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Reconstruction of 3.2Ga sea floor environment: Carbon and sulfur isotopic ratios of DXCL drill cores.

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In the Pilbara Coastal Greenstone Terrane in Western Australia, the Dixon Island and Cleaverville formations of 3.2-3.1 Ga is exposed. DXCL Drilling Project was performed in 2007 and 2011 for the purpose of the high-resolution reconstruction of the change of past sedimentary environment in this area, and four core samples (DX, CL1, CL2, and CL3) were acquired. Through these cores except for CL3, previous study revealed carbon isotopic ratio (=δ^{13}C) with about -30 ‰ and sulfur isotopic ratio (=δ^{34}S) of black shale from DX core obtained by combustion method with wide range of fluctuation and had very high values (δ^{34}S=-10.1∼+26.8 ‰, n=93: Sakamoto, MS2010; Kobayashi, MS2013). This is dissimilar to the previously reported sulfur isotopic ratio of sedimentary sulfides of the early Archean (δ^{34}S=-16.8∼+8.7 ‰, n=351: Strauss, 2003).

In this study, we evaluated the change of carbon and sulfur isotopic ratio through whole DXCL cores. Moreover, in order to clarify the cause of positive shift and dispersion, we performed in situ analysis with NanoSIMS focusing minute spherical pyrites observed in the DX core.

Three cores (CL2: 44.4m, CL1: 66.1m, CL3: 200m to the top) were collected from the Cleaverville Formation which consists of lower Black Shale Member and upper Banded Iron Formation Member. DX core (100.40m) of the upper part of Dixon Island Formation is composed of black shale, gray chert, and alternated pyrite layers. Especially, the DX core contains the layer of tens-hundreds micrometer euhedral pyrites and the layer of the minute spherical pyrites (about 10 μm in diameter) which are fulfilled with silica. We considered that the minute spherical pyrites formed at early stage of sedimentation from their morphology and occurence.

We did whole-rock analysis of sulfur isotope by NA 1500NCS (EA) manufactured by FISONS and DELTA plus XL (IRMS) manufactured by Thermo Finnigan. The instruments are equipped in Organic Geochem. & Cosmochem. Lab., Kyushu University. In situ analysis of sulfur isotope was performed using NanoSIMS50 manufactured by CAMECA at Atmosphere and Ocean Research Institute, Tokyo University. Carbon isotope analysis was performed using Delta Plus Advantage (EA/IRMS) manufactured by Thermo Finnigan at the Center for Advanced Marine Core Research, Kochi University.

As a result, minute spherical pyrites were revealed to have 5∼10 ‰ isotopic fractionation on the inside, showing distribution that area of high value is in ring-shape on the inside and area of low value is in the outer side and the central part of the crystal. Besides, CL3 core (n=27) showed δ^{34}S=+1.33∼+21.52 ‰, $\delta^{13}C_{org}$=-30.79∼-28.57 ‰, C_{org}=0.09∼1.65wt%.

In this analysis, most of carbon isotopic data had value between -30 to -28 ‰ in about 400m forming the Dixon island to Cleaverville formations. The carbon isotope result indicates that the same kind of carbonaceous material was deposited on the seafloor and the value corresponds with photosynthetic bacteria like cyanobacteria origin. Besides, pyrites formed in the anoxic marine sediment rich in organic matter. Particularly, closed system to sulfate was formed and Rayleigh fractionation was promoted by sulfate reducing bacteria. As a result, the feedback occurred and pyrites isotopically heavier than contemporary seawater sulfate (+2 ‰: Ohmoto, 1992) formed on the inside of pyrite shell. Although generally, in case sulfate reducing bacteria is concerned, sulfur isotopic ratio of sulfides has negative value, but +20 ‰ or more is observed in these sequence. It is possible that sedimentary sulfides in that time were in a condition that they had high sulfur isotopic ratio.

Keywords: Archean, carbon isotopic ratio, sulfur isotopic ratio, pyrite, SIMS, sulfate reducing bacteria