Paleoarchaean sulfur cycling as revealed by multiple sulfur isotopes, Barberton Greenstone Belt, South Africa

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Archaean and Early Proterozoic sedimentary rocks show both mass-dependent (MDF-S: $\delta^{34}S$) as well as mass-independent fractionation of sulfur isotopes (MIF-S: $\Delta^{33}S$) [1]. Positive $\Delta^{33}S$ values characterize photochemically derived elemental sulfur, negative $\Delta^{33}S$ values indicate an origin as atmospherically derived sulfate. Traditional $\delta^{34}S$ values reveal inorganic and microbial sulfur cycling in terrestrial environments. Different combinations of MIF-S and MDF-S signatures preserved in terrestrial rocks >2.4 Ga old can therefore identify different sulfur sources and processes.

Multiple sulfur isotopes were determined for pyrites from the BARB4 and BARB5 drill cores drilled by ICDP through the Mapepe Formation (3.26-3.23 Ga), Fig Tree Group, Barberton Supergroup, South Africa. Both cores show MIF-S signals with a typical $\Delta^{36}S/\Delta^{33}S \approx -1$, implying an atmospheric origin of the pyrite sulfur. BARB4 samples show values of 0.28 to 1.87 with an average of 1.14 ‰ for $\Delta^{33}S$ and -0.85 to 4.90 around an average of 0.9 ‰ for $\delta^{34}S$ (V-CDT), respectively, indicating a photolytic elemental sulfur source for sedimentary pyrite sulfur. The small spread in $\delta^{34}S$ is generally consistent with microbial processing of this elemental sulfur source. BARB5 samples display values of -0.38 to 2.31 with an average of 0.64 ‰ for $\Delta^{33}S$ and -6.78 to 3.55 averaging at 0.58 ‰ for $\delta^{34}S$ (V-CDT), respectively, whereas a subset of these BARB5 samples exhibits highly variable $\delta^{34}S$ and mostly negative $\Delta^{33}S$ values suggesting that the sulfur source was atmospherically derived sulfate, which subsequently underwent microbial sulfate reduction. Extreme fractionations such as strongly negative $\delta^{34}S$ and strongly positive $\Delta^{33}S$ values as presented by Philippot et al. (2012) [2] for the same sedimentary succession could not be confirmed with samples studied here.

Generally, multiple sulfur isotopes for the BARB drill cores indicate an atmospheric sulfur source (MIF-S) and subsequent microbial processing imparting an MDF-S signal on the pyrite sulfur.

[1] Johnston. (2011), *Earth Sci. Rev.* **106**, 161-183. [2] Philippot *et al.* (2012), *Nature Geoscience* **5**, 668-674.