

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）

A Dissertation Submitted for the Degree of Doctor of Philosophy

December 2020

令和2年12月博士（理学）申請

Department of Earth and Planetary Science, Graduate School of Science

The University of Tokyo

東京大学大学院理学系研究科地球惑星科学専攻

Jiwon Eom

嚴 智瑗

博士論文（要約）

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

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

令和2年12月博士（理学）申請

東京大学大学院理学系研究科

地球惑星科学専攻

巖 智瑗

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 ($-0.83 \pm 0.09\text{‰}$, Ling et al., 2011) is isotopically heavy relative to the riverine input ($-1.09 \pm 0.05\text{‰}$, 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.

- 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.

Acknowledgements

I would like to express my appreciation to professor Hodaka Kawahata for everything through the doctoral course. It was very lucky to meet him in my life, not to mention as an academic advisor and his support has been indispensable. I am very grateful to Dr. Toshihiro Yoshimura who tried to guide me to my research and I could learn basics of Mg isotopes from him. Dr. Norikatsu Akizawa offered precious Oman peridotites and spent countless hours to teach me petrology and geochemical analyses. I would like to deeply appreciate Professor Toshitaka Gamo for sharing invaluable seafloor hydrothermal vent fluid samples and constructive advices, Dr. Daisuke Araoka for the analyses of Mg isotope compositions and helpful discussion and Dr. Kyoko Yamaoka for sharing her data and her idea.

I owe a great dept of gratitude to those in JAMSTEC, Kochi. Dr. Tsuyoshi Ishikawa allowed me to do my experiments, gave great discussion, and also offered his lovely boninite sample. Dr. Shigeyuki Wakaki taught me the analyses of Sr, Nd, and Mg isotope compositions and helped my Kochi life, the days never to be forgotten. I also received technical support from Dr. Tatsuya Kawai and Dr. Kazuya Nagaishi.

I greatly appreciate those in Niigata university. Professor Eiichi Takazawa and professor Toshiyuki Kurihara kindly shared their valuable Oman samples and I could improve my thesis from their constructive discussion. Professor M. Satish Kumar gave me a chance to measure S isotope compositions that was one of my aspirations for a long time. During analyses of S isotope compositions, I received support from Mr. Shun Mihira and Mr. Silpa A. S.

I greatly acknowledge professor Yuji Sano, professor Susumu Umino, professor Yohei Suzuki, and professor Junichiro Kuroda for their reviews and insightful comments.

My special thanks are expressed to members of the Department of Ocean Floor GeoScience, Atmosphere and Ocean Research Institute, the University of Tokyo for everything in my Kashiwa life. I also deeply appreciate Japanese Government and Mr. J. S. Hwang.

Finally, I am indebted to my family for their support of my life.

Contents

Chapter I. General introduction	1
--	---

Chapter II. Magnesium isotopic composition of submarine vent fluids from arc and back-arc hydrothermal systems in the western Pacific	15
--	----

II-1. Introduction	16
--------------------------	----

II-2. Geological setting and samples	17
--	----

II-2.1. Manus Basin (Vienna Woods, PACMANUS).....	17
---	----

II-2.2. Izu-Bonin Arc (Suiyo Seamount).....	18
---	----

II-2.3. Mariana Trough (Alice Springs, Forecast Vent)	18
---	----

II-2.4. North Fiji Basin	19
--------------------------------	----

II-2.5. Okinawa Trough	19
------------------------------	----

II-3. Analytical method	23
-------------------------------	----

II-4. Results	24
---------------------	----

II-5. Discussion	27
------------------------	----

II-5.1. Mg isotopic behavior during high-temperature seawater-rock interactions	27
---	----

II-5.2. Estimating the fractionation factor	35
---	----

II-5.3. Estimating the oceanic Mg budgetii.....	38
---	----

II-6. Summary and conclusion	41
------------------------------------	----

Chapter III. Magnesium isotopic composition of sediment, crust, and mantle in the Oman ophiolite	43
---	----

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	45
---	-----------

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 General introduction.....	47
--	-----------

References	52
-------------------------	-----------

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 ($\text{W/R} \leq 50$), 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 ($\text{W/R} > 50$) 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:

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

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.

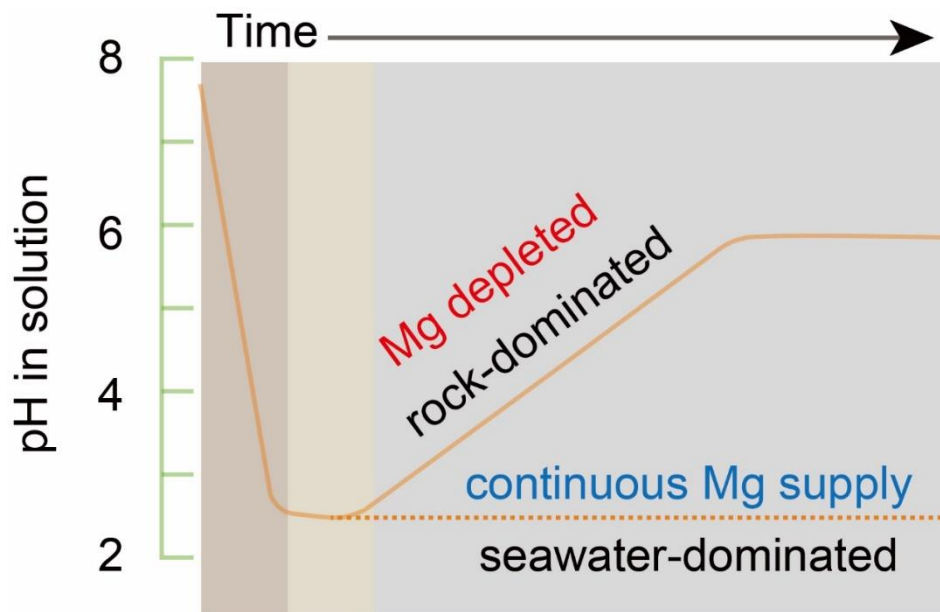


Fig. I-1. Idealized illustration of the pH change with time during reaction of seawater with basalt at rock-rock dominated and seawater-dominated system. Modified after Seyfried and Mottl, 1982.

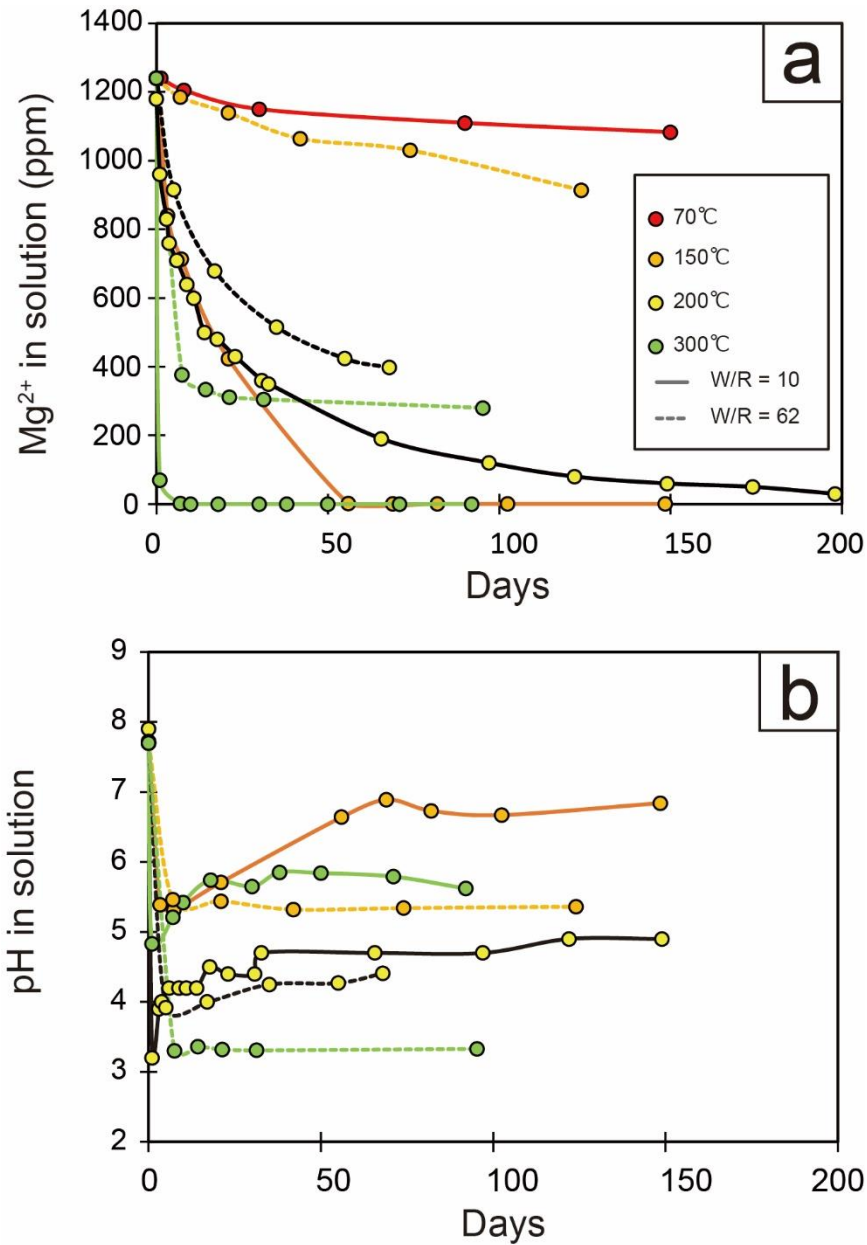


Fig. I-2. a) Concentration of Mg²⁺ and b) pH in solution with time in hydrothermal experiments reacting seawater with basalt. Conditions are at 70 °C, 1atm, and 150 °C, 200 °C and 300 °C at 500 bars. Data are from Bischoff and Dickson (1975), Seyfried and Bischoff (1979 and 1981) and Seyfried and Mottl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

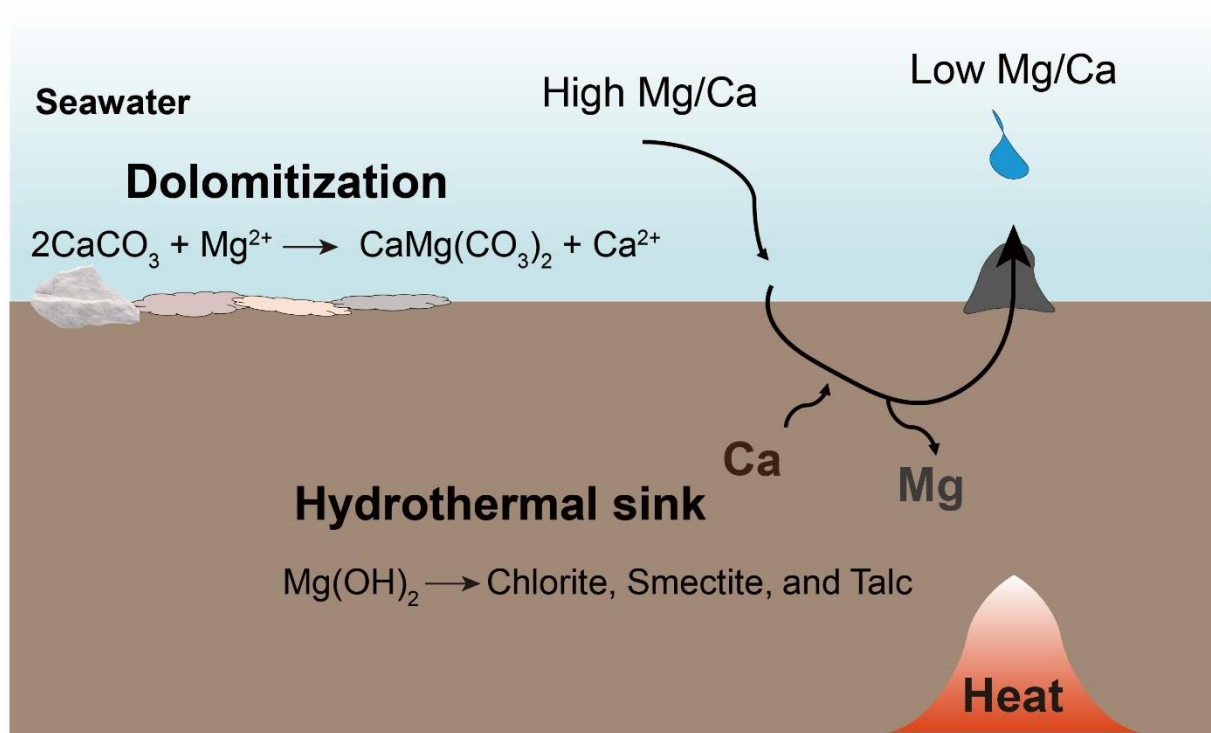


Fig. I-3. Illustration of the main seafloor Mg sinks at the seafloor environment. Both the dolomite sink and the hydrothermal sink remove Mg and supply Ca to the seawater, lowering Mg/Ca ratios in seawater.

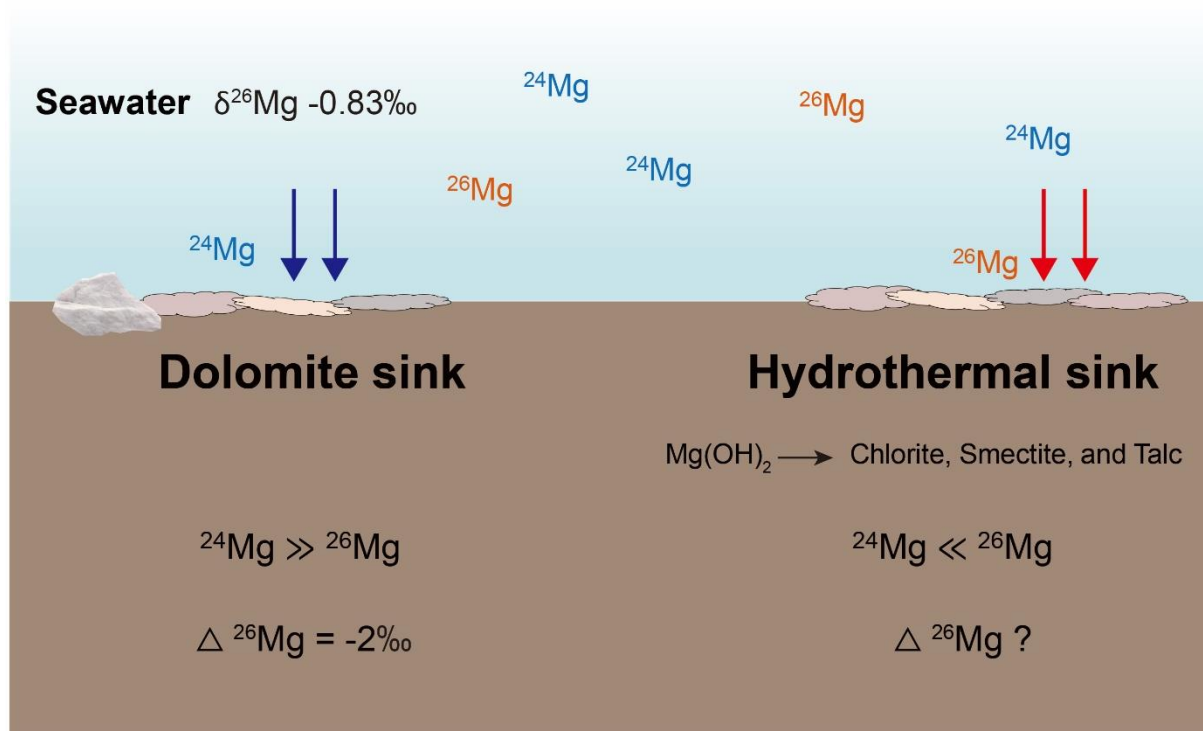


Fig. I-4. Illustration of the main seafloor Mg sinks at the seafloor environment. Dolomite sink and hydrothermal sink remove Mg in the seawater but they are isotopically differentiated. Dolomite sink prefers light Mg isotopes while heavy Mg isotopes are preferentially removed by hydrothermal circulation.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

