

博士論文（要約）

Geochemical cycles of volatile elements in surface environment of the Earth

（地球表層における揮発性元素の物質循環）

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Abstract

Volcanic and hydrothermal activity discharge variable volatile species from the Earth's mantle to surface environment. Sulfur and carbon are major components of volcanic gases and they significantly affect atmospheric and oceanic chemistry. Halogens form variable chemical compounds in surface environments due to their high chemical activity. Therefore their fluxes are important to reveal Earth's evolution and to assess how much volcanic activity affects chemistry of surface environment. For sulfur and halogen fluxes, an approach using calibration against the reliable ^3He flux was applied for elucidating their cycles. Especially for chlorine, isotope compositions were determined using the new experimental method with high resolution applicable for microinclusions. Helium and carbon behavior related to eruption was investigated based on gas chemistry.

In order to estimate sulfur flux at mid-ocean ridges (MOR), I focused on the volatile components preferentially released from magmas through film rupturing processes in ascending magmas. Such components are expected to be retained in vesicles of MORB glasses, and they are analyzed with the currently established crushing technique based on the conventional noble gas analyses. Sulfur fluxes were calibrated against ^3He using datasets of MORB vesicles, submarine hydrothermal fluids, and volcanic gases. Carbon fluxes were also calibrated against ^3He fluxes based on MORB and volcanic gas datasets. The obtained sulfur flux at MOR is less than their volcanic fluxes at arc volcanoes (ARC). Wedge mantle contributions to ARC fluxes were deconvolved, and the mantle fluxes combining MOR and ARC were calculated for sulfur and carbon. The estimated C/S flux ratio is close to the C/S ratio in the present surface inventory, suggesting their mantle origins. To balance the mass between surface environment and the mantle, fluxes of sulfur and carbon subducted into the mantle and not immediately returned to the surface were assessed.

Halogen cycles were also discussed. In order to estimate halogen fluxes at MOR, I focused on the volatile components preferentially released from magmas as sulfur, and analyzed MORB glasses. The complete halogens and helium datasets in MORB vesicles were obtained by combinations of some independent analyses, providing halogen fluxes at MOR by calibrating against the well documented ^3He flux.

This part will be published in five years.

この部分については、5年以内に雑誌等で刊行予定のため非公開。

Geochemical cycles of variable volatile elements and approaches to investigate them are described in this dissertation.

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Chapter 1

General introduction

1. Volatile flux from the mantle and evolution of atmosphere and ocean

“How surface environment of the Earth was constructed” is one of the long-lasting theme of geoscience. Volcanic and hydrothermal activity discharges volatile elements such as sulfur, carbon, and halogens from the Earth’s mantle to the surface, which has formed atmosphere and ocean. Therefore in order to constrain surface environmental evolution, it is important to assess volatile behavior between the interior and the surface of Earth and its degassing histories. In particular, estimations of volatile flux from the mantle to the surface enable us to calculate residence times of volatiles in surface environment as follows:

$$T_V = S_V / F_V \quad (1-1)$$

where the subscript “V” shows a target volatile element; T_V , S_V , and F_V indicate the residence time, the surface inventory at present, and the mantle flux of V, respectively. We may discuss Earth’s degassing and atmospheric evolutionary histories by comparing calculated residence times of volatiles and the Earth’s age of 4.54×10^9 years (Tera, 1981). When residence times are longer than the Earth’s age, they imply catastrophic degassing histories of the volatile elements, which is consistent with the argon degassing history (Hamano & Ozima, 1978; Pujol et al., 2013; briefly depicted in Fig. 1-1). The argon degassing and evolutionary history has been well constrained based on argon isotopic compositions in the atmosphere and the mantle. One might calculate the duration of the early catastrophic degassing event of argon and the degassing fraction using the first-order rate box model focusing on mantle degassing and argon isotopic composition in the atmosphere (Hamano & Ozima, 1978). Parameters used in the model were isotopic compositions and abundance of argon in the atmosphere and the mantle, potassium contents in the crust and the mantle, decay constants of ^{40}K which produces ^{40}Ar as a daughter isotope, masses of the crust and the mantle, and the degassing rate. They concluded that more than ~80% of ^{36}Ar in today’s atmosphere was discharged by 4.0×10^9

