

Doctoral Dissertation (Censored)

博士論文（要約）

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)

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Abstract

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 (~ 0 mM) 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 (~ 0 mM) show ^{26}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% to 0.00% 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% and -0.23%) 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% to -0.04% 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

± 0.04 ‰ (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 ‰ to -0.07 ‰. 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 the 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 the 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.

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Chapter I

General introduction

Magnesium (Mg) plays an important role in addressing the long-term global carbon cycle which is supported by the covariation between seawater Mg/Ca and climate (Stanley and Hardie, 1998; Ries et al., 2006). Continuous changes throughout geologic time in the marine mineralogy are also regarded as a result of variation in seawater Mg chemistry (Hardie, 1996; Higgins and Schrag, 2015; Wilkinson and Algeo, 1989). Conversely, the modern oceans have a constant Mg concentration (53 mM, Holland et al., 1986) and isotopic composition ($-0.83 \pm 0.09\%$, Ling et al., 2011) with a residence time of ~ 10 million years (Berner and Berner, 2012). Continental runoff is the major source of Mg into the oceans; the largest Mg flux is delivered by rivers (5.5 Tmol/yr, Berner and Berner, 2012). There is little agreement on the oceanic Mg cycle, however, because the magnitude and mechanisms regarding the removal of Mg in the ocean are poorly constrained. Only the Mg processes that occur at surface environments (low temperature) were considered; carbonate formation, ion exchange in clay minerals, glauconite formation, Mg-Fe exchange, and burial of interstitial water. These processes account for only 50% of the total riverine Mg input. This mass imbalance had been called the “Mg problem” (Drever, 1974) for decades.

The existence of the hydrothermal system on the seafloor had been expected at spreading centers due to the discrepancy between observed and theoretical values of heat flow. This heat flow anomaly had drawn the idea of the heat transport to the seafloor by hydrothermal circulation (Lister, 1972; Williams et al., 1974; Anderson and Hobart, 1976). After the first hot water ($\sim 60^\circ\text{C}$) was discovered from the Galapagos Spreading Center (Lonsdale, 1977), in 1979, the team at the Scripps Institution of Oceanography found black smokers with hot vent fluids at East Pacific Rise (EPR) 21°N (Spiess et al., 1980). Since the concentration of Mg in high-temperature hydrothermal vent fluids decreases to near zero, it has now been recognized that seafloor hydrothermal systems are responsible for a considerable amount of Mg removal.

Earlier experimental studies where basalts reacted with seawater demonstrated that the hydrothermal Mg sink at variable conditions at temperatures of 25 to 500°C , pressures of 1 to

1,000 bars, water/rock ratios of 11 to 125, and a duration time of 11 to 602 days (Bischoff and Dickson, 1975; Mottl and Holland, 1978; Mottl and Seyfried, 1980; Seyfried and Bischoff, 1977, 1979 and 1981; Seyfried and Mottl, 1982). At the initial stage, dissolved Mg in seawater precipitates into the form brucite ($\text{Mg}(\text{OH})_2$, the secondary mineral precursor), which produces H^+ by hydrolysis, turning the seawater into acid (Bischoff and Dickson, 1975) (Fig. I-1 and Fig. I-2). As the reaction progresses, the dissolution and the formation of brucite equilibrate and pH is constant. In the rock-dominated condition ($W/R \leq 50$), the mass of dissolved Mg is small relative to that of rock. Therefore, Mg is completely removed from the seawater. Then, the dissolution of brucite becomes dominant and the pH increases (Seyfried and Bischoff, 1977). On the other hand, in the water-dominated condition ($W/R > 50$) where Mg is continuously supplied, Mg still exists in the fluid. Therefore, the liquid phase remains acidic (Seyfried and Mottl, 1982; Mottl and Seyfried, 1980). These experiments succeeded in producing fluids similar to actual hydrothermal fluids collected from seafloor hydrothermal vent sites. The most noticeable feature of these experiments is the rapid removal of magnesium (Mg) from seawater at $>300^\circ\text{C}$. The brucite changes to smectite ($(\text{Na,Ca})_{0.25}\text{Mg}_3(\text{Si,Al})_4\text{O}_{10}(\text{OH})_2 \cdot n\text{H}_2\text{O}$), chlorite ($\text{Mg}_5\text{Al}_2\text{Si}_3\text{O}_{10}(\text{OH})_8$), amphibole ($\text{Mg}_7\text{Si}_8\text{O}_{22}(\text{OH})_2$), and talc ($\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$).

Several estimates support the hydrothermal Mg sink, which forms Mg-containing secondary minerals, comprising more than half of the riverine Mg flux (Milliman, 1974; Elderfield and Schultz, 1996; Tipper et al., 2006b; Beinlich et al., 2014). Even now, there is little consensus on the Mg cycle in the ocean because Mg concentrations in the fluids were the only factor. The reconstruction of the ancient seawater Mg/Ca ratios has been usually conducted from the amount of dolomite deposition. Unfortunately, the major Mg sinks - the dolomite sink and the hydrothermal sink result in the same Mg/Ca behavior. Both mechanisms supply Ca to the seawater during Mg sinks, decreasing Mg/Ca ratios. Therefore, the causal relationship for the reconstructed ancient seawater Mg/Ca ratio has not been clear, which makes it difficult to distinguish between the dolomite sink and the hydrothermal sink (Fig. I-3).

Mg has three stable isotopes (^{24}Mg , ^{25}Mg , and ^{26}Mg). Isotope ratios are reported using the delta notation:

$$\delta^{26}\text{Mg} = \left[\left(\frac{^{26}\text{Mg}}{^{24}\text{Mg}} \right)_{\text{sample}} / \left(\frac{^{26}\text{Mg}}{^{24}\text{Mg}} \right)_{\text{STD}} - 1 \right] \times 1000$$

where STD refers to the DSM-3 Mg standard. Early Mg isotope studies focused on mass independent anomalies because excess ^{26}Mg was discovered from calcium-, aluminum-rich inclusion (CAI) of Allende chondrite (Lee et al., 1976) and partly because there had been a technical limitation. ^{26}Mg produced by ^{26}Al radioactive decay suggests the presence of ^{26}Al in the early solar system. Therefore, ^{26}Al - ^{26}Mg geochronology has been used to study the evolution of the early solar system (Young and Galy, 2004). In the 2000s, the development of Mg isotope measurement techniques broadened the understanding of Mg behavior. Relatively large mass differences between Mg isotopes facilitate isotopic fractionation by low-temperature processes. For example, the high-temperature geological processes - including planetary accretion processes, partial melting and magmatic differentiation - do not significantly change Mg isotopic compositions, leading to homogeneity (Teng et al., 2010). Since, the coordination number of Mg in major mafic rock-forming minerals (olivine, orthopyroxene, clinopyroxene, hornblende, and biotite) is the same of 6, the partial melting and the magmatic differentiation produce limited inter-mineral Mg isotopic fractionation (Hu et al. 2016; Lai et al., 2015; Wang et al., 2016). Therefore, the fresh oceanic crust, such as the mid-oceanic ridge basalt (MORB) and oceanic island basalt (OIB), has $\delta^{26}\text{Mg}$ values similar to that of the mantle ($-0.25 \pm 0.04\%$, Teng et al., 2010). On the contrary, Mg isotopic studies of the low-temperature geological processes such as secondary mineral formations (Galy et al., 2002; Tipper et al., 2006a) and weathering (de Villiers et al., 2005; Tipper et al., 2006a, 2006b; Pogge von Strandmann et al., 2008) showed large Mg isotopic variations.

$\delta^{26}\text{Mg}$ is a suitable proxy for determining mass-balance considerations of the oceanic input and output fluxes of Mg. In general, the net flux of $\delta^{26}\text{Mg}$ from terrestrial weathering has

been negative (-1.09 ± 0.05 ‰, Tipper et al., 2006b) relative to seawater; this isotopic offset is inherited from lower $\delta^{26}\text{Mg}$ outputs in the ocean, caused by either a Mg isotope fractionation of low-temperature Mg-bearing carbonates/clays or high-temperature hydrothermal alteration of primary silicate minerals. Previous studies showed the variable $\delta^{26}\text{Mg}$ values of the ocean floor environment. In deep sea sediments, the precipitation of Mg-bearing minerals leads to the decrease in Mg concentrations of pore-fluids with depth; but $\delta^{26}\text{Mg}$ values tend to change depending on different minerals (Higgins and Schrag, 2010): silicate minerals are enriched in the heavy Mg isotopes, while dolomite formation, regarded as one of the major Mg sinks in the oceans, prefers the light Mg isotopes (Fig. I-4). Now, the dolomite sink and the hydrothermal sink are isotopically differentiated.

The fluid-rock interaction is an essential mechanism in the evolution of the oceanic lithosphere. It involves magmatic accretion of the new crust and elemental distributions between seawater and the oceanic lithosphere (hydrothermal alteration). Oceanic lithospheres are recycled into the subduction zone, and subducting hydrous materials react with overlying mantle, producing geochemical heterogeneities (subduction related alteration) (Fig. I-5).

For studies of fluid-rock interactions, the oceanic crust can be acquired by dredging and drilling. Until today, these samples are largely pillow basalts and sheeted dyke diabase. Hole 504B is the deepest scientific drill hole in the oceans, down to depth of 1,837 m. However, the bottom of the hole just lies within the lower portion of the sheeted dike complex (Alt et al., 1996). Although the samples have been dredged along fracture zones, the stratigraphic position of these samples is uncertain. Even samples recovered by drilling are not always consistent with the stratigraphic order from the normal mid-ocean ridge crust (Alt and Shanks, 1998; Arai and Matsukage, 1996; Arai et al., 1997).

Ophiolites are the ancient analogue of the oceanic lithosphere and are presently exposed on land (Fig. I-6). They can offer the chance to access the continuous section from crust to mantle and provide constraints of the oceanic lithosphere evolution, including structural,

magmatic and metamorphic processes (Dilek and Flower, 2003; Dilek and Furnes, 2011; Nicolas et al., 1989). The study of the Oman ophiolite has been actively conducted over the last few decades (Coleman, 1981; Lippard et al., 1986; Boudier and Juteau, 2000; Styles et al., 2006). The tectonic setting responsible for the Oman ophiolite formation is still debatable. Early studies reported that the Oman ophiolite consists of the classic ophiolite sequence (the pillow lavas, sheeted dyke complex, gabbros, and serpentinized peridotites) (Lippard et al., 1986). Consequently, the Oman ophiolite has been considered as an analogue of the mid-ocean ridge formed at seafloor spreading. However, many igneous rocks crosscutting the original sequence in northern Oman ophiolite proposed that the Oman ophiolite experienced at least two different phases of magmatism. The early magmatism (referred to as V1 of Ernewein et al., 1988, Geotimes of Alabaster et al., 1982, and Phase 1 of Goodenough et al., 2014) occurred at a spreading center, mainly considered as a mid-ocean ridge. Petrological and geochemical observations show that the later magmatism with the hydrous magma (referred to as V2 of Ernewein et al., 1988, Lasail of Alabaster et al., 1982, and Phase 2 of Goodenough et al., 2014) was related to the initial stage of the arc magmatism above a subduction zone. This later magmatism is commonly observed in the northern to central Oman ophiolite but rare in the southern part of the Oman ophiolite. Rioux et al. (2016) estimated the age of the V1 magmatism at ca. 96.12 to 95.50 Ma, and the V2 magmatism at ca. 96.16 to 94.82 Ma. The chronological studies demonstrated the initial ridge magmatism and subsequent thrusting/subduction associated arc magmatism (Warren et al., 2005; Rioux et al., 2012; 2016).

Studies relating to the fluid-rock interactions of the Oman ophiolite have mainly focused on the crustal section, mantle/crust boundary and basal mantle section as they preserve hydrothermal alteration-related distinct changes in chemical composition and petrology. Previous studies suggested that the hydrothermal circulation at mid-ocean ridge have reached at least to the mantle/crust boundary (Akizawa et al., 2014; Bosch et al., 2004; Dygert et al., 2017; Kawahata et al., 2001; Python et al., 2007), and subduction-related metasomatism is

preserved in the basal mantle section (Khedr et al., 2014; Prigent et al., 2018; Takazawa et al., 2003; Yoshikawa et al., 2015). On the contrary, the inner mantle section itself has received little attention so far. The lack of pervasive data from isotopic perspectives hindered our understanding of the fluid-mantle interactions and the scale of the modification in the mantle.