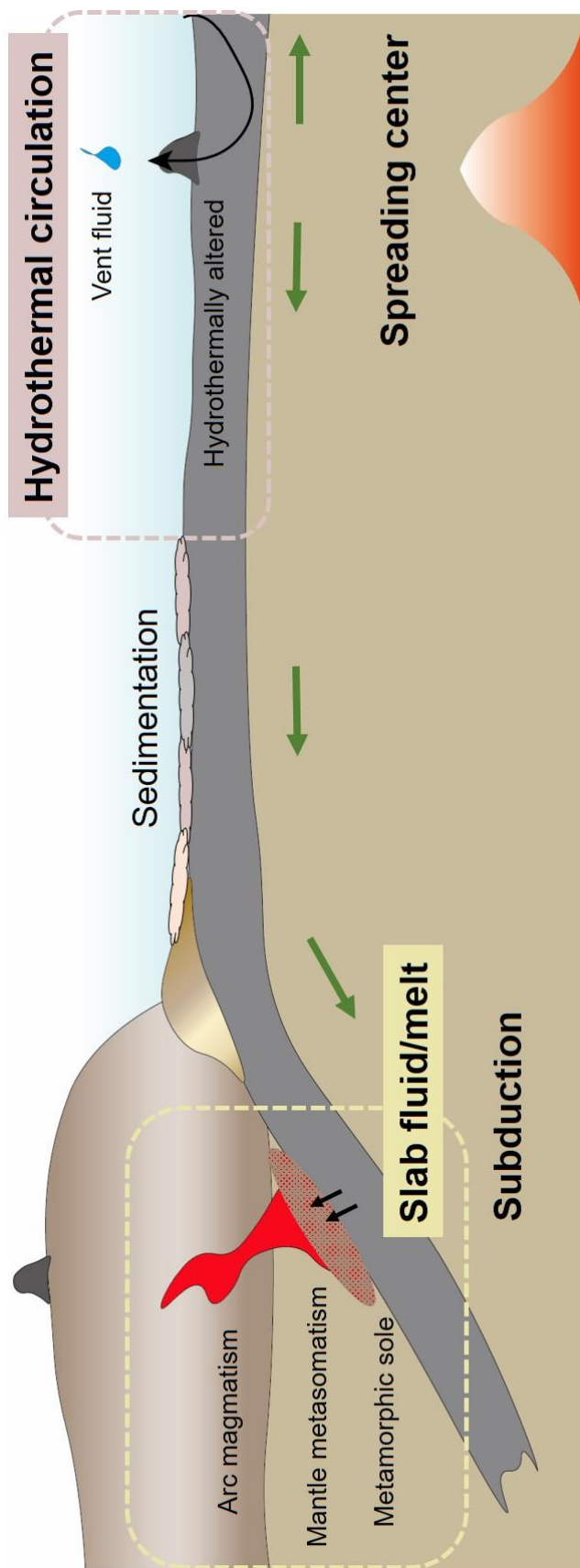


Fig. I-5. Illustration of the main fluid-rock interactions at oceanic lithospheres. Oceanic lithospheres experience the hydrothermal alteration at the spreading center and are recycled at the subduction zone. At the subduction zone, subducting materials (slab) react

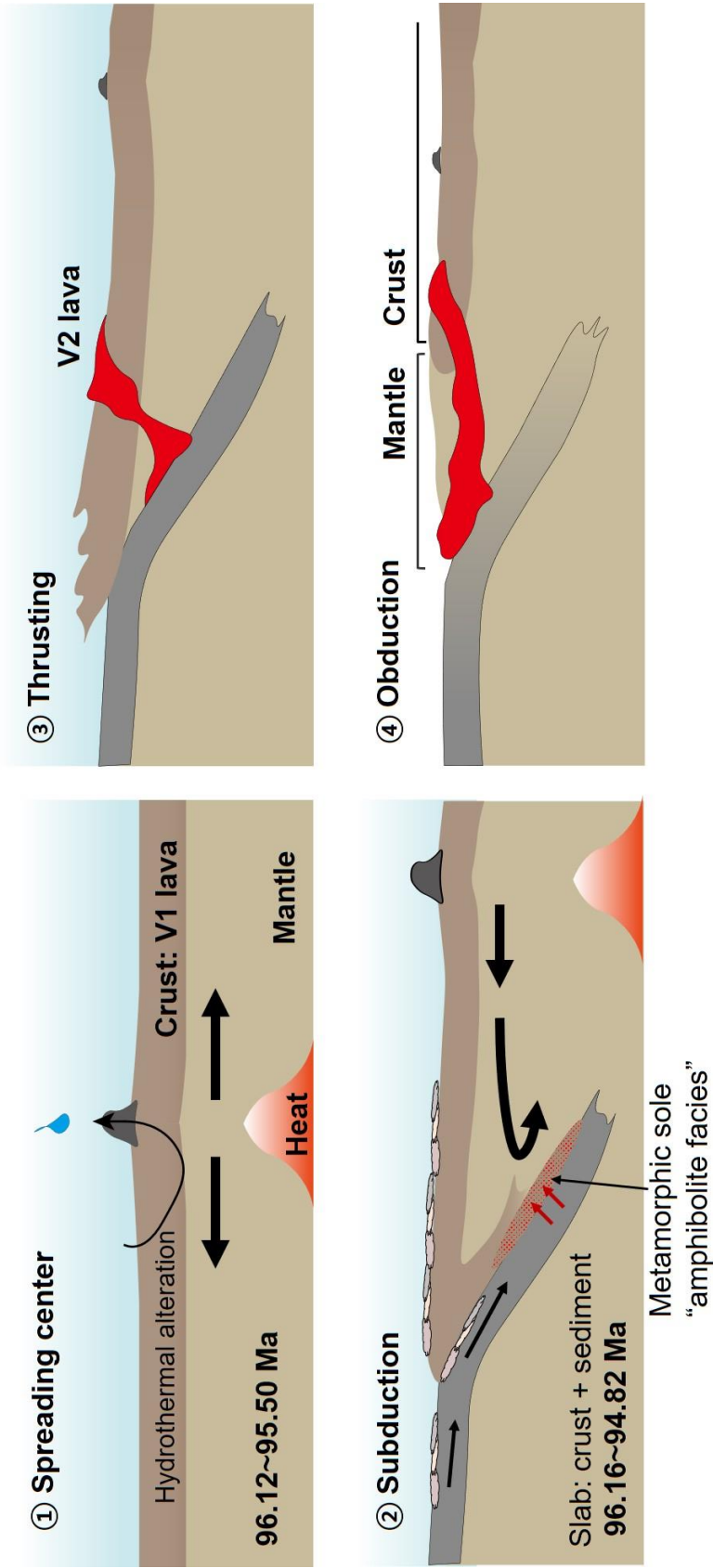


Fig. I-6. Illustration of the Oman ophiolite formation. The Oman ophiolite was probably produced at the spreading center, and subducted into the other oceanic lithosphere. After thrusting, it was obducted onto the other plate. Presently, it is exposed on land. Geochronological data is from Coleman, 1981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

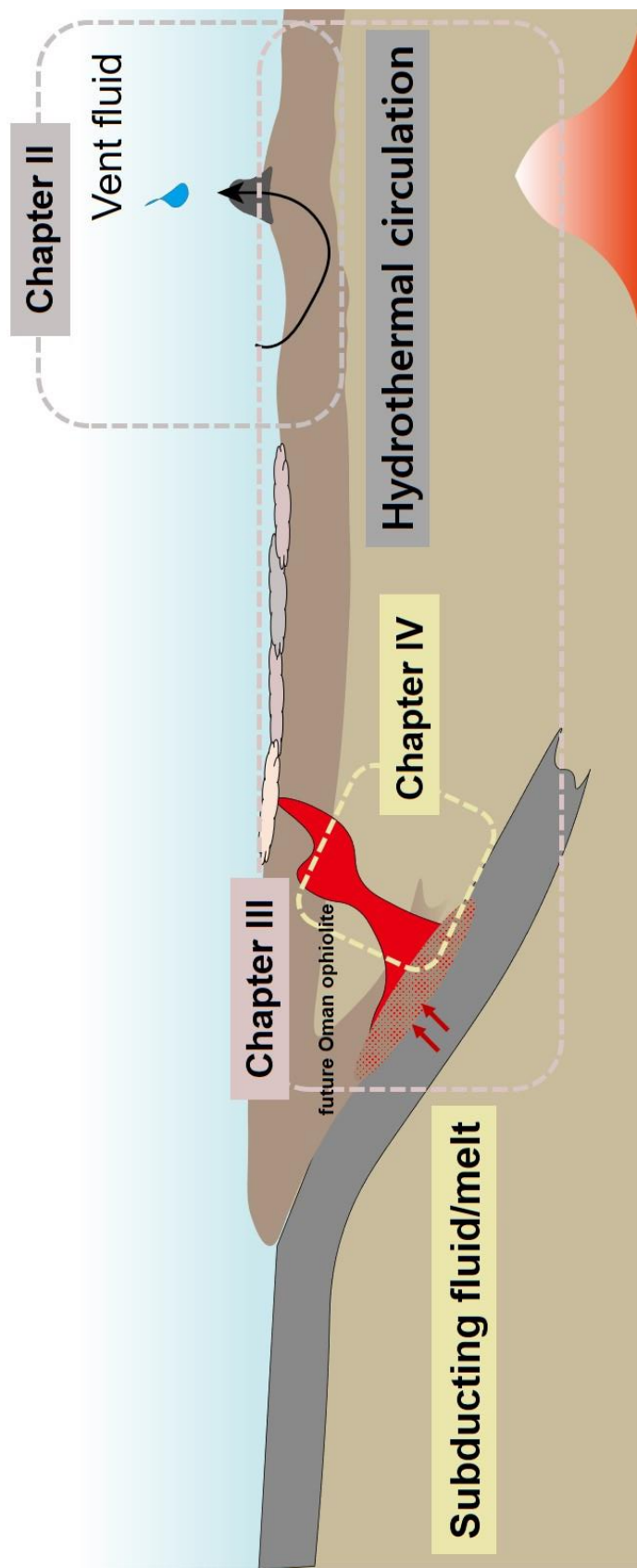


Fig. I-7. The structure of this dissertation. In regards to the Mg behavior, Mg isotopic compositions of the high-temperature vent fluid from the western Pacific and Oman rock samples were measured. Mg behavior inferred from vent fluids (return flux) and Mg sink by hydrothermal circulation are discussed in Chapter II and III, respectively. Chapter III also covers Mg transfer by subduction. In Chapter IV, mantle modifications suggested by Mg isotopes in Chapter III are described by using Sr, Nd, and S isotopes.

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 ($-0.83 \pm 0.09\text{‰}$, Ling et al., 2011) which is distinct from the major Mg input into oceans (Riverine input of $-1.09 \pm 0.05\text{‰}$, 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 $+0.21\text{‰}$ (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).

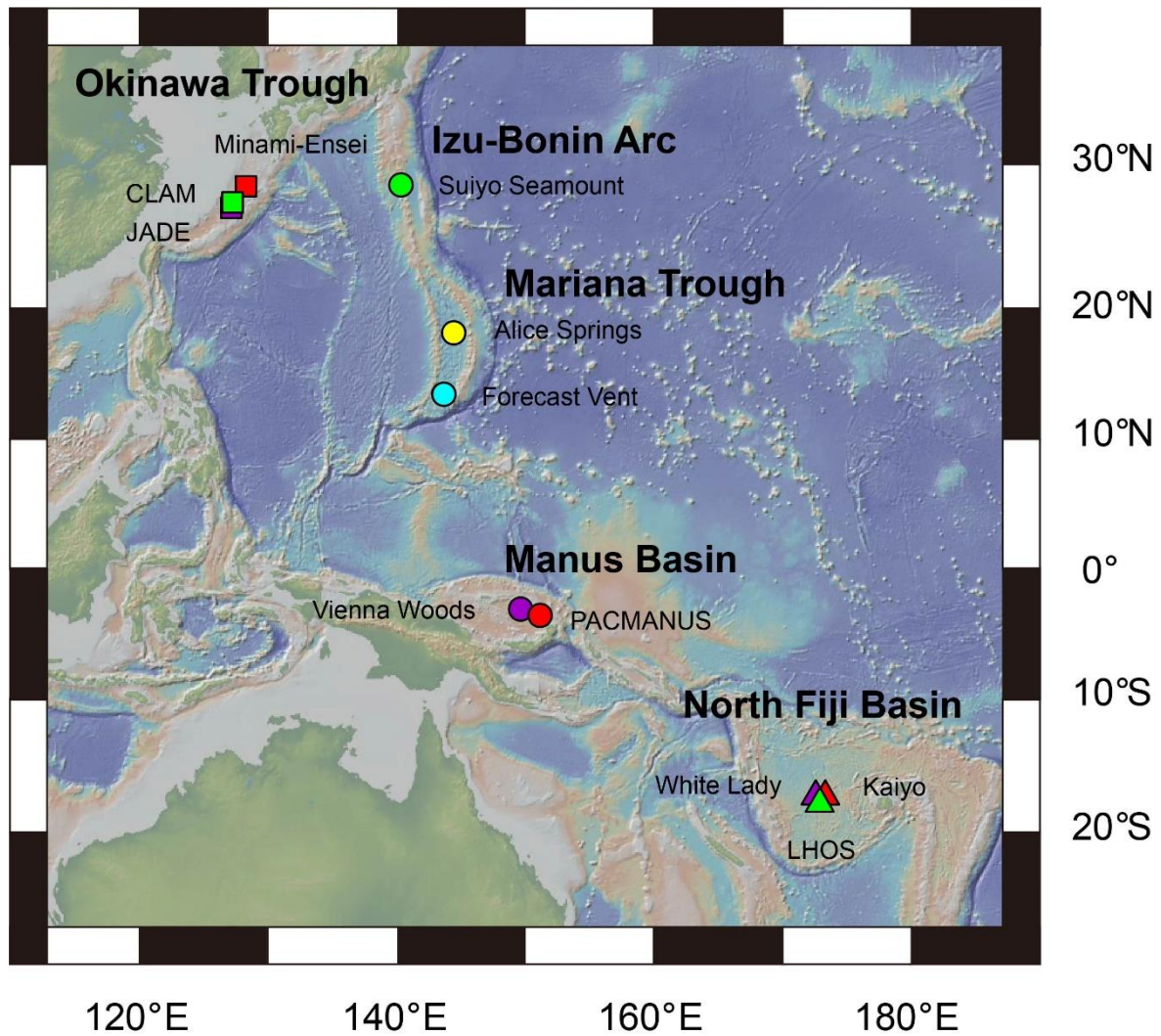


Fig. II-1. The map of sampling sites of submarine vent fluid in arc and back-arc hydrothermal systems, the western Pacific. Circles (\circ), triangles (\triangle) and squares (\square) indicate sediment-starved, phase-separated and sediment-hosted sites, respectively. Characteristics of each site are 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 mLmin⁻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 7mL 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).

