

## Geological and geochemical studies about the Eoarchaean-aged Banded Iron Formations in Nain Province, Northern Labrador.

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Banded iron formations (BIFs) are chemical sediments, deposited in seawater before the Paleoproterozoic, and are often utilized as proxies for chemical compositions of seawater. However, the scarcity of >3.6 Ga supracrustal rocks including BIFs hampers the use of BIFs for estimate of the seawater composition, especially bioessential elements, in the early earth. Recently, Konhauser et al. (2009) showed secular change of Ni/Fe ratios of BIFs through geologic time, and suggested that the Archean seawater was enriched in dissolved Ni, suitable for methanogenic bacteria. But, their data show quite large variations in Ni/Fe ratios at the same ages from the modern value to about ten times value. Therefore, more comprehensive investigation of the BIFs through geological time is necessary to estimate secular change of chemical composition of seawater. For the purpose, we performed comprehensive investigations of geology, geochronology, stratigraphy and geochemistry of the oldest supracrustal rocks, in >3.96 Ga Nulliak Supracrustal rocks in the Nain Province, Northern Labrador, Canada (Shimojo et al., 2013).

Based on the lithostratigraphy and accompanied rocks, we classified into two types of BIFs: BIFs interlayered with metabasite in the Nulliak Island and BIFs accompanied with carbonate and/or chert layers, respectively. The former are Algoma-type BIFs, which was deposited in deep-sea near basaltic volcanism. The latter are uncommon in the Early Archaean, which are possibly formed in shallow-water environment.

Their PAAS-normalized REE+Y patterns display positive La, Eu and Y anomalies, suggesting that they were deposited in a mixing zone of seawater and hydrothermal water. In addition, transitional element contents such as Ni and Zn (>50 ppm) are high, similar to other Archean BIFs (Konhauser et al., 2009, Mloszewska et al., 2012). But, HFSE (e.g. 1~20 ppm in Zr contents) and Al<sub>2</sub>O<sub>3</sub> (0.5~2 wt%) contents are variable, and positively correlated with REE+Y and the transitional element contents, suggesting that the variation in the REE+Y contents is due to detrital inputs so that samples with low Zr and Al<sub>2</sub>O<sub>3</sub> contents preserve the detritus-free compositions. The samples with low detritus inputs show a negative correlation between Eu/Eu\* and REE and Y/Fe ratios, and between Eu/Eu\* and LREE/REE and Y ratios, respectively. The similar correlations are reported for iron-rich suspended particulates collected from the TAG hydrothermal field (German et al., 1990). Therefore, the REE+Y variations can be explained by continuous scavenging processes by iron-oxyhydroxide particles. Moreover, no Ce/Ce\* anomaly is consistent with anoxic seawater in the Early Archaean.

In addition, transition metals (Ni, Zn, Co)/Fe ratios correlate negatively with Eu/Eu\*. The correlations were also shown in BIFs in the Isua Supracrustal Belts and the Nuvvuagittuq Supracrustal Belts (Bolhar et al., 2004; Mloszewska et al., 2012), suggesting that their variations are due to same scavenging processes by iron-oxyhydroxide particles as REE+Y. Namely, the transition metals/Fe ratios of BIFs don't provide direct estimate of those concentrations of seawater. We normalize their transitional metals by rare earth elements (e.g. Sm), which are adsorbed on iron-oxyhydroxide similar to the transition metals. Sm-normalised transitional metals contents of the Archaean BIFs are higher than those of Proterozoic BIFs, suggesting that the Archaean seawater was enriched in transitional metals such as Ni and Zn, which are essential for protein synthesis of the early life.

**Reference** : Konhauser et al., 2009. *Nature* 458, 750-754. ; Shimojo et al., 2013. *Goldschmidt 2013*, Florence, Italy.; German et al., 1990. *Nature* 345, 516-518. ; Bolhar et al., 2004. *EPSL* 222, 43-60. ; Mloszewska et al., 2012. *EPSL* 317-318, 331-342.

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