In this dissertation, I focus on two main fluid-rock interactions during oceanic lithospheric evolution; the hydrothermal circulation at spreading centers and the subduction related alteration (Fig. I-7). Chapter II and III deal with the Mg behavior. The objective of Chapter II is to constrain high-temperature hydrothermal Mg sink and global oceanic Mg budget. This was achieved by measuring Mg isotopic composition of vent fluids from western Pacific. In Chapter III, Mg isotopic compositions from sediment, crust and mantle in the Oman ophiolite are measured to investigate the reconstruction of the Cretaceous seawater Mg isotopic composition, the hydrothermal Mg sink at the spreading center and the Mg transfer by the subduction. In chapter IV, I focus on the mantle modification suggested by Mg isotopes. Discussions are based on the measurements of strontium (Sr), neodymium (Nd), and sulfur (S) isotopes where these conventional isotopes enable us to trace processes fluid-rock interactions. Finally, Chapter V summarizes the conclusion of this dissertation.

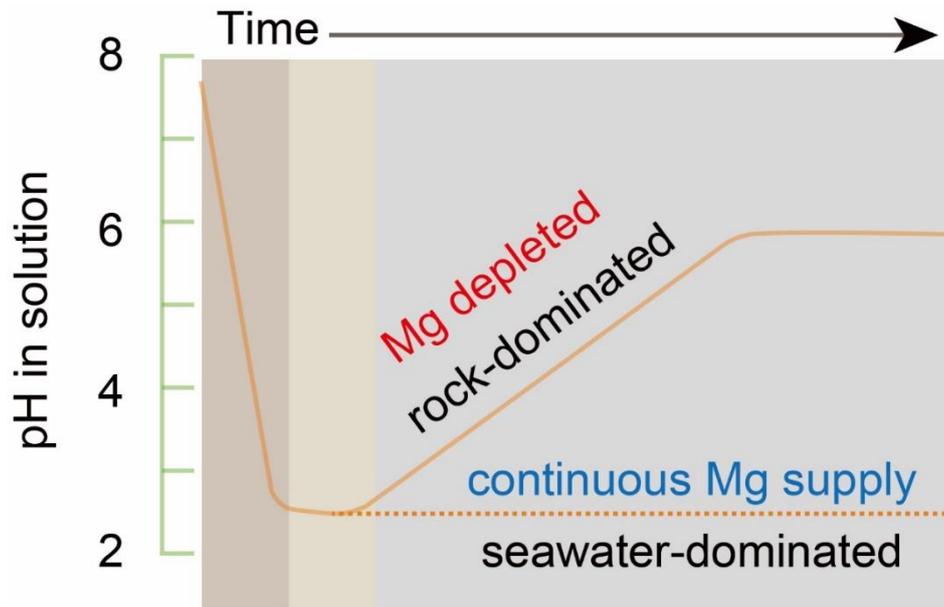


Fig. I-1. Idealized illustration of the pH change with time during reaction of seawater with basalt at rock-rock dominated and seawater-dominated system. Modified after Seyfried and Mottl, 1982.

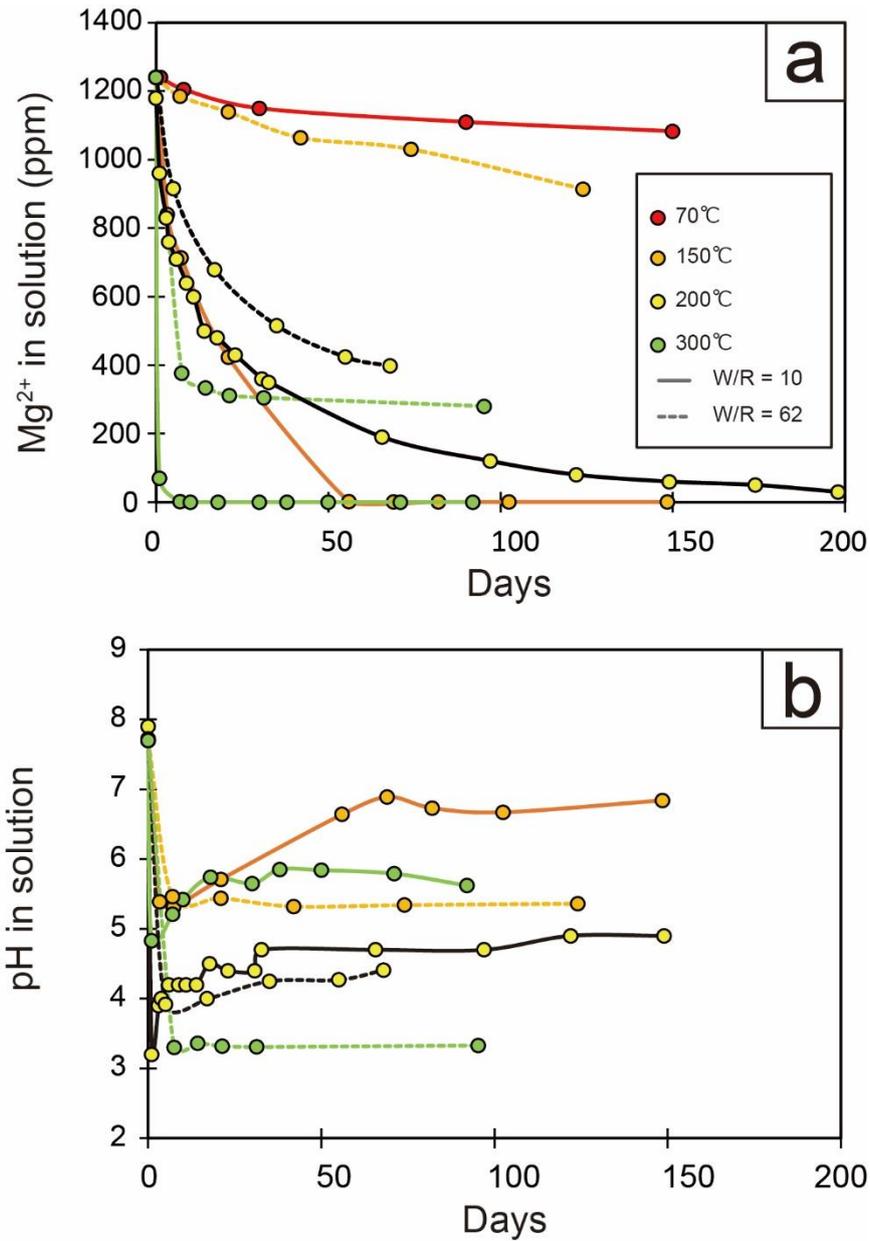


Fig. I-2. a) Concentration of Mg²⁺ and b) pH in solution with time in hydrothermal experiments reacting seawater with basalt. Conditions are at 70 °C, 1atm, and 150 °C, 200 °C and 300 °C at 500 bars. Data are from Bischoff and Dickson (1975), Seyfried and Bischoff (1979 and 1981) and Seyfried and Mottl (1982).

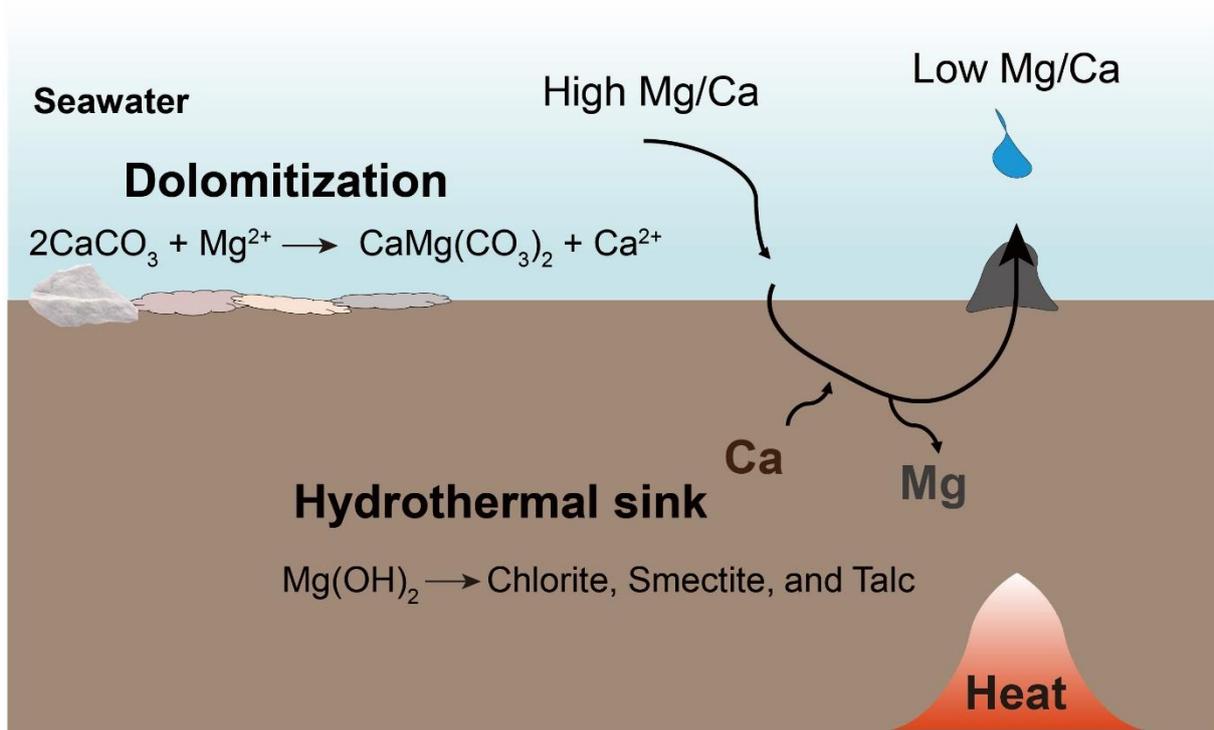


Fig. I-3. Illustration of the main seafloor Mg sinks at the seafloor environment. Both the dolomite sink and the hydrothermal sink remove Mg and supply Ca to the seawater, lowering Mg/Ca ratios in seawater.

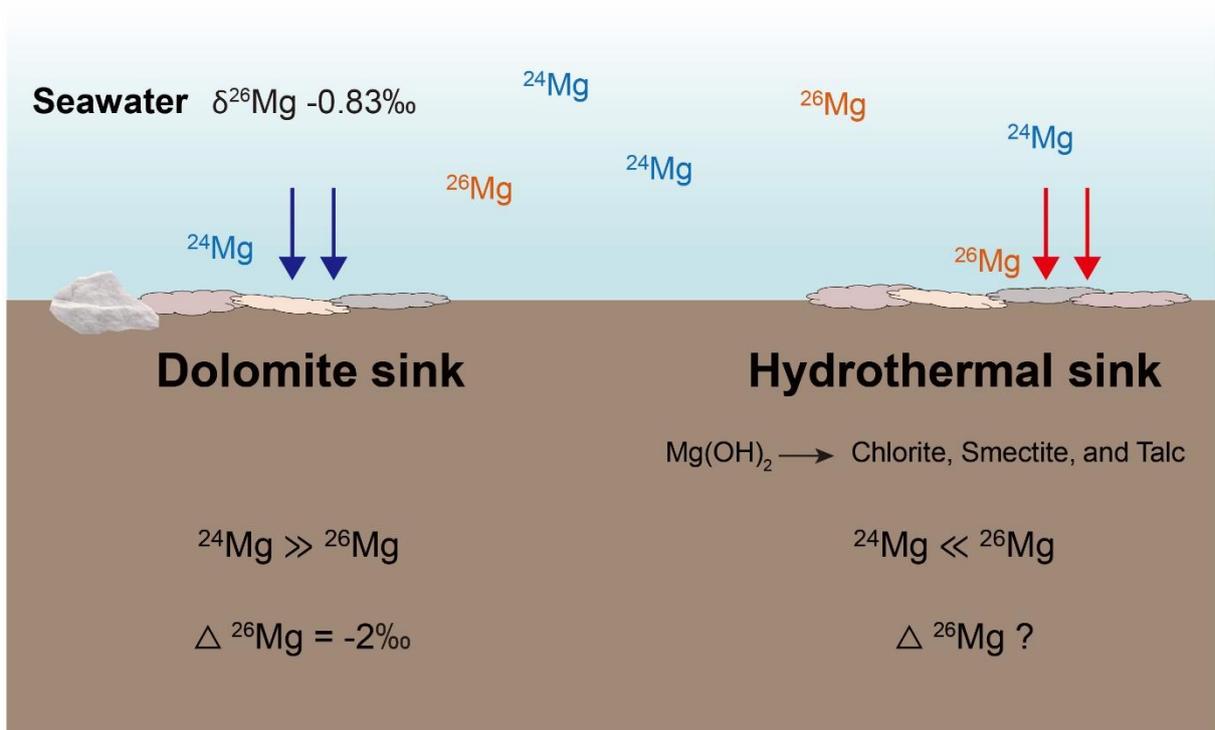


Fig. I-4. Illustration of the main seafloor Mg sinks at the seafloor environment. Dolomite sink and hydrothermal sink remove Mg in the seawater but they are isotopically differentiated. Dolomite sink prefers light Mg isotopes while heavy Mg isotopes are preferentially removed by hydrothermal circulation. $\Delta^{26}\text{Mg}$ fractionation factor of dolomite and related water is from Li et al., 2015.

