論文の内容の要旨

論文題目

Geology and geochemistry of the Eoarchean carbonate rocks: Implications for co-evolution of life and transitional element contents in the seawater through geologic time

（初期太古代炭酸塩岩の地質学・地球化学的研究：生命と海洋遷移金属元素組成の共進化）

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The evolution of life is the key issue in the history of the Earth. Many geologists and biologists think that trace elements utilized in modern lives' metalloenzymes commonly reflect the availability of trace elements in ancient seawater when those metalloenzymes first emerged. The idea that an organism's trace element requirements are dependent on the environment in which the organism evolved stems from the simple observation that the biogeochemical cycling of many bioessential elements can vary dramatically under different aqueous conditions.

Geochemistry of chemical sedimentary rocks such as banded iron formation (BIF) is commonly utilized to estimate surface environmental conditions such as seawater composition during the Archean. For example, Konhauser et al. (2009) suggested that Ni concentration of the ocean was high during the Eoarchean due to furious hydrothermal Ni influx from komatiite to the ocean. Moreover, they argued that high Ni content in the Archean ocean led a prosperity of methanogens, because Ni is contained in cofactor F_{430} used by methanogen.

However, many problems remain to be solved regarding geochemical studies of ancient chemical sedimentary rocks. The main problem is that only a few Eoarchean rocks are preserved throughout the world, and that most Eoarchean rocks have undergone severe deformation, metamorphism, and metasomatism. In addition, an estimation of ocean composition with BIF has some difficulties. For example, trace element concentration the BIF depends not only those in ambient seawater but also sedimentary rates, involvement of detrital materials, kinetic effect caused by adsorption rate of trace element on iron-oxyhydroxide, and other interference elements such as Si.

Yet, despite these problems with BIF, there is still no study on the secular change in seawater composition through geologic time using carbonate rocks. This is because it was reported that the Eoarchean carbonate rocks could be formed secondary to igneous rocks due to an alteration. Therefore, when estimating seawater composition using the Eoarchean carbonate rocks, it is necessary to clarify their origin based on occurrence, petrography, and geochemistry.

In the Chapter 2, I studied the carbonate rocks of the *ca*. 3.8 Ga Nuvvuagittuq supracrustal belt. The carbonate rocks in the area were classified into four types based on their occurrence. Their geological occurrence strongly suggested that all types of carbonate rocks were formed by an alteration of igneous rocks. Some carbonate rocks in this area had positive La and Y anomalies. Since the positive La and Y anomalies are formed by the reaction of water with iron-oxides, these anomalies indicate that the carbonate rocks were derived from chemical sedimentary rocks precipitated from the ocean. The contradiction between the occurrence and geochemistry suggested that iron-oxide precipitated within hydrothermal fluid, and Y and Ho were fractionated *in-situ*. The results of this chapter proposed that that it is important not to use geochemistry blindly, but to use geological occurrence and geochemistry complementarily.

In the Chapter 3, I studied the carbonate rocks of the *ca*. 3.9 Ga Nulliak supracrustal rocks. The carbonate rocks in the area were classified into two types, based on their occurrence: Those

accompanied with mafic rocks or BIF and those accompanied with pelitic rocks. The geological occurrence suggests that the formers were formed around hydrothermal fields, whereas the latters were formed near a continental margin. To estimate an origin of the carbonate rocks, less-altered samples were selected using a combined filter of the SiO_2, TiO_2, Al_2O_3, Zr, and Ba contents. The selected carbonate rocks had positive La, Eu, and Y anomalies. The La and Y anomalies suggested that they originate from chemical sediments precipitated from seawater and the Eu anomaly suggested that the seawater was globally affected by hydrothermal fluids because even the carbonate rocks formed near a continent had a positive Eu anomaly.

In addition, V, Co, Ni, and Zn contents of the carbonate rocks were analyzed. Assuming that the SiO_2 contents in the carbonate rocks were supplied by only the contamination of detrital material and silicification, an influx of SiO_2 contents by silicification into carbonate rock accounts for $ca.$ 95% of a total SiO_2 contents estimated by their SiO_2 and Al_2O_3 contents. This ratio was used to calculate the V, Co, Ni, and Zn contents of the carbonate rock composition before silicification. And then, the ideal carbonate rock composition without the contamination of detrital material was estimated, based on assuming that aluminum and zirconium are hardly dissolved in the ocean.

In the Chapter 4, I studied the carbonate rocks of the $ca.$ 3.8 Ga Isua supracrustal belt. The carbonate rocks occur as layers alternating with chert layers and with conglomerate layers. The geological occurrence indicates that the formers formed in hydrothermal fields or in pelagic areas, whereas the latters were deposited near a continental margin. Based on petrography and geochemistry, I selected less-altered samples. Selected samples had positive La, Eu and Y anomalies. The La and Y anomalies suggested that they originate from chemical sediments precipitated from seawater and the Eu anomaly suggested that the seawater was globally affected by hydrothermal fluids because even the carbonate rocks formed near a continental margin had a positive Eu anomaly.

Besides, V, Co, Ni, and Zn contents of the carbonate rocks were analyzed. The ideal carbonate rock composition was estimated by calculating in the same manner as in the Chapter 3.

In the Chapter 5, aforementioned methods were applied to the Neoarchean and modern carbonate rocks to estimate the secular change of V, Co, Ni, and Zn contents in the carbonate rocks through geologic time. Assuming that the partition coefficients for transitional elements between seawater and carbonate minerals were the same through geologic time, the secular change in the carbonate rock composition can be regarded as the secular change in the seawater composition.

The Eoarchean carbonate rocks have higher V content than the modern equivalent. Vanadium is contained in nitrogenase enzymes, and phylogenetic analysis suggested that type containing V appeared in the final stage of nitrogenase evolution. This study implied that the evolution of nitrogenase was independent of seawater composition. The Eoarchean carbonate rocks have higher Co content than the modern equivalent. Cobalt is contained in vitamin B_{12} which is used to synthesis of methionine, and the enzyme is available only to prokaryotes. Therefore, the results of this study implied that a secular variation of Co composition in the seawater was associated with the evolutions of methionine synthesis by prokaryotes and eukaryotes. The Eoarchean carbonate rocks have higher Ni content than the modern equivalent. Nickel is bioessential element for methanogens, which are candidate for early life, because Ni is contained in coenzyme, cofactor F_{430}, hydrogenase, and carbon monoxide dehydrogenase. This study suggested that the use of Ni by methanogens was associated with seawater composition.

The results of this doctoral dissertation showed that life and transitional element contents in the seawater may have co-evolved. At the same time, however, the results also showed examples where life and seawater composition did not co-evolve. This reflects the possibility that the evolution of life depends on biological factors as well as seawater composition.