

## In-situ iron isotope analysis of pyrites in ~3.7 Ga sedimentary protoliths from the Isua supracrustal belt

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The timing of the emergence of life remains one of the principal unresolved questions in the Earth sciences. Putative relicts of microorganisms in the Eoarchean (ca. 3.6-3.85 Ga) high-grade metamorphic terranes do not preserve morphological evidence for early life, but some relicts can be identified by their geochemical signatures created by metabolic processes. Among the oldest rocks of sedimentary origin (ca. 3.8 Ga) occur in the Isua supracrustal belt (ISB), southern West Greenland; these have undergone metamorphism up to the amphibolite facies. Despite intense metamorphism, the carbon isotope compositions of graphite clots from the Isua metasedimentary rocks suggest biological carbon fixation and provide the oldest evidence for this biological process. Microbial dissimilatory iron reduction (DIR) is considered to be an early form of metabolism. The microbial DIR produced  $\text{Fe}^{2+}_{aq}$  with a lower  $\delta^{56}\text{Fe}$  value from a precursor  $\text{Fe}^{3+}$ -bearing iron mineral. However,  $\delta^{56}\text{Fe}$  values lower than -1 ‰ are not found in sedimentary rocks prior to about 2.9 Ga. Here, we report in-situ iron isotope analysis of pyrites in sedimentary rocks from the ISB, using a near infrared-femtosecond-laser ablation-multicollector-ICP-MS (NIR-fs-LA-MC-ICP-MS). A large variation of  $\delta^{56}\text{Fe}$  values from -2.41 to +2.35 ‰, was documented from 190 points within pyrite grains from 11 rock specimens, including those interpreted to be banded iron-formations (BIF), chert, amphibole-rich chert, quartz-rich clastic sedimentary rocks, mafic clastic sedimentary rocks, carbonate rocks and conglomerates. We found that the distribution of  $\delta^{56}\text{Fe}$  values depends on the lithology, whereas there is no correlation between their  $\delta^{56}\text{Fe}$  values and the metamorphic grade. The  $\delta^{56}\text{Fe}$  values of pyrites in BIFs range from +0.25 to +2.35 ‰, indicating partial oxidation in the deep ocean. Especially, the high  $\delta^{56}\text{Fe}$  values, up to +2.35 ‰, suggest that the BIF was formed through interaction of ferruginous seawater with a highly alkaline hydrothermal fluid under anoxic conditions. Pyrite grains in a conglomerate, carbonate rocks, mafic clastic sedimentary rocks, and amphibole-rich cherts show negative  $\delta^{56}\text{Fe}$  values around -1.5 ‰, down to -2.41 ‰, pointing to microbial DIR in the Eoarchean shallow sea. In addition, the relatively low  $\delta^{56}\text{Fe}$  values of pyrites in the shallow water sediments suggest anoxic, anoxygenic photoautotrophic iron oxidation in the photic zone.

Keywords: Eoarchean, Isua supracrustal belt (ISB), pyrite, microbial dissimilatory iron reduction (DIR)