

## 博士論文 (要約)

### **Molybdenum isotope study on modern marine hydrothermal iron and manganese deposits: Implications for Archean and Paleoproterozoic ocean redox condition**

(現世熱水性鉄マンガン酸化物を対象としたモリブデン同位体研究: 太古代・原生代前期における海洋酸化還元環境への示唆)

平成 29 年 2 月論文博士 (理学) 申請

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Oxygen (O<sub>2</sub>) is the second most abundant gas, and makes up 21% of the atmosphere on the modern Earth. However, the atmospheric O<sub>2</sub> levels (*p*O<sub>2</sub>) were likely less than 10<sup>-5</sup> PAL for the first two billion years of the Earth's history. Oxygen is fundamentally sourced from O<sub>2</sub>-producing photosynthesis, and can significantly influence various biogeochemical processes on the surface environment. Hence, a detailed reconstruction of redox evolution in ancient ocean-atmosphere system would provide unique insights into co-evolution of the Earth's environment and life. On the basis of chemical compositions (e.g., U content and I and Fe speciation) of sedimentary rocks, recent studies have proposed an oxygen overshoot immediately after the first rise of atmospheric O<sub>2</sub> (the Great Oxidation Event) in the early Paleoproterozoic. That is, *p*O<sub>2</sub> may rise from <10<sup>-5</sup> PAL to >~10<sup>-2</sup> PAL at ~2.3 Ga, but dropped to <10<sup>-3</sup>–10<sup>-1</sup> PAL at ~2.06 Ga. Such a highly oxidizing condition between ~2.3 and ~2.1 G may be consistent with the extreme positive δ<sup>13</sup>C excursion (called the Lomagundi event) found from carbonates rocks deposited during that period and recent findings of fossil records for multicellular life, possibly eukaryotic organisms, from ~2.1 Ga sedimentary rocks. However, the idea of O<sub>2</sub> overshoot relies on the geochemical records that allow several different interpretations, and hence has yet to be evaluated.

The isotopic compositions of Mo (δ<sup>98/95</sup>Mo) in seawater is sensitive to ocean redox condition. As marine sedimentary rocks can directly and/or indirectly record seawater δ<sup>98/95</sup>Mo at the time of deposition, their δ<sup>98/95</sup>Mo may provide constraints on global paleoredox conditions of ocean-atmosphere system. δ<sup>98/95</sup>Mo of Archean and Paleoproterozoic Fe- and Mn-rich sedimentary rocks are

currently receiving attention in studies assessing ocean paleoredox conditions. Previous studies reported light  $\delta^{98/95}\text{Mo}$  values from those sedimentary rocks which are indicative of Mo adsorption onto Fe- and/or Mn oxides. Those findings may serve as evidence of local  $\text{O}_2$  production as early as ~2.95 Ga. However, due to our limited knowledge on Mo isotope variations among modern marine Fe- and Mn-rich sedimentary rocks, the previous studies failed to discuss changes in global redox. Mechanism responsible for  $\delta^{98/95}\text{Mo}$  variations among Fe- and Mn-rich sedimentary rocks and its relationship to global redox condition should be further elucidated through a detailed study of Mo isotope on modern marine oxides.

In the present study, we conducted the following three experiments to understand the history of atmosphere-ocean redox variations and its impacts on biological evolution: (1) development of Mo isotope analysis based on double spike technique and MC-ICP-MS measurement at the Geological Survey of Japan, (2) investigations of  $\delta^{98/95}\text{Mo}$  variation among modern marine hydrothermal Fe- and Mn-oxides, and (3) reconstruction of ocean-redox condition during the early Paleoproterozoic based on trace element and Re-Os and Mo isotope analyses of the ~2.2 Ga Nsuta Mn deposits. Below, our findings are summarized.

***Mo isotope analysis:*** A new double spike enriched with  $^{100}\text{Mo}$  and  $^{97}\text{Mo}$  were prepared, and calibrated during the present study. Using this new double spike,  $\delta^{98/95}\text{Mo}$  of reference solutions were measured repeatedly. The external reproducibility of the reference solutions was better than 0.03‰ which is similar or superior to those reported by previous studies. The isotopic compositions of

reference Mn nodules (Nod A-1, Nod P-1, and JMn-1) and modern hydrogenous Fe-Mn crusts were also analyzed after separation and purification of Mo by two-stages of ion exchange chemistry.  $\delta^{98/95}\text{Mo}$  of the reference Mn nodules materials and hydrogenous Fe-Mn crusts were consistent with previously reported values. These results verify the accuracy and precision of method used in the present study.