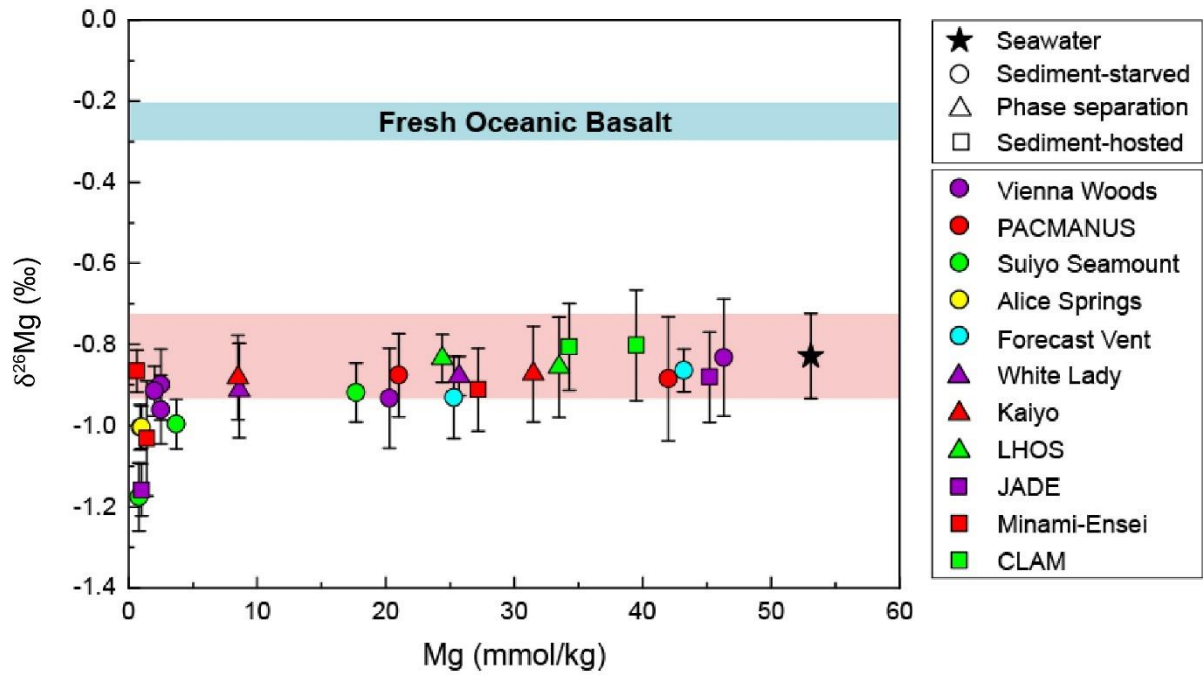


Fig. II-2. $\delta^{26}\text{Mg}$ -Mg concentration diagram showing hydrothermal fluid compositions used in this study. The samples can be roughly divided into two groups: first, with enough Mg concentrations having $\delta^{26}\text{Mg}$ value close to seawater and the second, having little or no Mg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

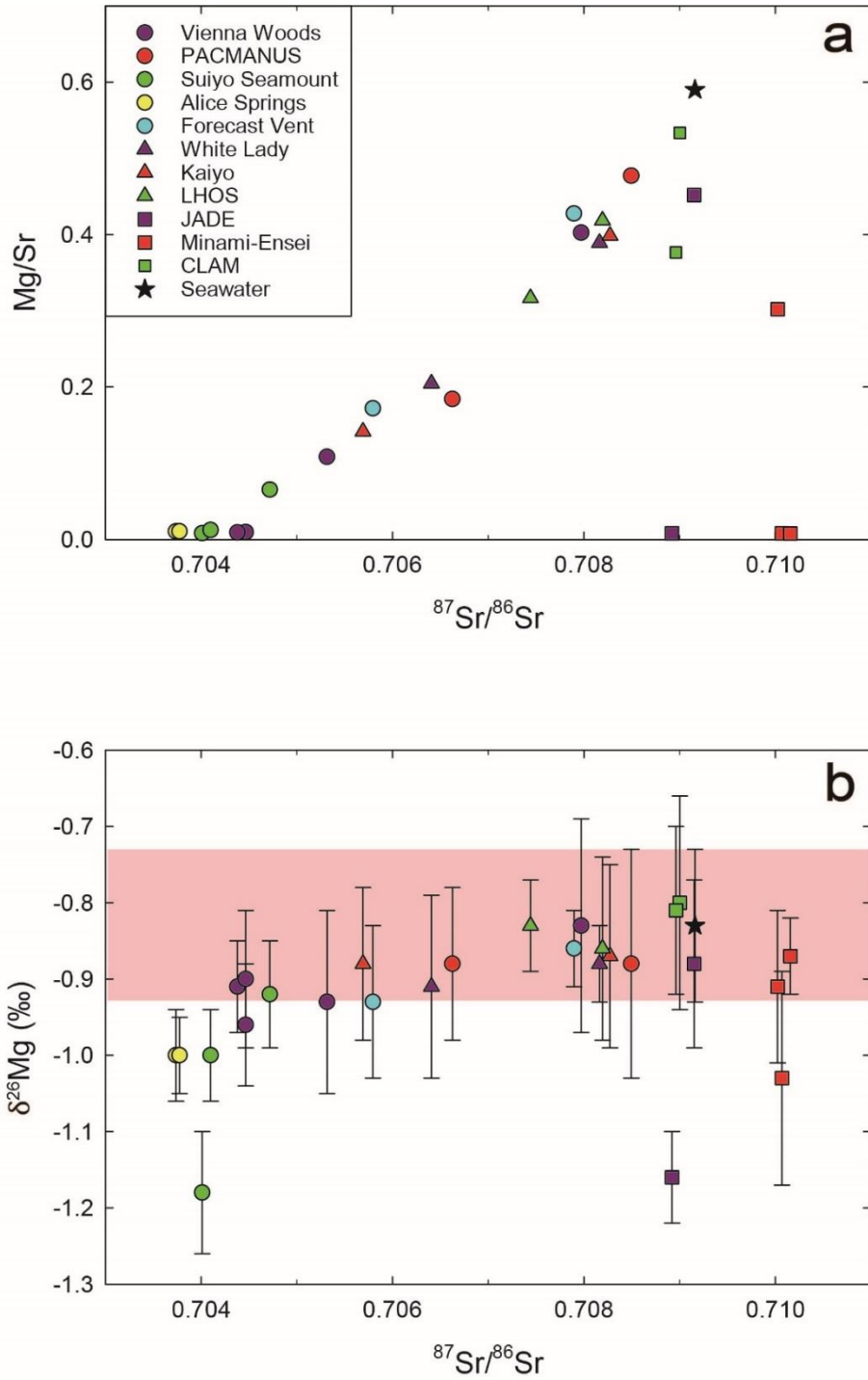


Fig. II-3. Plots of (a) $^{87}\text{Sr}/^{86}\text{Sr}$ ratios versus Mg/Sr ratios and (b) $\delta^{26}\text{Mg}$ versus $^{87}\text{Sr}/^{86}\text{Sr}$ ratios for vent fluids. Except for samples from sediment-hosted sites (\square), the linear trends shown in (a) and (b) suggest the entrainment of seawater.

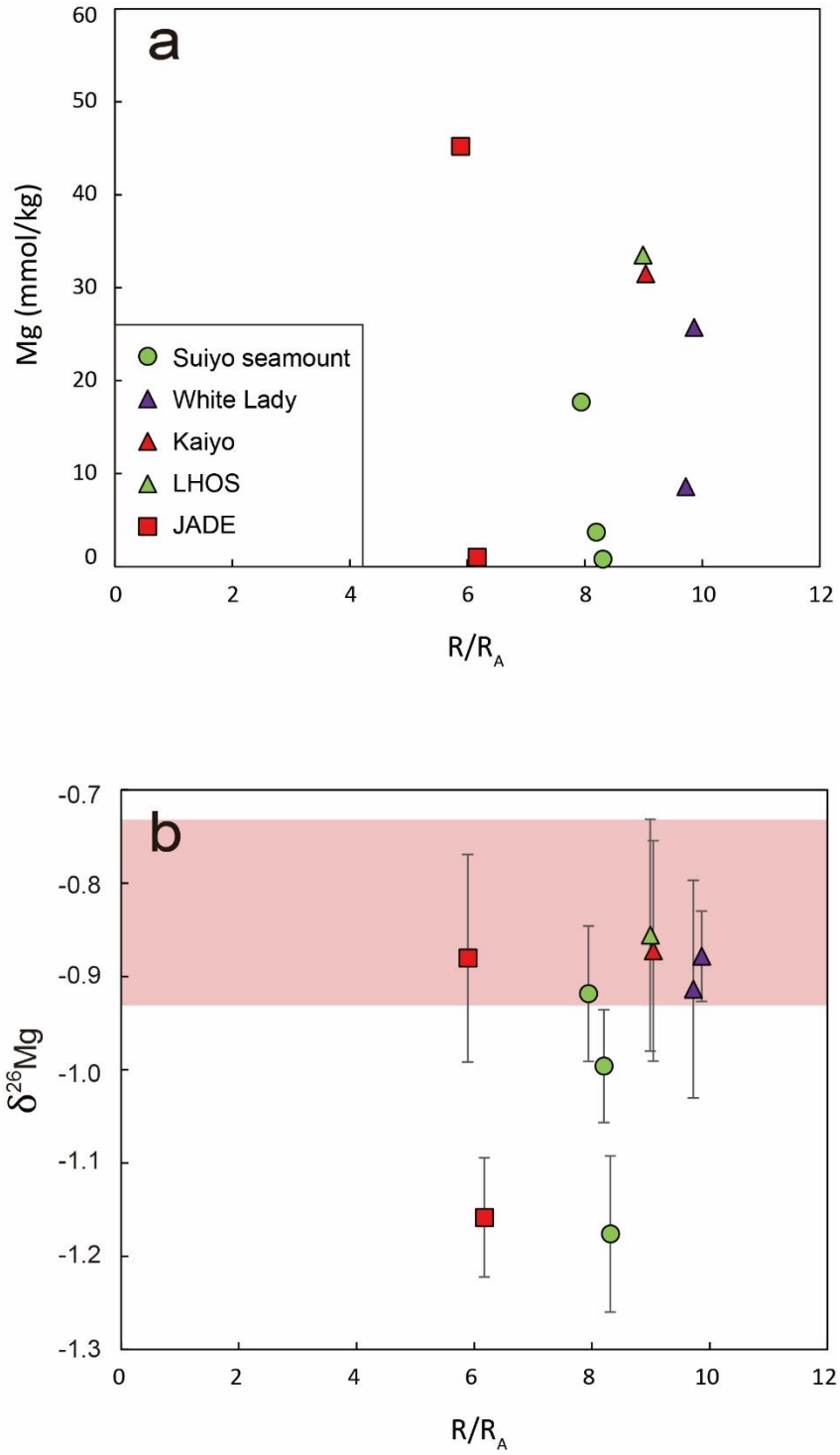


Fig. II-4. Plots of (a) Mg concentration and (b) $\delta^{26}\text{Mg}$ versus R/R_A ($R = {}^3\text{He}/{}^4\text{He}$ in vent fluid and $R_A = {}^3\text{He}/{}^4\text{He}$ in atmosphere). R/R_A data are from Tsunogai et al., 1994; Ishibashi et al., 1994b and 1995.

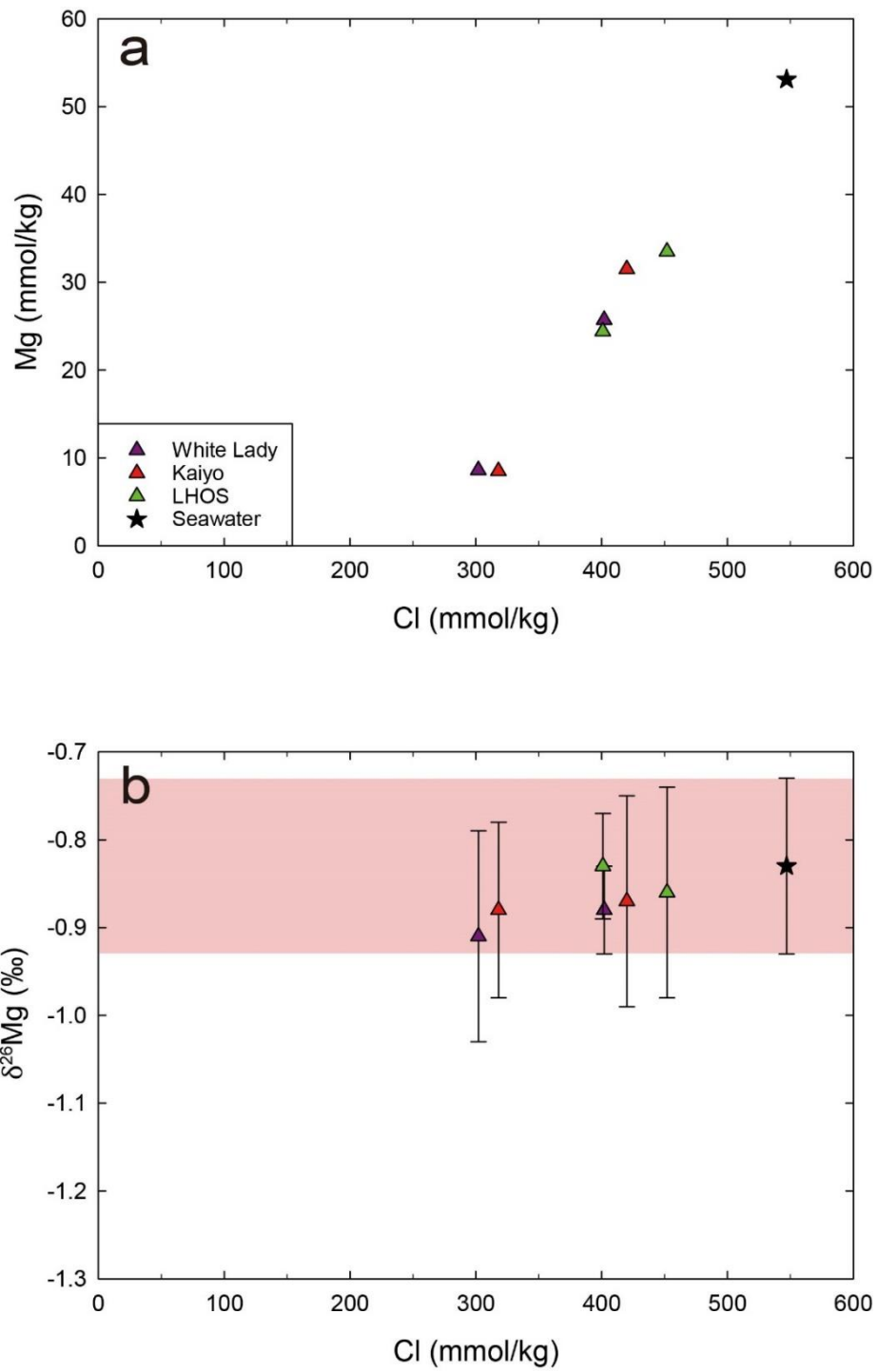


Fig. II-5. Plots of (a) Mg concentration and (b) $\delta^{26}\text{Mg}$ versus Cl concentration from phase-separated sites.

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 $+0.03\text{‰}$. 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 ($-0.28 \sim -0.14\text{‰}$) and the mantle ($-0.25 \pm 0.04\text{‰}$, 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.

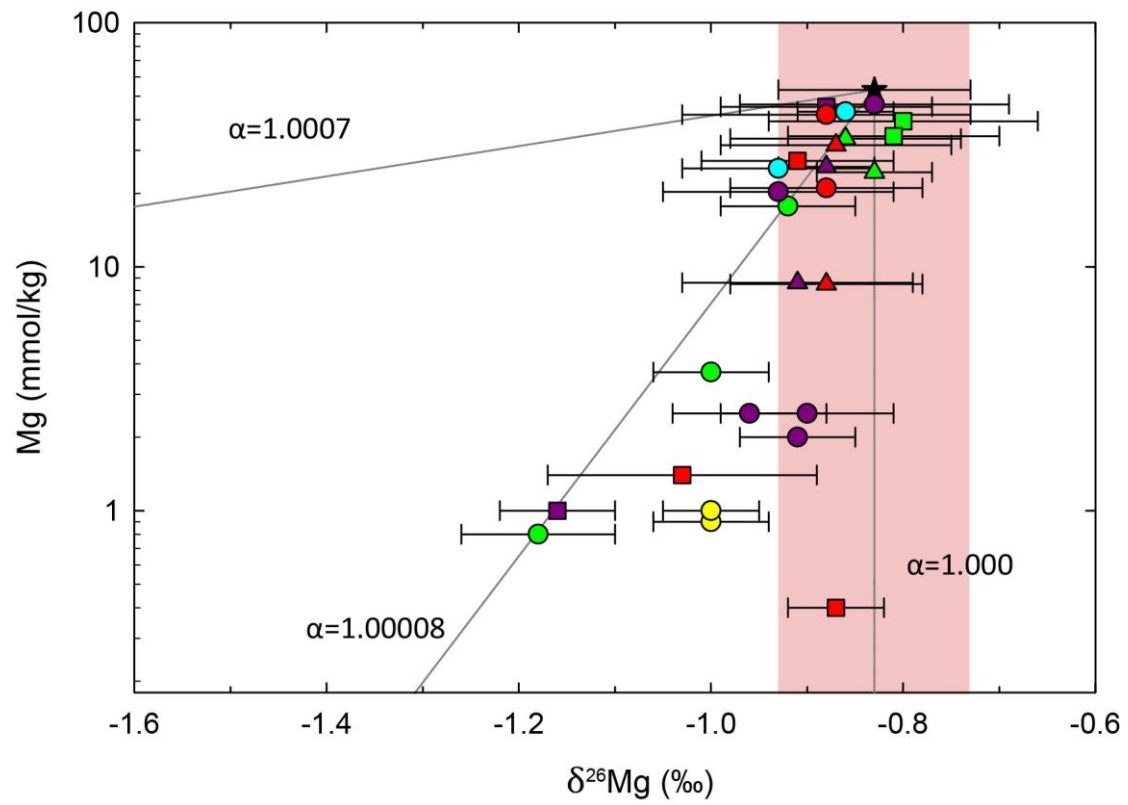


Fig. II-6. $\delta^{26}\text{Mg}$ -Mg concentration diagram with fractionation curves. The fractionation factors at low- T and high-T (Higgins and Schrag, 2015) are shown.

