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Reconstruction of 3.2Ga seafloor: Carbon and Sulfur isotopic analysis for DXCL drill cores of Pilbara, Western Australia

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3.2∼3.1Ga oceanic sedimentary sequences, the Dixon Island and the Cleaverville formations are exposed at the coastal Pilbara terrane in the Western Australia. They are well preserved in low-grade metamorphism (Shibuya et al., 2007). In order to reconstruct sedimentary environment in high-precision, we performed DXCL Drill Project on land in 2007 and 2011, and 4 cores were obtained: DX, CL1, CL2 and CL3 (Kiyokawa et al., 2012; Yamaguchi et al., 2009).

In this study, we measured carbon and sulfur content (C_{org}, TS) and isotopic ratio ($\delta^{13}C_{org}$, $\delta^{13}C_{carb}$, $\delta^{34}S$) of CL3. Then we compiled them with previous works for DX to CL2 (Sakamoto, MS2010; Kobayashi et al., 2012; Teraji, MS2013). In addition, for DX core showing wide range of $\delta^{34}S$, we tried microrange analysis for pyrite grains using Secondary Ion Mass Spectrometry (NanoSIMS 50L).

The Cleaverville formation consists of the Black Shale (CL1, 2 and lower CL3) and the BIF (Banded Iron Formation; upper CL3) members. In the BIF member, iron carbonate (siderite: $FeCO_3$) and oxide (Hematite: Fe_2O_3; Magnetite: Fe_3O_4) alternate with chert predominantly in lower part and upper part, respectively. The DX core represents Dixon Island formation and is composed of alternation of black shale and gray chert with pyrite layer.

In microscopic observation in pyrite, we can find layers of microscale spherical shell pyrite of 10μm in diameter and 2μm in shell thickness. Their morphology and occurrence compared with euhedral ones imply that they have formed in the early stage of diagenesis.

For carbon analysis, we analyzed C_{org}, $\delta^{13}C_{org}$ and $\delta^{13}C_{carb}$. $\delta^{13}C_{org}$ showed a constant value of -30±1 ‰ in the Black Shale member. On the other hand, $\delta^{13}C_{carb}$ indicated a value of -10 ‰ in the BIF member which showed very low C_{org} value.

We also performed sulfur analysis. For powder samples, we measured $\delta^{34}S$ and TS for SO_2 gas after combustion. $\delta^{34}S$ of the Black Shale member revealed to have a wide range of 0∼+20 ‰ while that of the BIF member showed small range of +5∼+10 ‰. In terms of microscale spherical pyrites in DX, we performed $\delta^{34}S$ mapping in the scale of 10x10μm. As a result, we found microscale $\delta^{34}S$ heterogeneity of +5∼+10 ‰ in microscale spherical shell pyrites.

$\delta^{13}C_{org}$ value of -30 ‰ in black shale corresponds with the range of that of photosynthetic bacteria such as cyanobacteria (-31∼-18 ‰) and Chromatiaceae spp(one kind of purple sulfur bacteria; -36∼-26 ‰), and methane-related bacteria(-41∼-5 ‰ $<$) (Schidlowski, 1987). Regular fine parallel-laminations in organic-rich sediment indicates that organic matter is precipitated remains of bacteria. It can be considered that photosynthesis was probably active at that time and the same kind of remains of bacteria had continued to deposit.

$\delta^{13}C_{carb}$ of BIF(-15∼-5 ‰) accorded with that of siderite(-15∼-0.5 ‰) from anaerobic respiration by iron reducing bacteria (Fischer et al., 2009). This bacteria obtains energy by means of reduction of Fe^{3+} (e.g., iron hydroxide) into Fe^{2+} while decomposing organic matter. Therefore, iron hydroxide which is essential to life of iron reducing bacteria needs to have deposited at first. Although the main cause of forming of iron hydroxide is not clear, there are possibilities that surface water was weekly oxic or anoxygenic photosynthetic iron oxidizing bacteria was active.

Moreover, microscale $\delta^{34}S$ heterogeneity indicates an activity of sulfate reducing bacteria. TS/C_{org} plot for black shale slightly implies euxinic water, so bacterial sulfate reduction may have been active in the water column. However, taking $\delta^{34}S$ value (∼+20 ‰) higher than that of sulfate around 3.2Ga(+5.4 ‰, 3.3Ga: Strauss, 1993; +4.3 ‰, 3.0Ga: Hoering et al., 1989) into consideration, isotopic composition of sulfate could have been rich in ^{34}S. Besides, sediments could have been so stagnant that the supply of sulfate was restricted and Rayleigh fractionation occurred.

Keywords: Archean, sulfur isotope, carbon isotope, sulfate reducing bacteria, NanoSIMS