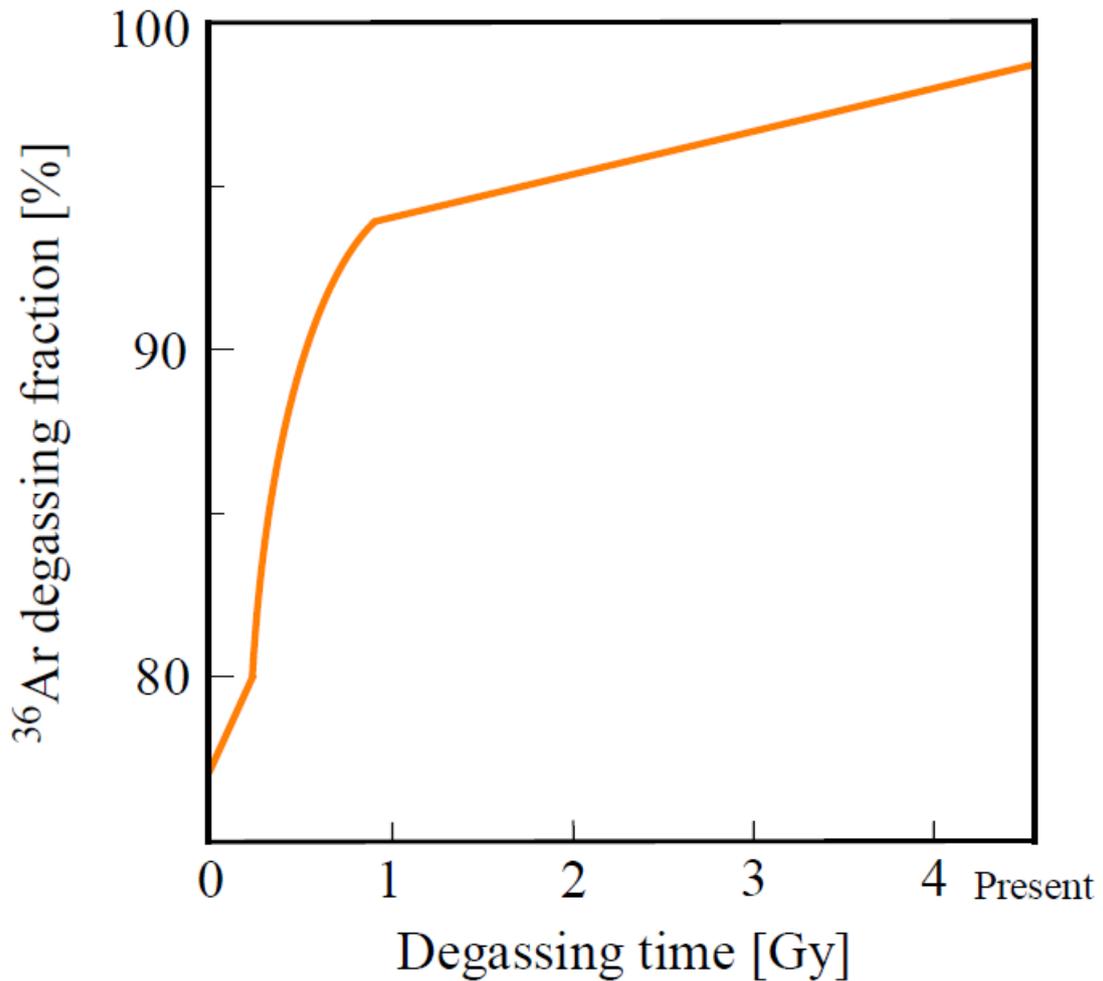


Figure 1-1. An example of ³⁶Ar degassing history.

The brown solid curve indicates minimum degassing fractions of ³⁶Ar contained in the Earth. The minimum degassing fractions for 0-0.9 Gy are values estimated by Hamano & Ozima (1978), while those for 0.9-4.54 Gy are estimated values under the assumption that 80% of ³⁶Ar remaining in the Earth has been degassed continuously during the past 3.64×10^9 years.

years ago. The growth history of the continental crust was recently assessed based on argon analyses of Archean hydrothermal quartz (3.5 Ga) and the atmospheric argon evolution model of Hamano & Ozima (1978), suggesting the catastrophic mantle degassing during the Earth's first 170 My and formation of the significant volume of the crust comparable to 80+/-10% of its present abundance between 3.8 Ga and 2.5 Ga (Pujol et al., 2013). The catastrophic mantle degassing event in the early Earth is widely accepted in the geoscience field.

Volatiles are injected from the mantle to the surface through submarine and land volcanisms. In the present Earth, the main mantle flux of volatile elements seems to be derived from submarine volcanisms related to mid-ocean ridges (MOR), which are the dominant divergent plate boundaries with the length of 1.5 times (Uyeda & Kanamori, 1979) longer than that of the total arc trench at convergent boundaries. Volatile flux at MOR has been determined mainly based on volatile contents in submarine glasses and the production rate of oceanic crust as follows:

$$F_V = F_{MORB} \times [V] \quad (1-2)$$

In this equation, the target volatile is indicated as "V". F_V and F_{MORB} indicate flux of V and the production rate of MORB (MOR basalt, i.e., oceanic crust), respectively. $[V]$ indicates V concentration in the carrier (i.e., MORB glass here). In this case, flux is calculated under the assumption that the all the volatile in the oceanic crust are finally released into the ocean. Therefore in the case of volatile elements which tends to stay in the oceanic crust and is not easily released into the ocean, more accurate MOR flux is estimated as follows:

$$F_V = F_{MORB} \times [V] \times R_V \quad (1-3)$$

This equation is derived from modification of eq. 1-2. F_V , F_{MORB} , and $[V]$ are the same as those explained for eq. 1-2, and R_V is a ratio of the volatile "V" amount released from the mantle into the ocean relative to the total V amount in the oceanic crust. However quantifying R_V is not easy for variable elements because it may be succeeded by isotope exchange-based calculations, which requires high precision isotope analyses and cannot

be applied for elements with only one stable isotope such as fluorine. When a precise volatile flux from the mantle cannot be easily calculated multiplying the MORB flux and volatile concentrations therein, another possible way is the calculation based on a well determined flux of a specific volatile element as follows:

$$F_{V1} = F_{V2} \times [V1]/[V2] \quad (1-4)$$

V1 is the target volatile element, while V2 is a volatile element whose mantle flux is well determined somehow. F_{V1} and F_{V2} are mantle fluxes of V1 and V2, respectively. [V1] and [V2] indicate respectively V1 and V2 concentrations in the same reservoir (i.e., mantle derived materials at ridges in this equation). ^3He can be conventionally applied as V2 because its MOR flux is well determined based on excess ^3He in deep seawater and $^3\text{He}/\text{CO}_2$ ratios in fresh MORB (e.g., Craig et al., 1975; Jean-Baptiste, 1992; Saal et al., 2002; Cartigny et al., 2008; Bianchi et al., 2010). In particular, high ^3He excess in deep seawater can be explained only by ^3He injection from the mantle because it is primordial in origin and is not produced by radioactivity efficiently. Thus ^3He anomaly in deep seawater well reflects the ^3He flux at ridges. The recent study reported the MOR ^3He flux of (527 ± 102) mol/y comparing World Ocean Circulation Experiment datasets of helium isotopes in deep seawater with depths greater than 1000m and calculated ^3He and radiocarbon compositions in deep seawater based on a suite of ocean general circulation models (Bianchi et al., 2010), which is a half value of (1070 ± 270) ^3He mol/y (Craig et al., 1975) conventionally accepted. In addition, the global ^3He flux at volcanic arcs (ARC) is calculated to be (105 ± 20) mol/y as the 20% value of MOR ^3He flux (Torgerson, 1989). We therefore obtain the global ^3He cycle (Fig. 1-2). This obvious geochemical cycle and inert chemistry of noble gases enable ^3He to be one of the most useful geochemical tracers, and its mantle flux has been conventionally used for calculations of other volatile fluxes as follows:

