Occurrence and chemical composition of carbonate rocks in the Nuvvuagittuq supracrustal belt, Quebec, Canada: Implications for chemical composition of the Eoarchean hydrothermal fluid

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The Earth is a unique planet where liquid water and life exist through the geologic time. Therefore, an estimate of surface environmental conditions of the surface environment of the early Earth is an important issue to reveal early life. However, we know little about the early Earth, because the first 500-million-year records of the Earth was almost lost.
Recent studies suggested that the Nuvvuagittuq supracrustal belt (NSB) in Quebec, Canada, was formed 4.28 billion years ago (O'Neil et al., 2008). Therefore, the NSB has gained attention in the decoding of the early Earth history.
Previous studies showed that the origin of BIF occurred in the NSB is originated from chemically sedimentary rock based on their Post-Archean Average Shale (PAAS)-normalized rare earth element (REE) patterns, including positive La, Eu, and Y anomalies (Mloszewska et al., 2012; 2013). The La and Y positive anomalies are recognizable in the modern seawater, and the positive Eu anomaly is a diagnostic signature of hydrothermal fluid. Therefore, these features are regarded as powerful proxies in discussing the origin of metamorphosed and altered Archean sedimentary rocks (e.g. Bolhar et al., 2004). In particular, it is considered that the positive Y anomaly is mainly formed by precipitation of iron oxides in the ocean (e.g. Nozaki et al., 1997). Mloszewska et al. (2013) also described occurrence of carbonate rocks in the NSB, and argued that it was formed through metasomatic alteration based on its occurrence. However, they did not estimate the chemical compositions of hydrothermal fluids that caused metasomatic alternation. Therefore, we try to decode the Eoarchean hydrothermal fluid chemical composition using the carbonate rocks in the NSB.
In 2018, we found some new outcrops of carbonate rocks in the NSB. Most of the carbonate rocks in the NSB occur as vein within mafic rocks or silicic sedimentary rocks. As suggested by the previous study, it is considered that the carbonate rocks were formed through metasomatism. We analyzed major and trace element (e.g. REE and Zr) contents of whole rocks of the carbonate rocks using X-ray Fluorescence for major elements and High-Resolution Inductively Coupled Plasma Mass Spectrometry for trace elements at the University of Tokyo, respectively. Some carbonate rocks have high SiO_2, Al_2O_3, and Zr contents, possibly due to involvement of detrital and volcanic materials with/without silicification. We selected the carbonate rocks with low SiO_2, Al_2O_3, and Zr contents in order to remove influence of the silicification and contamination of the detrital materials. The PAAS-normalized REE patterns of the almost all of the carbonate rocks show LREE-depleted patterns with positive La, Eu (Eu/Eu*: 1.01-2.87) and Y (Y/Ho: 34.3-48.1) anomalies and some samples show a negative Ce anomaly.
Generally speaking, positive La and Y anomalies of carbonate rocks indicate that they originate from chemical sediments precipitated from seawater (e.g. Webb and Kamber, 1999; Bolhar et al., 2004). Although the carbonate rocks in the NSB have the La and Y anomalies, their geologic occurrence suggests that these carbonate rocks were formed through metasomatism. Namely, their chemical signatures are inconsistent with the geological occurrence. The inconsistency may indicate that the Y and La anomalies are not necessarily robust proxies for origins of the Eoarchean sedimentary rocks. A combination of their chemical composition and geological occurrence is essential for the estimate of origins.

In general, it is considered that a Ce anomaly can be formed by oxidation of trivalent Ce to less soluble tetravalent Ce and then the subsequent absorption of Ce to Fe oxide. However, our result suggests that metamorphic fluids have the Ce anomaly because the carbonate rocks in the NSB have the negative Ce anomaly. If the hydrothermal fluids in the Eoarchean were more alkaline than previously expected, the Ce would be tetravalent. Also in this case, Ce is adsorbed to iron oxide and removed as described above. Hofmann and Harris (2008) reported the negative Ce anomaly from the Eoarchean altered basalt in the Barberton greenstone belt, and interpreted that Ce was removed by iron oxides in the hydrothermal system. Our result supports the mechanism.
A negative Y anomaly have been reported in carbonated or weathered basalts (e.g. Nakamura and Kato, 2004; Babechuk et al., 2015), but generation processes of the anomaly is still unknown. Therefore, further studies of causes of the positive Y anomaly in the Eoarchean carbonated basalt will be required.

Keywords: Nuvvuagittuq supracrustal belt, Carbonate rock, Eoarchean

