

## Geochemical studies about late Paleoproterozoic ocean environment: The Cape Smith belt, Canada

Kento Motomura<sup>1</sup>, Shoichi Kiyokawa<sup>1</sup>, Minoru Ikehara<sup>2</sup>, Kentaro Tanaka<sup>3</sup>, Takashi Sano<sup>4</sup>, Yukiyasu Tsutsumi<sup>4</sup>, Yuji Sano<sup>3</sup>

<sup>1</sup>*Kyushu Univ.*

<sup>2</sup>*Kochi Univ.*

<sup>3</sup>*Univ. of Tokyo*

<sup>4</sup>*National Museum of Nature and Science*

Paleoproterozoic is one of the periods which Earth's surface environment was changed dramatically. For instance, Great Oxidation Event (GOE) occurred ca. 2.4 Ga is well known. GOE caused oxidative weathering of continent, and it results in accumulation of sulfate in the ocean (Scott et al., 2014). Although it is suggested that the seawater sulfate which accumulated in the ocean was decreased till ca. 2.0 Ga, there are few studies about ocean redox condition and sulfate level after 2.0 Ga. We studied about 50 m thick sandstone-black shale sequence from the Nuvilic Formation, Povungnituk Group at the Cape Smith belt to reconstruct sedimentary environment. The sedimentary rocks in the group was deposited at the northern margin of the Superior craton. In this presentation, we report detailed observation of the sequence and result of organic carbon ( $\delta^{13}\text{C}_{\text{org}}$ ), sulfur ( $\delta^{34}\text{S}$ ) isotopes and trace element compositions analysis to clarify the sedimentary environment such as sulfate level and biological activities of the formation.

The drilling core no. 718.3333 which consists of an alternation of sandstone and black shale are used for our chemical analysis. The core includes two upward fining which changes sandstone dominant to shale dominant sequences and an upward coarsening structures. Black shale includes silt size quartz, as a main mineral, white mica and pyrrhotite as accessory minerals. Pyrrhotite is subdivided into three types from the morphology, vein-type, syngenetic, and authigenic. The First type is often observed in the upper portion of the core. The type composes vein-like band which thickness is usually 5 mm and is coarse and euhedral. The second is in the lower portion of the core, which is less than 10  $\mu\text{m}$ . The third is present throughout the core and about 50  $\mu\text{m}$ .

The  $\delta^{13}\text{C}_{\text{org}}$  value ranges from -33 to -30 ‰ which reflects the activity of cyanobacteria, purple sulfur and methanogenic bacteria. Furthermore, the  $\delta^{13}\text{C}_{\text{org}}$  decrease from -30 to -33 ‰ at the lower portion of the core, which might indicate the transition of inorganic carbon isotopes caused by oxidative weathering of the organic matter on the continent. The  $\delta^{34}\text{S}$  value changes from heavier (+15 ‰) to lighter (-5 ‰) at the lower portion of the core, simultaneously with the  $\delta^{13}\text{C}_{\text{org}}$  transition, and then, return gently at the middle. Higher  $\delta^{34}\text{S}$  value, more than +7 ‰, suggests the activity of the sulfate reducing bacteria in the sulfate poor environment because isotope fractionation between sulfate and sulfide will less than 10 ‰ when ocean sulfate level is smaller than 1 mM (Canfield et al., 2010). On the other hand, enrichment in  $^{32}\text{S}$  is likely to relate to the increase of oceanic sulfate. Therefore, sulfur isotope transition in the sequence suggests increasing of seawater sulfate and subsequent decrease. Trace element composition analysis cleared redox sensitive metal such as Ni and V increased at the lower portion, which indicates increase of free sulfide or dissolved metal. In conclusion, our  $\delta^{13}\text{C}_{\text{org}}$ ,  $\delta^{34}\text{S}$  and trace element composition analysis revealed that oxidative weathering of the continent where host organic matter and sulfides caused enrichment in sulfate and bacterial sulfate reducing acted as negative feedback.

### References

- C. Scott, B.A. Wing, A. Bekker, N. J. Planavsky, P. Medvedev, S.M. Bates, . . . T. W. Lyons, Pyrite multiple-sulfur isotope evidence for rapid expansion and contraction of the early Paleoproterozoic seawater sulfate reservoir. *Earth and Planetary Science Letters*, 389, 95-104, 2014.
- D.E. Canfield, J. Farquhar and A.L. Zerkle, High isotope fractionations during sulfate reduction in a low-sulfate euxinic ocean analog. *Geology*, 38(5), 415-418. 2010.