$$F_V = F_{\text{helium-3}} \times [V]/[^3\text{He}] \quad (1-5)$$

This equation is a modified version of eq. 1-4. F_V and $F_{\text{helium-3}}$ are fluxes of volatile “V” and ^3He , respectively. This equation can be applied for flux calculations when $V/^3\text{He}$

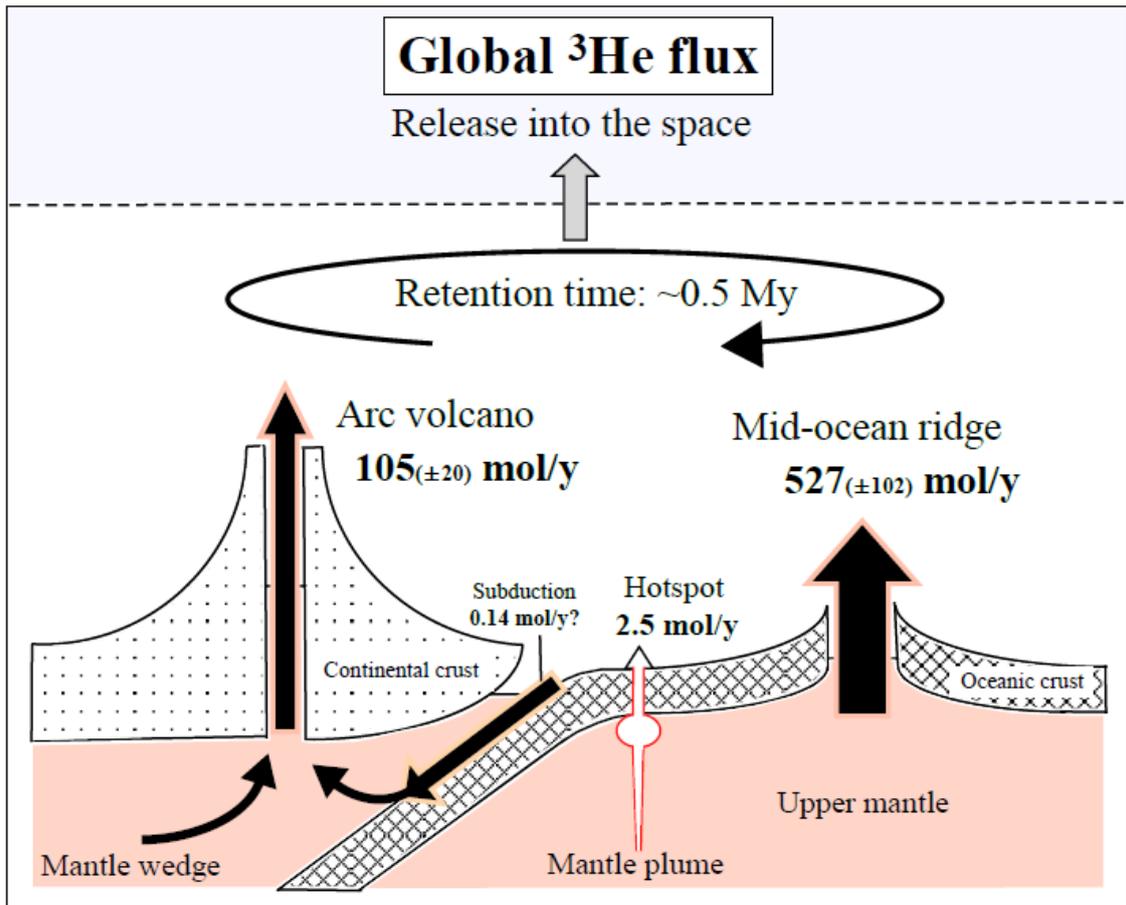


Figure 1-2. Global ^3He fluxes among the Earth's interior and surface.

The mid-ocean ridge flux is the value reported by Bianchi et al. (2010). The flux from arc volcanoes was calculated multiplying MOR flux by 20% which is the arc flux ratio relative to MOR flux (Torgersen, 1989). Subscripts indicate errors of the fluxes. The hotspot flux is the value reported by Torgersen (1989). The subducting ^3He flux is the value reported by Hilton et al. (2002) under the assumption that there is only terrestrial ^3He in marine sediment. The residence time of ^3He is the half of that of ^4He (~ 1 My; Ozima & Podosek, 2002). Atmospheric ^3He continuously escapes into the space due to its small atomic weight. Helium-3 fluxes could be easily determined because its behavior is basically unidirectional from the mantle to surface.

ratios are not affected by fractionation through degassing procedures. [V] and [^3He] are concentrations of V and ^3He in the same reservoir such as MORB glasses. In particular, carbon flux has been well constrained by calibrating against ^3He flux (e.g., Marty & Jambon, 1987; Marty & Tolstikhin, 1998). Mantle fluxes and geochemical cycles of volatile elements will be estimated based on the calculation methods explained in the current section.

