Occurrence and chemical compositions of the Eoarchean carbonate rock: Implications for the composition of the Eoarchean seawater

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The Earth is a unique planet where liquid water and life exist through the geologic time. Therefore, estimating the surface environment of the early Earth is very important for understanding the early life. However, we have little knowledge about the early Earth, because the first 500 million years history of the Earth was almost lost.

Recent geological study suggested that Nulliak supracrustal rocks in the Saglek Block, Labrador, Canada were formed around 3.95 Ga. That means that the Nulliak supracrustal rocks were the oldest supracrustal rocks.

We estimate chemical composition of the Eoarchean seawater from the carbonate rocks in the Nulliak supracrustal rocks. We collected the carbonate rocks in four groups. The carbonate rocks in the St. John’ s Harbour South area sporadically occur near the ultramafic rocks within the metabasaltic bodies. The carbonate rocks in the St. John’ s Harbour East area, are interlayered with pelitic rocks. The carbonate rocks in the Big Island are accompanied with pelitic rocks, and display lithostratigraphic transition from pure carbonate rock to pelitic rock. The carbonate rocks in the Pangertok Inlet are interlayered with the BIF. The differences in occurrence are possibly related with their depositional environments. The carbonate rocks in the St. John's Harbor South and the Pangertok Inlet were deposited in hydrothermal fields where basaltic magmatism was active, whereas those in the St. John's Harbor East and the Big Island were deposited near continental margin where detrital materials were deposited together.

We analyzed major and trace element (rare earth element (REE), Y and Zr) contents of the whole rock in the carbonate rocks by X-ray Fluorescence (XRF) for major elements and Inductively Coupled Plasma Quadrupole Mass Spectrometry (ICP-QMS) for trace elements. Some carbonate rocks have high Zr, Ti, Al, Si, and Fe contents, possibly due to involvement of detrital and volcanic materials and ferruginous minerals, and/or silicification. We selected the carbonate rocks with low Zr, Ti, Al, Si, and Fe contents in order to remove the influence of the silicification and contamination of the detrital materials or ferruginous materials.

Their PAAS (Post-Archean Average Shale)-normalized REE and Y patterns display flat to slightly LREE-depleted patterns with positive La and Y anomalies. Samples in the St. John’ s Harbour East and the Big Island, which were accompanied with pelitic rocks, have no large Eu anomaly.

The positive Y anomalies indicate that the carbonate rocks originate from chemical sediments precipitated from seawater. In addition, the variation of the positive Eu anomalies, which ranges from large Eu anomaly for samples deposited near the hydrothermal vents to small Eu anomaly for those deposited near continental margin, suggests that the hydrothermal activities reached only near the hydrothermal vents. Previous geochemical studies of carbonate rocks in the Isua supracrustal belt (3.81 Ga) also found the positive Eu anomalies for the carbonate rocks. However, since the compositions of the

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seawater were considered to be homogenous in these studies, there was no discussion on which place in the Eoarchean ocean was affected by hydrothermal activities.

We also measured the concentration of transition metal elements (V, Cr, Co, Ni, Cu, and Zn) in the carbonate rocks of the Nulliak supracrustal rocks by ICP-Sector Field Mass Spectroscopy (ICP-SFMS). The the carbonate rocks with low Si, and Fe contents range from 0.45 to 9.0 ppm for V contents, from 2.0 to 24 ppm for Cr contents, from 0.8 to 4.8 ppm for Co contents, from 3.4 to 25 ppm for Ni contents, from 1.7 to 27 ppm for Cu contents and from 8.7 to 46 ppm for Zn contents respectively.

We compared them with those in the modern carbonate sediments precipitated in the Pacific, Atlantic and Indian Oceans. The Al_2O_3 variation diagrams for V, Cr, Co, Ni and Zn contents show the Nulliak carbonate rocks with low Si and Fe contents are more enriched in those elements than the modern carbonate sediments at given Al contents. Especially, the Nulliak carbonate rocks have higher V, Cr, Co, Ni, and Zn than the modern carbonate sediments at 0% in Al_2O_3 contents by 1.5, 2, 3, 1.5, and 2.7 times respectively.
Assuming that the partition coefficients for the transition metal elements between seawater and carbonate did not change between the Eoarchean and the present, the results imply that the Eoarchean seawater was more enriched in the V, Cr, Co, Ni and Zn than the modern seawater. Especially, the enrichment of Ni content in the ancient seawater may be consistent with a hypothesis that early life was methanogen with an enzyme methyl coenzyme M reductase, Cofactor F430.

Keywords: Eoarchean, Paleoseawaer , carbonate rock, Nulliak supracrustal rocks, Saglek Block

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