Large fractionations in Fe, Cu and Zn isotopes associated with Archean microbially-mediated sulphides

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Perhaps the most important potential application of transition metal isotope geochemistry is in the study of biogeochemical processes, particularly early in Earth history where morphological evidence for life is rare, equivocal or absent. Early studies have shown that biological systems consistently use the lighter isotopes preferentially. Given the potential for non-biological fractionation of the transition metals, however, the greatest degree of success in utilising these systems will probably come from a multi-isotopic approach. Here we present a combined Fe-Cu-Zn isotopic dataset from sulphide grains and black shales from the 2.7Ga Belingwe Belt, Zimbabwe, associated with sulphate-reducing microbial communities.

We have tested these techniques using analyses of USGS basalt BCR-1. In common with previous studies of Fe (Beard and Johnson 1999) and Zn (Marechal et al. 2000) isotopes in terrestrial basalts we have observed very small fractionations for this sample. We have measured δ^{56}Fe of +0.11±0.04 ‰, δ^{66}Zn of 0.2±0.06 ‰ and δ^{65}Cu of 0.1±0.06 ‰ (relative to IRMM-14 Fe, Lyons JMC Zn and NIST 976 Cu respectively).

In contrast, organic-carbon-rich black shales from Belingwe exhibit extreme depletions in heavy Fe and Cu isotopes relative to IRMM-14 and NIST 976 – with δ^{56}Fe = -2.9 ‰, δ^{65}Cu = -1.0 ‰. Zinc isotopes exhibit positive fractionations in the black shales - δ^{66}Zn = +1.1‰. 15 individual sulphide grains from the same section spread along correlations between BCR-1 and the Belingwe black shales, with δ^{56}Fe exhibiting a range of -1.2 to -2.7 ‰, δ^{65}Cu varying between –0.1 and -1.0 ‰ and δ^{66}Zn = +0.3 to +1.1‰. Furthermore, these data are correlated with depletions in ^{34}S of up to 18‰ (Grassineau et al. 2001). The negatively skewed nature of the Fe isotopic dataset, in combination with the positive Zn (cf. Marechal et al. 2000) and negative Cu, strongly suggest involvement of biological processes. However, fractionation of Fe isotopes is not, *a priori*, expected during microbially-mediated sulphide precipitation itself but probably reflects the operation of repeated reduction and re-oxidation cycles.

References

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Geochemical model of the granite-bentonite-groundwater at Äspö (LOT experiment)

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In the nuclear waste repository designed by SKB, bentonite is considered as a barrier between the geologic environment and the canister containing the spent nuclear fuel. The use of bentonite as a barrier has a double motivation. First, it isolates the nuclear waste from groundwater due to its swelling capacity as it saturates with water. Second, in case the isolation fails, it could retard the radionuclide migration outside the system due to its sorption capacity on the clay surface.

In this context, it is very important to know how bentonite responds to some geochemical processes, which are likely to occur in an underground repository. For this reason, SKB financed the LOT experiment in Äspö, Sweden (Karnland et al., 2000). The aim of this experiment is to understand how bentonite reacts to changes produced by a thermal gradient and/or to the addition of some substances at different bentonite blocks, such as NaCl, KCl, gypsum, calcite, and cement, among others.

We modelled some of the special cases of the LOT experiment. The calculations were performed using a two-dimensional reactive-transport model with the code PHAST (Parkhurst et al., 2000). The results indicate that calcite is buffering pH in almost all cases, except where cement is present. In this case the equilibrium with portlandite implies a very alkaline pH and the precipitation of sulphides leads to reducing conditions. The calcite dissolution-precipitation is governed by the calcium in solution, which is mainly controlled by the cation exchange in the bentonite. The effect of adding KCl or NaCl to the bentonite results in an acidification of the solution. This is because Ca in solution increases due to the cation exchange, leading to a large precipitation of calcite.

Acknowledgements: This work has been financed by SKB.

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