2. Research objectives and strategies

In this research, for assessing how Earth's degassing has been producing atmosphere and ocean, I estimate global mantle fluxes of sulfur, carbon, and halogens which form various chemical compounds and significantly affect surface environment on the Earth. Based on the estimated mantle fluxes, their geochemical cycles and degassing histories are also discussed. This study constrains volatile geodynamics and degassing histories based on the well accepted ^3He fluxes in the surface.

In *Chapter 2*, I discuss sulfur and carbon geochemical cycles and degassing histories. The currently established crushing technique enables direct comparison of sulfur and helium retained in MORB vesicles, which may be a component preferentially released at MOR. Applying data of MORB and hydrothermal fluids around the world, sulfur and carbon fluxes at MOR are calculated in this chapter. In addition, the wedge mantle contribution to volcanic gases is deconvolved in order to calculate the mantle fluxes at ARC. Comparing MOR and ARC fluxes, geochemical cycles and degassing histories of sulfur and carbon are constrained.

In *Chapter 3*, I discuss halogen geochemical cycles and degassing histories. The crushing method used in *Chapter 2* is applied for comparing fluorine, chlorine, and helium in MORB vesicles directly. In addition, the neutron irradiation method converting halogens into proxy noble gas isotopes is also applied for calculating halogen concentrations and inter-halogen ratios in MORB glasses. Based on these datasets, mantle fluxes of halogens are estimated in this chapter. Comparing MOR and ARC fluxes, halogen geochemical cycles and degassing histories are constrained.

Chapter 2

Geochemical cycles of sulfur and carbon

1. Introduction

Volcanic and hydrothermal activity discharges variable volatile species from the Earth's mantle to surface. Sulfur and carbon, which are both major components of volcanic gases, are injected into the surface in forms of SO_2 , H_2S , CO_2 , and CH_4 , and significantly affect atmospheric and oceanic chemistry and their evolution. In order to reveal Earth's evolution and to assess how much volcanic activity affects chemistry of surface environment, previous studies were trying to estimate sulfur and carbon fluxes between the Earth's interior and the surface. However, only a small number of studies have discussed global mass balances of sulfur and carbon (Hilton et al., 2002; Wallace, 2005; see reported sulfur fluxes in Table 2-1) while other studies have focused only on local ridges and arcs. It should be noted that elucidating individual volcanic and hydrothermal activity is very important for assessing their effects on human society (hazard mitigation), and is also essential for estimating global volatile cycles by comparing themselves as representatives of volcanic activity around the world. I will discuss sulfur and carbon cycles among Earth's surface and interior reservoirs based on chemistry of ridges and arcs worldwide.

In surface environment, sulfur and carbon are stored as gases (SO_2 , H_2S , CO_2 , CH_4 etc.) in the atmosphere, dissolved matters (SO_4^{2-} , HCO_3^- , CO_3^{2-} etc.) in seawater, and are also retained as solid materials (FeS_2 , CaCO_3 etc.) in sedimentary reservoirs. They finally move to the mantle owing to subduction of oceanic plates at trenches, which makes a part of them recycled back into the mantle (e.g., Hilton et al., 2002), while other parts are returned to the atmosphere and ocean again. It is important to estimate sulfur and carbon fluxes between the mantle and the surface for revealing histories of Earth's degassing and atmospheric evolution. In particular, when the mantle flux of sulfur is obtained, applying eq. 1-1, I can estimate the residence time of sulfur. Thus I can discuss the sulfur degassing history by comparing the calculated residence time and the Earth's age of 4.54×10^9 years (Tera, 1981).

Table 2-1. Reported sulfur global fluxes at ridges and residence times.

S flux [Gmol/y]	Residence time [Gy]	Flux estimation method	Ref.
2670	0.2	Loss of total sulfur in MORB	Hilton et al. (2002)
1640	0.3	Loss of total sulfur in MORB	Hansen & Wallmann (2003)
144	3.7	Alteration of ~10% of MORB	Sakai & Matsuhisa (1996); Tajika (1998)
78	6.8	Based on altered oceanic crust compositions	Alt (1995)

NOTE: Sulfur surface inventory of 5.3×10^{20} mol (Hilton et al., 2002) was applied for residence time calculations.

The global flux of sulfur from sub-aerial arc volcanoes is well constrained (Hilton et al., 2002; Bluth et al., 1993) based on measurements of SO₂ gas from volcanoes using correlation spectrometry abbreviated as COSPEC (Stoiber & Jepsen, 1973), UV spectroscopy, and satellite remote sensing (Bluth et al., 1993). Carbon flux from volcanic arcs can be also obtained multiplying global SO₂ flux and a representative CO₂/SO₂ ratio in volcanic gases, or following another estimation method discussed later. However, the main mantle flux of volatile elements seems to be derived from submarine volcanisms related to MOR as discussed in *Chapter 1*. Therefore, we need to discuss MOR flux together with sub-aerial flux to evaluate a mass balance of sulfur and carbon on the Earth's surface precisely. However MOR volatile flux cannot be determined by direct observations in ways similar as those for arc volcanoes such as COSPEC and satellite remote sensing because the measurement of ocean-bottom hydrothermal systems is technically very difficult to succeed. It seems that MOR fluxes can be calculated based on volatile concentrations in MORB and the MORB production rate (eq. 1-2), but such bulk concentration-based flux is often inconsistent with the catastrophic degassing history of Earth expected from atmospheric argon evolution (Hamano & Ozima, 1978; Pujol et al., 2013; Fig. 1-1). In the case of sulfur, based on its concentration in the oceanic crust, fluxes of 2.67×10^{12} mol/y and 1.64×10^{12} mol/y at MOR were evaluated by Hilton et al. (2002) and Hansen & Wallmann (2003), respectively. Applying these fluxes and the sulfur surface inventory of 5.33×10^{20} mol (Hilton et al., 2002) to eq. 1-1, residence times of sulfur in the surface reservoir are calculated to be 2.0×10^8 years and 3.3×10^8 years, respectively. These residence times are significantly shorter than the Earth's age of 4.54×10^9 years, which seems to imply that there were no need to have a significant degassing event in the early Earth. It seems, however, that if only a part of total sulfur in the oceanic crust is finally released into the ocean by alteration of the crust, the net sulfur flux from the mantle to the ocean is lower than the flux calculated using sulfur contents in the oceanic crust and the MORB flux. This is why we have to calculate MOR flux of volatiles including sulfur more precisely in another way.