*$\delta^{98/95}\text{Mo}$  in modern marine hydrothermal Fe- and Mn-oxides:* Hydrothermal Fe oxides composed mainly of goethite have  $\delta^{98/95}\text{Mo}$  of 0.65–0.88‰ (relative to NIST SRM 3134) which is 1.21–1.44‰ lighter than that of present-day seawater. Hydrothermal Mn oxides show large variations in  $\delta^{98/95}\text{Mo}$  ranging from –1.7 to 0.5‰, but most of their isotopic compositions are  $2.7 \pm 0.3\%$  lighter than present-day seawater  $\delta^{98/95}\text{Mo}$ . These offsets from the present-day seawater value are consistent with the isotope fractionations observed by previous adsorption experiments of Mo onto Fe and Mn oxides. Hence, our results indicate that seawater is the dominant source of Mo for modern hydrothermal Fe and Mn deposits. Based on our new  $\delta^{98/95}\text{Mo}$  data, we proposed a new framework to interpret  $\delta^{98/95}\text{Mo}$  variations of Fe- and Mn-rich sedimentary rocks in  $\delta^{98/95}\text{Mo}$ –Fe/Mn diagram. We developed a simple mass balance model that considers Mo isotope fractionations during adsorption onto Fe and Mn oxides to explain. A theoretical line (modern theoretical line) obtained by the calculation using the present-day seawater  $\delta^{98/95}\text{Mo}$  showed good agreement with our new  $\delta^{98/95}\text{Mo}$  data of hydrothermal Fe and Mn oxides. In addition, our calculation demonstrated that the previously reported  $\delta^{98/95}\text{Mo}$  of ancient Fe- and Mn-rich sediments were generally explained by our new model

assuming a seawater  $\delta^{98/95}\text{Mo}$  value of 1.5‰ (inferred from 2.5-Ga pyritic black shales) at the time of deposition. Our model indicates that deviation ( $\Delta^{98/95}\text{Mo}$ ) of each  $\delta^{98/95}\text{Mo}$  data from the modern theoretical line reflect difference between present-day seawater  $\delta^{98/95}\text{Mo}$  and seawater  $\delta^{98/95}\text{Mo}$  at the time of deposition. These observations suggest that  $\Delta^{98/95}\text{Mo}$  could be a promising new tool to reconstruct paleo-seawater  $\delta^{98/95}\text{Mo}$  values

***Geochemistry of the ~2.2 Ga Nsuta Mn deposit:*** Geochemical features of Mn ore and phyllite samples from the Nsuta deposit are follows: (1) Mo concentration is high in the Mn ore samples compared to the phyllite samples, (2) the Mn ore samples show both positive Eu and Ce anomalies in the PAAS-normalized REE pattern, whereas the phyllite samples only show the positive Eu anomaly, (3) the composite Re-Os isochron yields an age of  $2232 \pm 120$  Ma with a low initial  $^{187}\text{Os}/^{188}\text{Os}$  ratio of  $0.22 \pm 0.07$ , and (4)  $\delta^{98/95}\text{Mo}$  values of the Mn ore samples are lighter than 2.5 Ga, ~1.9–1.8 Ga, and present-day seawater, although the values show large variation. The obtained geochemical data can be explained by precipitation of Mn oxides from ascending hydrothermal fluids at ~2.2 Ga, although the large  $\delta^{98/95}\text{Mo}$  variation suggests that bulk  $\delta^{98/95}\text{Mo}$  value of several samples was influenced by Mo associated with organic materials, hydrothermally derived Mo, and early diagenesis. Samples which likely adsorbed most of their Mo from ambient seawater were calculated for  $\Delta^{98/95}\text{Mo}$ , and their  $\Delta^{98/95}\text{Mo}$  values were compared to  $\Delta^{98/95}\text{Mo}$  of other ancient Fe- and Mn-rich sedimentary rocks. We found that the mean  $\Delta^{98/95}\text{Mo}$  of the Nsuta deposit was similar to those of 2.35-Ga IFs and ~2.1 Ga Mn deposit. However, it was significantly heavier than those in pre-2.5 Ga and 1.88 Ga IFs.

As seawater  $\delta^{98/95}\text{Mo}$  values are heavy under high Mo fluxes into Mn oxides, the heavy mean  $\Delta^{98/95}\text{Mo}$  values during 2.35–2.1 Ga suggest the development of anomalously oxidizing condition during the period. Hence,  $\delta^{98/95}\text{Mo}$  of the Nsuta deposit support the occurrence of oxygen overshoot during the early Paleoproterozoic.

***Implications for biological evolution:*** Given the marine Mo isotope systematics, the heavy  $\Delta^{98/95}\text{Mo}$  values between 2.35 and 2.1 Ga most likely reflect widespread oxygenation of ocean-atmosphere system that allows precipitation and preservation of Mn oxides on seafloor, rather than local  $\text{O}_2$  production. In the modern ocean, such an oxidative Mn cycle requires oxidizing bottom water that contains  $[\text{O}_2] > 10 \mu\text{M}$ , which may be sufficient to sustain early eukaryotic organisms. The first appearance of possible eukaryotic fossil records roughly corresponds with the widespread oxidation during the oxygen overshoot, whereas the major diversification of eukaryotic organism took place at ~800 Ma. These results imply that the  $\text{O}_2$  rise played a key role for the evolution of eukaryotes during the early Paleoproterozoic; however, because of the instability of that highly oxidizing condition, the evolution and activity of eukaryotic organisms were depressed till the second major rise of atmospheric  $\text{O}_2$  at ~800 Ma.