.09‰. The ^{δ65}Cu_{goethite-solution} values for the two experiments are 0.37 ± 0.11‰ and 0.34 ± 0.10‰ and indicate that the heavier Cu isotope is sorbed onto goethite. Previous XANES has shown that the Cu complex sorbed onto goethite is similar to that of [Cu(H₂O)₆²⁺], which suggested Cu is octahedrally coordinated to O (Parkman et al. 1999). This is analogous to that discovered for Zn sorption onto goethite (^{δ66}Zn_{goethite-solution} = 0.15 ± 0.08‰) in which EXAFS proved octahedral coordination for sorbed Zn and for Zn in solution (Cacaly et al. 2004). Further Cu isotopic studies in conjunction with XAS are planned in order to decipher isotopic effects that depend in part on speciation and the bonding environment.

References

- Cacaly, S., Marechal, C., Juillot, F., Guyot, F. and Benedetti, M. (2004). *Geochim. Cosmochim. Acta*, A366.
Parkman, R.H., Charnock, J.M., Bryan, N.D., Livens, F.R. and Vaughan, D.J. (1999). *Am. Mineral.* **84**(3), 407-419.