One of ways to estimate volatile flux from the mantle very precisely is evaluating isotopic exchange between oceanic crust and seawater. A sulfur flux of 7.8×10^{10} mol/y from the volcanic section in the oceanic crust to the ocean was calculated from seawater–basalt sulfur exchange during hydrothermal alteration based on sulfur isotope

measurements in Ocean Drilling Program Hole 504B samples (Alt, 1995). This flux is markedly lower than the estimate of 2.67×10^{12} mol/y and 1.64×10^{12} mol/y discussed above (Hilton et al., 2002; Hansen & Wallmann, 2003). This isotope exchange-based flux is very close to the flux of 1.44×10^{11} mol/y estimated under the assumption that only 10% of sulfur retained in the oceanic crust are finally released into the ocean (Sakai & Matsuhisa, 1996). Though the 10%-release of sulfur from the oceanic crust (i.e., $R_V = 0.1$ in eq. 1-3) is just an assumption and is not a value derived from a rigorous estimate, this flux may be much more reliable as a net sulfur flux relative to those calculated under the assumption that all the sulfur in the oceanic crust are released into the ocean. However, quantifying the reliable R_V is very difficult as discussed in *Chapter 1*, and more data for more sampling sites are needed to investigate the global sulfur flux precisely.

In this study, I will estimate sulfur flux in a different way. A precise sulfur flux from the mantle cannot be easily calculated multiplying the MORB flux and sulfur concentrations therein, thus I will calculate it by calibrating against the well determined ^3He flux at MOR (Bianchi et al., 2010; Fig. 1-2; eq. 1-5). Carbon flux are also constrained in the same way using ^3He flux (e.g., Marty & Jambon, 1987; Marty & Tolstikhin, 1998). Therefore mantle fluxes and geochemical cycles of sulfur and carbon will be discussed based on ^3He flux in this chapter.

2. Carbon cycle

Carbon fluxes from the mantle to the atmosphere and the ocean have been already documented, but the conventional estimate (Marty & Talstikhin, 1998) depends on the old ^3He flux from the mantle reported in 1970's (Craig et al., 1975). The MOR ^3He flux has been recently modified (Bianchi et al., 2010), thus one might recalculate global carbon fluxes based on the newly estimated ^3He flux from the mantle. The method to estimate global carbon cycles will be also useful for investigating sulfur cycles.

2.1. Carbon flux at mid-ocean ridges

Mantle carbon flux of 2×10^{12} mol/y was derived from the MOR ^3He flux and $\text{C}/^3\text{He}$ ratio in MOR basalt glass (Marty & Jambon, 1987), but the most accepted carbon flux at MOR was estimated by Marty & Tolstikhin (1998). They calculated carbon flux based on $\text{C}/^3\text{He}$ ratios in submarine glasses and hydrothermal fluids at MOR. They treated their $\text{C}/^3\text{He}$ ratios as a single population and obtained the average $\text{C}/^3\text{He}$ ratio of $(2.2 \pm 0.7) \times 10^9$. This ratio was multiplied by the MOR ^3He flux of (1000 ± 250) mol/y derived from a single oceanic model (Craig et al., 1975; Welhan & Craig, 1983), providing MOR carbon flux of $(2.2 \pm 0.9) \times 10^{12}$ mol/y (Marty & Talstikhin, 1998). However, the ^3He flux has been recalculated to be (527 ± 102) mol/y (Bianchi et al., 2010) based on the data and models more sophisticated than those used in Craig et al. (1975), which requires re-estimation of carbon flux at ridges. Now, one might calculate carbon flux to be $(1.2 \pm 0.4) \times 10^{12}$ mol/y (Fig. 2-1) multiplying the representative upper mantle $\text{C}/^3\text{He}$ ratio of $(2.2 \pm 0.7) \times 10^9$ and the MOR ^3He flux of (527 ± 102) mol/y (Bianchi et al., 2010).

2.2. Carbon flux at arc volcanoes

The carbon and helium behaviors in individual volcano are well studied (see *Appendix C* for an example at Ontake volcano). Following the same way as the MOR flux calculation, the global carbon flux at arc volcanoes can be estimated multiplying $\text{C}/^3\text{He}$ ratios in volcanic gases and the determined ^3He flux of (105 ± 20) mol/y at ARC (Fig. 1-2). There are many subaerial volcanoes in the circum-Pacific region due to tectonic settings of convergent plate boundary (Fig. 2-2; see also Table 2-2). Helium and carbon isotopic compositions in high temperature ($>200\text{C}$) volcanic gases and steam wells are

