

### 3.2 Ga seawater sulfate implied from sulfur isotopic compositions of barite crystals in Pilbara, Western Australia

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Sulfur isotopic ratio ( $\delta^{34}\text{S}$ ) 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 because of the limited occurrences of sulfate deposits. Therefore, we focused on newly discovered sedimentary barite ( $\text{BaSO}_4$ ) layers from the 3.2Ga Dixon Island Formation, which is considered to have been deposited in a relatively deep open sea environment [1].

The Dixon Island Formation is located in the coastal Pilbara terrane, Western Australia and shows low metamorphic grade [2]. Barite layers alternate with black chert layers in the Black Chert Member of the Dixon Island Formation that overlies hydrothermal vein networks. Though most of them are silicified [1], there exist small crystals of barite (less than 200  $\mu\text{m}$  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.

As a result, we obtained scattered  $\delta^{34}\text{S}$  values of  $-2.1 \pm 1.1$  to  $+18.7 \pm 0.9\text{‰}$  (Avg. =  $+6.5 \pm 6.3\text{‰}$ ) from twelve crystals. On the other hand, averages in each rock sample were  $+3.4 \pm 5.8$ ,  $+7.8 \pm 8.0$  and  $+8.4 \pm 3.6\text{‰}$ .

There are two possible causes of the dispersion of  $\delta^{34}\text{S}$  of barite crystals: 1) change in hydrothermal activities or 2) a gradual microbial sulfate reduction in a sulfate-limited condition (Rayleigh fractionation). However, no change in mineral occurrences and rock facies eliminate the former. Moreover, fluctuations of bulk  $\delta^{34}\text{S}$  [3] and micro-meter scale heterogeneity of  $\delta^{34}\text{S}$  of pyrite [4] possibly supports the latter.

[1] Kiyokawa *et al.* (2006) *Geol Soc Am Bull* **118**, 3-22. [2] Kiyokawa & Taira (1998) *Precambrian Res* **88**, 109-142. [3] Sakamoto (2010) *Master's thesis*, unpublished. [4] Miki (2015) *Master's thesis*, unpublished.