

Microbial activity below Archean seafloor constrained by 4 sulfur isotopes analysis of pyrite in ca. 3.5 Ga basalts from

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Microbial sulfate reduction is one of the most ubiquitous metabolisms on Earth [Canfield, 1998]. In modern environment, it is well known that microbial sulfate reduction takes place below seafloor [e.g. Kallmeyer et al., 2012]. Aoyama et al. [2014] showed microbial sulfate reduction takes place not only in quiescent seafloor (i.e. non-hydrothermal), but also in active hydrothermal system. On the other hand, the oldest evidence of microbial sulfate reduction has been reported from ca. 3.5 Ga Dresser Formation, Western Australia by using quadruple sulfur stable isotopes analyses of sulfate and sulfide minerals related to hydrothermal environment [Ueno et al., 2008; Shen et al., 2009]. However, the isotopic compositions of sulfides and sulfate minerals through history show small isotopic fractionation (~ 20 ‰) before the rise of oxygen (c. 2450 Ma), possibly because of low sulfate concentration in the Archean seawater ($< 200 \mu\text{M}$) [Habicht et al., 2002]. Microbial sulfate reduction below Archean seafloor might have yield larger sulfur isotopic fractionation owing to enhanced sulfate concentration. In order to test this scenario, we analyzed quadruple sulfur isotopic compositions of pyrite grains (from 10 to 40 μg) of seafloor basalts. For studying isotopic variation within sample, we used newly developed micro-fluorination technique.

The observed variations within each rock have positive correlations between the $\delta 34\text{S}$ and $\delta 33\text{S}$, and negative correlations between the $\delta 34\text{S}$ and $\delta 36\text{S}$, suggesting these trends are derived from mixing or fractionation. Pyrite within silica dykes penetrating seafloor basalts, which are the most plausible end-member within pyrite in basalts, however, cannot explain the observed variations. On the other hand, the slope of the observed $\delta 36\text{S}/\delta 33\text{S}$ (-9.3) and large variations within small volume rocks (~ 10 ‰) suggest microbial sulfate reduction took place in Archean hydrothermal system. The observed intensive $\delta 34\text{S}$ depletions only in Unit-I, and mass dependent compositions imply the substrate sulfate was different from Archean seawater suggested by bedded barite in upper part of the Unit-I. Thus the Archean hydrothermal system may have host microbial activity by enhanced sulfate.