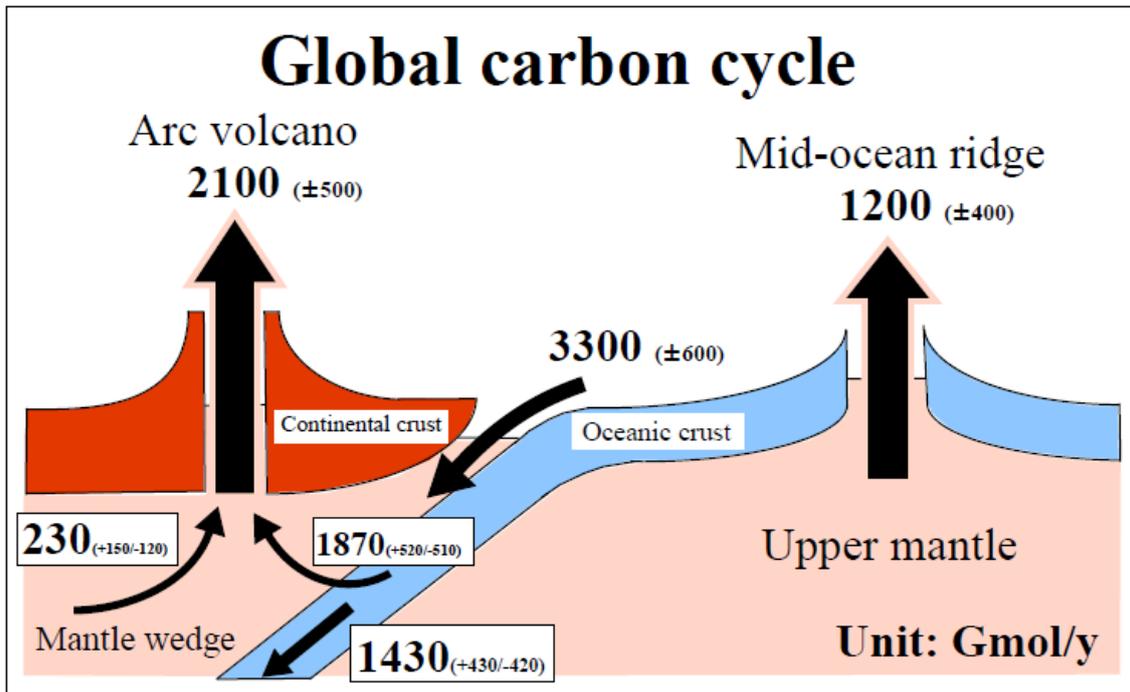


Figure 2-1. Global carbon fluxes among the Earth's interior and surface environment.

Numbers are carbon fluxes among reservoirs with errors as subscripts. They are described in the unit of Gmol/y. See text for calculations of fluxes at mid-ocean ridges (1200 Gmol/y) and arc volcanoes (2100 Gmol/y), and the mantle contribution to the ARC flux (230 Gmol/y). Other fluxes related to recycle and return were calculated under the assumption of the steady-state surface environment of carbon.

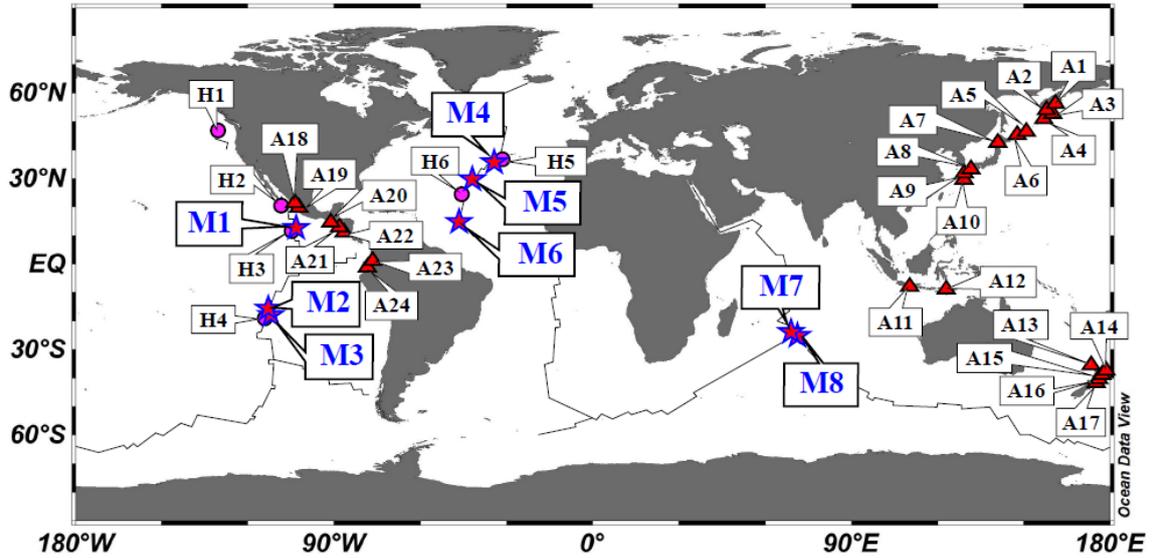


Figure 2-2. Sites of MORB, submarine hydrothermal fluids, and arc volcanoes considered in this study.

Stars, circles, and triangles indicate sites of MORB glasses, submarine high temperature (>200C) hydrothermal fluids, and high temperature (>200C) volcanic gases, respectively. Names of each site and sample are described in Table 2-2. This figure was prepared using the Ocean Data View software (Schlitzer, 2013).

Table 2-2. Sample or site names considered for flux calculations in Chapter 1.

