

## Reconstruction of the 3.2 Ga depositional environment of black shale and siderite/oxide BIF at Pilbara, Western Australia

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The Dixon Island and Cleaverville formations, 3.2 to 3.1 Ga oceanic sedimentary sequences, are exposed at the coastal Pilbara terrane in the Western Australia. They are well preserved in low-grade metamorphic greenstone belt. In order to reconstruct sedimentary environment in high-precision, DXCL Drilling Project on land was operated and four drill cores were obtained: DX, CL1, CL2, and CL3. The DX of Dixon Island Formation is composed of alternation of black shale and grey siliceous shale with pyrite layers. The Cleaverville Formation consists of the Black Shale (the CL1 and the CL2) and the BIF (Banded Iron Formation) Members, from the bottom to the top. In the BIF Member, iron carbonate (siderite:  $\text{FeCO}_3$ ) and oxides (Hematite:  $\text{Fe}_2\text{O}_3$ ; Magnetite:  $\text{Fe}_3\text{O}_4$ ) alternates with chert predominantly in lower and upper part, respectively.

In this study, organic and inorganic carbon isotopic analyses (bulk) and sulfur isotopic analyses for pyrite (bulk and *in situ*) and barite (*in situ*) were performed in addition to macroscopic and microscopic observation for mainly drill cores and barite layers on land. From these results, depositional setting was reconstructed.

Increase in size of clastic particles of black shale and frequency of coarser grains through the DXCL drill cores suggest that depositional setting got shallower from deep anoxic environment to shallower oxic BIF-forming area.

The  $\delta^{13}\text{C}_{\text{org}}$  through the DXCL drill cores except for the BIF Member showed constant values indicating some photosynthetic bacteria, probably  $\text{O}_2$  generating cyanobacteria. Thus, iron oxyhydroxide could have formed in the surface euphotic zone due to oxidization of ferrous iron discharged from proximate hydrothermal systems.

The  $\delta^{13}\text{C}_{\text{carb}}$  of siderite in the upper part of BIF Member in the CL3 were lower than that of typical marine carbonate. This can be partly traced to the  $\delta^{13}\text{C}_{\text{org}}$  of organic matter oxidized by iron reducing bacteria. The bacteria would have reduced iron oxyhydroxide into siderite by their metabolism using organic matter as electron donor.

The  $\delta^{34}\text{S}$  of pyrite (bulk and *in situ*) in the DXCL drill cores and that of barite-associated pyrite (*in situ*) in the barite-yielding layers in the lower Black Chert Member of the Dixon Island Formation were characterized by high values. On the other hand, that of barite (*in situ*) in the barite-yielding layers was characterized by rather low  $\delta^{34}\text{S}$  than previously estimated values for 3.2 to 3.1 Ga barite. Common explanation for “heavy” pyrites and “light” barites by Rayleigh fractionation model requires also

“light” pyrites. However, those “light” pyrites are still not found in the Dixon Island and Cleaverville Formations, and even in the Mesoarchean records. Thus, in this depositional environment, some unknown processes producing “heavy” pyrites other than Rayleigh fractionation could have been operated.

10  $\mu\text{m}$ -sized spherical pyrites in the DX had internal  $\delta^{34}\text{S}$  heterogeneity of about 6 ‰ with the heaviest domain in the shape of a ring. With inferred growing process of these pyrites from their morphologies, they grew both inward and outward beginning from thin spherical shell. However, although supply of sulfate or sulfide into the shell is required to fill the inside with pyrite, isotopically heavy pyrite could not have formed in an open system on sulfate via Rayleigh fractionation. As original sulfate is considered to be isotopically light from barite analysis in this study, the same/different enigmatic processes producing “heavy” pyrites could have been operated even in  $\mu\text{m}$ -scale.

Summarizing the lithology and carbon and sulfur isotope results, findings include the following: (1) shallowing from deep anoxic environment to BIF forming setting, (2) formation of iron oxyhydroxide by oxygen produced by cyanobacteria in the surface seawater and formation of siderite by iron reducing bacteria in the reductive seafloor, (3) possibility of isotope fractionation other than Rayleigh process in the unique environment where  $\delta^{34}\text{S}$  of sulfide is high and that of barite is low, and (5) existence of the process which raise  $\delta^{34}\text{S}$  of pyrite in the  $\mu\text{m}$ -scale.

キーワード：太古代、縞状鉄鉱層、炭素同位体、硫黄同位体、菱鉄鉱、黄鉄鉱

Keywords: Archean, banded iron formation, carbon isotope, sulfur isotope, siderite, pyrite