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 ($-1.09 \pm 0.05\text{‰}$, Tipper et al., 2006) is lower than that of seawater ($-0.83 \pm 0.09\text{‰}$, 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 $\delta^{26}\text{Mg}_{\text{vent fluid}} = -1.18\text{‰}$ 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 $\sim -0.825\text{‰}$. 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 ($-0.83 \pm 0.09\text{‰}$, Ling et al., 2011) than the riverine Mg input into oceans ($-1.09 \pm 0.05\text{‰}$, 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

References

Chapter I

- Akizawa, N. and Arai, S. (2014) Petrology of mantle diopsidite from wadi Fizh, northern Oman ophiolite: Cr and REE mobility by hydrothermal solution. *Island Arc* 23, 312-323.
- Alabaster, T., Pearce, J. A., and Malpas, J. (1982) The volcanic stratigraphy and petrogenesis of the Oman ophiolite complex, *Contributions to Mineralogy and Petrology* 81 (3), 168-183.
- Alt, J.C., Zuleger, E., and Erzinger, J. A. (1996) Mineralogy and stable isotopic compositions of the hydrothermally altered lower sheeted dike complex, Hole 504B, Leg 140. *Proceedings of the Ocean Drilling Program, Scientific Results* 137/140, 155-156.
- Alt, J. C. and Shanks, W. C. (1998) Sulfur in serpentinized oceanic peridotites: Serpentinization processes and microbial sulfate reduction. *Journal of Geophysical Research* 103, 9917-9929.
- Anderson, R. N., and Hobart, M. A. (1976) The relation between heat flow, sediment thickness, and age in the eastern Pacific. *Journal of Geophysical Research* 81, 2968-2989.
- Arai, S., and Matsukage, K. (1996) Petrology of the gabbro-troctolite-peridotite complex from Hess Deep, equatorial Pacific: Implications for mantle-melt interaction within the oceanic lithosphere. *Proceedings of the Ocean Drilling Program, Scientific Results* 147, 135-155.
- Arai, S., Matsukage, K., Isobe, E., and Vysotskiy, S. (1997) Concentration of incompatible elements in oceanic mantle: effect of melt/wall interaction in stagnant or failed melt conduits within peridotite. *Geochimica et Cosmochimica Acta* 61, 671-675.
- Beinlich, A., Mavromatis, V., Austrheim H and Oelkers E. H. (2014) Inter-mineral Mg isotope fractionation during hydrothermal ultramafic rock alteration—Implications for the global Mg-cycle. *Earth and Planetary Science Letters* 392, 166–176.
- Berner, E. K. and Berner, R. A. (2012) *Global Environment: Water, Air, and Geochemical Cycles*. Princeton University Press, Princeton, p. 488.
- Bischoff, J. L., and Dickson, F. W. (1975) Seawater-basalt interaction at 200°C and 500 bars: implications for origin of sea-floor heavy-metal deposits and regulation of seawater chemistry. *Earth and Planetary Science Letters* 25, 385-397.
- Bosch, D., Jamais, M., Boudier, F., Nicolas, A., Dautria, J.-M., and Agrinier, P. (2004) Deep and high-temperature hydrothermal circulation in the Oman ophiolite: Petrological and isotopic evidence. *Journal of Petrology*, 45(6), 1181-1208. doi:10.1093/petrology/egh010
- Boudier, F. and Juteau, T. (2000) The ophiolite of Oman and United Arab Emirates. *Marine Geophysical Researches* 21, 145-407.
- Coleman, R. G. (1981) Tectonic setting of ophiolite obduction in Oman. *Journal of Geophysical*

Research 86, 2497-2508.

- de Villiers, S., Dickson, J. A. D. and Ellam, R. M. (2005) The composition of the continental river weathering flux deduced from seawater Mg isotopes. *Chemical Geology* 216, 133-142.
- Dilek, Y. and Flower, M. F. J. (2003) Arc-trench rollback and forearc accretion: 2. A model for ophiolites in Albania, Cyprus, and Oman. In *Ophiolite in Earth History* (Dilek, Y. and Robinson, P. T., Eds). Geological Society, London, Special Publications 218, 43-68.
- Dilek, Y. and Furnes, H. (2011) Ophiolite genesis and global tectonics: Geochemical and tectonic fingerprinting of ancient oceanic lithosphere, *Geological Society of America Bulletin* 123, 387-411.
- Drever, J. I. (1974) The magnesium problem, in *The Sea*, vol. 5, E. D. Goldberg (ed), pp.337-358, Wiley Interscience, New York.
- Dygert, N., Kelemen, P. B. and Liang, Y. (2017) Spatial variations in cooling rate in the mantle section of the Samail ophiolite in Oman: Implications for formation of lithosphere at mid-ocean ridges. *Earth and Planetary Science Letters* 465, 134-144.
- Elderfield, H. and Schultz, A. (1996) Mid-ocean ridge hydrothermal fluxes and the chemical composition of the ocean, *Annual Review of Earth and Planetary Sciences* 24, 191-224.
- Ernewein, M., Pflumio, C., and Whitechurch, H. (1988). The death of an accretion zone as evidenced by the magmatic history of the Sumail ophiolite (Oman). *Tectonophysics*, 151(1-4), 247-274.
- Galy, A., Bar-Matthews, M., Halicz, L., and O’Nions, R. K. (2002) Mg isotopic composition of carbonate: insight from speleothem formation. *Earth and Planetary Science Letters* 201, 105-115.
- Goodenough, K. M., Thomas, R. J., Styles, M. T., Schofield, D. I., and MacLeod, C. J. (2014). Records of ocean growth and destruction in the Oman-UAE ophiolite. *Elements*, 10(2), 109-114.
- Hardie, L. A. (1996) Secular variation in seawater chemistry: An explanation for the coupled secular variation in the mineralogies of marine limestones and potash evaporates over the past 600 m.y. *Geology* 24, 279-283.
- Higgins, J. A. and Schrag, D. P. (2010) Constraining magnesium cycling in marine sediments using magnesium isotopes. *Geochimica et Cosmochimica Acta* 74, 5039-5053.
- Higgins, J. A. and Schrag, D. P. (2015) The Mg isotopic composition of Cenozoic seawater-evidence for a link between Mg-clays, seawater Mg/Ca, and climate. *Earth and Planetary Science Letters* 416, 73-81.
- Holland, H. D., Lazar, B. and McCaffrey, M. (1986) Evolution of the atmosphere and oceans. *Nature* 320, 27-33.
- Hu, Y., Harrington, M. D., Sun, Y., Yang, Z., Konter, J., and Teng, F.-Z, (2016) Magnesium isotopic homogeneity of San Carlos olivine: a potential standard for Mg isotopic analysis by multi-collector

- inductively coupled plasma mass spectrometry. *Rapid Communications in Mass Spectrometry* 30 (19), 2123–2132.
- Kawahata, H., Nohara, M., Ishizuka, H., Hasebe, S. and Chiba, H. (2001) Sr Isotope Geochemistry and Hydrothermal Alteration of the Oman Ophiolite. *Journal of Geophysical Research* 106, 11,083–11,099.
- Khedr, M. Z., Arai, S., Python, M., and Tamura, A. (2014) Chemical variations of abyssal peridotites in the central Oman ophiolite: Evidence of oceanic mantle heterogeneity. *Gondwana Research* 25, 1242–1262.
- Lai, Y.-J., Pogge von Strandmann, P. A. E., Dohmen, R., Takazawa, E., and Elliot, T. (2015) The influence of melt infiltration on the Li and Mg isotopic composition of the Horoman Peridotite Massif. *Geochimica et Cosmochimica Acta* 164, 318–332.
- 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.
- Lee, T., Papanastassiou, D. A., Wasserburg, G. J. (1976) Demonstration of ^{26}Mg excess in Allende and evidence for ^{26}Al . *Geophysical Research Letters* 3, 109–112.
- Lister, C. R. B. (1972) On the thermal balance of a mid-ocean ridge. *Geophysical Journal International* 26, 515–535.
- Lippard, S. J., Shelton, A. W., and Gass, I. G. (1986) *The Ophiolite of Northern Oman*. Blackwell Scientific Publications, Oxford
- Lonsdale, P. (1977) Clustering of suspension-feeding macrobenthos near abyssal hydrothermal vents at oceanic spreading centers. *Deep-Sea Research* 24 (9) 857–863.
- Milliman, J. D., (1974) *Marine Carbonates-Recent Sedimentary Carbonates*, Part I, Berlin, Springer-Verlag, 375 p.
- Mottl, M. J. and Holland, H. D. (1978) Chemical exchange during hydrothermal alteration of basalt by seawater —1. Experimental results for major and minor components of seawater. *Geochimica et Cosmochimica Acta* 42, 1103–1115.
- Mottl, M. J. and Seyfried, W. E. (1980) Subseafloor hydrothermal systems: Rock- vs. seawater-dominated, In *Seafloor spreading centers: Hydrothermal systems*, 66–82. P. A. Rona and R. P. Lowell (eds) Stroudsburg, Pennsylvania: Dowden, Hutchinson and Ross, Inc.
- Nicolas, A. (1989) *Structure of Ophiolites and Dynamics of the Oceanic Lithosphere*. Kluwer Acad., Norwell Mass.
- Pogge von Strandmann, P. A. E. (2008) Precise magnesium isotope measurements in core top planktic and benthic foraminifera. *Geochemistry Geophysics Geosystems* 9, 1–13.

- Prigent, C., Guillot, S., Agard, P., Lemarchand, D., Soret, M., and Ulrich, M. (2018) Transfer of subduction fluids into the deforming mantle wedge during nascent subduction: Evidence from trace elements and boron isotopes (Semail ophiolite, Oman). *Earth and Planetary Science Letters* 484, 213-228.
- Python, M., Ceuleneer, G., Ishida, Y., Jean-Alix Barrat and Arai, S. (2007) Oman diopsidites: a new lithology diagnostic of very high temperature hydrothermal circulation in mantle peridotite below oceanic spreading centres. *Earth and Planetary Science Letters* 255, 289-305.
- Rioux, M., Bowring, S., Kelemen, P., Gordon, S., Dudás, F. and Miller, R. (2012) Rapid crustal accretion and magma assimilation in the Oman–U.A.E. ophiolite: High precision U-Pb zircon geochronology of the gabbroic crust. *Journal of Geophysical Research* 117, B07201.
- Rioux, M., Garber, J., Bauer, A., Bowring, S., Searle, M., Kelemen, P. and Hacker, B. (2016) Synchronous formation of the metamorphic sole and igneous crust of the Semail ophiolite: New constraints on the tectonic evolution during ophiolite formation from high-precision U-Pb zircon geochronology. *Earth and Planetary Science Letters* 451, 185-195.
- Ries, J. B., Stanley, S. M. and Hardie, L. A. (2006) Scleractinian corals produce calcite, and grow more slowly, in artificial Cretaceous seawater. *Geology*, 34, 525-528.
- Seyfried, W. E. and Bischoff, J. L. (1977) Hydrothermal transport of heavy metals by seawater: The role of seawater/basalt ratio. *Earth and Planetary Science Letters* 34, 71-77.
- Seyfried Jr, W. E. and Bischoff, J. L. (1979) Low temperature basalt alteration by seawater: an experimental study at 70°C and 150°C. *Geochimica et Cosmochimica Acta* 43, 1937-1947.
- Seyfried, W. E. and Bischoff, J. L. (1981) Experimental seawater-basalt interaction at 300°C and 500 bars: Chemical exchange, secondary mineral formation and implications for the transport of heavy metals. *Geochimica et Cosmochimica Acta* 45, 135-147.
- Seyfried, W. E. and Mottl, M. J. (1982) Hydrothermal alteration of basalt by seawater under seawater-dominated conditions. *Geochimica et Cosmochimica Acta* 46, 985-1002.
- Spiess, F. N., Macdonald, K. C., Atwater, T. et al. (1980) East Pacific Rise: Hot Springs and Geophysical Experiments. *Science* 207, 1421-1433.
- Stanley, S. M. and Hardie, L. A. (1998) Secular oscillations in the carbonate mineralogy of reef-building and sediment-producing organisms driven by tectonically forced shifts in seawater chemistry. *Paleogeography, Paleoclimatology, Paleoecology* 144, 3-19.
- Styles, M.T. and 10 coauthors (2006) *Geology and Geophysics of the United Arab Emirates*. British Geological Survey, Keyworth, Nottingham
- Takazawa, E., Okayasu, T., and Satoh, K. (2003) Geochemistry and origin of the basal lherzolites from the northern Oman ophiolite (northern Fijah block). *Geochemistry Geophysics Geosystems* 4(2),

1021.

- 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. and Bickle, M. J. (2006a) Riverine evidence for a fractionated reservoir of Ca and Mg on the continents: Implications for the oceanic Ca cycle. *Earth and Planetary Science Letters* 247, 267-279.
- 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.
- Wang, S.-J., Teng, F.-Z., Scott, J. (2016) Tracing the origin of continental HIMU-like intraplate volcanism using magnesium isotope systematics. *Geochimica et Cosmochimica Acta* 185, 78-87.
- Warren, C. J., Parrish, R. R., Waters, D. J., and Searle, M. P. (2005). Dating the geologic history of Oman's Semail ophiolite: Insights from U-Pb geochronology. *Contributions to Mineralogy and Petrology* 150(4), 403-422.
- Wilkinson, B. H. and Algeo, T. J. (1989) Sedimentary carbonate record of calcium-magnesium cycling. *American Journal of Science* 289, 1158-1194.
- Williams, D. L., Von Herzen, R. P., Sclater, J. G. and Anderson, R. N. (1974) The Galapagos spreading centre: Lithospheric cooling and hydrothermal circulation, *Geophysical Journal of International* 38, 587-608.
- Yoshikawa, M., Python, M., Tamura, A., Arai, S., Takazawa, E., Shibata, T., Ueda, A., and Sato, T. (2015) Melt extraction and metasomatism recorded in basal peridotites above the metamorphic sole of the northern Fizz massif, Oman ophiolite. *Tectonophysics* 650, 53–64.
- Young, E. D., and Galy, A. (2004) The isotope geochemistry and cosmochemistry of magnesium. In *Geochemistry of Non-traditional Stable Isotopes. Reviews in Mineralogy & Geochemistry*. Eds C. M. Hohnson, B. L. Beard and F. Albarede. Mineralogical Society of America, 197-230.

Chapter II

- Alt, J. C. (1995) Subseafloor processes in mid-ocean ridge hydrothermal systems, *Seafloor Hydrothermal Systems, Physical, Chemical, Biological, and Geological Interactions*, Geophysical Monograph 91, S. E. Humphris et al., 85-114, AGU, Washington, D. C.
- Araoka, D., Nishio, Y., Gamo, T., Yamaoka, K. and Kawahata, H. (2016) Lithium isotopic systematics of submarine vent fluids from arc and back-arc hydrothermal systems in the western Pacific, *Geochemistry, Geophysics, Geosystems* 17, 3835-3853, doi:10.1002/ 2016GC006355.

