



In-situ Fe and S isotope analyses of pyrite from the Lower Mapepe Formation (3.26-3.23 Ga), Barbeton Greenstone Belt, South Africa

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The Archaean oceans differed from today in being anoxic, Fe-rich and S-poor. Despite the low abundance of marine sulfate, significant amounts of sedimentary pyrite are associated with shales and sandstones deposited in Palaeoarchean time. Combined Fe and S isotopes can be used in pyrite to trace element sources as well as pathways of mineral formation and environmental redox processes since they record the changes in redox state in abiotic and biological processes. In this study, Fe and S isotopes were measured in pyrite from sedimentary rocks sampled by diamond drilling in the Lower Mapepe Formation (3.26-3.23 Ga, Lowe, 1999)¹ of the Archaean Barbeton Greenstone Belt, South Africa. We performed in situ Fe and multiple S isotopic analysis by secondary ionization mass spectrometry (SIMS) of single mineral grains. The grain size range from 10 to several hundreds of micrometers. The stratigraphy consists of barite-chert units and barite-free terrigenous clastic sediments with pyrites occurring in both types of lithologies. The complete range of pyrite $\delta^{56}\text{Fe}$ data vary from -2.61 to +2.74 ‰. Most individual pyrite samples showed iron isotopic variability of between 1.0-1.5 ‰ consistent with the range induced by abiotic pyrite precipitation (Guilbaud et al. 2012)², whilst one sample contained more extreme variability of close to 5 ‰. Clear correlations with multiple S isotopes were not seen in individual samples, but there was a clear shift in average Fe isotope values and mixing trends in multiple S isotopes on going from the barite-free to the barite-rich part of the drill core. Pyrites in barite-free lithologies show slightly more positive $\delta^{56}\text{Fe}$ value than those in close association with the barite. This suggests different sources of iron in the lower and upper parts of the stratigraphy, with a possible hydrothermal source for the pyrite associated with the barite. The origin of the more negative $\delta^{56}\text{Fe}$ values (up to -2.61 ‰) is unclear but might result from microbial activity or mixing with a light iron pool. Pyrites with a positive $\delta^{56}\text{Fe}$ signature could suggest involvement of $\delta^{56}\text{Fe}$ enriched oxyhydroxides. Our in situ Fe isotope data reveal fractionation, mixing and inherited variability on a scale that would be difficult to resolve using bulk rock analyses. This microscale approach is critical to better constrain iron biogeochemistry in the Mid-Archaean environment.

¹ Lowe, D. R., 1999. Geologic evolution of the Barbeton Greenstone Belt and vicinity. *Geol. Soc. Am. Spec. Pap.* 329, 287-312

² Guilbaud, I.R., Butler, I.B., Ellam, R.M. 2011. Abiotic pyrite formation produces a large Fe isotope fractionation. *Science* 332, 1528-1551