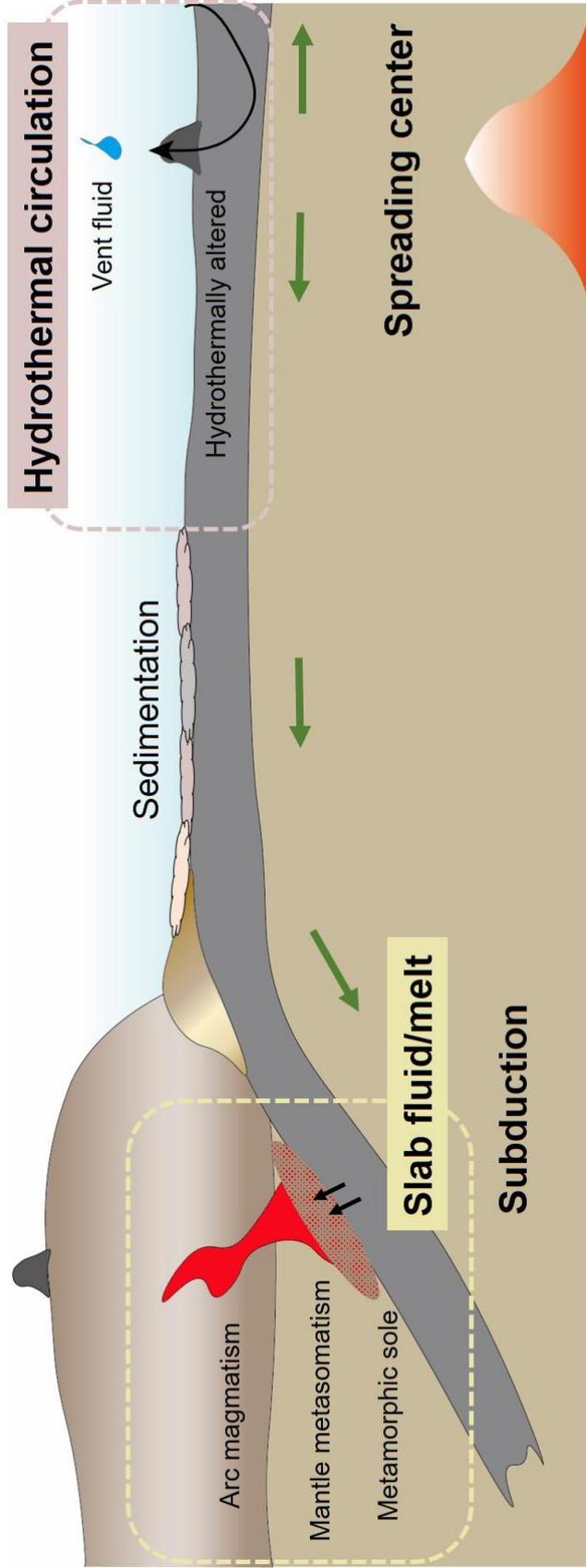


Fig. 1-5. Illustration of the main fluid-rock interactions at oceanic lithospheres. Oceanic lithospheres experience the hydrothermal alteration at the spreading center and are recycled at the subduction zone. At the subduction zone, subducting materials (slab) react

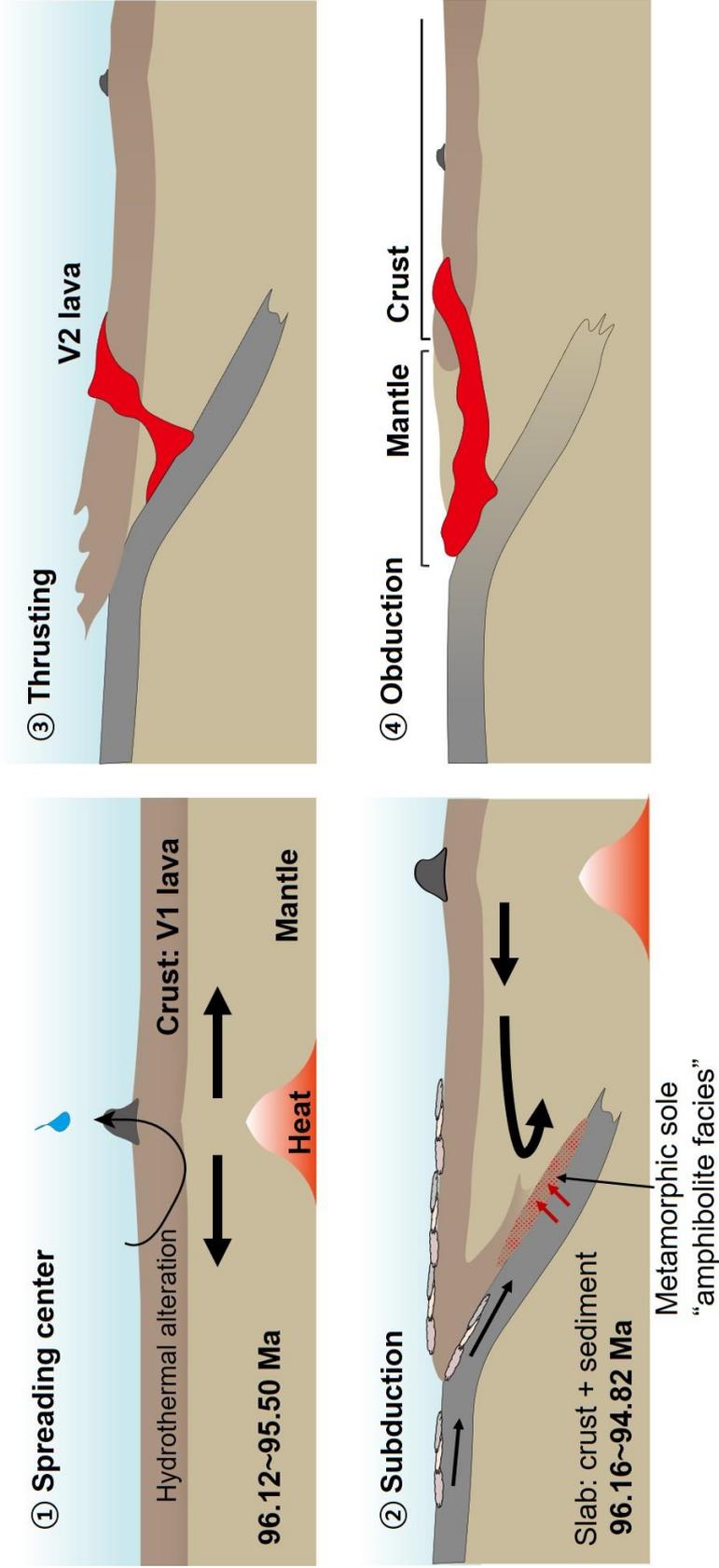


Fig. I-6. Illustration of the Oman ophiolite formation. The Oman ophiolite was probably produced at the spreading center, and subducted into the other oceanic lithosphere. After thrusting, it was obducted onto the other plate. Presently, it is exposed on land. Geochronological data is from Coleman, 1981 and Rioux et al., 2016.

Chapter II

Magnesium isotopic composition of submarine vent fluids from arc and back-arc hydrothermal systems in the western Pacific

II-1. Introduction

The isotope fractionation effects have been used to identify differences in element source and reactions. Seawater has a uniform Mg isotopic composition ($-0.83 \pm 0.09\%$, Ling et al., 2011) which is distinct from the major Mg input into oceans (Riverine input of $-1.09 \pm 0.05\%$, Tipper et al., 2016). The relative importance of the hydrothermal sink to the net oceanic Mg sink can be resolved as a function of the difference of the $\delta^{26}\text{Mg}$ of the hydrothermal and dolomite sinks. The Mg isotopic fractionation during hydrothermal ultramafic rock alteration suggests that sub-seafloor hydrothermal carbonation may contribute significantly to the Mg isotopic composition of seawater (Beinlich et al., 2014). A recent study demonstrated that formation of secondary minerals, saponite and calcite results in variable $\delta^{26}\text{Mg}$ values of the altered oceanic crust ranging from -2.76 to $+0.21\%$ (Huang et al., 2018). This indicates that significant Mg isotopic fractionation occurs during low-temperature alteration of the oceanic crust. Although high-temperature basalt alteration represents a sink in the global Mg mass-balance (10-40% loss of the riverine Mg input, thermal estimation by Mottl and Wheat, 1994), effects of host rock type, phase separation, and overlying sediment on Mg isotope fractionation and variations in the $\delta^{26}\text{Mg}$ values of the hydrothermal fluids are still under debate.

Much of the early research on the oceanic Mg sink was related to the missing Mg flux, and little attention was given to the behavior of Mg isotopes during high-temperature seafloor hydrothermal processes. This is because high-temperature hydrothermal systems completely remove Mg from the fluid, suggesting that Mg isotopic fractionation could be negligible (Higgins and Schrag, 2015). On the contrary, Beinlich et al. (2014) insisted that the vent fluid would have elevated Mg isotopic compositions than seawater, based on the ^{24}Mg enriched carbonation during hydrothermal circulation.

In order to investigate the Mg isotopic behavior during high-temperature hydrothermal circulation and quantify its contribution to the global Mg cycle, we present $\delta^{26}\text{Mg}$ data for eleven submarine vent sites from five arc and back-arc hydrothermal systems in the western

Pacific. These are classified under three categories: sediment-starved sites (Vienna Woods and PACMANUS in the Manus Basin, Suiyo Seamount in the Izu-Bonin Arc, Alice Springs and Forecast Vent in the Mariana Trough), phase-separated sites (White Lady, Kaiyo, and LHOS in the North Fiji Basin) and sediment-hosted sites (JADE, Minami-Ensei, and CLAM in the Okinawa Trough). Our research can provide constraints on the seawater Mg chemistry in modern hydrothermal systems, mainly at back-arc tectonic spreading centers in different types of hydrothermal settings.

II-2. Geological setting and samples

Research cruises were conducted in the 1990s that collected high-temperature hydrothermal vent fluid samples from arc and back-arc settings in the western Pacific (Fig. II-1). Using these samples, previous studies have published a wide range of geochemical studies on hydrothermal systems such as boron and lithium isotopes (e.g., Chiba et al., 1993; Gamo et al., 1991, 1997a, 1997b; Grimaud et al., 1991; Sakai et al., 1990a, 1990b; Ishibashi et al., 1994a, 1994b; Yamaoka et al., 2015; Araoka et al., 2016). The geological setting and the chemical characteristics of the hydrothermal vent fluids are summarized in Table II-1.

II-2. 1. Manus Basin (Vienna Woods, PACMANUS)

The Manus Basin is located between the inactive Manus Trench and the active New Britain Trench (Taylor et al., 1994). It is known for its young age (ca. 3.5Ma old) and rapid spreading rate (up to 13.7 cm/yr, Tregoning, 2002). The spreading axis consists of three NE-SW trending segments (Taylor et al., 1994; Martinez and Taylor, 1996). The Vienna Woods site on the Manus Spreading Center was discovered in 1990 where vigorous hydrothermal activity has been reported (Tufar, 1990). The host rock is basaltic and the chemical properties of the fluids are analogous to those of the mid-oceanic ridge system (Lisitsyn et al., 1993; Gamo et

al., 1997a). PACMANUS, discovered in 1991, is situated in the eastern part of the Manus Basin. The hydrothermal system is influenced by magmatic input and subsurface mixing with seawater (Bach et al., 2003; Paulick et al., 2004; Paulick and Bach, 2006). The observed maximum temperature of the hydrothermal fluids in Vienna Woods and PACMANUS were 302 °C and 268 °C, respectively (Gamo et al., 1996, 1997a). PACMANUS fluids are solutions with highly concentrated mobile elements, such as Li, B and K, compared to those of Vienna Woods, implying the influence of dacitic host rocks (Gamo et al., 1996; Reeves et al., 2011).

II-2. 2. Izu-Bonin Arc (Suiyo Seamount)

The Izu-Bonin Arc is present in the eastern margin of the Philippine Sea Plate. It has resulted from the subduction of the Pacific Plate beneath the Philippine Sea Plate. The arc is 1200 km long, stretching from Izu Peninsula, Honshu Island to the northern end of the Mariana Arc (Yuasa, 1985). The Suiyo Seamount is a submarine volcano on the Izu-Bonin Arc front. The temperature of the hydrothermal fluids reported previously showed a maximum of 311 °C (Ishibashi et al., 1994c). The host rock is dacite with the low K alkaline rock series, which caused the difference in chemical characteristics from typical MORs (Nagaoka et al., 1992). Therefore, the vent fluids are higher in B, Ca and Sr than those of the East Pacific Rise. Additionally, CO₂ gas and He isotope ratio enrichment in the vent fluids are presumed to be affected by the subducting slab (Ishibashi et al., 1994c; Tsunogai et al., 1994).

