

# 論文の内容の要旨

## Study on fluid-rock interactions in oceanic crust and upper mantle using isotope geochemistry

(同位体地球化学に基づく海洋地殻と上部マントルにおける  
水-岩石相互作用に関する研究)

氏 名 巖 智 瑗

Magnesium (Mg) is a major element in both the silicate Earth and hydrosphere. It is important in understanding the chemical evolution of the oceans and the lithospheres, as well as changes in global climate inferred from the co-variation between seawater Mg/Ca and climate throughout geologic time. In general, Mg is transferred from continents to the oceans via river and is removed mainly by the carbonate deposition and the hydrothermal alteration of the oceanic crust on the spreading centers. Even now, there is little consensus on the Mg cycle in the ocean regarding sink fluxes because Mg concentrations were the only factor. In the 2000s, the development of Mg isotope measurement techniques has broadened the understanding of Mg behavior. Mg isotopes are noticeable tracers for the fluid-rock interactions because each Mg reservoir has a different  $\delta^{26}\text{Mg}$  value and because they do not fractionate by magmatic

processes. Importantly, Mg behaviors between the carbonation and the hydrothermal sink are isotopically differentiated.

This dissertation focuses on Mg isotopes at the two main fluid-rock interactions at the oceanic lithosphere (the hydrothermal circulation at spreading centers and the subduction related alteration). Conventional isotopes (Sr, Nd, and S) are also supportive of Mg isotopic geochemistry. High-temperature vent fluids from the western Pacific and the Oman ophiolite are investigated as the example of the fluid and the rock, respectively. The high-temperature vent fluids are characterized by extremely depleted Mg concentrations compared to the seawater (53 mM of Mg, Holland et al., 1986), which enables us to investigate Mg behavior by hydrothermal circulation and constrain the global Mg fluxes in the oceans. On the other hand, the Oman ophiolite is the ancient oceanic lithosphere, presently exposed on land. It has been considered that the Oman ophiolite has experienced variable tectonic events from spreading and subduction to obduction, which records not only the hydrothermal alteration at the spreading stage but also the subduction related modification. Additionally, the Oman ophiolite enable us to infer the scale of the modification since it is easily accessible and an exposed, large ophiolitic body with the full sequence.

Seawater ( $-0.83 \pm 0.09\%$ , Ling et al., 2011) is isotopically heavy relative to the riverine input ( $-1.09 \pm 0.05\%$ , Tipper et al., 2006), requiring isotopically fractionated Mg sinks in the oceans. In this dissertation,  $\delta^{26}\text{Mg}$  values of high-temperature vent fluids in seafloor hydrothermal systems are measured for the first time. Due to the isotopically fractionated Mg fixation into secondary minerals during hydrothermal circulation, some vent fluids (return flux) with significantly low Mg concentration ( $\sim 0$  mM) show  $^{26}\text{Mg}$  depletion (down to  $-1.18\%$ ) compared to seawater Mg. By contrast, addition of Mg to the permeable sub-seafloor during venting is the probable reason for others having seawater  $\delta^{26}\text{Mg}$  value. This confirms that the high-temperature hydrothermal sinks have a less significant effect on the oceanic Mg isotopic composition, since almost all the Mg in seawater entering high-temperature hydrothermal circulation is precipitated (high-temperature Mg sink). Based on the simple steady state

equations and low-temperature hydrothermal sinks of Mg ( $-0.25\text{‰}$  to  $0.00\text{‰}$  of  $\delta^{26}\text{Mg}$ ), 7-26% of the riverine Mg input is presumed to be removed through the high-temperature sink. This is lower than the thermal estimation proposed by Mottl and Wheat (1994), which was 10-40%. Thus, other Mg sinks such as the low-temperature hydrothermal sink and/or the dolomite sink need to be considered to explain seawater  $\delta^{26}\text{Mg}$  value.

