Tracking the metabolic pathways by *in situ* iron and sulphur isotope analyses of sedimentary pyrite

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Microbial iron reduction (MIR) and microbial sulphate reduction (MSR) are the two most important processes in oxidizing organic matter in the modern ocean, and may represent the earliest evolved metabolic pathways in the Earth. Fe^{2+} and H_2S, the products of MIR and MSR, are eventually buried as sedimentary pyrite (FeS_2). Thus, MIR and MSR might be tracked from sedimentary pyrite. In this study, we conducted *in situ* iron ($\delta^{56}Fe$) and sulphur ($\delta^{34}S$) isotope analyses of pyrite crystals from 635-million-year old sedimentary rocks. Both $\delta^{34}S$ and $\delta^{56}Fe$ show the rim-to-core intra-crystalline variation, and there is an anti-correlation between $\delta^{34}S$ and $\delta^{56}Fe$. For pyrite derived from *in situ* MSR in sediment, $\delta^{34}S$ and $\delta^{56}Fe$ display the increasing and decreasing core-to-rim trends, respectively, while pyrite precipitation with H_2S supplied from *in vitro* MSR would demonstrate the opposite trends. We suggest that the intra-crystalline $\delta^{34}S$ and $\delta^{56}Fe$ core-to-rim variations may constrain the process of pyrite formation. Unlike traditional isotope analyses on bulk sample, which likely obscure the signal of microbial metabolic processes, the *in situ* isotope analyses on a single pyrite crystal can reveal the signature of microbial activities. When applied to ancient samples, the *in situ* iron and sulphur isotope analyses on a pyrite crystal can track the metabolic pathways of early life.