II-2. 3. Mariana Trough (Alice Springs, Forecast Vent)

The Mariana Trough is a back-arc basin in the western Pacific and is actively spreading (Hussong and Uyeda, 1982). It shows different spreading rates depending on the location, from 1.5 cm/yr in the wide central basin to 4.5 cm/yr in the southern part of the trough (Kato et al., 2003). The Alice Springs site nestles on the flank of an axial basaltic-andesitic volcano in the

middle of the basin and the Forecast Vent site at the summit of the seamount in the southern tip of the Mariana Trough (Gamo et al., 1994). Fluid samples from both sites were enriched in CO₂ gas, indicating that these areas were influenced by subducting materials (Gamo et al., 1997b; Ishibashi et al., 2015). The temperatures of the sampled hydrothermal fluids were 202-280 °C due to mixing with ambient seawater (Gamo et al., 1994;1997b).

II-2. 4. North Fiji Basin

The North Fiji Basin is an active back-arc basin in the southwestern Pacific. The formation of the basin began about 10 Ma ago (Auzende et al., 1988) and complex tectonic events led to its present location. The New Herbrides Arc lies on the west, the Hunter Ridge and Fracture Zone to the south, the Fiji Platform to the east and the Vitiaz Paleosubduction Zone to the north. The spreading ridge is 800 km long, divided into four segments and generally shows N-MORB-like composition with the local influence of OIB (Tanahashi et al., 1994; Eissen et al., 1991, 1994; Nohara et al., 1994). The White Lady site was discovered at the northern end of the north-central segment near a triple junction (Grimaud et al., 1991). The Kaiyo and the LHOS sites are 150 m southwestward from the White Lady site. The vent fluids from the North Fiji Basin have lower concentrations of Cl, Fe and Mg than the normal vent fluids, implying that this hydrothermal system experienced phase separation (Grimaud et al., 1991; Ishibashi et al., 1994a). The sampled hydrothermal fluids showed temperatures ranging from 285 to 291 °C (Grimaud et al., 1991; Ishibashi et al., 1994a, 1994b).

II-2. 5. Okinawa Trough

The Okinawa Trough is a back-arc basin behind the Ryukyu Arc-Trench system in the East China Sea near the Okinawa Island. The ridges consist of basaltic to rhyolitic volcanic rocks (Kimura et al., 1986). Thick sediments covering top of the study area were composed of terrigenous clays and marine biogenic carbonates (Halbach et al., 1993). In the middle the

Okinawa Trough, the JADE site was discovered on the eastern wall of the Izena Cauldron and the CLAM site was at the foot of the Iheya Ridge (Halbach et al., 1989; Ishibashi et al., 1995). The Minami-Ensei site is located at a rifting center in the northern Okinawa Trough (Chiba et al., 1993). Since the overlying sediments consisted of organic materials, vent fluids from the Okinawa Trough hydrothermal system were distinctively high in CH₄, H₂S and NH₄ (Chiba et al., 1993; Gamo et al., 1991; Sakai et al., 1990a, 1990b). The maximum temperature of the sampled hydrothermal fluid was 320°C (Sakai et al., 1990a, 1990b).

Table II-1. Characteristics of the study area.

	Geological setting	Rock type	Latitude	Longitude	Water depth (m)	Max. Temp. (°C)	pH (25°C)	Sampling year
Sediment-starved								
Manus Basin	Vienna Woods ^{a, b}	Basalt	3°10'S	150°17'E	2500	302	4.0-4.5	1995
	PACMANUS ^c	Dacite	3°43'S	151°41'E	1710	268	2.5	1995
Izu-Bonin Arc	Suiyo Seamount ^{d, e}	Dacite	28°34'N	140°39'E	1380	311	3.7	1992
Mariana Trough	Alice Springs ^{f, g}	Basalt	18°13'N	144°42'E	3600	280	3.9	1992
	Forecast Vent ^{g, h}	Basalt	13°24'N	143°55'E	1490	202	-	1993
Phase-separated								
North Fiji Basin	White Lady ^{i, j}	Basalt	16°59'S	173°55'E	1970	285	4.7	1989
	Kaiyo ^j	Basalt	16°59'S	173°55'E	2000	291	4.7	1991
	LHOS ^j	Basalt	16°59'S	173°55'E	2000	291	4.7	1991
Sediment-hosted								
Okinawa Trough	JADE ^{k, l}	Rhyolite-Andesite	27°16'N	127°04'E	1340	320	4.7	1989
	Minami-Ensei ^m	unknown	28°23'N	127°38'E	710	278	4.9-5.1	1992
	CLAM ⁿ	Basalt	27°33'N	126°58'E	1390	220	5.3	1989

Table II-1. Characteristics of the study area. ^a Lisitsyn et al. (1993); ^b Gamo et al. (1997b); ^c Gamo et al. (1996); ^d Tsunogai et al. (1994); ^e Ishibashi et al. (1994c); ^f Campbell et al. (1987); ^g Gamo et al. (1997b); ^h Gamo et al. (1994); ⁱ Grimaud et al. (1991); ^j Ishibashi et al. (1994a, 1994b); ^k Sakai et al. (1990a, 1990b); ^l Ishibashi et al. (1995); ^m Chiba et al., (1993) and Chiba (1997); ⁿ Gamo et al. (1991).

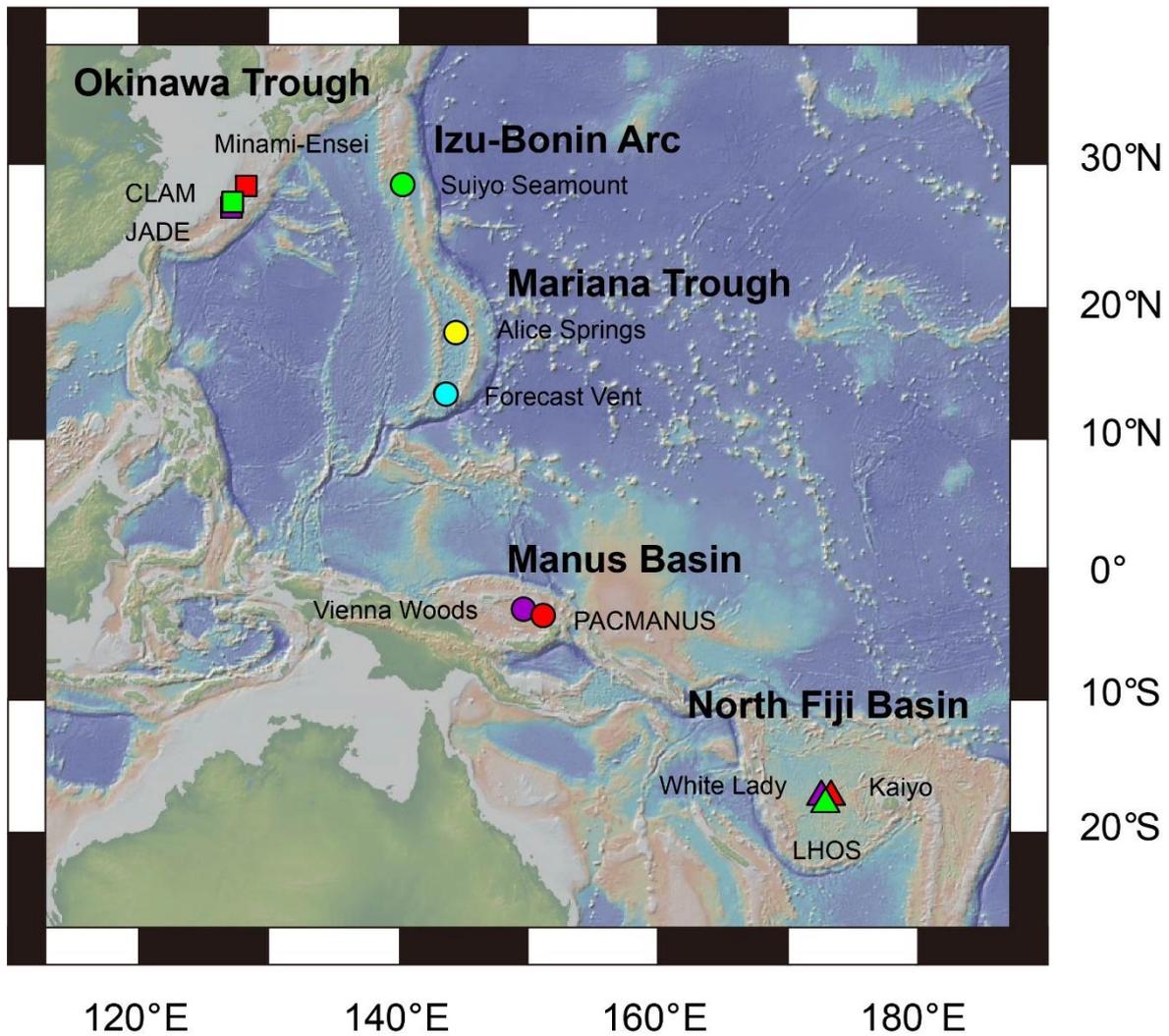


Fig. II-1. The map of sampling sites of submarine vent fluid in arc and back-arc hydrothermal systems, the western Pacific. Circles (\circ), triangles (\triangle) and squares (\square) indicate sediment-starved, phase-separated and sediment-hosted sites, respectively. Characteristics of each site are listed in Table II-1.

II-3. Analytical method

After being collected in the 1990s, the vent fluids used in this study have been stored carefully at the laboratory. Before conducting the isotopic analysis, I remeasured the fluid chemistry to assess whether their initial conditions have been preserved. The original concentrations of major elements in the fluids were found to be consistent with previous data (Yamaoka et al., 2015; Araoka et al., 2016).

The Mg isotopic composition of the samples was determined by following a procedure reported by Yoshimura et al. (2018). We used an offline method for the purification of Mg using an ion chromatograph (IC) coupled to an automated fraction collector prior to the stable isotope measurements. Samples were introduced into the IC on a Metrohm 930 Compact IC Flex (Metrohm AG, Herisau) instrument coupled to an Agilent 1260 Infinity II Bio-Inert analytical-scale FC system (Agilent Technologies, Santa Clara). Subsequently, they were loaded into 0.8 Mm ultrapure HNO₃ acid (TAMAPURE AA-100, Tama Chemical, Kawasaki) and passed through a Metrohm Metrosep C6-260/4.0 column (packed with silica gel functionalized with carboxyl groups) at a flow rate of 0.9 mL min⁻¹. The detection was performed by an electrical conductivity detector and a diode array detector. The temperature of the column made with polyetheretherketone was maintained at 35 °C. The IAPSO (International Association for the Physical Sciences of Oceans) standard seawater reference was used to confirm the accuracy of this procedure. The purified samples were pooled in 7 mL Teflon vials, then dried out. The dried residue was dissolved in 0.3 M ultrapure HNO₃ for isotope analysis. Additionally, I conducted the separation procedure in a class-1000 clean bench, to avoid contamination. The accuracy of the purification method for different matrix/Mg relative to seawater was also verified by Araoka and Yoshimura (2019). Several reference materials with wide range of Mg compositions (0.02-26.9%) were evaluated to demonstrate if Mg are successfully separated from the interference matrices, including high concentration of Na derived from sodium tetraborate flux. Mg, as well as Li and Sr, isotopic compositions of silicate and carbonate

reference materials are in excellent agreement with previously reported data obtained by means of acid sample decomposition and multistep chromatographic separation with cation exchange resins, indicating almost lossless recovery of Mg and no isotopic fractionation during this purification process.

Mg isotope ratios were measured by MC-ICP-MS (Neptune Plus, Thermo Fisher Scientific, Waltham) at the Geological Survey of Japan, National Institution of Advanced Industrial Science and Technology. Instrumental mass fractionation was calibrated by a standard-sample bracketing method. The repeatability was better than $\pm 0.12\text{‰}$ (2 SD) for $\delta^{26}\text{Mg}$, as estimated from the long-term measurements of mono-element standard solutions: $-2.60 \pm 0.07\text{‰}$ (2 SD, n=9) for Mg standard Cambridge 1. The isotopic composition of Mg from seawater was $\delta^{26}\text{Mg}_{\text{DSM-3}} = -0.83 \pm 0.10\text{‰}$ (2 SD), and the results agreed with the data published by Foster et al. (2010).

