3.2 Ga sedimentary environment implied from heterogeneity of sulfur isotopic compositions of barite beds in Pilbara, Western Australia

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Sulfur isotopic ratio ($\delta^{34}S$) of past sulfate minerals is a good proxy for redox state and microbial sulfate reducing system in the Precambrian. However, reports of $\delta^{34}S$ of Archean sulfate are scarce because of the limited occurrences of sulfate deposits and difficulties in analyses for trace amounts of sulfate. 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 [1].

The Dixon Island Formation is located in the coastal Pilbara terrane, Western Australia and shows low metamorphic grade [2]. We can see pyrite layers of a few millimeters thick which make an alternate layers with black chert layers in the Varicolored Chert Member. The bulk $\delta^{34}S$ values of these layers are -10.1 to +26.8‰ [3] and micro-meter scale heterogeneity of $\delta^{34}S$ can be seen in minute spherical shell pyrite which was formed at early stage of diagenesis [4]. On the other hand, barite layers in the Black Chert Member of the Dixon Island Formation overlies hydrothermal vein networks. Though most of them are silicified [1], 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 three to five fine barite grains respectively and twelve in total, and performed micro-meter scale $\delta^{34}S$ analyses using a NanoSIMS.

We used five sedimentary barites as working standards which are considered to have $\delta^{34}S$ homogeneity in each crystal determined by an isotope ratio mass spectrometer. 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 $\delta^{34}S$ values of -2.1 ± 1.1 to +18.7 ± 0.9‰ (Avg. = +6.5 ± 6.3‰) from twelve crystals. On the other hand, averages in each rock sample were +3.4 ± 5.8, +7.8 ± 8.0 and +8.4 ± 3.6‰.

Averages for each rock sample are similar to literature values of Archean sulfate (ca. +5-10‰, e.g. [5]). Meanwhile, focusing on the range of values of each crystal, lower ones were near $\delta^{34}S$ of mantle-originated sulfur (ca. 0‰). Besides, higher ones were near $\delta^{34}S$ of modern seawater sulfate (+22‰) and thus higher than Archean sulfate. There are two possible causes of the dispersion of $\delta^{34}S$ of barite crystals in the same beds: 1) change in hydrothermal activities or 2) effect of 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 $\delta^{34}S$ and micro-meter scale heterogeneity of $\delta^{34}S$ of pyrite possibly supports the latter.

References:

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