- Araoka, D., and Yoshimura, T. (2019) Rapid purification of alkali and alkaline-earth elements for isotope analysis ($\delta^{26}\text{Li}$, $\delta^{26}\text{Mg}$, $^{87}\text{Sr}/^{86}\text{Sr}$, and $\delta^{88}\text{Sr}$) of rock samples using borate fusion followed by Ion chromatography with a fraction collector system, *Analytical Sciences*, vol. 35, 751-757.
- Auzende, J. M., Rissen, J. P., Lafoy, Y., Gente, P. and Charlou, J. L. (1988), Seafloor spreading in the North Fiji Basin (Southwest Pacific), *Tectonophysics*, 146, 317–352.
- Bach, W., Roberts, S., Vanko, D.A., Binns, R., Yeats, C., Craddock, P., and Humphries, S. E. (2003) Controls on fluid chemistry and complexation on rare-earth element contents of anhydrite from the Pacmanus sub seafloor hydrothermal system, Manus basin, Papua New Guinea: *Mineralium Deposita* 38, 916–935.
- Beinlich, A., Mavromatis, V., Austrheim H and Oelkers E. H. (2014) Inter-mineral Mg isotope fractionation during hydrothermal ultramafic rock alteration—Implications for the global Mg-cycle. *Earth and Planetary Science Letters* 392, 166–176.
- Bowers, T. S., Campbell, A. C., Measures, C. I., Spivack, A. J., Khadem, M. and Edmond J. M. (1988) Chemical controls on the composition of vent fluids at 13°-11° and 21°N, East Pacific Rise, *Journal of Geophysical Research* 93, 4522-4536.
- Butterfield, D. A., Massoth, G. J., McDuff, R. E., Lupton, J. E. and Lilley, M. D. (1990) Geochemistry of hydrothermal fluids from Axial Seamount Hydrothermal Emissions Study Vent Field, Juan de Fuca Ridge: Subseafloor boiling and subsequent fluid-rock interaction, *Journal of Geophysical Research* 95, 12,895-12,921.
- Campbell, A. C., Edmond, J. M., Colodner, D., Palmer, M. R. and Falkner, K. K. (1987) Chemistry of hydrothermal fluids from the Mariana Trough back-arc basin in comparison to mid-ocean ridge fluids. *Eos Trans. AGU* 68, V31B-05.
- Campbell, A. C., Bowers, T. S., Measures, C. I., Falkner, K. K., Khadem, M. and Edmond, J. M. (1988) A time series of vent fluid compositions from 21°N, East Pacific Rise (1979, 1981, 1985), and the Guaymas Basin, Gulf of California (1982, 1985), *Journal of Geophysical Research* 93, 4537-4549.
- Chiba, H., Nakashima, K., Gamo, T., Ishibashi, J., Tsunogai, U. and Sakai, H. (1993) Hydrothermal activity at the Minami-Ensei Knoll, Okinawa Trough: chemical characteristics of hydrothermal solutions, *Proceeding of the JAMSTEC Symposium Deep Sea Research* 9, 271-282 (in Japanese with English abstract)
- Chiba, H. (1997) Geochemistry of active hydrothermal systems in Okinawa Trough Back Arc Basin, *JAMSTEC Journal of Deep Sea Research*, Special Volume, 63-68.
- Eissen, J.-P., Lefe`vre, C., Maillet, P., Morvan, G. and Nohara, M. (1991) Petrology and geochemistry of the central North Fiji Basin spreading center (Southwest Pacific) between 16°S and 22°S. *Marine Geology* 98, 201–239.
- Eissen, J.-P., Nohara, M., Cotten, J. and Hirose, K. (1994) North Fiji Basin basalts and their magma

- sources: Part I. Incompatible element constraints. *Marine Geology* 116, 153–178.
- Elderfield, H. and Schultz, A. (1996) Mid-ocean ridge hydrothermal fluxes and the chemical composition of the ocean, *Annual Review of Earth and Planetary Sciences* 24, 191-224.
- Fantle, M. S. and Higgins, J. (2014) The effects of diagenesis and dolomitization on Ca and Mg isotopes in marine platform carbonates: Implications for the geochemical cycles of Ca and Mg. *Geochimica et Cosmochimica Acta* 142, 458-481.
- Foster, G. L., Pogge von Strandmann, P. A. E. and Rae, J. W. B. (2010) Boron and magnesium isotopic composition of seawater. *Geochemistry, Geophysics, Geosystems* 11, Q08015.
- Galy, A., Carder, E. and Elderfield, H. (2006) Insights from magnesium isotopic compositions on the Oceanic Hydrothermal Circulation: Is seamount weathering the solution? In *American Geophysical Union*, Fall Meeting 2006, San Francisco, CA, USA.
- Gamo, T., Sakai, H., Kim, E.-S., Shitashima, K. and Ishibashi, J. (1991) High alkalinity due to sulfate reduction in the CLAM hydrothermal field, Okinawa Trough. *Earth and Planetary Science Letters* 107, 328-338.
- Gamo, T., Chiba, H., Fryer, P., Ishibashi, J., Ishii, T., Johnson, L. E., Kelly, K., Masuda, H., Ohta, S., Reysenbach, A.-L., Rona, P. A., Shibata, T., Tamaoka, J., Tanaka, H., Tsunogai, U., Yamaguchi, T., Fujioka, K., (1994) Mariana 1992 diving surveys by Shinkai 6500 (Y9204 cruise): revisits to the mid-Mariana Trough hydrothermal area and discovery of hydrothermal vents in the southern Mariana region. *JAMSTEC Journal of Deep Sea Research* 10, 153–162 (in Japanese with English abstract).
- Gamo, T., Okamura, K., Charlou, J. L., Urabe, T., Auzende, J.-M., Ishibashi, J., Shitashima, K., 1996. Chemical exploration of hydrothermal activity in the Manus Basin, Papua New Guinea (Manus Flux Cruise). *JAMSTEC Journal of Deep Sea Research* 12, 336–345 (in Japanese with English abstract).
- Gamo, T., Okamura, K., Charlou, J.L., Urabe, T., Auzende, J.-M., Ishibashi, J., Shitashima, K., Kodama, Y. and Shipboard Sci. Party of the Manus Flux Cruise (1997a) Acidic and sulfate-rich hydrothermal fluid from the Manus back-arc basin, Papua New Guinea. *Geology* 25, 139–142.
- Gamo, T., Tsunogai, U., Ishibashi, J., Masuda, H. and Chiba, H. (1997b) Chemical characteristics of hydrothermal fluids from the Mariana Trough. *JAMSTEC Journal of Deep Sea Research*, Special volume: Deep Sea Research in Subduction Zones, Spreading Centers and Backarc Basins, JAMSTEC, 69-74, .
- German, C. R. and Von Damm, K. L. (2003) Hydrothermal processes, in *Treatise on Geochemistry*, vol. 6, edited by Elderfield, H., pp. 181-222. Elsevier/Pergamon, Oxford.
- Geske, A., Goldstein, R. H., Mavromatis, V., Richter, D. K., Buhl, D., Kluge, T., John, C. M. and Immenhauser, A. (2015) The magnesium isotope ($\delta^{26}\text{Mg}$) signature of dolomites. *Geochimica et*

- Cosmochimica Acta 149, 131-151.
- Grimaud, D., Ishibashi, J.-I., Lagabriele, Y., Auzende, J.-M. and Urabe, T. (1991) Chemistry of hydrothermal fluids from the 17 S active site on the North Fiji Basin Ridge (SW Pacific). *Chemical Geology* 93, 209-218.
- Halbach, P., Nakamura, K., Wahsner, M., Lange, J., Sakai, H., Kaselitz, L., Hansen, R.-D., Yamano, M., Post, J., Prause, B., Seifert, R., Michaelis, W., Teichmann, F., Kinoshita, M., Marten, A., Ishibashi, J., Czerwinski, S. and Blum, N. (1989) Probable modern analogue of Kuroko-type massive sulphide deposits in the Okinawa Trough back-arc basin. *Nature* 338, 496–499.
- Halbach, P., Pracejus, B. and Marten, A. (1993) Geology and mineralogy of massive sulfide ores from the Central Okinawa Trough, Japan. *Economic Geology* 88, 2210–2225.
- Higgins, J. A. and Schrag, D. P. (2010) Constraining magnesium cycling in marine sediments using magnesium isotopes. *Geochimica et Cosmochimica Acta* 74, 5039-5053.
- Higgins, J. A. and Schrag, D. P. (2015) The Mg isotopic composition of Cenozoic seawater-evidence for a link between Mg-clays, seawater Mg/Ca, and climate. *Earth and Planetary Science Letters* 416, 73-81.
- Holland, H. D. (2005) Sea level, sediments and the composition of seawater, *American Journal of Science* 305, 220-239.
- Hu, Y., Harrington, M. D., Sun, Y., Yang, Z., Konter, J., and Teng, F.-Z. (2016) Magnesium isotopic homogeneity of San Carlos olivine: a potential standard for Mg isotopic analysis by multi-collector inductively coupled plasma mass spectrometry. *Rapid Communications in Mass Spectrometry* 30 (19), 2123–2132.
- Huang, J., Ke, S., Gao, Y., Xiao, Y. and Li, S. (2015) Magnesium isotopic compositions of altered oceanic basalts and gabbros from IODP site 1256 at the East Pacific Rise. *Lithos* 231, 53-61.
- Huang, K.-J., Teng, F.-Z., Plank, T., Staudigel, H., Hu, Y. and Bao, Z.-Y (2018) Magnesium isotopic composition of altered oceanic crust and the global Mg cycle. *Geochimica et Cosmochimica Acta* 238, 357-373.
- Hussong, D. M., and Uyeda, S. (1982) Tectonic processes and the history of the Mariana arc: A synthesis of the results of Deep Sea Drilling Project Leg 60, Initial Reports of the Deep Sea Drilling Project 60, 909–929, Deep Sea Drilling Project, Washington, D.C.
- Ishibashi, J., Grimaud, D., Nojiri, Y., Auzende, J.-M. and Urabe, T. (1994a) Fluctuation of chemical compositions of the phase-separated hydrothermal fluid from the North Fiji Basin Ridge. *Marine Geology* 116, 215–226.
- Ishibashi, J.-I., Wakita, H., Nojiri, Y., Grimaud, D., Jean-Baptiste, P., Gamo, T., Auzende, J.-M. and Urabe, T. (1994b) Helium and carbon geochemistry of hydrothermal fluids from the North Fiji

- Basin spreading ridge (southwest Pacific). *Earth and Planetary Science Letters* 128, 183-197.
- Ishibashi, J., Tsunogai, U., Wakita, H., Watanabe, K., Kajimura, T., Shibata, A., Fujiwara, Y. and Hashimoto, J. (1994c) Chemical composition of hydrothermal fluids from the Suiyo and the Mokuyo Seamounts, Izu-Bonin Arc. *JAMSTEC Journal of Deep Sea Research* 10, 89-97 (in Japanese with English abstract).
- Ishibashi, J., Sano, Y., Wakita, H., Gamo, T., Tsutsumi, M. and Sakai, H. (1995) Helium and carbon geochemistry of hydrothermal fluids from the Mid-Okinawa Trough Back Arc basin, southwest of Japan. *Chemical Geology* 123, 1–15.
- Ishibashi, J.-I., Tsunogai, U., Toki, T., Ebina, N., Gamo, T., Sano, Y., Masuda, H. and Chiba, H. (2015) Chemical composition of hydrothermal fluids in the central and southern Mariana Trough backarc basin. *Deep-sea Research II* 121, 126-136.
- Kato, T., Beavan, J., Matsushima, T., Kotake, Y., Camacho, J. T. and Nakao, S. (2003) Geodetic evidence of back-arc spreading in the Mariana Trough, *Geophysical Research Letters* 30, 1625.
- Kelemen, P. B. Hanghoj, K. and Greene, A. R. (2003) One view of the geochemistry of subduction-related magmatic arcs, with an emphasis on primitive andesite and lower crust. In: Rudnick, R. L. (ed.) *The Crust*, Vol.3. In: Holland, H. D. & Turekian, K. K. (eds) *Treatise on Geochemistry*. Oxford: Elsevier-Pergamon, pp. 593-659.
- Kimura, M., Kaneoka, I., Kato, Y., Yamamoto, S., Kushiro, I., Tokuyama, H., Kinoshita, H., Isezaki, N., Masaki, H., Ohsida, A., Uyeda, S., Hilde, T.W.C. (1986) Report on DELP 1984 cruise in the middle Okinawa Trough, Part V: topography and geology of the central grabens and their vicinity. *Bulletin of the Earthquake Research Institute, the University of Tokyo* 61, 269–310.
- Kurz, M. D., Jenkins, W. J., Schilling, J. G. and Hart, S. R. (1982) Helium isotopic variations in the mantle beneath the central North Atlantic Ocean. *Earth and Planetary Science Letters* 58, 1-14.
- Li, W.-Y., Teng, F.-Z., Wing, B. A. and Xiao, Y. (2014) Limited magnesium isotope fractionation during metamorphic dehydration in metapelites from the Onawa contact aureole, Maine. *Geochemistry, Geophysics, Geosystems* 15, 408-415.
- Li, W., Beard, B. L., Li, C., Xu, H. and Johnson, C. M. (2015) Experimental calibration of Mg isotope fractionation between dolomite and aqueous solution and its geological implications. *Geochimica et Cosmochimica Acta* 157, 164–181.
- 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.
- Lisitsyn, A. P., Crook, K. A. W., Bogdanov, Yu. A., Zonenshayn, L. P., Murav'yev, K. G., Tufar, W., Gurvich, Y. G., Gordeyev, V. V. and Ivanov, G. V. (1993) A hydrothermal field in the rift zone of the Manus Basin, Bismarck Sea. *International Geology Review* 35, 105–126.

- Martinez, F. and Taylor, B. (1996) Backarc spreading, rifting, and microplate rotation, between transform faults in the Manus Basin. *Marine Geophysical Researches* 18, 203–224.
- Marumo, K., Urabe, T., Goto, A., Takano, Y. and Nakaseama, M. (2008) Mineralogy and isotope geochemistry of active submarine hydrothermal field at Suiyo Seamount, Izu-Bonin Arc, West Pacific Ocean. *Resource Geology* 58, 220-248.
- Milliman, J. D., (1974) *Marine Carbonates-Recent Sedimentary Carbonates*, Part I, Berlin, Springer-Verlag, 375 p.
- Mottl, M. J. and Wheat, C. G. (1994) Hydrothermal circulation through mid-ocean ridge flanks: Fluxes of heat and magnesium. *Geochimica et Cosmochimica Acta*, 58, 2225-2237.
- Nagaoka, N., Kasuga, S. and Kato, Y. (1992) Geology of Mokuyo Smt., Doyo Smt., and Suiyo Smt. in the Shichiyo Seamounts on the Ogasawara Arc. *Proceeding of JAMSTEC Symposium on Deep Sea Research* 8, 237–248 (in Japanese with English abstract).
- Noguchi, T., Shinjo, R., Ito, M., Takada, J. and Oomori, T. (2011) Barite geochemistry from hydrothermal chimneys of the Okinawa Trough: insight into chimney formation and fluid/sediment interaction. *Journal of Mineralogical and Petrological Sciences*, 106(1), 26-35.
- Nohara, M., Hirose, K., Eissen, J.-P., Urabe, T. and Joshima, M. (1994) The North Fiji Basin basalts and their magma sources: Part II. Sr-Nd isotopic and trace element constraints. *Marine Geology* 116, 179–195.
- Paulick, H., Vanko, D. A., and Yeats, C. (2004) Drill core-based facies reconstruction of a deep-marine, felsic volcano hosting an active hydrothermal system (Pual Ridge, Papua New Guinea, ODP Leg 193): *Journal of Volcanology and Geothermal Research* 130, 31–50.
- Paulick, H. and Bach, W. (2006) Phyllosilicate alteration mineral assemblages in the active subsea-floor PACMANUS hydrothermal system, Papua New Guinea, ODP Leg 193. *Economic Geology* 101, 633-650.
- Reeves, E. P., Seewald, J. S., Saccocia, P., Bach, W., Craddock, P. R., Shanks, W. C., Sylva, S. P., Walsh, E., Pichler, T. and Rosner, M. (2011), Geochemistry of hydrothermal fluids from the PACMANUS, Northeast Pual and Vienna Woods hydrothermal fields, Manus Basin, Papua New Guinea, *Geochimica et Cosmochimica Acta* 75, 1088–1123.
- Ryu, J.-S., Vigier, N., Decarreau, A., Lee, S.-W., Lee, K.-S., Song, H. and Petit, S. (2016) Experimental investigation of Mg isotope fractionation during mineral dissolution and clay formation. *Chemical Geology* 445, 135-145.
- Sakai, H., Gamo, T., Kim, E.S., Shitashima, K., Yanagisawa, F., Tsutsumi, M., Ishibashi, J., Sano, Y., Wakita, H. and Tanaka, T. (1990a) Unique chemistry of the hydrothermal solution in the mid-Okinawa Trough Backarc Basin. *Geophysical Research Letters* 17, 2133-2136.