II-4. Results

Mg isotopic compositions of vent fluids are presented in Table II-2 along with the major element concentrations and Sr isotope ratios from previous data (Araoka et al., 2016; Chiba, 1997; Gamo et al., 1991, 1997b; Grimaud et al., 1991; Ishibashi 1994a). All samples in this study have lower Mg concentrations (0.4 - 46.3 mM) compared to seawater (53.1 mM). The $\delta^{26}\text{Mg}$ ranges from -1.18‰ to -0.80‰ (Fig. II-2). There was no significant and systematic variability of Mg isotopic compositions at the different sampling sites. Based on the Mg isotopic ratios, the results can be divided into two groups: indistinguishable from seawater value (-0.83‰) and lighter isotopic compositions. Fluids with low Mg concentrations (< 3.7 mM) tend to be enriched in light isotopes while all fluids with Mg concentrations > 8.5 mM fall within the 2 SD of seawater $\delta^{26}\text{Mg}$ value.

Table II-2. Magnesium and Strontium isotopic compositions of vent fluids from the study areas.

	Sample	Mg (mmol/kg) ^a	$\delta^{26}\text{Mg}$	2sd	Cl (mmol/kg) ^a	Sr ($\mu\text{mol/kg}$) ^b	$^{87}\text{Sr}/^{86}\text{Sr}$ ^b
Manus Basin							
Vienna Woods	303-TS1	46.3	-0.83	0.14	565	115	0.70797
	307-1	20.3	-0.93	0.12	623	187	0.70532
	307-2	2.5	-0.9	0.09	687	256	0.70447
	307-2	2.5	-0.96	0.08	687	256	0.70447
	308-2	2	-0.91	0.06	707		0.70438
PACMANUS	301-8	21.02	-0.88	0.1	565	114	0.70663
	304-1	42	-0.88	0.15	543	88	0.70850
Izu-Bonin Arc							
Suiyo Seamount	D630-3	17.7	-0.92	0.07		270	0.70472
	D631-2	0.8	-1.18	0.08		307	0.70401
	D631-6	3.7	-1	0.06		295	0.70410
Mariana Trough							
Alice Springs	D154-2	0.9	-1	0.06	582	84	0.70374
	D154-5	1	-1	0.05	548	94	0.70377
Forecast Vent	D182-4	43.2	-0.86	0.05		101	0.70790
	D187-2	25.3	-0.93	0.1		147	0.70579
North Fiji Basin							
White Lady	IST5-2	8.6	-0.91	0.12	302	42	0.70641
	IST6-1	25.7	-0.88	0.05	402	66	0.70816
Kaiyo	D80-3	31.5	-0.87	0.12	420	79	0.70827
	D80-4	8.5	-0.88	0.1	318	60	0.70569
LHOS	D93-3	24.4	-0.83	0.06	401	77	0.70744
	D93-4	33.5	-0.86	0.12	452	80	0.70820
Okinawa Trough							
JADE	D423-3	1	-1.16	0.06	528	180	0.70892
	D423-5	45.2	-0.88	0.11	503	100	0.70915
Minami-Ensei	D621-5	27.2	-0.91	0.1	550	90	0.71002
	D622-2	1.4	-1.03	0.14	550	252	0.71007
	D622-4	0.4	-0.87	0.05			0.71016
CLAM	D426-6	39.5	-0.8	0.14		74	0.70900
	D427-6	34.3	-0.81	0.11	517	91	0.70896

^a Data are from Chiba (1993), Gamo et al. (1991, 1996, 1997b), Grimaud et al. (1991), Ishibashi et al. (1994a, 1994c), Sakai et al. (1990a, 1990b); ^b Araoka et al. (2016).

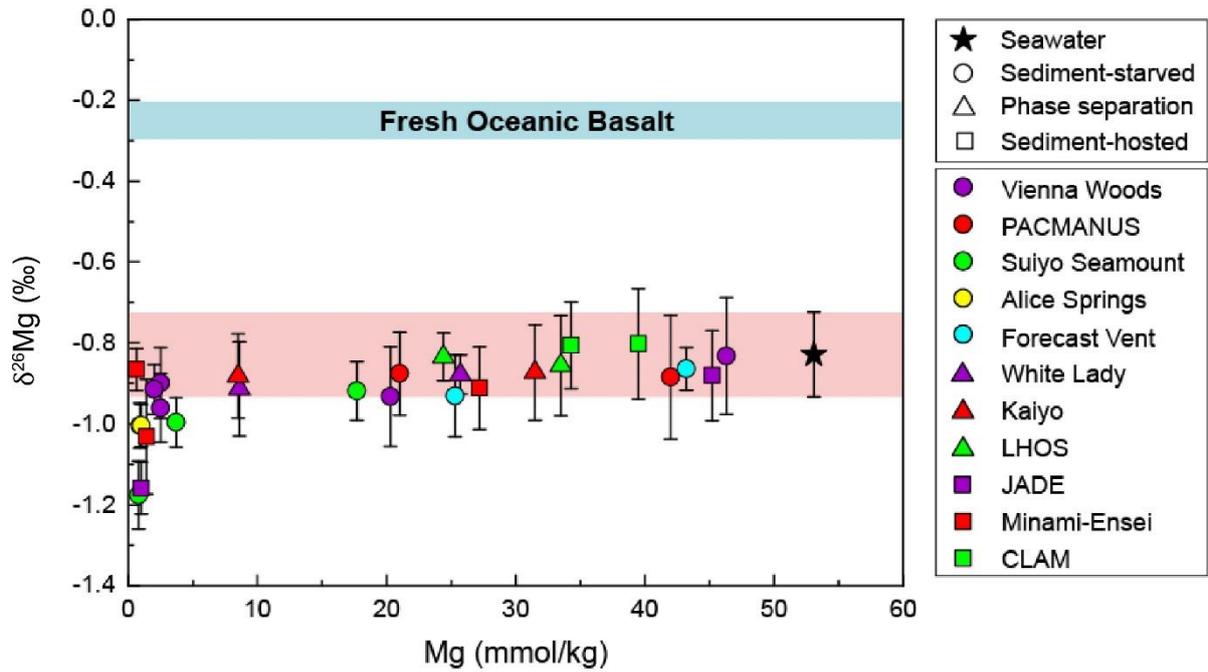


Fig. II-2. $\delta^{26}\text{Mg}$ -Mg concentration diagram showing hydrothermal fluid compositions used in this study. The samples can be roughly divided into two groups: first, with enough Mg concentrations having $\delta^{26}\text{Mg}$ value close to seawater and the second, having little or no Mg content with lower $\delta^{26}\text{Mg}$ values.

II-5. Discussion

II-5. 1. Mg isotopic behavior during high-temperature seawater-rock interactions

In hydrothermal circulation systems along the MOR, Mg behavior in fluids is influenced by its hydrothermal path, especially by the formation of Mg-bearing secondary minerals (Alt, 1995; Seyfried and Bischoff, 1977 and 1979; Seyfried and Mottl, 1982). The Mg is removed from seawater to form smectite and a mixed layer of smectite/chlorite at low-temperatures (< 200 °C); greenschist facies minerals such as chlorite and actinolite form at higher temperatures (> 200 °C) in the recharge zone (Alt, 1995; German and Von Damn, 2003). Experimental studies suggest that the isotopically heavy Mg is preferentially incorporated into the octahedral sheets in clay minerals such as chlorite. Thus, newly formed clay minerals are enriched in heavy Mg isotopes, reducing the $\delta^{26}\text{Mg}$ value and the Mg concentration of hydrothermal fluids (Wimpenny et al., 2014; Ryu et al., 2016). Much of the studies assumed that the Mg concentrations of endmember fluids would be zero (Araoka et al., 2016; Bowers et al., 1988; Butterfield et al., 1990; Campbell et al., 1988; Gamo et al., 1991; Grimaud et al., 1991; Ishibashi et al., 1994a and 1994c; Reeves et al., 2011, Yamaoka et al., 2015). However, none of the vent fluids presented here showed zero Mg concentrations, suggesting the incomplete removal of Mg from fluids or addition of Mg from external sources.

Generally, the host rock composition is related to its geological characteristics, which affects seawater-rock interactions. The host rock in the sampling sites was mainly basalt but dacite was present at PACMANUS (back-arc) and the Suiyo Seamount (arc). The dacite host rocks have less Mg than basaltic rocks because of the incorporation of the subducting slab (0.67-2.37 MgO wt.% for the PACMANUS, Paulick et al., 2006; 0.59-2.41 MgO wt.% for the Suiyo Seamount, Marumo et al., 2008). Our results show that Mg isotopic compositions of vent fluids from dacite-hosted and basalt-hosted hydrothermal systems are not significantly different. Given the low concentration of Mg in fluids during high-temperature seawater-rock interactions, the behavior of Mg isotopes may not depend significantly on the host rock type.

$^{87}\text{Sr}/^{86}\text{Sr}$ values of the vent fluids are good proxies to estimate the mixing with ambient seawater. I compared the $^{87}\text{Sr}/^{86}\text{Sr}$ values of the vent fluids with the $\delta^{26}\text{Mg}$ values and Mg/Sr ratios; the endmember fluids usually reflect host rock $^{87}\text{Sr}/^{86}\text{Sr}$ ratio which is much lower than that of seawater (Fig. II-3). In Fig. II-3. (a), fluids from sediment-starved sites and phase-separated sites were plotted on the mixing line of endmember at Mg/Sr = 0 and seawater. From this, substantial entrainments of water are suggested to fluids (> 8.5 mM), which is consistent with their homogeneous $\delta^{26}\text{Mg}$ values in Fig. II-3. (b). Fluids (< 3.7 mM) might be considered as endmember fluids since they are plotted to near Mg/Sr = 0. For fluids with light Mg concentrations (< 3.7 mM), some have fractionated $\delta^{26}\text{Mg}$ values and others have seawater $\delta^{26}\text{Mg}$ values. Since the latter is a little more radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ values of endmember than that of the former, this figure points out that other process might have been involved to the latter.

Considering the error sizes, only half of the fluids with low Mg concentrations (<3.7 mM) display lighter $\delta^{26}\text{Mg}$ values (D631-2 and D631-6 from Suiyo Seamount, D514-2 and D514-5 from Alice Springs, and D423-3 from JADE) than that of seawater. $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of these fluids have 0.7037-0.7041 values (Table II-2) which are similar to average oceanic rock value of 0.70389 (Kelemen et al., 2003) and the venting temperatures (Table II-1, 311 °C for Suiyo Seamount and 280 °C for Alice Springs) were high enough for Sr to be dissolved from host rocks by water-rock interaction. Thus, it is likely that lighter $\delta^{26}\text{Mg}$ with extremely low Mg concentration reflects the result of high-temperature water-rock interaction with little or no seawater interference, and these samples are comparable to endmember fluids. Other samples with low Mg concentrations (< 2.5 mM, 307-2 and 308-2 from Vienna Woods) have $\delta^{26}\text{Mg}$ of seawater. Possible explanations for the inconsistency are 1) incomplete removal of Mg with no isotopic fractionation, 2) Mg leaching from host rock, 3) Mg input from seawater. Unlike other isotopes controlled by isotopic equilibrium reaction such as B and Li, removal of Mg is kinetically controlled during high-temperature water-rock interactions. The variable $\delta^{26}\text{Mg}$

values from altered oceanic crusts and the lighter $\delta^{26}\text{Mg}$ with extremely low Mg concentration from this study support that fractionation of Mg is inevitable with regardless of completion of Mg removal. It is probable that the fluids with low Mg concentration with $\delta^{26}\text{Mg}$ of seawater are affected by 2) and/or 3). Dissolution of Mg from host rock increases Mg concentration of a fluids. Light Mg is preferentially leached from silicate minerals (Wimpenny et al., 2010). Mg-bearing primary minerals contain higher $\delta^{26}\text{Mg}$ values ($\delta^{26}\text{Mg}_{\text{clinopyroxene}}: -0.23 \pm 0.04\text{‰}$, $\delta^{26}\text{Mg}_{\text{orthopyroxene}}: -0.22 \pm 0.05\text{‰}$ and $\delta^{26}\text{Mg}_{\text{olivine}}: -0.24 \pm 0.03\text{‰}$, Hu et al., 2016), similar to that of the host rocks ($\delta^{26}\text{Mg}_{\text{MORB}}: -0.25 \pm 0.06\text{‰}$, $\delta^{26}\text{Mg}_{\text{OIB}}: -0.26 \pm 0.08\text{‰}$ and $\delta^{26}\text{Mg}_{\text{peridotites}}: -0.26 \pm 0.08\text{‰}$, Teng et al., 2010). Hence, if the silicate mineral dissolution is involved, the fluid always has a light $\delta^{26}\text{Mg}$ values relative to reacting host rocks and increased Mg concentrations (Wimpenny et al., 2010). The assumption that endmember fluids gain small amount of Mg derived from host rocks agrees well with the Li concentration and Li isotopic composition of 307-2 (Araoka et al., 2016), suggesting minimal effect of entrainment seawater. However, it is not clear that leaching of Mg from host rock actually occurred and that modified seawater was involved.