Number in Fig. 1-4	Sample/site name	Lat.	Lon.	Depth [m]
(MORB)				
M1	CL DR01	12.75oN	103.93oW	2610
M2	ND 18-1	17.42oS	113.20oW	2578
M3	RY380-R03b	17.44oS	113.22oW	2580
M4	CH31 DR12	36.87oN	33.25oW	2895
M5	CH98 DR12	30.17oN	41.92oW	4150
M6	418R002	15.36oN	46.63oW	4944
M7	KH10-6 DR15-glass	24.48oS	69.92oE	2242
M8	KH10-6 DR16-glass	24.53oS	69.93oE	2268
(Submarine hydrothermal fluids >200°C)				
H1	Juan de Fuca Ridge (47N-48N)	48.0N	129.1W	
H2	East Pacific Rise (21N)	20.8N	109.1W	
H3	East Pacific Rise (11N-13N)	11.0-12.8N	103.5-104.0W	
H4	East Pacific Rise (17S-19S)	17-19S	113.5W	
H5	Mid-Atlantic Ridge (36N-38N)	36.2-37.8N	31-33.9W	
H6	Mid-Atlantic Ridge (23N-26N)	23.4-26.1N	45W	
(Arc volcanoes)				
A1	Klyuchevskoy	56.06N	160.64E	
A2	Koryak	53.32N	158.69E	
A3	Avacha	53.26N	158.83E	
A4	Mutnovsky	52.45N	158.2E	
A5	Chirpoy	46.5N	151E	
A6	Kudryavy	46N	148E	
A7	Usu	42.53N	140.83E	
A8	Kuju	33.1N	131.3E	
A9	Unzen	32.75N	130.3E	
A10	Satuma-Iwojima	30.8N	130.3E	
A11	Merapi	7.52S	110.43E	
A12	Lewoto	8.27S	123.5E	
A13	Ngawha	35.4S	173.85E	
A14	White Island	37.52S	177.18E	
A15	Ohaaki	38.51S	176.29E	
A16	Mokai	38.52S	175.91E	
A17	Ngauruhoe	39.15S	175.63E	
A18	La Primavera	20.62N	103.52W	
A19	Colima	19.50N	103.62W	
A20	Pacaya	14.37N	90.6W	
A21	Cerro Negro	12.5N	86.7W	
A22	Momotombo	12.41N	86.52E	
A23	Galeras	1.22N	77.37W	
A24	Cumbal	0.95N	77.89W	

NOTE: Numbers correspondent to those in Fig. 2-2. Names of MORB are sample names, while others are site names.

Table 2-3. Helium and carbon isotopic compositions in high temperature (>200C) geothermal fluids in the circum-Pacific region.

Name	Lat.	Lon.	Location	Temp. (°C)	³ He/ ⁴ He (Ratm)	δ ¹³ C (‰)	C/ ³ He	Reference
Klyuchevskoy	56.06N	160.64E	Kamchatka	250	6.8	-11.6	1.1E+10	Taran et al. (1991); Taran (2009)
Koryak	53.32N	158.69E	Kamchatka	220	5.3	-11.8	3.6E+10	Taran et al. (1997); Taran (2009)
Avacha	53.26N	158.83E	Kamchatka	473	7.1	-5.7	2.3E+10	Taran et al. (1997); Taran (2009)
Mutnovsky	52.45N	158.2E	Kamchatka	543	8.2	-9.9	1.3E+10	Taran et al. (1992); Taran (2009)
Chirpoy	46.5N	151E	Kuril	344	6.3		5.9E+10	Taran et al. (1995); Taran (2009)
Kudryavy	46N	148E	Kuril	920	6.8	-7.2	9.0E+09	Fischer et al. (1998); Taran (2009)
Usu	42.53N	140.83E	Japan	750	5.4	-4.4	1.0E+10	Marty et al. (1989)
Kuju	33.1N	131.3E	Japan	351	7.6	-7.9	1.4E+10	Nagao et al. (1981); Saito et al. (2002)
Unzen	32.75N	130.3E	Japan	803	7.3	-6.1	8.1E+09	Sano & Williams (1996)
Satuma-Iwojima	30.8N	130.3E	Japan	885	7.9	-5.5	6.3E+09	Marty et al. (1989); Taran (2009)
Merapi	7.52S	110.43E	Indonesia	803	7.4	-3.9	1.4E+10	Javoy et al. (1986); Taran (2009)
Lewoto	8.27S	123.5E	Indonesia	490	3.6	-3.9	1.3E+10	Varekamp et al. (1992)
Ngawha	35.4S	173.85E	New Zealand	269	6.0	-8.7	2.8E+10	Giggenbach et al. (1993); Lyon and Hulston (1983)
White Island	37.52S	177.18E	New Zealand	495	6.1	-2.0	3.6E+10	Marty & Giggenbach (1990)
Ohaaki	38.51S	176.29E	New Zealand	280	5.0		6.9E+10	Giggenbach et al. (1993)
Mokai	38.52S	175.91E	New Zealand	300	6.8		1.3E+10	Giggenbach et al. (1993)
Ngauruhoe	39.15S	175.63E	New Zealand	516	6.7	-10.4	7.9E+09	Giggenbach et al. (1993); Giggenbach (1996); Fischer (2008)
La Primavera	20.62N	103.52W	Mexico	260	6.2	-3.9	6.2E+09	Taran et al. (2002)
Colima	19.50N	103.62W	Mexico	814	6.6	-6.3	6.1E+09	Sano & Williams (1996); Taran (2009)
Pacaya	14.37N	90.6W	Guatemala	965	4.2	-6.9	2.0E+10	Sano & Williams (1996)
Cerro Negro	12.5N	86.7W	Nicaragua	350	6.8	-2.5	3.3E+10	Sano & Williams (1996)
Momotombo	12.41N	86.52E	Nicaragua	747	7.1	-2.8	1.6E+10	Javoy et al. (1986); Taran (2009)
Galeras	1.22N	77.37W	Colombia	222	8.4	-7.6	1.5E+10	Sano & Williams (1996)
Cumbal	0.95N	77.89W	Colombia	257	6.8	-4.9	1.2E+10	Sano & Williams (1996)

