Experimental study of copper isotope fractionation between aqueous Cu(II) and Cu(I) sulphide

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We report here initial results of a study of the geologically important copper isotope ($^{65}Cu/^{63}Cu$) fractionation between aqueous Cu(II) and solid Cu(I) sulphide. Experiments were made in anaerobic conditions by precipitating Cu(I) sulphide from excess copper sulphate solution by the addition of aliquots of sodium sulphide solution. After separation of the precipitate by filtration, the residual bulk copper in solution was precipitated by the addition of excess sulphide. Isotopic analyses of both copper fractions were made relative to the SRM 976 standard on a Nu Instruments MC-ICP-MS using sample-standard bracketing, after dissolution and diluting to give 1 ppm Cu in 0.1M HNO_3 solution matrix. Independent studies show that Cu(II) reduction by sulphide to Cu(I) occurs in solution prior to precipitation of the solid Cu(I)S phase (Luther et al, 2002).

The results of a series of experiments at 20°C give a mean fractionation of $\Delta^{65}Cu$ (Cu(II) – Cu(I)S) = 3.0 ± 0.18 ‰. This value is independent of ageing of the precipitate, CuS precipitate/bulk solution ratio or the filter membrane size (0.45 and 0.02 μm). Additional experiments made at 2°, 10° and 40°C show that the fractionation factor varies inversely with temperature ($\Delta(\Delta^{65}Cu) \approx 0.2*10^{6}T^{-2}$).

Although the lighter isotopic composition of the precipitated Cu(I)S could be compatible with either kinetic or equilibrium fractionation, the observed inverse temperature dependence is in accordance with the theory of equilibrium isotopic fractionation. The ~ 3‰ Cu(II)–Cu(I)S fractionation compares with the 4 ‰ value for the Cu(II)- Cuprous iodide fractionation at 22°C (Zhu et al, 2002) and the much smaller experimentally measured Cu(II)-malachite fractionation (-0.2 to -0.4‰) (Maréchal and Sheppard, 2002). Thus, redox state is to be expected a significant control of $^{65}Cu/^{63}Cu$ fractionation in low-temperature copper deposits.

References

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Late Archean Shallow- and Deepwater Sulfur Cycles: Molecuar and Isotopic Evidence

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We are investigating molecular records of ancient life in late-Archean core samples of shales and carbonates from the Hamersley Basin in Western Australia (2.8-2.6 Ga). Previously, researchers have documented molecular inputs from cyanobacteria and possible inputs from eukaryotic organisms. Our own lipid studies support these findings, and we observe molecular inputs from all three domains of life. Overall, the extreme carbon-isotope depletion of these units suggest active methane recycling by the ancient ecosystems, although other (or additional) origins of this depletion are possible. Here, we consider lipid, organic carbon and pyrite sulfur isotopic patterns with respect to lithologic facies.

Samples from the Jeerinah Formation are composed of finely laminated carbonaceous black shale, deposited in deep waters below storm-wave base. Some samples indicate inputs resulting from high-energy current transport, suggesting a mid- to deep-slope environment. The Carawine Dolomite conformably overlies the Jeerinah Formation, and consists of three lithofacies: 1) laminated black shale, intercalated shale and dolomitic siltstone and laminated dolomite; 2) massive and stromatolitic dolomite; and 3) massive carbonaceous black shale associated with the massive dolomite. These facies are interpreted to represent deposition in upper-to-middle ramp, peritidal platform and restricted lagoon environments, respectively.

Carbon isotopic values for kerogen in our samples range from –36.5 to –50.2 ‰. Typically, the shallower facies are represented by more enriched values, with –38.2±7 ‰ for the Carawine platform, -43.3±4.6 ‰ for the ramp facies, and -47.5±1.5 ‰ for the deep-water slope facies. The lagoonal massive black shale samples averaged –49.5±1.5 ‰, with the most depleted signatures. Sulfur isotopic patterns (Ono et al., submitted) follow these facies, with notably stronger and relatively more positive signatures of mass-independent fractionation (i.e., $\Delta^{33}S$ values) recorded in the deeper-water environments. Shallow-water $\Delta^{33}S$ and $\delta^{34}S$ data are consistent with active microbial sulfate reduction, probably under sulfate-limited conditions.

Kerogen carbon and pyrite sulfur isotopic data combined with molecular records reveal evidence for two means for sulfur cycling in these ancient settings. In deep waters, S was cycled between S^{o} and HS- by elemental sulfur reducers and sulfide-oxidating chemoautotrophic bacteria. Autotrophic recycling of respired CO_2 provides a pathway for the generation of isotopically depleted organic carbon recorded by these units. We suggest S in shallow waters was cycled between SO_4^{2}- and HS^{-}, with the presence of sulfate possibly fueled by more active oxygenic photosynthesis.