In terms of the Mg behavior in the rock,  $\delta^{26}\text{Mg}$  values are determined for sediments, crusts, and mantle peridotites in the northern Fizh massif, Oman ophiolite. The reconstruction of the  $\delta^{26}\text{Mg}$  value of the Cretaceous seawater was attempted by measuring the  $\delta^{26}\text{Mg}$  of the micrite limestone.  $\delta^{26}\text{Mg}$  values of micrite limestone ( $-0.52\text{‰}$  and  $-0.23\text{‰}$ ) are even heavier than those of modern seawater and are considered out of the isotopic equilibrium during its formation. Therefore, they could not be used for direct reconstruction of seawater  $\delta^{26}\text{Mg}$  in the Cretaceous time. In the crustal section,  $\delta^{26}\text{Mg}$  values ranging from  $-0.58\text{‰}$  to  $-0.04\text{‰}$  do not correlate with stratigraphic depth. Instead, the formation of clay minerals by hydrothermal circulations leads to a decrease in  $\delta^{26}\text{Mg}$  values from the global mantle  $\delta^{26}\text{Mg}$  value of  $-0.25 \pm 0.04 \text{‰}$  (Teng et al., 2010). This decrease indicates the intense hydrothermal alteration at high-temperatures. This high-temperature Mg sink is isotopically limited within 2 km of stratigraphic depth. The mantle section has slightly heterogeneous  $\delta^{26}\text{Mg}$  values, ranging from  $-0.39 \text{‰}$  to  $-0.07\text{‰}$ . The slightly heavier  $\delta^{26}\text{Mg}$  values than the global mantle can be attributed to the seafloor weathering. On the contrary, the peridotites in the proximity of slab/mantle interface and in the highly refractory zone have slightly lighter  $\delta^{26}\text{Mg}$  values than other samples. The subduction related fluid-rock interaction - mainly from subducted sediments - is considered to have left light  $\delta^{26}\text{Mg}$  values in local scale.

In order to constrain the mantle modification suggested by Mg isotopes and the scale of resultant mantle heterogeneity, Sr, Nd, and S isotopes are measured for the mantle peridotites from basal thrust to mantle/crust boundary. The peridotite samples with less radiogenic  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios than Cretaceous seawater ( $^{87}\text{Sr}/^{86}\text{Sr} < 0.7074$ ) can be found at the uppermost mantle of each massif and the  $\epsilon\text{Nd}-^{87}\text{Sr}/^{86}\text{Sr}$  suggests they are the product of deep-seated water circulation into the mantle. On the contrary, the peridotites with higher  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios than

Cretaceous seawater ( $^{87}\text{Sr}/^{86}\text{Sr} > 0.7074$ ) suggest the sediment Sr with highly radiogenic isotopic compositions was carried into the mantle section during subduction. The S isotopic variations in sulfides strongly support the involvement of a slab component. Since sulfide S in sediments can be the only source for the negative  $\delta^{34}\text{S}$  values, such negative  $\delta^{34}\text{S}$  values in the northern Fizh mantle section indicate that the mantle peridotite in the northern Oman ophiolite has been pervasively modified by sediment-derived fluids. These subduction-related isotopic signals are strong at the lower mantle section but the uppermost mantle section has  $\delta^{34}\text{S}$  values close to that of the primary mantle, implying the source for the modification originating from the basal mantle, the slab/mantle boundary. The main processes in the mantle wedge can be summarized by slab dehydration, transporting of hydrous fluid/melt, and enriched geochemical signals from the subducted slab to the mantle wedge. The different Sr, S and Mg isotopic distributions in the northern Fizh mantle may come from the elemental characteristics.

Holland, H. D., Lazar, B. and McCaffrey, M. (1986) Evolution of the atmosphere and oceans. *Nature* 320, 27-33.

Ling, M.-X., Sedaghatpour, F., Teng, F.-Z., Hays, P.D., Strauss, J., and Sun, W. (2011) Homogeneous magnesium isotopic composition of seawater: an excellent geostandard for Mg isotope analysis. *Rapid Communications in Mass Spectrometry* 25, 2828–2836.

Teng, F.-Z., Li, W.-Y., Ke, S., Marty, B., Dauphas, N., Huang, S., Wu, F.-Y., and Pourmand, A. (2010) Magnesium isotopic composition of the Earth and chondrites. *Geochimica et Cosmochimica Acta* 74, 4150–4166.

Tipper, E. T., Galy, A., Gaillardet, J., Bickle, M. J., Elderfield, H. and Carder, E. A. (2006b) The magnesium isotope budget of the modern ocean: Constraints from riverine magnesium isotope ratios. *Earth and Planetary Science Letters* 250, 241-253.