Helium (He) has been used as a proxy for seafloor hydrothermal reactions. Since He is inert, the mantles beneath the global mid-oceanic ridge (MOR) system have a narrow range of $^3\text{He}/^4\text{He}$, roughly eight times higher than the atmospheric value ($R/R_A \approx 8$, Kurz et al., 1982). To confirm the endmember fluid and constrain Mg isotope fractionation from He isotopes, I compared Mg concentration and isotopic composition with He isotopic values from the vent fluid samples. Fig. II-4 shows He isotopes are unequivocal tracer for the geological settings where sediment starved, phase-separated, and sediment covered sites are different He isotopic ratios. however, the relation between Mg concentration and isotopic composition is not likely. This is because the main processes during high-temperature hydrothermal circulations are quite different. Mg is removed from the fluids to secondary minerals while ^3He enrichment comes from the mantle volatile. Therefore, the He isotopic ratio could be an

effective proxy for a magmatic contribution to hydrothermal fluids, but not suitable for Mg circulation.

For the North Fiji basin, Cl concentrations of the vent fluids are mainly controlled by phase separation. The Cl concentration is plotted against the Mg concentration and $\delta^{26}\text{Mg}$ values in Fig. II-5, which suggests mixing with ambient seawater (Fig. II-5. (a)). Interestingly, all samples from the North Fiji basin have indistinguishable $\delta^{26}\text{Mg}$ values from seawater despite having different Cl concentrations (Fig. II-5. (b)). The high-temperature fluids with extremely low Mg concentration, comparable to the endmember fluid, is presumed to have lost its $\delta^{26}\text{Mg}$ values during venting. Conversely, vent fluids from the sediment-hosted sites showed different characteristics from other sites; the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios are within a narrow range while $\delta^{26}\text{Mg}$ values cover a relatively wider range (Fig. II-3. (b)). The seafloor sediments have abundant pore fluids with higher $^{87}\text{Sr}/^{86}\text{Sr}$ ratios sourced from host rocks (> 0.7085 , Noguchi et al., 2011). The $^{87}\text{Sr}/^{86}\text{Sr}$ data for the sediment-hosted vent fluids depend largely on changes in the contribution of Sr from sedimentary sources. This suggests that the sedimentary components significantly contribute to the total Sr. With respect to Mg, clay mineral formation in the sediments tends to decrease the Mg concentration and $\delta^{26}\text{Mg}$ in the sedimentary pore fluids during early diagenesis (Higgins and Schrag, 2010). The decrease in vent fluid Mg concentration from the Minami-Ensei site is not accompanied by a negative shift in Mg isotopic composition (-1.03 to -0.87% and 0.4 to 27.2 mmol/kg). The changes in the contribution of Mg from each source, such as binary mixing basal hydrothermal input versus sediment contribution may lead to the drift. The magnitude of secondary mineral precipitation may play a role in driving the dissolved Mg to cause higher $\delta^{26}\text{Mg}$ variations. However, it is challenging to distinguish each source that affects the Mg chemistry.

In short, Fig. II-3 and 5 show that the processes that alter Mg concentrations in hydrothermal systems contribute to minimize the range of $\delta^{26}\text{Mg}$ around the seawater $\delta^{26}\text{Mg}$ value. Processes, such as water-rock interaction, phase-separation and mixing with seawater

are applied to explain the variations in Mg concentration, $^{87}\text{Sr}/^{86}\text{Sr}$, and chlorinity. The absence of Mg isotopic fractionation suggests that effects of such processes are limited or offset in the case of Mg. The thing is that hydrothermal fluids are mixed with seawater, then they cannot hold endmember Mg isotopic compositions. Even if extremely small amount of seawater is added to endmember fluids, $\delta^{26}\text{Mg}$ of fluids are modified to seawater value due to relatively significant Mg enrichment in seawater while other endmember values could be partly preserved, make possible to estimate. This explains the lack of Mg isotopic fractionation shown in most fluid samples except for fluids with extremely low Mg concentrations.

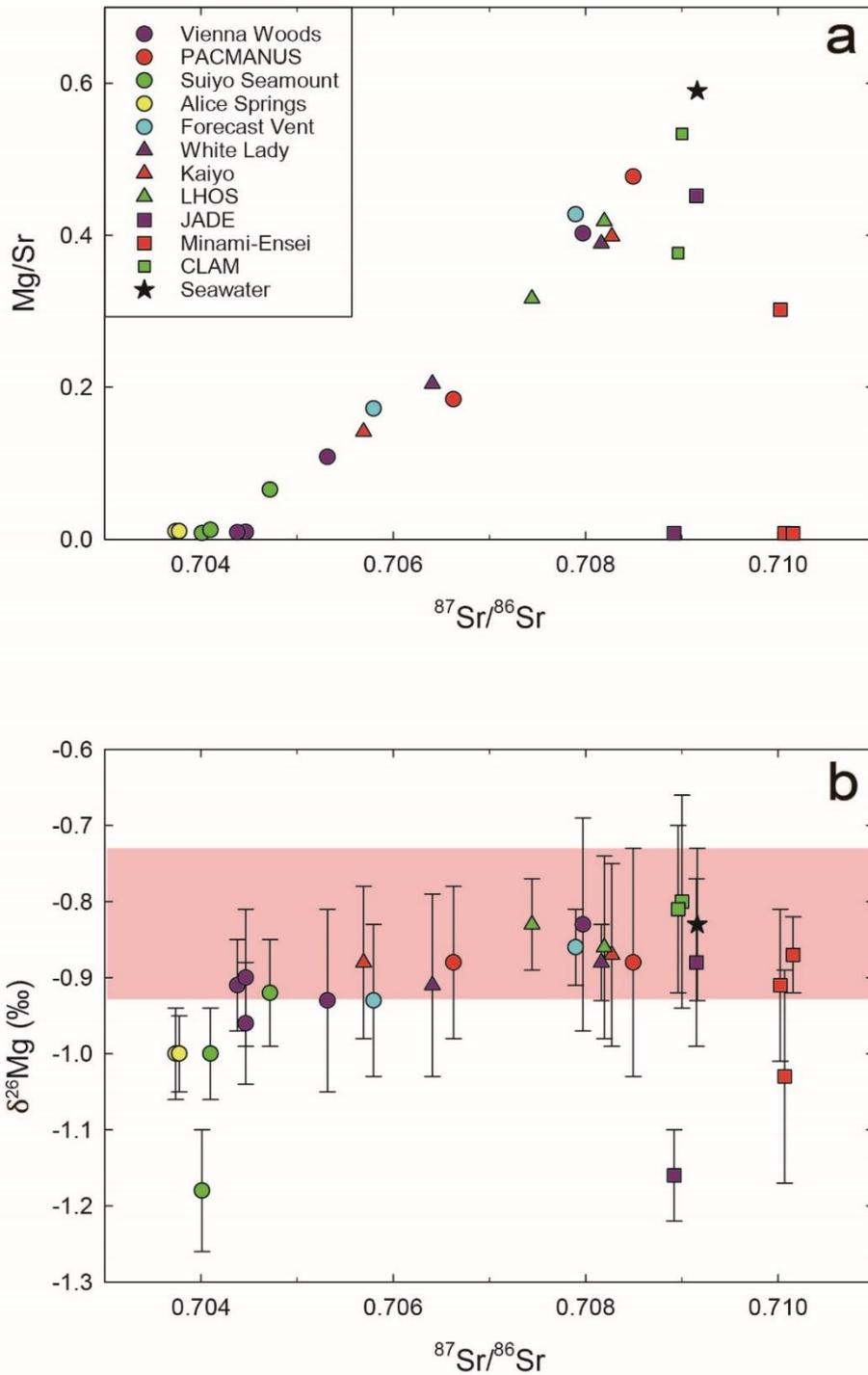


Fig. II-3. Plots of (a) $^{87}\text{Sr}/^{86}\text{Sr}$ ratios versus Mg/Sr ratios and (b) $\delta^{26}\text{Mg}$ versus $^{87}\text{Sr}/^{86}\text{Sr}$ ratios for vent fluids. Except for samples from sediment-hosted sites (\square), the linear trends shown in (a) and (b) suggest the entrainment of seawater.

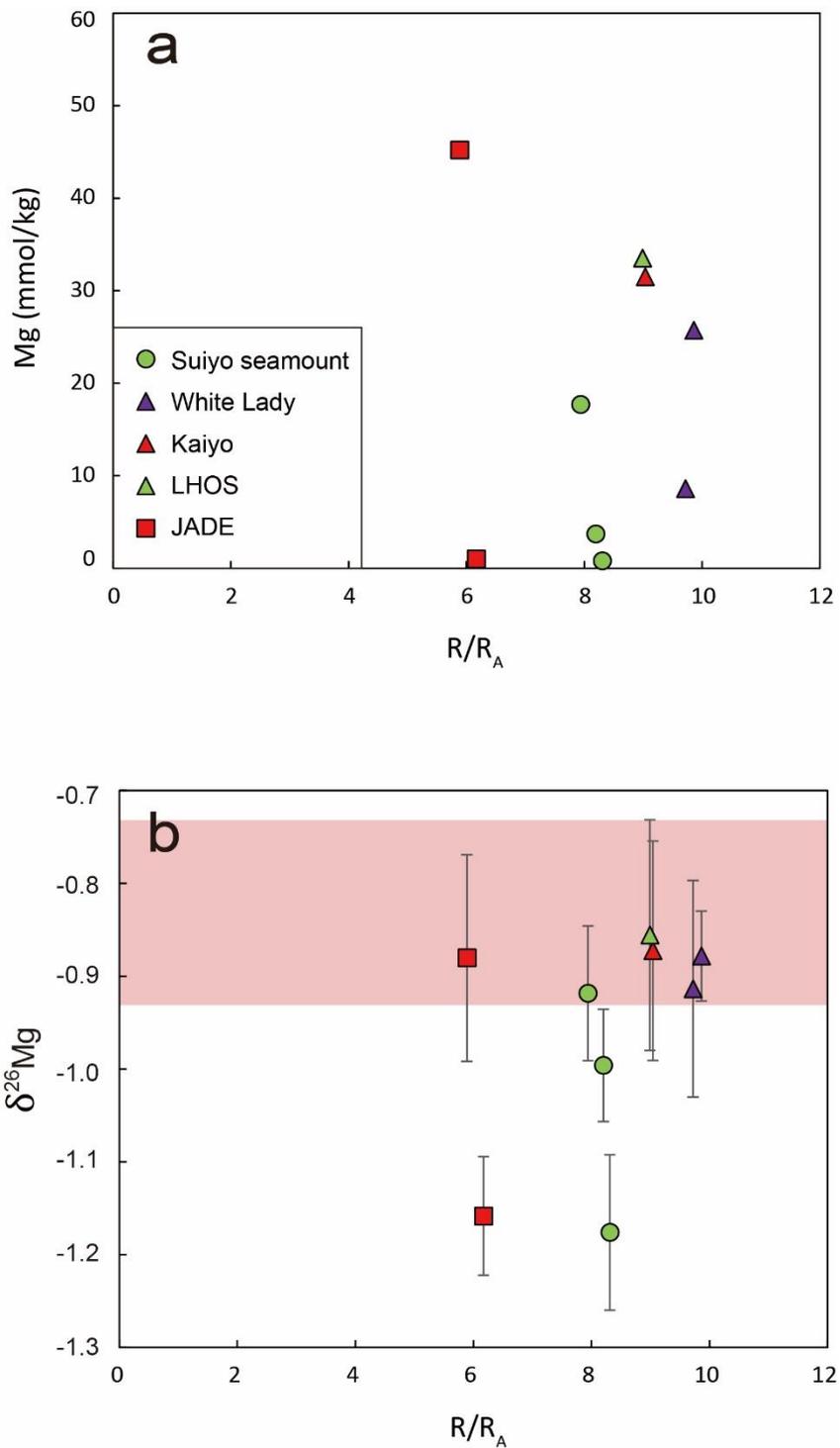


Fig. II-4. Plots of (a) Mg concentration and (b) $\delta^{26}\text{Mg}$ versus R/R_A ($R = {}^3\text{He}/{}^4\text{He}$ in vent fluid and $R_A = {}^3\text{He}/{}^4\text{He}$ in atmosphere). R/R_A data are from Tsunogai et al., 1994; Ishibashi et al., 1994b and 1995.