- Sakai, H., Gamo, T., Kim, E.-S., Tsutsumi, M., Tanaka, T., Ishibashi, J., Wakita, H., Yamano, M., Oomori, T., (1990b) Venting of carbon dioxide-rich fluid and hydrate formation in Mid-Okinawa Trough backarc basin. *Science* 248, 1093–1096.
- Seyfried, W. and Bischoff, J. L. (1977) Hydrothermal transport of heavy metals by seawater: the role of seawater/basalt ratio. *Earth and Planetary Science Letters* 34, 71-77.
- Seyfried Jr, W. E. and Bischoff, J. L. (1979) Low temperature basalt alteration by seawater: an experimental study at 70°C and 150°C. *Geochimica et Cosmochimica Acta* 43, 1937-1947.
- Seyfried Jr, W. E. and Mottl, M. J. (1982) Hydrothermal alteration of basalt by seawater under seawater-dominated conditions. *Geochimica et Cosmochimica Acta* 46, 985-1002.
- Su, B. X., Teng, F. Z., Hu, Y., Shi, R. D., Zhou, M. F., Zhu, B., Liu, F., Gong, X., Huang, Q., Xiao, Y., Chen, C. and He, Y. (2015) Iron and magnesium isotope fractionation in oceanic lithosphere and sub-arc mantle: Perspectives from ophiolites. *Earth and Planetary Science Letters* 430, 523-532.
- Tanahashi, M., Kisimoto, K., Joshima, M., Jarvis, P., Iwabuchi, Y., Ruellan, E. and Auzende, J.-M. (1994), 800-km-long N-S spreading system of the North Fiji Basin, *Marine Geology* 116, 5–24.
- Taylor, B., Crook, K. and Sinton, J. (1994) Extensional transform zones and oblique spreading centers, *Journal of Geophysical Research* 99, 19,707–19,718.
- 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.
- Teng, F.-Z. (2017) Magnesium isotope geochemistry. *Reviews in Mineralogy and Geochemistry* 82, 219-287.
- 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.
- Tregoning, P. (2002) Plate kinematics in the western Pacific derived from geodetic observations. *Journal of Geophysical Research* 107(B1), 2020, doi: 10.1029/2001JB000406.
- Tsunogai, U., Ishibashi, J., Wakita, H., Gamo, T., Watanabe, K., Kajimura, T., Kanayama, S., and Sakai, H., (1994) Peculiar features of Suiyo Seamount hydrothermal fluids, Izu-Bonin Arc: Differences from subaerial volcanism. *Earth and Planetary Science Letters* 126, 289–301.
- Tufar, W. (1990) Modern hydrothermal activity, formation of complex massive sulfide deposits and associated vent communities in the Manus Back-Arc Basin (Bismarck Sea, Papua New Guinea), *Mitteilungen der Österreichischen Geologischen Gesellschaft* 82, 183-210.
- Wimpenny, J., Gíslason, S. R., James, R. H., Gannoun, A., Pogge Von Strandmann, P. A. E., and Burton, K. W. (2010) The behavior of Li and Mg isotopes during primary phase dissolution and secondary

- mineral formation in basalt. *Geochimica et Cosmochimica Acta* 74, 5259-5279.
- Wimpenny, J., Harvey, J. and Yin, Q. (2012) The effects of serpentinization on Mg isotopes in Mid-Atlantic ridge peridotite. American Geophysical Union Fall Meeting, San Francisco
- Wimpenny, J., Colla, C. A., Yin, Q.-Z., Rustad, J. R. and Casey, W. H. (2014) Investigating the behaviour of Mg isotopes during the formation of clay minerals. *Geochimica et Cosmochimica Acta* 128, 178-194.
- Yamaoka, K., Hong, E., Ishikawa, T., Gamo, T. and Kawahata, H. (2015) Boron isotope geochemistry of vent fluids from arc/back-arc seafloor hydrothermal systems in the western Pacific, *Chemical Geology*, 392, 9-18.
- Yoshimura, T., Araoka, D., Tamenori, Y., Kuroda, J., Kawahata, H. and Ohkouchi, N. (2018) Lithium, magnesium and sulfur purification from seawater using an ion chromatograph with a fraction collector system for stable isotope measurements, *Journal of Chromatography A*, 1531, 157-162.
- Yuasa, M. (1985) Sofugan tectonic line, a new tectonic boundary separating northern and southern parts of the Ogasawara (Bonin) Arc, northwest Pacific in Formation of active ocean margin, edited by Nasu, N., Kobayashi, K., Uyeda, S., Kushiro, K. and Kagami, H, Terrapub, Tokyo, 483-496.

Chapter III

- Akizawa, N., Ozawa, K., Tamura, A., Michibayashi, K. and Arai, S. (2016) Three-dimensional evolution of melting, heat and melt transfer in ascending mantle beneath a fast-spreading ridge segment constrained by trace elements in clinopyroxenes from concordant dunites and host harzburgites of the Oman ophiolite. *Journal of Petrology* 57, 777-814.
- Alt, J. C. (1995) Subseafloor processes in mid-ocean ridge hydrothermal systems, Seafloor Hydrothermal Systems, In Physical, Chemical, Biological, and Geological Interactions. Geophysical Monograph 91, S. E. Humphris et al., 85-114, AGU, Washington, D. C.
- Ayers, J. C., Dittmer, S. K., Graham, D. L. (1997) Partitioning of elements between peridotite and H₂O at 2.0-3.0 GPa and 9000-1100°C, and application to models of subduction zone processes. *Earth and Planetary Science Letters* 150, 381-398.
- Beinlich, A., Mavromatis, V., Austrheim H and Oelkers E. H. (2014) Inter-mineral Mg isotope fractionation during hydrothermal ultramafic rock alteration-Implications for the global Mg-cycle. *Earth and Planetary Science Letters* 392, 166-176.
- Bosch, D., Jamais, M., Boudier, F., Nicolas, A., Dautria, J.-M., and Agrinier, P. (2004) Deep and high-temperature hydrothermal circulation in the Oman ophiolite: Petrological and isotopic evidence. *Journal of Petrology*, 45(6), 1181-1208.
- Boudier, F. and Coleman, R. G. (1981) Cross-section through the peridotite in the Samail ophiolite,

- southeastern Oman mountains. *Journal of Geophysical Research* 88, 2573-2592.
- Boudier, F. Ceuleneer, G., and Nicolas, A. (1988) Shear zones, thrusts and related magmatism in the Oman ophiolite: Initiation of thrusting on an oceanic ridge. *Tectonophysics* 151, 275-296.
- Braun, M. G. and Kelemen, P. B. (2002) Dunite distribution in the Oman ophiolite: Implications for melt flux through porous dunite conduits. *Geochemistry Geophysics Geosystems* 3, 1-21.
- Brenot, A., Cloquet, C., Vigier, N., Carignan, J., and France-Lanord, C. F. (2008) Magnesium isotope systematics of the lithologically varied Moselle river basin, France. *Geochimica et Cosmochimica Acta* 72, 5070-5089.
- Coleman, R. G. (1977) *Ophiolites*, Springer-Verlag, New York.
- Fantle, M.S. and Higgins, H. (2014) The effects of diagenesis and dolomitization on Ca and Mg isotopes in marine platform carbonates: Implications for the geochemical cycles of Ca and Mg. *Geochimica et Cosmochimica Acta* 142, 458-481.
- Godard, M. Jousselin, D. and Boudinier, J. -L. (2000) Relationships between geochemistry and structure beneath a paleo-spreading centre: a study of the mantle section in the Oman ophiolite. *Earth and Planetary Science Letters* 180, 133-148.
- Gaffin, S. (1987), Ridge volume dependence on seafloor generation rate and inversion using long term sealevel change. *American Journal of Science* 287, 596-611.
- German, C. R. and Von Damm, K. L. (2003) Hydrothermal processes, in *Treatise on Geochemistry*, vol. 6, edited by Elderfield, H., pp. 181-222. Elsevier/Pergamon, Oxford.
- Geske, A., Goldstein, R. H., Mavromatis, V., Richter, D. K., Buhl, D., Kluge, T., John, C. M. and Immenhauser, A. (2015) The magnesium isotope ($\delta^{26}\text{Mg}$) signature of dolomites. *Geochimica et Cosmochimica Acta* 149, 131-151.
- Gothmann, A.M., Stolarski, J., Adkins, J.F. and Higgins, J.A. (2017) A Cenozoic record of seawater Mg isotopes in well-preserved fossil corals. *Geology* 45, 1039-1042.
- Gregory, R. T. and Taylor, H. P. (1981) An oxygen isotope profile in a section of Cretaceous oceanic crust, Samail ophiolite, Oman: evidence for $\delta^{18}\text{O}$ buffering of the oceans by deep (>5km) seawater-hydrothermal circulation at mid-ocean ridges. *Journal of Geophysical Research* 86, 2737-2755.
- Hacker, B. R. and Mosenfelder, J. L. (1996) Metamorphism and deformation along the emplacement thrust of the Samail ophiolite, Oman. *Earth and Planetary Science Letter* 144, 435-451.
- Hanhøj, K. Kelemen, P. B., Hassler, D. and Godard, M. (2010) Composition and genesis of depleted mantle peridotites from the wadi Tayin massif, Oman ophiolite; Major and trace element geochemistry, and Os isotope and PGE systematics. *Journal of Petrology* 51, 201-227.
- Hara, K. and Kurihara, T. (2017) Radiolarian age and lithostratigraphy of late Cretaceous pelagic sediments overlying basaltic extrusive rocks, northern Oman mountains. *Ofioliti* 42 (1), 21-38.

- Hara, K (2017) Radiolarian biostratigraphy of Late Cretaceous pelagic sediments in the Oman Ophiolite: Environmental change based on the radiolarian faunal transition across the Cenomanian/Turonian boundary. Doctoral thesis of Niigata university, Japan.
- Hardie, L. A. (1996) Secular variation in seawater chemistry: An explanation for the coupled secular variation in the mineralogies of marine limestones and potash evaporates over the past 600 m.y. *Geology* 24, 279-283.
- Hasebe, S. (2001) Ocean-floor metamorphism and phase analyses of Oman ophiolite. M.S. thesis of the Kochi university, Japan.
- Higgins, J. A. and Schrag, D. P. (2010) Constraining magnesium cycling in marine sediments using magnesium isotopes. *Geochimica et Cosmochimica Acta* 74, 5039-5053.
- Higgins, J. A. and Schrag, D. P. (2012) Records of Neogene seawater chemistry and diagenesis in deep-sea carbonate sediments and pore fluids. *Earth and Planetary Science Letters* 357-358, 386-396.
- Higgins, J. A. and Schrag, D. P. (2015) The Mg isotopic composition of Cenozoic seawater – evidence for a link between Mg-clays, seawater Mg/Ca, and climate. *Earth and Planetary Science Letters* 416, 73-81.
- Hippler, D., Buhl, D., Witbaard, R., Richter, D. K. and Immenhauser, A. (2009) Towards a better understanding of magnesium isotope ratios from marine skeletal carbonates. *Geochimica et Cosmochimica Acta* 73, 6134-6146.
- Holland, H. D., Lazar, B. and McCaffrey, M. (1986) Evolution of the atmosphere and oceans. *Nature* 320, 27-33.
- Hu, Y., Teng, F.-Z., Zhang, H.-F., Xiao, Y., and Su, B.-X. (2016) Metasomatism-induced mantle magnesium isotopic heterogeneity: Evidence from pyroxenites. *Geochimica et Cosmochimica Acta* 185, 88-111.
- Huang, F., Zhang, Z., Lundstrom, C. C., and Zhi, X. (2011) Iron and magnesium isotopic compositions of peridotite xenoliths from Eastern China. *Geochimica et Cosmochimica Acta* 164, 298-317.
- Huang, J., Ke, S., Gao, Y., Xiao, Y. and Li, S. (2015) Magnesium isotopic compositions of altered oceanic basalts and gabbros from IODP site 256 at the East Pacific Rise. *Lithos* 231, 53-61.
- Huang, K.-J., Teng, F.-Z., Plank, T., Staudigel, H., Hu, Y. and Bao, Z.-Y (2018) Magnesium isotopic composition of altered oceanic crust and the global Mg cycle. *Geochimica et Cosmochimica Acta* 238, 357-373.
- Ishikawa, T., Fujisawa, S., Nagaishi, K., and Masuda, T. (2005) Trace element characteristics of the fluid liberated from amphibolite-facies slab: Influence from the metamorphic sole beneath the Oman ophiolite and implication for boninite genesis. *Earth and Planetary Science Letters* 240, 355-377.

- Kanke, N. and Takazawa, E. (2014) A kilometre-scale highly refractory harzburgite zone in the mantle section of the northern Oman ophiolite (Fizh Block): implications for flux melting of oceanic lithosphere mantle. *Geological Society, London, Special Publications* 392, 229-246.
- Kawahata H., Nohara M., Ishizuka H., Hasebe S. and Chiba H. (2001) Sr isotope geochemistry and hydrothermal alteration of the Oman ophiolite. *Journal of Geophysical Research* 106, 11083-11099.
- Khedr, M. Z., Arai, S., Python, M., and Tamura, A. (2014) Chemical variations of abyssal peridotites in the central Oman ophiolite: Evidence of oceanic mantle heterogeneity. *Gondwana Research* 25, 1242–1262.
- Koepke, J., Berndt, J., Feig, S. T., and Holtz, F. (2007) The formation of SiO₂-rich melts within the deep oceanic crust by hydrous partial melting of gabbros. *Contributions to Mineralogy and Petrology* 153, 67-84.
- Lai, Y.-J., Pogge von Strandmann, P. A. E., Dohmen, R., Takazawa, E., and Elliot, T. (2015) The influence of melt infiltration on the Li and Mg isotopic composition of the Horoman Peridotite Massif. *Geochimica et Cosmochimica Acta* 164, 318-332.
- Lanphere, M. A., Coleman, R. G. and Hopson, C. A. (1981) Sr isotopic tracer study of the Samail ophiolite, Oman. *Journal of Geophysical Research* 86(B4), 2709-2720.
- Li, W.-Y., Teng, F.-Z., and Xiao, Y. (2018) Magnesium isotope record of fluid metasomatism along the slab-mantle interface in subduction zones. *Geochimica et Cosmochimica Acta* 237, 312-319.
- Li, W., Chakraborty, S., Beard, B. L., Romanek, C. S., and Johnson, C. M. (2012). Magnesium isotope fractionation during precipitation of inorganic calcite under laboratory conditions. *Earth and Planetary Science Letters* 333-334, 304-316.
- Li, W.-Y., Teng, F.-Z., Wing, B. A., Xiao, Y. (2014) Limited magnesium isotope fractionation during metamorphic dehydration in metapelites from the Onawa contact aureole, Maine. *Geochemistry Geophysics Geosystems* 15, 408-415.
- 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.
- Lippard, S. J., Shelton, A. W. and Gass, I. G. (1986) *The Ophiolite of Northern Oman*. Geological Society, London, Memoirs, 178 pp.
- Liu, P.-P., Teng, F.-Z., Dick, H. J. B., Zhou, M.-F., and Chung, S.-L. (2017) Magnesium isotopic composition of the oceanic mantle and oceanic Mg cycling. *Geochimica et Cosmochimica Acta* 206, 151-165.
- Machel, H.G. (2004) Concepts and models of dolomitization: a critical reappraisal. In *The Geometry*

