3.2 Ga sulfur isotopic heterogeneity of barite and pyrite microcrystals in Dixon Island Formation, Pilbara, Western Australia.

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Mesoarchean is known as an environmental changing period in the Earth history with Banded Iron Formations within greenstone belt indicating gradual oxidation of atmosphere and ocean environments (Windley, 1995). One of the methods of estimation of sulfur cycle and redox environment uses sulfur isotopic ratio ($\delta^{34}S$(‰)=(($^{34}S/^{32}S)_{sample}$/ ($^{34}S/^{32}S)_{standard}$-1)×1000). The $\delta^{34}S$ values of each chemical species in each reservoir, such as mantle and ocean is generally in a state of equilibrium. However, they greatly change their values in case that they are mixed locally or change into different chemical species due to redox reaction. Therefore, fluctuations of $\delta^{34}S$ values of sulfide and sulfate minerals through geological time have a close relationship with atmospheric oxygen level and biological activity of sulfate reducing bacteria. Though reports of $\delta^{34}S$ of Archean sulfate are scarce because of the limited occurrences of sulfate deposits, a high precision microanalytical method which has been difficult have begun to be established.
In this study, we focused on newly discovered sedimentary barite ($BaSO_4$) layers and associated pyrite (FeS_2) from 3.2 Ga Dixon Island Formation in Pilbara, Western Australia and performed isotopic microanalysis in order to constrain ocean environment.
Dixon Island Formation is located in coastal Pilbara terrane, Western Australia and shows low metamorphic grade. It consists of Komatiite-rhyolite tuff Member, Black chert Member and Varicolored chert Member from the bottom to the top (Kiyokawa and Taira, 1998). Based on the DXCL drilling result for Varicolored chert Member, a few millimeters in thickness of pyrite layers were recognized in the black chert layers. The bulk $\delta^{34}S$ values of these layers are ranging from -10.1 to +26.8‰ (Sakamoto, MS2010).Micro-meter scale heterogeneity of $\delta^{34}S$ are recognized, in a range from +5 to +10‰, in the minute spherical shell pyrite (Miki, MS2015).
On the other hand, minor barite layers, which are now mostly silicified beds, are preserved in the black chert layers which overlie on hydrothermal deposits. Detail observations indicate that barite layers contain small relict crystals of barite (less than 200 μm in diameter). These preserved barite crystals are considered to be remnants of original barite. Besides, surrounding black chert of the barite pseudomorph contain minute pyrite grains. We performed micro-meter scale $\delta^{34}S$ analyses using a lateral high resolution mass spectrometry (NanoSIMS), housed at AORI of the University of Tokyo, on 29 barite grains and 19 pyrite grains which were from three representative samples of different horizons.
The $\delta^{34}S$ values of barite were ranging from -7.1 ±1.0 to +18.7 ±0.9‰ (Avg. = +0.4 ±1.3‰) in 29 grains. Associated pyrite $\delta^{34}S$ values showed +2.1 ±2.0 ~ +22.3 ±5.9 (Avg. = +11.4 ±2.8‰).
In general, pyrite formed by the sulfate reducing bacteria tend to have negative $\delta^{34}S$ value than that of abiogenic pyrite. However, this study revealed that pyrite with heavier $\delta^{34}S$ values than those of barite. Recent studies report that heavy $\delta^{34}S$ pyrites from the neighbor ages as well. To explain these enigmatic isotope signals of pyrite, we need to consider isotopic fractionation without sulfate reducing bacteria or influx from outside like volcanisms. Besides, shifting towards positive value by Rayleigh fractionation indicates sulfate-limited environment such as lagoon or ocean beneath the ice during snow ball earth. Identification of the cause of high $\delta^{34}S$ is important to reconstruct the environment.

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