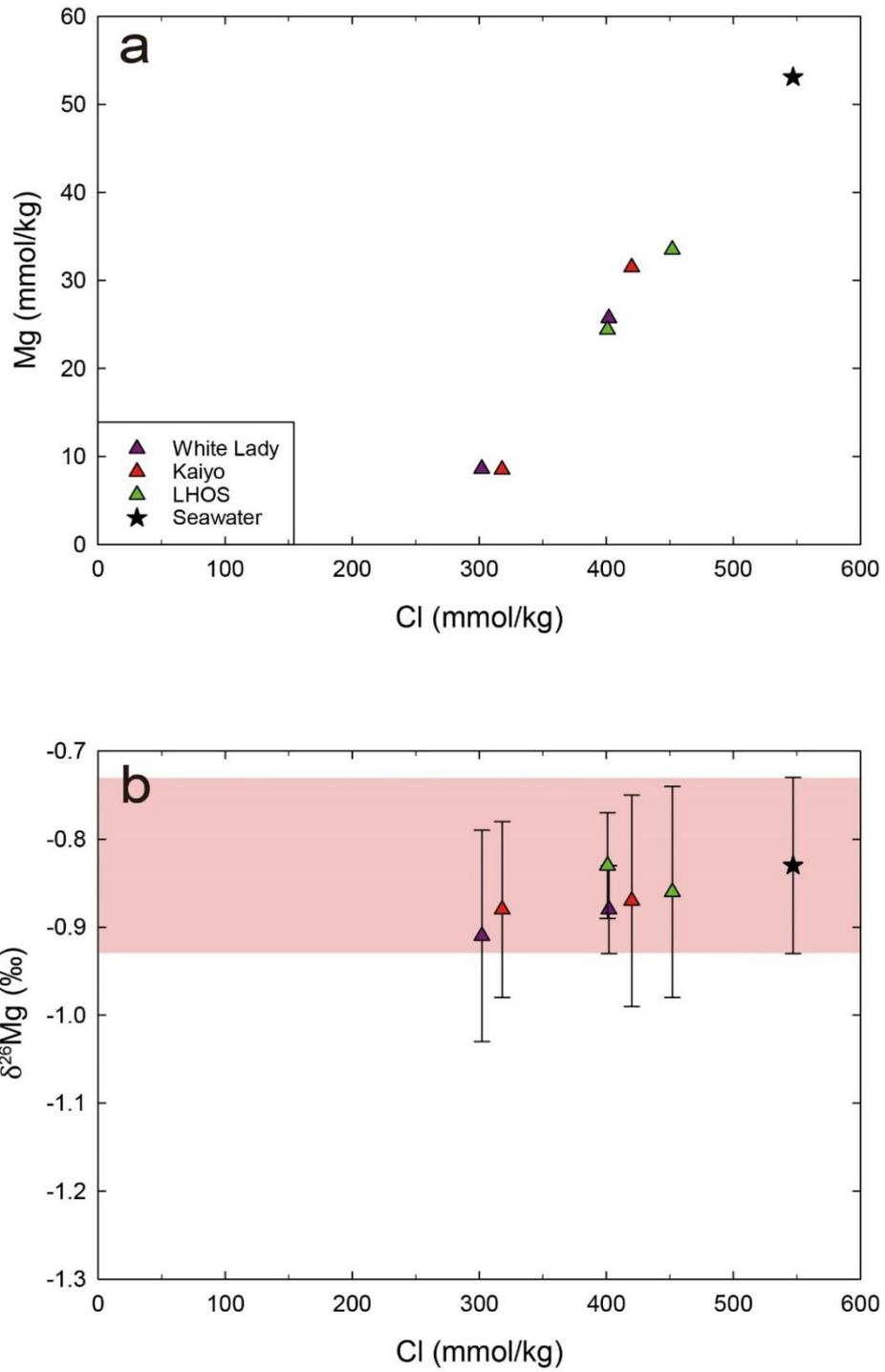


Fig. II-5. Plots of (a) Mg concentration and (b) $\delta^{26}\text{Mg}$ versus Cl concentration from phase-separated sites.

II-5. 2. Estimating the fractionation factor

Temperature is presumed to be the dominant contributor for isotope fractionation in the fluids (Seyfried and Bischoff, 1979). At high-temperatures, Mg in the fluids is regarded to be completely removed. Thus, the $\delta^{26}\text{Mg}$ value of the total high-temperature sink must be equal to that of seawater (Tipper et al., 2006; Higgins and Schrag, 2015). The altered abyssal peridotites from the Mid Atlantic Ridge, Gakkel Ridge, and Southwest Indian Ridge have $\delta^{26}\text{Mg}$ values ranging from -0.25 to $+0.03\%$. This is interpreted to be a result of seafloor weathering of peridotites and formation of clay (Teng, 2017 and references therein). Although the Mg isotopic data for ophiolites is sparse, a subtle difference in $\delta^{26}\text{Mg}$ between the Tibetan ophiolite ($-0.28 \sim -0.14\%$) and the mantle ($-0.25 \pm 0.04\%$, Teng, 2017) potentially reflects the Mg isotope fractionation during seafloor hydrothermal alteration (Su et al., 2015). The curves presented in Fig. II-6 are calculated using the Rayleigh fractionation equation which describes the one-sided transfer of Mg from the fluid to the mineral phase during fluid evolution. The samples used in this study recorded temperatures around 300°C during the sampling, so that our results are expected to be distributed near the high-temperature curve ($\alpha = 1.0000$, Higgins and Schrag, 2015). The measured data approaches $\alpha=1.000083$ which is significantly smaller than that estimated by Galy et al. (2006). However, in extreme cases, clay sinks could produce -0.35% Mg isotope variability in high-temperature hydrothermal systems. Compared to the seawater entering hydrothermal circulations, the vent fluids show lower Mg concentrations (near zero concentrations). This indicates that seafloor hydrothermal systems are closed systems and the fluids have a finite amount of Mg, if there is no addition of seawater during circulation. Therefore, complete Mg removal from the fluid results in total Mg isotope fractionation in the fluid at $\alpha = 1.0000$. Unfortunately, the kinetics of the temperature related fractionation for Mg-bearing minerals is not constrained well. Particularly, theoretical calculations and experimental/field data have focused on carbonate minerals (dolomite); whereas minerals related to hydrothermal systems have not been studied and there is no

comparable data. Currently, the direct measurement of $\delta^{26}\text{Mg}$ values in rocks from high-temperature hydrothermal vent sites have not been conducted. However, Huang et al. (2015) reported that $\delta^{26}\text{Mg}$ values of altered oceanic crust, involved with high-temperature hydrothermal circulation, do not change with depth. Moreover, the altered samples have identical $\delta^{26}\text{Mg}$ values to unaltered rocks, reflecting limited Mg isotope fractionation at the bulk-rock scale. As the Mg content in the fluid is relatively lower than in the host rocks, Mg precipitation by seawater-rock interactions cannot affect the $\delta^{26}\text{Mg}$ values of host rocks (Li et al., 2014; Huang et al., 2015). Conversely, Huang et al. (2018) reported minerals with average $\delta^{26}\text{Mg}$ values of $0.00 \pm 0.09\text{‰}$ for ODP Hole 801C. Therefore, it is challenging to trace Mg isotope behavior in high-temperature hydrothermal systems during fluid evolution. Thus, further studies are needed, both natural and experimental, on the Mg isotopic composition of the host rock, altered phase and fluid.

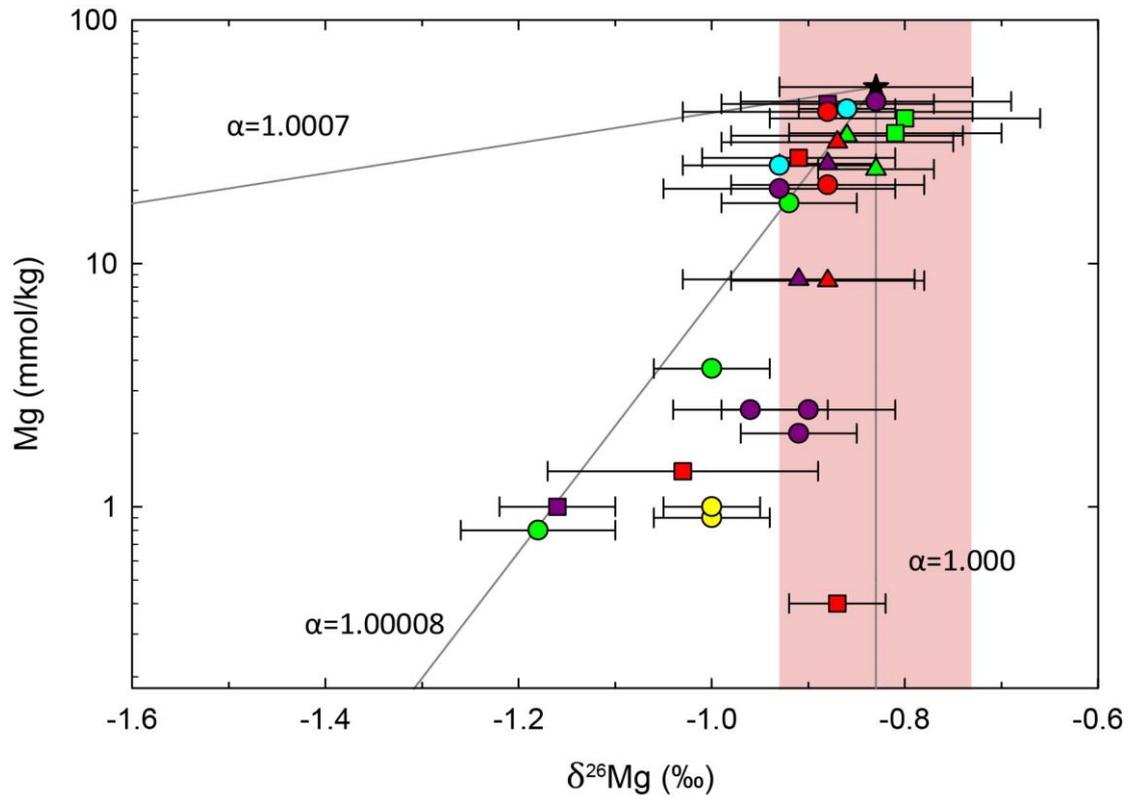


Fig. II-6. $\delta^{26}\text{Mg}$ -Mg concentration diagram with fractionation curves. The fractionation factors at low- T and high-T (Higgins and Schrag, 2015) are shown.

II-5. 3. Estimating the oceanic Mg budget

Most of Mg flux to the ocean is through continental runoff. The $\delta^{26}\text{Mg}$ values of river water ($-1.09 \pm 0.05\%$, Tipper et al., 2006) is lower than that of seawater ($-0.83 \pm 0.09\%$, Ling et al., 2011). It implies that Mg isotopes undergo fractionation in the oceans and/or that the modern oceanic Mg budget is not at steady state (Tipper et al., 2006). Hydrothermal systems along the MOR and its flanks are widely regarded as the places where considerable Mg removal occurs. Based on thermal calculations, Mottl and Wheat (1994) suggested that up to 40% of the riverine Mg flux could be removed through high-temperature seafloor hydrothermal circulation along the MOR axis. The rest is presumed to be removed by low-temperature hydrothermal circulation off the axis. Another factor governing the seawater Mg sink is the dolomite precipitation that leads to heavier Mg isotopic composition in the oceans. We estimate the $\delta^{26}\text{Mg}$ value of high-temperature hydrothermal sinks (formation of secondary minerals) according to the following equation:

$$\begin{aligned} & [\text{Mg}]_{\text{seawater}} \cdot \delta^{26}\text{Mg}_{\text{seawater}} \\ &= [\text{Mg}]_{\text{hydrothermal sink}} \cdot \delta^{26}\text{Mg}_{\text{hydrothermal sink}} + [\text{Mg}]_{\text{vent fluid}} \\ & \quad \cdot \delta^{26}\text{Mg}_{\text{vent fluid}} \end{aligned}$$

given that the $\delta^{26}\text{Mg}_{\text{vent fluid}} = -1.18\%$ and $[\text{Mg}]_{\text{vent fluid}} = 0.8 \text{ mM}$ from the sample D630-2, the lowest Mg concentration and isotopic composition in this study, $\delta^{26}\text{Mg}$ value of net hydrothermal sink from the high-temperature condition is calculated to be $\sim -0.825\%$. Here, there is no big difference from that of seawater, supporting the previous estimation that total hydrothermal sink through secondary mineral formation should have a $\delta^{26}\text{Mg}$ value of seawater (Tipper et al., 2006; Higgins and Schrag, 2015). This result suggests that the high-temperature hydrothermal sink does not significantly affect the oceanic Mg isotopic composition. To explain the modern seawater $\delta^{26}\text{Mg}$ value, further study on the dolomite and/or low-temperature hydrothermal sink is required.

