Unique sulfur isotope signatures in Neoarchean carbonates

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Archean sedimentary rocks (mostly black shales) have been intensively studied using sulfur isotopes but have not yielded strongly negative $\delta^{34}S$ and $\Delta^{33}S$. The lack of negative $\delta^{34}S$ was attributed either to an insignificant role of sulfate-reducing bacteria (SRB) or to low seawater sulfate concentrations in Arcehan [1]. MIF-S is accepted to be a product of atmospheric photochemistry of sulfur gases producing at least two pools with dinstinct sulfur isotopic compositions ($\delta^{34}S$ and $\Delta^{33}S$) [2]. The predominance of positive $\Delta^{33}S$ values in the Archean rock records raised a question about a "lost" negative MIF-S sink.

Our results from the ca. 2.5 Batatal Fm. (Brazil) demonstrate that two types of rocks (black shales and carbonates) have distinctive sulfur isotope signatures. Whole rock analysis of black shales mostly show small $\delta^{34}S$ variation with average -3.69±3.51‰ whilst carbonates possess $\delta^{34}S$ of -9.74±2.84‰. The $\Delta^{33}S$ values of black shales and carbonates average +0.24±0.86‰ and -1.70±0.51‰, respectively. In a part of the carbonate section there is an excursion to negative $\Delta^{33}S$ down to -3.1‰. Analyses of carbonate – associated pyrite using a micro drilling technique and also SIMS reveal more significant variation, and strongly negative $\delta^{34}S$ for some grains (down to to -38 ‰) with the most negative grains reaching a stable negative value for $\Delta^{33}S$. Since the inferred $\delta^{34}S$ of the sulfate pool is 10 ±5 ‰ [3], this yields a fractionation associated with sulfate reduction greater than 40‰ at this time in the late Archean. The observation of an apparent floor for $\Delta^{33}S$ suggests sulfate reduction by SRB from a well-mixed sulfate pool with negative $\Delta^{33}S$. Examination of the stratigraphic trends in $\Delta^{33}S$ for carbonates shows a stable value near -2 ‰ for this sulfate pool, but reveal a coherent trend to more negative $\Delta^{33}S$ (-3.15 ‰) over an interval of approximately 10m, which suggests a response time for this pool that is short relative to the deposition time of the ~70 m of carbonate interval. The existence of Archean carbonates with negative $\Delta^{33}S$ also raises the possibility that they carry a significant part of the "lost" reservoir of sulfur.

[1] Habicht *et al* (2002) *Science* **298**, 2372-2374. [2] Farquhar *et al* (2000) *Science* **289**, 756-758. [3] Ono *et al* (2003) *EPSL* **213**, 15-30.