- and Petrogenesis of Dolomite Hydrocarbon Reservoirs. Eds. C. J. R. Braithwaite, G. Rizzi and G. Darke. Geological Society, Special Publication, London, 235(1), 7-63.
- Manning, C. E. (2004) The chemistry of subduction-zone fluids. *Earth and Planetary Science Letters* 223, 1-16.
- Mavromatis, V., Meister, P., and Oelkers, E.H. (2014) Using stable Mg isotopes to distinguish dolomite formation mechanisms: A case study from the Peru Margin. *Chemical Geology* 385, 84-91.
- McCulloch, M. T., Gregory, R. T., Wasserburg, G. J., and Taylor, H. P. (1981) Sm-Nd, Rb-Sr and $^{18}\text{O}/^{16}\text{O}$ isotopic systematics in an oceanic crustal section: evidence from the Samail ophiolite. *Journal of Geophysical Research* 86, 2721-2735.
- Monnier, C., Girardeau, J., Le Mée, L. and Polvé, M. (2006) Along-ridge petrological segmentation of the mantle in the Oman ophiolite. *Geochemistry Geophysics Geosystems* 7(11), Q11008.
- Mottl, M. J. and Wheat, C. G. (1994) Hydrothermal circulation through mid-ocean ridge flanks: Fluxes of heat and magnesium. *Geochimica et Cosmochimica Acta*, 58, 2225-2237.
- Munnecke, A., and Samtleben, C. (1996) The formation of micritic limestones and the development of limestone-marl alternations in the Silurian of Gotland, Sweden. *Facies* 34, 159-176.
- Nicolas, A. (1989) *Structure of Ophiolites and Dynamics of the Oceanic Lithosphere*. Kluwer Acad., Norwell Mass.
- Nicolas, A., Boudier, F., Ildefonse, B. and Ball, E. (2000) Accretion of Oman and United Arab Emirates ophiolite: Discussion of a new structural map. *Marine Geophysical Researches* 21, 147-179.
- Pogge von Strandmann, P. A. E. (2008) Precise magnesium isotope measurements in core top planktic and benthic foraminifera. *Geochemistry Geophysics Geosystems* 9, 1-13.
- Prigent, C., Guillot, S., Agard, P., Lemarchand, D., Soret, M., and Ulrich, M. (2018) Transfer of subduction fluids into the deforming mantle wedge during nascent subduction: Evidence from trace elements and boron isotopes (Semail ophiolite, Oman). *Earth and Planetary Science Letters* 484, 213-228.
- Richter, F. M., Watson, E. B., Mendybaev, R., Dauphas, N., Georg, B., Watkins, J., and Valley, J. (2009) Isotopic fractionation of the major elements of molten basalt by chemical and thermal diffusion, *Geochimica et Cosmochimica Acta* 73, 4250-4263.
- Richter, F. M., Watson, E. B., Mendybaev, R., Teng, F. Z., and Janney, P. E. (2008) Magnesium isotope fractionation in silicate melts by chemical and thermal diffusion, *Geochimica et Cosmochimica Acta* 72, 206-220.
- Robertson, A. H. F. and Hudson, J. D. (1974) Pelagic sediments in the Cretaceous and Tertiary history of the Troodos Massif, Cyprus. In: K. J. Hsü and H. C. Jenkyns (Eds.), *Pelagic sediments: on land and under the Sea*. The International Association of Sedimentologists. 403-326.

- Stakes, D. S., and Taylor, H. P. (1992) The northern Semail ophiolite: an oxygen isotope, microprobe, and field study. *Journal of Geophysical Research* 97(B5), 7043-7080.
- Searle, M. P. and Cox, J. (1999) Tectonic setting, origin, and obduction of the Oman ophiolite. *Bulletin of the Geological Society of America* 111, 104-122.
- Searle, M. P. and Cox, J. (2002) Subduction zone metamorphism during formation and emplacement of the Semail ophiolite in the Oman mountains: *Geology Magazine* 139, 241-255.
- Searle, M. P. and Malpas, J. (1982) Petrochemistry and origin of sub-ophiolitic metamorphic and related rocks in the Oman Mountains, *Journal of the Geological Society* 139, 235-248.
- Seyfried, W. E., Shanks, W. C., and Dibble, W. E. (1978) Clay mineral formation in DSDP Leg 34 basalt. *Earth and Planetary Science Letters* 41, 265-276.
- Soret, M., Agard, P., Dubacq, B., Plunder, A. and Yamato, P. (2017) Petrological evidence for stepwise accretion of metamorphic soles during subduction infancy (Semail ophiolite, Oman and UAE). *Journal of Metamorphic Geology* 35, 1051-1080.
- Takazawa, E., Okayasu, T., and Satoh, K. (2003) Geochemistry and origin of the basal lherzolites from the northern Oman ophiolite (northern Fizz block). *Geochemistry Geophysics Geosystems* 4(2), 1021.
- 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. (2006) The magnesium isotope budget of the modern ocean: Constraints from riverine magnesium isotope ratios. *Earth and Planetary Science Letters* 250, 241-253.
- Umino, S., and Kushiro, I. (1989) Experimental studies on boninite petrogenesis, in *Boninite and related rocks*. Ed. A. J. Crawford, Unwin Hymn, London, 89-111.
- van der Laan, S. R., Flower, J. F. J., and van Groos, A. F. K. (1989) Experimental evidence for the origin of boninites: Near-liquidus phase relations to 7.5 kbar, in *Boninite and related rocks*. Ed. A. J. Crawford, Unwin Hymn, London, 112-147.
- Von Damm, K. L., Edmond, J. M., Grant, B., Measures, C. I., Walden, B. and Weiss, R. F. (1985) Chemistry of submarine hydrothermal solutions at 21°N, East Pacific Rise. *Geochimica et Cosmochimica Acta* 49, 2197-2220.
- Wang, S.-J., Teng, F.-Z., Williams, H. M., and Li, S. G. (2012) Magnesium isotopic variations in cratonic eclogites: origins and implications. *Earth and Planetary Science Letters* 359-360, 219-226.
- Wang, S.-J., Teng, F.-Z., Li, S.-G. (2014) Tracing carbonate-silicate interaction during subduction using magnesium and oxygen isotopes. *Nature communications* 5, 5328.

- Xiao, Y., Teng, F.-Z., Zhang, H.-F., and Yang, W. (2013) Large magnesium isotope fractionation in peridotite xenoliths from eastern North China craton: Product of melt-rock interaction. *Geochimica et Cosmochimica Acta* 115, 241-261.
- Yang, W., Teng, F.-Z., Zhang, H.-F., and Li, S.-G. (2012) Magnesium isotopic systematics of continental basalts from the North China Craton: implications for tracing subducted carbonate in the mantle. *Chemical Geology* 328, 185-194.
- Yamaoka, K., Ishikawa, T., Matsubaya, O., Ishiyama, D., Nagaishi, K., Hiroyasu, Y., Chiba, H. and Kawahata, H. (2012) Boron and oxygen isotope systematics for a complete section of oceanic crustal rocks in the Oman ophiolite. *Geochimica et Cosmochimica Acta* 84, 543-559.
- Yokoyama, T., Makishima, A. and Nakamura, E. (1999) Evaluation of the coprecipitation of incompatible trace elements with fluoride during silicate rock dissolution by acid digestion. *Chemical Geology* 157, 175-187.
- Yoshikawa, M., Python, M., Tamura, A., Arai, S., Takazawa, E., Shibata, T., Ueda, A., and Sato, T. (2015) Melt extraction and metasomatism recorded in basal peridotites above the metamorphic sole of the northern Fizh massif, Oman ophiolite. *Tectonophysics* 650, 53–64.
- Yoshimura, T., Tanimizu, M., Inoue, M., Suzuki, A., Iwasaki, N., and Kawahata, H. (2011). Mg isotope fractionation in biogenic carbonates of deep-sea coral, benthic foraminifera, and hermatypic coral. *Analytical and Bioanalytical Chemistry* 401(9), 2755-2769.
- Young, E. D., and Galy, A. (2004) The isotope geochemistry and cosmochemistry of magnesium. In *Geochemistry of Non-traditional Stable Isotopes. Reviews in Mineralogy & Geochemistry*. Eds C. M. Hohnson, B. L. Beard and F. Albarede. Mineralogical Society of America, 197-230.

Chapter IV

- Akizawa, N., Arai, S., Tamura, A., Uesugi J. and Python M. (2011) Crustal diopsidites from the northern Oman ophiolite: Evidence for hydrothermal circulation through suboceanic Moho. *Journal of Mineralogical and Petrological Sciences* 106, 261-266.
- Akizawa, N., Arai, S. and Tamura, A. (2012) Behavior of MORB magmas at uppermost mantle beneath a fast-spreading axis: an example from Wadi Fizh of the northern Oman ophiolite. *Contributions to Mineralogy and Petrology* 164, 601-625.
- Akizawa, N., Ozawa, K., Tamura, A., Michibayashi, K. and Arai, S. (2016a) Three-dimensional evolution of melting, heat and melt transfer in ascending mantle beneath a fast-spreading ridge segment constrained by trace elements in clinopyroxenes from concordant dunites and host harzburgites of the Oman ophiolite. *Journal of Petrology* 57, 777-814.
- Akizawa, N., Tamura, A., Fukushi, K., Yamamoto, J., Mizukami, T., Python, M. and Arai, S. (2016b) High-temperature hydrothermal activities around suboceanic Moho: An example from diopsidite

- and anorthosite in Wadi Fizh, Oman ophiolite. *Lithos* 263, 66-87.
- Alt, J. C., Shanks, W. C. and Jackson, M. C. (1993) Cycling of sulfur in subduction zones: The geochemistry of sulfur in the Mariana island arc and back-arc trough. *Earth and Planetary Science Letters* 119, 477-494.
- Alt, J. C. and Shanks, W. C. (1998) Sulfur in serpentinitized oceanic peridotites: Serpentinization processes and microbial sulfate reduction. *Journal of Geophysical Research: Solid Earth* 103 (5), 9917-9929.
- Alt, J. C. and Shanks, W. C. (2003) Serpentinization of abyssal peridotites from the MARK area, Mid-Atlantic Ridge: sulfur geochemistry and reaction modeling. *Geochimica et Cosmochimica Acta* 67 (4), 641-653.
- Alt, J. C. and Shanks, W. C. (2006) Recycling of water, carbon, and sulfur during subduction of serpentinites: A stable isotope study of Cerro del Almirez, Spain. *Earth and Planetary Science Letters* 327-328, 50-60.
- Alt, J. C., Shanks, W. C., Bach, W., Paulick, H., Garrido, C. J. and Beaudin, G. (2007) Hydrothermal alteration and microbial sulfate reduction in peridotite and gabbro exposed by detachment faulting at the Mid-Atlantic Ridge, 15°20'N (ODP Leg 209): A sulfur and oxygen isotope study. *Geochemistry Geophysics Geosystems* 8 (8), Q08002.
- Alt, J. C., Garrido, C. J., Shanks, W. C., Turchyn, A., Padrón-Navarta, J. A., Sánchez-Vizcaíno, V. L., Pugnaire, M. T. G. and Marchesi, C. (2012) Recycling of water, carbon, and sulfur during subduction of serpentinites: A stable isotope study of Cerro del Almirez, Spain. *Earth and Planetary Science Letters* 327-328, 50-60.
- Anders, E., and Grevesse, N. (1989) Abundances of the elements: Meteoritic and solar, *Geochimica et Cosmochimica Acta* 53, 197-214.
- Asimow, P. D. (1999) A model that reconciles major- and trace-element data from abyssal peridotites. *Earth and Planetary Science Letters* 169, 303-319.
- Bach, W., Garrido, C. J., Paulick, H., Harvey, J. and Rosner, M. (2004) Seawater-peridotite interactions: First insight from ODP Leg 209, MAR 15°N. *Geochemistry Geophysics Geosystems* 5 (9), Q09F26.
- Benn, K., Nicolas, A. and Reuber, I. (1988) Mantle-crust transition zone and origin of wehrlitic magmas, Evidence of Oman Ophiolite. *Tectonophysics* 151, 75-85.
- Benoit, M., Ceuleneer, G. and Polvé, M. (1999) The remelting of hydrothermally altered peridotite at mid-ocean ridges by intruding mantle diapirs. *Nature* 402, 514-518.
- Bosch, D., Jamais, M., Boudier, F., Nicolas, A., Dautria, J.-M., and Agrinier, P. (2004) Deep and high-temperature hydrothermal circulation in the Oman ophiolite: Petrological and isotopic evidence.

- Journal of Petrology, 45(6), 1181-1208. doi:10.1093/petrology/egh010
- Boschi, C., Dini, A., Früh-Green, G. L. and Kelley, D. S. (2008) Isotopic and element exchange during serpentinization and metasomatism at the Atlantis Massif (MAR 30°N): Insights from B and Sr isotope data. *Geochimica et Cosmochimica Acta* 72, 1801-1823.
- Boudier, F., Ceuleneer, G. and Nicolas, A. (1988) Shear zones, thrusts and related magmatism in the Oman ophiolite: Initiation of thrusting on an oceanic ridge. *Tectonophysics* 151, 275-296.
- Boudier, F., Godard, M. and Ambruster, C. (2000) Significance of noritic gabbros in the gabbro section of the Oman ophiolite. *Marine Geophysical Research* 21, 307-326.
- Brique, L., Mevel, C., and Boudier, F. (1991) Sr, Nd and Pb isotopic constraints in the genesis of a calc-alkaline plutonic suite in the Oman ophiolite related to the obduction process. In Peters T., Nicolas, A., and Coleman, R. G. (eds) *Ophiolite genesis and evolution of the oceanic lithosphere*. Kluwer, The Netherlands, pp 517-542.
- Canfield, D. E., Raiswell, R., Westrich, J. T., Reaves, C. M. and Berner, R. A. (1986) The use of chromium reduction in the analysis of reduced inorganic sulfur in sediments and shales. *Chemical Geology* 54, 149-155.
- Cowan, R. J., Searle, M. P. and Waters, D. J. (2014) Structure of the metamorphic sole to the Oman ophiolite, Sumeini Window and Wadi Tayin: Implications for ophiolite obduction processes. *In* Rollinson, H. R., Searle, M. P., Abbasi, I. A., Al-Lazki, A. and Kindi, M. H. (eds.) *Tectonic Evolution of the Oman Mountains*. Geological Society of London, Special Publication 392, 155-175.
- Cox, J., Searle, M. and Pedersen, R. (1999) The petrogenesis of leucogranitic dykes intruding the northern Semail ophiolite, United Arab Emirates: field relationship, geochemistry and Sr/Nd isotope systematics. *Contributions to Mineralogy and Petrology* 137, 267-287.
- Delacour, A., Früh-Green, G. L., Frank, M., Gutjahr, M. and Kelley, D. S. (2006) Sr- and Nd-isotope geochemistry of the Atlantis Massif (30°N, MAR): Implications for fluid fluxes and lithospheric heterogeneity. *Chemical Geology* 254, 19-35.
- Delacour, A., Früh-Green, G. L., Bernasconi, S. M. and Kelly, D. S. (2008) Sulfur in peridotites and gabbros at Lost City (30°N, MAR): Implications for hydrothermal alteration and microbial activity during serpentinization. *Geochimica et Cosmochimica Acta* 72, 5090-5110.
- Deschamps, F., Godard, M., Guillot, S. and Hattori, K. (2013) Geochemistry of subduction zone serpentinites; A review, *Lithos* 178, 96-127.
- de Hoog, J. C. M., Taylor, B. E. and van Bergen, M. J. (2001) Sulfur isotope systematics of basaltic lavas from Indonesia: Implications for the sulfur cycle in subduction zones. *Earth and Planetary Science Letters* 298, 1-13.