Tipper et al. (2006) estimated the relative importance of the dolomite and hydrothermal sink in a simplified oceanic system. Their study assumed the modern ocean to be at steady state regarding the Mg budget and isotopic composition. Moreover, the Mg sink was confined to dolomite formation and hydrothermal circulation, using straightforward mass balance equations: $J_{riv} = J_{dol} + J_{hyd}$ and $\delta_{riv}J_{riv} = \delta_{dol}J_{dol} + \delta_{hyd}J_{hyd}$; J_i is the flux of i ; δ_i is the $\delta^{26}\text{Mg}$ value of i ; subscripts riv, dol, and hyd represent riverine input, dolomite sink and hydrothermal sink, respectively. However, they did not discriminate between high and low-temperature hydrothermal systems, even though the high-temperature systems generally differ from low-temperature systems in terms of heat and chemical fluxes (Mottl and Wheat, 1994). Consequently, high-temperature hydrothermal systems completely remove Mg from fluids, resulting in a fractionation factor of $\alpha = 1.0000$; however, this may not be the case in low-temperature hydrothermal systems where the degree of Mg removal from the fluids varies considerably. Hydrothermally altered rocks enriched in isotopically heavy Mg relative to unaltered rocks also indicates that the return flux to the seawater would be enriched in light Mg (Wimpenny et al., 2012). Thus, we adopted the mass balance equations from Tipper et al. (2006) and Huang et al. (2018), splitting each hydrothermal term to detail the oceanic cycling of Mg. At steady state,

$$\begin{aligned} \frac{dN_{Mg}}{dt} &= J_{riv} - J_{dol} - J_{high T} - J_{low T} \\ N_{Mg} \frac{d\delta_{seawater}}{dt} &= (\delta_{riv} - \delta_{seawater})J_{riv} - (\delta_{dol} - \delta_{seawater})J_{dol} - (\delta_{high T} \\ &\quad - \delta_{seawater})J_{high T} - (\delta_{low T} - \delta_{seawater})J_{low T} \end{aligned}$$

where J_i is the flux of i ; δ_i is the $\delta^{26}\text{Mg}$ value of i ; subscripts riv, dol, high T and low T represent riverine input, dolomite sink, high-temperature and low-temperature hydrothermal sink, respectively. Present global riverine input is 5.5 Tmol/yr with a $\delta^{26}\text{Mg}$ value of -1.09‰ (Tipper

et al., 2006). The dolomite sink is 1.7 Tmol/yr (Holland, 2005) but natural dolomite shows Mg isotope variations ($\Delta^{26}\text{Mg}_{\text{dolomite-fluid}}$ fractionation factor ranges from -2.7‰ to $+0.1\text{‰}$, Higgins and Schrag, 2010; Fantl and Higgins, 2014; Geske et al., 2015). Based on the experimentally derived $\Delta^{26}\text{Mg}$ fractionation factor of dolomite and related water (Li et al., 2015), we assumed the $\Delta^{26}\text{Mg}$ fractionation of -2.0‰ . For high-temperature hydrothermal fluxes, we set a $\Delta^{26}\text{Mg}$ fractionation of 0.0‰ confirmed in this study. There are uncertainties in Mg isotopic composition in the low-temperature hydrothermal sink. Huang et al. (2015) concluded that limited Mg isotope fractionation occurs during the alteration of oceanic crust in the EPR at a bulk scale. However, Huang et al. (2018) reported an average $\delta^{26}\text{Mg}$ value of $0.00 \pm 0.09\text{‰}$ for ODP Hole 801C. Wimpenny et al. (2012) reported elevated $\delta^{26}\text{Mg}$ values, up to 0.02‰ at ODP Leg 209. On the contrary, Beinlich et al. (2014) suggested that hydrothermal carbonation is attributed to the isotopically light Mg sink ($-0.96 \pm 0.31\text{‰}$). To balance this uncertainty, I adopted these values (-0.96 , -0.25 , and 0.00‰) and approximated the relative importance of each sink. The total hydrothermal sink is calculated to be 3.8 Tmol/yr and is about 69% of the annual riverine input which is smaller than previous estimations (98%, Milliman, 1974; 80-87%, Elderfield and Schultz, 1996 and Tipper et al., 2006; 86-93%, Beinlich et al., 2014). When we assumed the $\delta^{26}\text{Mg}_{\text{low T}}$ value of 0.00‰ , the relative importance of the high and low hydrothermal sinks was 26% and 43%, respectively. $\delta^{26}\text{Mg}_{\text{low T}}$ value of -0.25‰ would be 7% for the high-temperature flux and 62% for the low-temperature flux. This range (7-26%) matches the 10-40% loss of the riverine Mg input by high-temperature systems along the ridge axis (Mottl and Wheat, 1994). As $\delta^{26}\text{Mg}_{\text{low T}}$ value approaches seawater $\delta^{26}\text{Mg}$ value of -0.83‰ , the low-temperature system is indistinguishable from the high-temperature system as a Mg sink. The $\delta^{26}\text{Mg}_{\text{low T}}$ value of -0.96‰ (Beinlich et al., 2014) would be beyond the scope of the discussion, resulting in a negative flux in the low-temperature sink. To meet Beinlich's data, it is inevitable to adjust dolomite flux to < 0.71 Tmol/yr (less than 13% of riverine input), which differs from the modern value of 1.7 Tmol/yr (Holland, 2005). Focusing on the Mg isotopic

control by hydrothermal carbonation, Beinlich et al. (2014) mentioned that the return flux to the seawater should have a $\delta^{26}\text{Mg}$ value greater than -0.83‰ , which is contrary to our result. This contradiction might arise from disregarding the ensuing talc production by hydrothermal carbonation, which is enriched in heavy Mg isotopes. The approach adopted by Beinlich et al. (2014), stating that hydrothermal carbonation leads to Mg isotopic fractionation forming ^{24}Mg -enriched carbonate and ^{26}Mg -enriched talc is acceptable. However, we are skeptical as to whether the hydrothermal carbonation represents the hydrothermal sink.

II-6. Summary and conclusion

I measured the Mg isotopic composition of the vent fluids from 11 sites in arc and back-arc hydrothermal systems in the western Pacific for the first time.

The vent fluids showed lighter $\delta^{26}\text{Mg}$ values (-1.18 to -0.80‰) and low Mg concentrations compared to seawater, indicating isotopic fractionation during high-temperature hydrothermal circulation. Only fluids with extremely low Mg concentrations show Mg isotope fractionation and they can represent hydrothermal endmember fluid. For the samples with $\delta^{26}\text{Mg}$ value of seawater (-0.83‰), correlation between $\delta^{26}\text{Mg}$ and proxies for seawater mixing ($^{87}\text{Sr}/^{86}\text{Sr}$ and Cl concentrations) support that Mg from seawater and/or sediments was introduced into the endmember vent fluids.

At high-temperatures, Mg in the hydrothermal fluids is dominantly controlled by removal mechanisms such as mineral formations, so that host rock compositions have little influence on the $\delta^{26}\text{Mg}$ values of the vent fluids. Measured $\delta^{26}\text{Mg}$ values approach a fractionation factor of $\alpha = 1.00008$, indicating almost complete Mg removal from the seawater.

The $\delta^{26}\text{Mg}$ value of high-temperature hydrothermal sinks has been calculated to be $\sim -0.825\text{‰}$, suggesting that the high-temperature hydrothermal sink and the accompanying return flux do not greatly affect seawater $\delta^{26}\text{Mg}$ values. In a steady state, 7-26% of riverine Mg input into the oceans may be removed by the high-temperature hydrothermal sink. This is smaller

than the thermal estimation of 10-40% by Mottl and Wheat (1994). Thus, other Mg sink mechanisms, including low-temperature hydrothermal sinks and/or dolomite sinks need to be considered in terms of relative importance and isotopic fractionation to explain modern seawater $\delta^{26}\text{Mg}$ values.

Chapter III

Magnesium isotopic composition of sediment, crust, and mantle in the Oman ophiolite

第III章については、5年以内に雑誌などで刊行予定のため、非公開

Chapter IV

Pervasive mantle modification by subduction inferred from Strontium, Neodymium, and Sulfur isotopes

第IV章については、5年以内に雑誌などで刊行予定のため、非公開

Chapter V

Summary and conclusion

In this dissertation, I aim to investigate two main fluid-rock interactions at oceanic lithosphere (the hydrothermal circulation at spreading centers and the subduction related alteration) using isotope geochemistry. Mg isotope geochemistry is the main method and other conventional isotopes (Sr, Nd and S) are also applied to support Mg isotope geochemistry. The active submarine vent fluids from the western Pacific and the Oman ophiolite were selected as the fluid and the rock, respectively.

Seawater has heavier Mg isotopic composition ($-0.83 \pm 0.09\%$, Ling et al., 2011) than the riverine Mg input into oceans ($-1.09 \pm 0.05\%$, Tipper et al., 2016b), which requires fractionated Mg sink (Fig. IV-1). In Chapter II, to constrain Mg isotopic behavior during high-temperature hydrothermal circulation and to quantify its contribution on the global oceanic Mg cycle, I apply Mg isotope geochemistry to submarine vent fluids from arc and back-arc hydrothermal systems in the western Pacific. Some vent fluids with extremely depleted Mg contents (~ 0 mM) have fractionated $\delta^{26}\text{Mg}$ values lighter than that of seawater. This result demonstrates that the high-temperature hydrothermal circulations have little 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). 7-26% of the riverine Mg input is estimated to be removed via high-temperature hydrothermal sink. This is smaller than the thermal estimation of 10-40% (Mottl and Wheat, 1994).

In Chapter III, I apply Mg isotope geochemistry to the Oman ophiolite. The sediment samples were expected to reconstruct the Cretaceous seawater $\delta^{26}\text{Mg}$ but instead the sediment samples were out of equilibrium with seawater during their formation. Therefore, the Cretaceous seawater $\delta^{26}\text{Mg}$ could not be reconstructed. $\delta^{26}\text{Mg}$ results from the crustal section demonstrate that the high-temperature Mg sink in Chapter II is isotopically limited within 2 km of stratigraphic depth. In the mantle section, slightly heavy $\delta^{26}\text{Mg}$ values resulted from seafloor weathering whereas the subduction related fluid-rock interaction left depleted $\delta^{26}\text{Mg}$ values in local scale.

In Chapter IV, I focus on the mantle modification suggested by Mg isotopes in Chapter III and discuss how these modifications are preserved with respect to the Sr, Nd, and S isotope compositions and their spatial distributions. The peridotite samples with less radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ ratios than Cretaceous seawater ($^{87}\text{Sr}/^{86}\text{Sr} < 0.7074$) are mostly focused at the mantle/crust boundary at 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. The peridotites with higher $^{87}\text{Sr}/^{86}\text{Sr}$ ratios than the Cretaceous seawater ($^{87}\text{Sr}/^{86}\text{Sr} > 0.7074$) suggests the sediment Sr with highly radiogenic isotopic compositions was carried into the mantle section during subduction. The enriched sulfide S contents and negative sulfide $\delta^{34}\text{S}$ values to -20.0% provide convincing evidence for the sediment sulfide S input and these subduction-related signals are strong at the lower mantle section. Moreover, the spatial distribution of combined Sr, Nd, and S isotopic variation in the northern Fizh massif demonstrate the pervasive mantle modification.

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. Slab-derived aqueous fluids are thought to be an effective agent for transporting elements from the slab to the mantle wedge, and the fluids can infiltrate the mantle wedge. The different Sr, S and Mg isotopic distributions in the northern Fizh mantle might come from the elemental characteristics. Sr is a strongly incompatible and highly moderate fluid-mobile element. Therefore, Sr is easily transported from the slab to the fluid by slab dehydration, and move upward, carrying slab-derived signals through the mantle. In addition, Sr can substitute Ca in the rock-forming minerals without isotopic fractionation. Slab-derived signals might be found in the entire peridotite section. On the contrary, S is a volatile element and sensitive to the oxidation state ($f\text{O}_2$). S is carried by fluids and behaves as an incompatible element during melting. The negative to positive changes in $\delta^{34}\text{S}$ in the northern Fizh mantle might reflect significant S isotopic fractionation by melt oxidation. The lack of a ^{34}S -rich slab signature in the uppermost mantle and boninite may be attributed to the equilibration of

metasomatized fluid with mantle material during a long pathway from the slab (Alt et al., 1993). Unlike Sr and S, Mg is a compatible element, and therefore, the slab-derived signals with Mg could not go further and just remain on a local scale where intense melting occurred by metasomatized fluids.

Fig. V-1. この図については、5年以内に雑誌などで刊行慣行予定のため、非公開

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Chapter I

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Chapter IV

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Chapter V

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