Iron and sulfur cycling in an early Archean basin: coupling of bulk rock and pyrite isotope data

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Fe and S isotopes are useful tools to trace sources, mixing and (bio)geochemical redox processes in the Fe-rich and S-poor Archaean oceans. Here we present bulk Fe isotopes and *in situ* Fe and multiple S isotopes from rocks of Middle Mapepe Formation of the Fig Tree Group from the BARB5 drill core of the Barberton Greenstone Belt drilling project, South Africa. We analyzed 43 whole rock samples for δ^{56}Fe by MC-ICPMS spanning deep water and shallow basinal settings. Representative samples were selected to produce 160 *in situ* pyrite measurements for multiple S isotopes (32,33,34,36) by SIMS. The aim was to identify pathways of pyrite formation, sources of Fe and S, and potential redox reactions in the Mapepe basin in Mid-Archaean times.

δ^{56}Fe (relative to IRMM 014), in bulk rocks varies from 0.42‰ to -0.46‰ with an average value of ca. 0 ‰. A weak trend was observed between more negative values deeper in the core, where deposition occured in deep anoxic water column, and slightly more positive values in a shallower water alluvial fan setting at the core top. This represents mixing between Fe derived from the water column and detrital Fe minerals weathered from the hinterland. Multiple S isotopes vary from -13.‰ to 6 ‰ for δ^{34}S, -2 ‰ to 4 ‰ for Δ^{33}S and from -5 ‰ to 1 ‰ for Δ^{36}S. Correlations indicate intensive mixing processes of different S sources as well as the operation of microbial sulfate reduction in the basin. A negative excursion in δ^{56}Fe and δ^{34}S correpsonds to a litharenite unit interbedded with chert, barite and carbonate and volcanic ash deposits. We interpret this as related to Fe drawdown from the basin during increased sulfide production due to microbial sulfate reduction. Our data show that coupling Fe isotopes with S and general geochemisty and petrology of Archaean sedimentary rocks is an extremely valuable tool in tracing the early Earth environments.