- Dilek, Y. and Flower, M. F. J. (2003) Arc-trench rollback and forearc accretion: 2. A model for ophiolites in Albania, Cyprus, and Oman. In *Ophiolite in Earth History* (Dilek, Y. and Robinson, P. T., Eds). Geological Society, London, Special Publications 218, 43-68.
- Dilek, Y. and Furnes, H. (2011) Ophiolite genesis and global tectonics: Geochemical and tectonic fingerprinting of ancient oceanic lithosphere, *Geological Society of America Bulletin* 123, 387-411.
- Dygert, N., Kelemen, P. B. and Liang, Y. (2017) Spatial variations in cooling rate in the mantle section of the Samail ophiolite in Oman: Implications for formation of lithosphere at mid-ocean ridges. *Earth and Planetary Science Letters* 465, 134-144.
- Elderfield, H. and Schultz, A. (1996) Mid-ocean ridge hydrothermal fluxes and the chemical composition of the ocean. *Annual Review of Earth and Planetary Sciences* 24, 191-224.
- Foustoukos, D., Savov, I. P. and Janecky D. R. (2008) Chemical and isotopic constraints on water/rock interactions at the Lost City hydrothermal field, 30°N Mid-Atlantic Ridge. *Geochimica et Cosmochimica Acta* 72, 5457-5474.
- Garuti, G., Alfonso, P., Proenza, J. A., and Zaccarini, F. (2009) Sulfur-isotope variations in sulfide minerals from massive sulfide deposits of the northern Apennine ophiolites: inorganic and biogenic constraints. *Ophioliti* 34, 43-62.
- Godard, M. Joussetin, D. and Boudinier, J. -L. (2000) Relationships between geochemistry and structure beneath a paleo-spreading centre: a study of the mantle section in the Oman ophiolite. *Earth and Planetary Science Letter* 180, 133-148.
- Godard, M., Bosch, D. and Einaudi, F. (2006) A MORB source for low-Ti magmatism in the Semail ophiolite. *Chemical Geology* 234, 58-78.
- Gregory, R. T. (2003) Ophiolites and global geochemical cycles: implications for the isotopic evolution of seawater. In *Ophiolites in Earth History* (Dilek, Y and Robinson P. T., Eds) Geological Society, London, Special publications 218, 353-368.
- Hanghøj, K. Kelemen, P. B., Hassler, D. and Godard, M. (2010) Composition and genesis of depleted mantle peridotites from the wadi Tayin massif, Oman ophiolite; Major and trace element geochemistry, and Os isotope and PGE systematics. *Journal of Petrology* 51, 201-227.
- Ishikawa, T., Nagaishi, K. and Umino, S. (2002) Boninitic volcanism in the Oman ophiolite: Implications for thermal condition during transition from spreading ridge to arc. *Geology* 30, 899-902.
- Ishikawa, T., Fujisawa, S., Nagaishi, K. and Masuda, T. (2005) Trace element characteristics of the fluid liberated from amphibolite-facies slab: Influence from the metamorphic sole beneath the Oman ophiolite and implication for boninite genesis. *Earth and Planetary Science Letters* 240, 355-377.

- Jégo, S. and Dasgupta, R. (2013) Fluid-present melting of sulfide-bearing ocean-crust: Experimental constraints on the transport of sulfur from subducting slab to mantle wedge. *Geochimica et Cosmochimica Acta* 110, 106-134.
- Kanke, N. and Takazawa, E. (2014) A kilometre-scale highly refractory harzburgite zone in the mantle section of the northern Oman ophiolite (Fizh Block): implications for flux melting of oceanic lithosphere mantle. *Geological Society, London, Special Publications* 392, 229-246.
- Kawahata, H., Nohara, M., Ishizuka, H., Hasebe, S. and Chiba, H. (2001) Sr isotope geochemistry and hydrothermal alteration of the Oman ophiolite. *Journal of Geophysical Research* 106, 11083-11099.
- Koepke, J., Schoenborn, S., Oelze, M., Wittmann, H., Feig, S. T., Hellebrand, E., Boudier, F. and Schoenberg, R. (2009) Petrogenesis of crustal wehrlites in the Oman ophiolites: Experiments and natural rocks. *Geochemistry Geophysics Geosystems* 10, Q10002.
- Koga, K. T., Kelemen, P. B., and Shimizu, N. (2001) Petrogenesis of the crust-mantle transition zone and the origin of lower crustal wehrlite in the Oman ophiolite. *Geochemistry Geophysics Geosystems* 2, 2000GC000132.
- Konrad-Schmolke, M. and Halama, R. (2014) Combined thermodynamic-geochemical modeling in metamorphic geology: Boron as tracer of fluid-rock interaction. *Lithos* 208-209, 393-414.
- Kusano, Y., Hayashi, M., Adachi, Y., Umino, S., and Miyashita, S. (2014) Evolution of volcanism and magmatism during initial arc stage: constraints for the tectonic setting of the Oman ophiolite. In H. R. Rollinson, M. P. Searle, I. A. Abbasi, A. Al-Lazki, M. H. Al Kindi (Eds.) *Tectonic Evolution of the Oman Mountains* (pp. 177-193), Geological Society, London, Special Publications (Vol. 392), London. doi:10.1144/SP392.9
- Kusano, Y., Umino, S., Shinjo, R., Ikei, A., Adachi, Y., Miyashita, S., and Arai, S. (2017) Contribution of slab-derived fluid and sedimentary melt in the incipient arc magmas with development of the paeol-arc in the Oman ophiolite. *Chemical Geology* 449, 206-225.
- Lanphere, M. A., Coleman, R. G. and Hopson, C. A. (1981) Sr isotopic tracer study of the Samail ophiolite, Oman. *Journal of Geophysical Research* 86(B4), 2709-2720.
- Li, J. -L., Schwarzenbach, E. M., John, T., Ague, J. J., Huang, F., Gau, J., Klemm, R., Whitehouse, M. J. and Wang, X. -S. (2020) Uncovering and quantifying the subduction zone sulfur cycle from the slab perspective. *Nature Communications* 11, 514.
- Lippard, S. J., Shelton, A. W. and Gass, I. G. (1986) *The Ophiolite of Northern Oman*. Geological Society, London, Memoirs, 178 pp.
- Mandeville, C. M., Sasaki, A., Saito, G., Faure, K., King, R. and Hauri, E. (1998) Open-system degassing of sulfur from Krakatau 1883 magma. *Earth and Planetary Science Letters* 160, 709-722.

- Masterson, A. L., Wing, B. A., Paytan, A., Farquhar, J. and Johnston, D. T. (2016) The minor sulfur isotope composition of Cretaceous and Cenozoic seawater sulfate. *Paleoceanography and Paleoclimatology* 31 (6), 779-788.
- McArthur, J. M., Howarth, R. J. and Bailey, T. R. (2001) Strontium isotope stratigraphy: LOWESS Version 3: Best fit to the marine Sr-isotope curve for 0-509 Ma and accompanying look-up table for deriving numerical age. *The Journal of Geology* 109, 155-170.
- McCulloch, M. T., Gregory, R. T., Wasserburg, G. J., Taylor, H. P. J. (1980) A neodymium, strontium, and oxygen isotopic study of the Cretaceous Samail ophiolite and implications for the petrogenesis and seawater-hydrothermal alteration of oceanic crust. *Earth and Planetary Science Letters* 46, 201-211.
- McCulloch, M. T., Gregory, R. T., Wasserburg, J., and Taylor, H. P. (1981) Sm-Nd, Rb-Sr and $^{18}\text{O}/^{16}\text{O}$ isotopic systematics in an oceanic crustal section: evidence from the Samail ophiolite. *Journal of Geophysical Research* 86, 2721-2736.
- McDonough, W. F., and Sun, S.-S. (1995) The composition of the Earth, *Chemical Geology* 120, 223-253.
- Mével, C. (2003) Serpentinization of abyssal peridotites at mid-ocean ridges. *C. R. Geoscience* 335, 825-852.
- Michibayashi, K. Gerbert-Gaillard, L. and Nicolas, A. (2000) Shear sense inversion in the Hilti mantle section (Oman ophiolite) and active mantle uprise. *Marine Geophysical Researches* 21, 259-268.
- Monnier, C. Girardeau, J., Le Mée, L. and Polvé, M. (2006). Along ridge petrological segmentation of the mantle in the Oman ophiolite. *Geochemistry, Geophysics, Geosystems* 7, Q11008.
- Mottl, M. J. and Wheat, C. G. (1994) Hydrothermal circulation through mid-ocean ridge flanks: Fluxes of heat and magnesium. *Geochimica et Cosmochimica Acta* 58, 2225-2237.
- Nicolas, A. Rueber, I. and Benn, K. (1988) A new magma chamber model based on structural studies in the Oman ophiolite. *Tectonophysics* 151, 87-105.
- Nicolas, A., Boudier, F., Ildefonse, B. and Ball, E. (2000) Accretion of Oman and United Arab Emirates ophiolite: Discussion of a new structural map. *Marine Geophysical Researches* 21, 147-179.
- Nicolas, A., Mainprice, D. and Boudier, F. (2003) High temperature seawater circulation through the lower crust of ocean-ridges: A model derived from the Oman ophiolites. *Journal of Geophysical Research* 108 (B8), 2371.
- Niu, Y. (2004) Bulk-rock major and trace element compositions of abyssal peridotites: implications for mantle melting, melt extraction and post-melting processes beneath mid-ocean ridges. *Journal of Petrology* 45, 2423-2458.
- Oeser, M., Strauss, H., Wolff, P. E., Koepke, J., Peters, M., Garbe-Schönberg, D and Dietrich, M. (2012)

- A profile of multiple sulfur isotopes through the Oman ophiolite. *Chemical Geology* 312-313, 27-46.
- Ohmoto, H and Rye, R. O. (1979) Isotopes of sulfur and carbon. *In* *Geochemistry of hydrothermal ore deposits* (ed. H. L. Barnes), second ed. Wiley, New York, pp. 509-567.
- Ohmoto, H and Lagasa, A. C. (1982) Kinetics of reactions between aqueous sulfates and sulfides in hydrothermal systems. *Geochimica et Cosmochimica Acta* 46, 1727-1745.
- Parkinson, I. J. and Pearce, J. A. (1998) Peridotites from the Izu-Bonin-Mariana forearc (ODP Leg 125): Evidence for mantle melting and melt-mantle interaction in a supra-subduction zone setting. *Journal of Petrology* 39, 1577-1618.
- Peters, M., Strauss, H., Farquhar, J., Ockert, C., Eickmann, B., and Jost, C. L. (2010) Sulfur cycling at the Mid-Atlantic Ridge: a multiple sulfur isotope approach. *Chemical Geology* 269, 180-196.
- Plank, T. and Langmuir, C. H. (1998) The chemical composition of subducting sediment and its consequences for the crust and mantle. *Chemical Geology* 145, 325-394.
- Prigent, C., Guillot, S., Agard, P., Lemarchand, D., Soret, M. and Ulrich, M. (2018) Transfer of subduction fluids into the deforming mantle wedge during nascent subduction: Evidence from trace elements and boron isotopes (Semail ophiolite, Oman). *Earth and Planetary Science Letters* 484, 213-228.
- Python, M., Ceuleneer, G., Ishida, Y., Jean-Alix Barrat and Arai, S. (2007) Oman diopsidites: a new lithology diagnostic of very high temperature hydrothermal circulation in mantle peridotite below oceanic spreading centres. *Earth and Planetary Science Letters* 255, 289-305.
- Rees, C. E., Jenkins, W. J. and Monster, J. (1978) The sulphur isotopic composition of ocean water sulphate. *Geochimica et Cosmochimica Acta* 42, 377-381.
- Regelous, M., Weinzierl, C. G., and Hasse, K. M. (2016) Controls on melting at spreading ridges from correlated abyssal peridotite — mid-ocean ridge basalt compositions, *Earth and Planetary Science Letters* 449, 1-11.
- Rioux, M., Bowring, S., Kelemen, P., Gordon, S., Dudás, F. and Miller, R. (2012) Rapid crustal accretion and magma assimilation in the Oman-U.A.E. ophiolite: High precision U-Pb zircon geochronology of the gabbroic crust. *Journal of Geophysical Research* 117, B07201.
- Rospabé, M., Ceuleneer, G., Benoit, M., Abily B., and Pinet, P. (2017) Origin of the dunitic mantle-crust transition zone in the Oman ophiolite: The interplay between percolating magmas and high-temperature hydrous fluids. *Geology* 45, 471-474.
- Sakai, H., Des Marais, D. J., Ueda, A. and Moore, J. G. (1984) Concentrations and isotope ratios of carbon, nitrogen and sulfur in ocean-floor basalts. *Geochimica et Cosmochimica Acta* 48, 2433-2441.

- Scambelluri, M., Fiebig, J., Malaspina, N., Müntener, O., Pettke, T. (2004) Serpentinite subduction: Implications for fluid processes and trace-element recycling. *International Geology Review* 46, 595-613.
- Schwarzenbach, E. M., Früh-Green, G. L., Bernasconi, S. M., Alt, J. C., Shanks, W. C., Gaggero, L. and Crispini, L. (2012) Sulfur geochemistry of peridotite-hosted hydrothermal systems: Comparing the Ligurian ophiolites with oceanic serpentinites. *Geochimica et Cosmochimica Acta* 91, 283-305.
- Shanks, W., Böhlke, J.K. and Seal, R.R. (1995) Stable isotopes in mid-ocean ridge hydrothermal systems: Interactions between fluids, minerals, and organisms. *In* *Seafloor Hydrothermal Systems: Physical, Chemical, Biological, and Geological Interactions*, vol. 70 (eds. S. E. Humpries, R. A. Zierenberg, L. S. Mullineaux and R. E. Thomson). American Geophysical Union, Washington DC, pp. 194-221.
- Takazawa, E., Okayasu, T., Satoh, K. (2003) Geochemistry and origin of the basal lherzolites from the northern Oman ophiolite (northern Fizh block). *Geochemistry Geophysics Geosystems* 4(2), 1021.
- Ueda, A. and Sakai, H. (1984) Sulfur isotope study of Quaternary volcanic rocks from the Japanese Islands Arc. *Geochimica et Cosmochimica Acta* 48, 1837-1848.
- Vils, F., Tonarini, S., Kalt, A. and Seitz, H. -M. (2009) Boron, lithium and strontium isotopes as tracers of seawater-serpentinite interaction at Mid-Atlantic ridge, ODP Leg 209. *Earth and Planetary Science Letters* 286, 414-425.
- Wakaki, S. and Ishikawa, T. (2018) Isotope analysis of nanogram to sub-nanogram sized Nd samples by total evaporation normalization thermal ionization mass spectrometry. *International Journal of Mass Spectrometry* 424, 40-48.
- Walters, J. B., Cruz-Urbe, A. M. and Marschall, H. R. (2019) Isotopic compositions of sulfides in exhumed high-pressure terranes: Implications for sulfur cycling in subduction zones. *Geochemistry Geophysics Geosystems* 20, 3347-3374.
- Yamaoka, K., Ishikawa, T., Matsubaya, O., Ishiyama, D., Nagaishi, K., Hiroyasu, Y., Chiba, H. and Kawahata, H. (2012) Boron and oxygen isotope systematics for a complete section of oceanic crustal rocks in the Oman ophiolite. *Geochimica et Cosmochimica Acta* 84, 543-559.
- Yamasaki, T., Maeda, J., and Mizuta, T. (2006) Geochemical evidence in clinopyroxenes from gabbroic sequence for two distinct magmatisms in the Oman ophiolite. *Earth and Planetary Science Letters* 251, 52-65.
- Yoshikawa, M., Nakamura, E. and Takahashi, N. (1993) Rb-Sr isotope systematics in a phlogopite-bearing spinel lherzolite and its implications for age and origin of metasomatism in the Horoman peridotite complex, Hokkaido, Japan. *Journal of Mineralogy Petrology and Economic Geology* 88, 548-561.

- Yoshikawa, M., Python, M., Tamura, A., Arai, S., Takazawa, E., Shibata, T., Ueda, A. and Sato, T. (2015) Melt extraction and metasomatism recorded in basal peridotites above the metamorphic sole of the northern Fizh massif, Oman ophiolite. *Tectonophysics* 650, 53-64.
- Ziegler, U. R. F., Stoessel, G. F. U., and Peters T. (1991) Isotopic (Rb-Sr and Sm-Nd) and geochemical studies of the metamorphosed volcanic rocks in the metamorphic series below the Semail ophiolite in the Dibba zone (United Arab Emirates). *Schweiz. Mineral. Mitt.* 71, 19-33.
- Zihlmann, B., Müller, S., Coggon, R. M., Koepke, J., Garbe-Schönberg, D and Teagle, D. A. H. (2018) Hydrothermal fault zones in the lower oceanic crust: An example from Wadi Gideah, Semail ophiolite, Oman. *Lithos* 323, 103-124.

Chapter V

- Alt, J. C., Shanks, W. C. and Jackson, M. C. (1993) Cycling of sulfur in subduction zones: The geochemistry of sulfur in the Mariana island arc and back-arc trough. *Earth and Planetary Science Letters* 119, 477-494.
- 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.
- Tipper, E. T., Galy, A., Gaillardet, J., Bickle, M. J., Elderfield, H. and Carder, E. A. (2006) The magnesium isotope budget of the modern ocean: Constraints from riverine magnesium isotope ratios. *Earth and Planetary Science Letters* 250, 241-253.