

Isotopic disequilibrium in sulfide mineral pairs from multiple sulfur isotopes

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We present a framework to investigate the sources of ore-forming fluids and to evaluate isotopic disequilibrium in Archean ore deposits with measurements of multiple isotopes (³²S, ³³S, ³⁴S). This technique is analogous to experimental tests for disequilibrium in multiple isotope systems (cf. ¹⁶O, ¹⁷O, ¹⁸O [1]), and it relies on two limiting assumptions: (1) the slopes of any secondary mass fractionation lines are generally concordant with the terrestrial fractionation line (TFL); and (2) there are natural, isotopically-labelled S sources that lie off of the TFL. The TFL can be defined by the quantity $\Delta^{33}\text{S} = 0$, where $\Delta^{33}\text{S} = \ln(\delta^{33}\text{S}/1000+1) - {}^{33}\lambda_{\text{TFL}} \times \ln(\delta^{34}\text{S}/1000+1)$ and ${}^{33}\lambda_{\text{TFL}} = 0.515$.

We demonstrate this method with sulfur multiple isotope measurements of ore sulfides from the ~2.7 Ga Kidd Creek volcanogenic massive sulfide (VMS) deposit in Ontario, Canada, since the formation of sulfides in this VMS deposit is thought to have included both juvenile sulfur and seawater sulfate. Recent studies demonstrate that the defining characteristic of the Archean sulfur cycle was the presence of sulfides and sulfates with multiple isotope compositions offset from the TFL [2,3]. We also use this method to test hypotheses about different generations of sulfides that are thought to have formed from different fluids, but presently reside in the same hand samples.

Results of isotopic analyses from Kidd Creek sulfides indicate the presence of different fluids during ore formation. Measurements of $\Delta^{33}\text{S}$ are used to indicate which minerals formed from the same sulfur sources and their approach to isotopic equilibrium, which has consequences for isotopic thermometry. The significance of these results will be discussed in the context of the evolution of the hydrothermal system and ore formation at Kidd Creek.

References

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The absence of mass independent fractionation of sulfur isotopes in Archean sedimentary rocks: An insignificant phenomenon?

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The presence of large mass independent fractionation (MIF) of S isotopes in pre-~2.3 Ga rocks and the absence of MIF in younger rocks have been regarded by many recent investigators as definitive evidence for a dramatic change in atmospheric chemistry, from anoxic to oxic, at ~2.3 Ga. This is because the MIF of S has been linked to the atmospheric photochemical reactions of volcanic SO₂ in the absence of an ozone shield to produce S⁰ with large positive $\Delta^{33}\text{S}$ values (>50‰) and SO₄²⁻ with negative $\Delta^{33}\text{S}$ values (<10‰). A serious problem with the above model is our recent findings of the absence of MIF-S in the 2.76 Ga Hardey Formation (lacustrine shales) and the 3.0 Ga Mosquito Creek Formation (marine shales) in Western Australia. The $\delta^{34}\text{S}$ values of ~30 bulk-rock samples vary more than 10‰, but their $\Delta^{33}\text{S}$ values fall within a range of 0±0.3‰. The absence of MIF-S has also been recognized in the entire Huronian sequence in Canada, including the ~2.4 Ga Living Creek Formation that underlie uraniferous conglomerate beds (Tachibana *et al.*, 2004). These data suggest either: (i) the Archean atmosphere fluctuated between oxic and anoxic, or (ii) large MIF values in geologic samples were not caused by atmospheric reactions. The second possibility is suggested from: (a) the recognition of strong correlations between the MIF-S values and the degree of hydrothermal alteration in samples analyzed by previous researchers; and (b) the recent findings by nuclear chemists (e.g., Fujii *et al.*, 2002) of MIF of many elements during non-photochemical reactions.