

Estimation of 3.2 Ga seawater-hydrothermal environment from sulfur isotopic analyses of barite crystals in Dixon Island Formation, Western Australia

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Fluctuations of sulfur isotopic ratio ($\delta^{34}\text{S}$) and concentrations of seawater sulfate through geological time have a close relationship with atmospheric oxygen level and biological activity of sulfate reducing bacteria. For example, in the Archean $\delta^{34}\text{S}$ values of sulfate was +4.6‰ (3.47Ga; Shen et al., 2009) and seawater sulfate concentration was <2.5 μM (>2.4Ga; Crowe et al., 2014b). However, after major increase in oxygen levels in the Paleoproterozoic, the concentration became larger up to 1-2mM (>1.6Ga; Kah et al., 2004). Besides, increased sulfate level promoted microbial sulfate reduction and isotopically light ^{32}S in sulfate was selectively used for metabolism and moved into sulfide, resulting in high $\delta^{34}\text{S}$ sulfate. Therefore, $\delta^{34}\text{S}$ of Archean sulfate is low compared to that of the Proterozoic (e.g. Canfield and Farquhar, 2009).

In this way, $\delta^{34}\text{S}$ of past sulfate minerals is a good proxy for redox state and microbial sulfate reducing systems in the Precambrian. However, reports of $\delta^{34}\text{S}$ of Archean sulfate are scarce and localities and ages of research are partial. Therefore, we focused on newly discovered sedimentary barite (BaSO_4) layers from the 3.2Ga Dixon Island Formation, which is considered to have been deposited in a relatively deep open sea environment (Kiyokawa et al., 2006).

The Dixon Island Formation is located in the coastal Pilbara terrane, Western Australia and shows low metamorphic grade (Kiyokawa and Taira, 1998). Barite layers alternate with black chert layers in the Black Chert Member of the Dixon Island Formation that overlies hydrothermal vein networks. Barite is considered to have formed during precipitation of black chert. Though most of them are silicified (Kiyokawa et al., 2006), there exist small crystals of barite (less than 200 μm in diameter) which are regarded to be remnants of original barite. We crushed three rock samples from different horizons, separated twelve fine barite grains in total, and performed micro-meter scale $\delta^{34}\text{S}$ analyses using a NanoSIMS.

We used five sedimentary barites as working standards which are considered to have $\delta^{34}\text{S}$ homogeneity in each crystal determined by an IsoPrime. For measuring samples, we performed raster analyses of two or three spots for each crystal, and values were averaged. As a result, we obtained scattered $\delta^{34}\text{S}$ values of -2.1 to +18.7‰ (Avg.=+6.5‰, $1\sigma=6.3\%$) from twelve crystals. On the other hand, averages in each rock sample were +3.4, +7.8 and +8.4‰. Measurement errors were $\pm 0.87\%$ to $\pm 3.72\%$. Average $\delta^{34}\text{S}$ values for each rock sample are similar to literature values of Archean sulfate (+5-10‰, Canfield and Farquhar, 2009). Meanwhile, focusing on the range of values of each crystal, lower ones were near $\delta^{34}\text{S}$ of mantle-originated sulfur (ca. 0‰), which may reflect $\delta^{34}\text{S}$ of hydrothermal-originated sulfate. Besides, higher ones were near $\delta^{34}\text{S}$ of modern seawater sulfate (+22‰) and thus higher than Archean sulfate. There are two possible causes of high $\delta^{34}\text{S}$: 1) extreme microbial sulfate reduction in an environment closed with respect to sulfate (Rayleigh fractionation) or 2) hydrothermal fluid supplying isotopically heavy sulfate.

This study is the first attempt of in situ $\delta^{34}\text{S}$ analyses for Archean barite microcrystals. We detected isotopic heterogeneity in individual barite crystals within three single barite beds. Conventional combustion method for S isotope analysis may mix this heterogeneity and provide us

with averaged values. There is a possibility that $\delta^{34}\text{S}$ dispersion in each barite bed shows isotopic heterogeneity of seawater sulfate at that time.

Keywords: Archean, sulfur isotopes, barite, SIMS