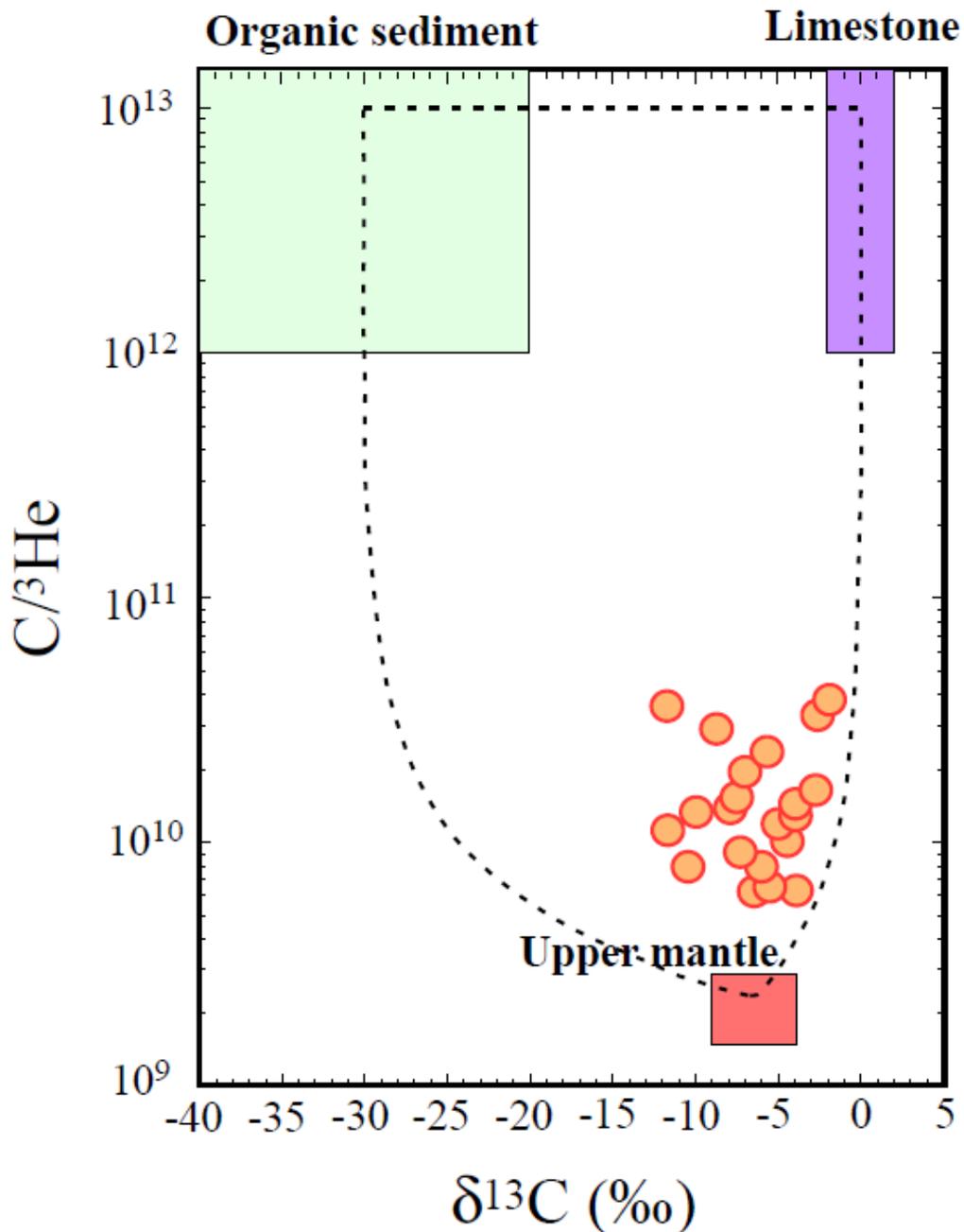


Figure 2-3. Carbon and helium compositions in volcanic gases and their end-members.

Volcanic gas data described in Table 2-3 and 2-4 are shown as red circles. Three square zones are end-members of volcanic gases: The upper mantle component; organic sediment; and limestone with slab carbonate abbreviated as “limestone”. Mixing lines of three end-members are depicted as dashed curves. Dashed lines are derived by the medium upper mantle composition and medium $\delta^{13}\text{C}$ values of organic sediment and limestone. This figure shows that all the data of volcanic gases are explained by mixing of the three end-members as suggested by Sano & Marty (1995).

compiled in Table 2-3. An average value of $C/{}^3\text{He}$ ratios in 24 subaerial volcanoes in Table 2-3 is calculated to be $(2.0\pm 0.3)\times 10^{10}$, providing the ARC carbon flux of $(2.1\pm 0.5)\times 10^{12}$ mol/y by multiplication of the ${}^3\text{He}$ flux of (105 ± 20) mol/y and the $C/{}^3\text{He}$ ratio of $(2.0\pm 0.3)\times 10^{10}$ at ARC. This ARC flux is consistent with the recent estimate using volcanic gas observations worldwide (Fischer, 2008).

2.3. Deconvolution of carbon flux at ARC

In order to estimate the carbon flux from the mantle to the surface through arc volcanisms, I deconvolved magmatic carbon into the mantle component and other end-members. Volatiles in volcanic gases are derived from magmas which have mainly two sources: components derived from the mantle and subducting materials. Deconvolution of the source contributions to volcanic gases is important to estimate net volatile fluxes from the mantle. In particular, carbon and helium mixing at subduction zone has been well studied. Sano & Marty (1995) compared carbon and helium isotopic compositions in surface reservoirs and the mantle, and concluded that those isotopic compositions in volcanic gases are produced by three-component mixing: the upper mantle component represented by MORB, organic sediment, and marine limestone with slab carbonate (abbreviated as “limestone” hereafter) (see also Fig. 2-3). Following Sano & Marty (1995), $\delta^{13}\text{C}$ values of -6.5 ± 2.5 ‰ in the upper mantle, -30 ± 10 ‰ in organic sediment, and 0 ± 2 ‰ in limestone were used as end-member compositions. The $C/{}^3\text{He}$ ratio in the upper mantle is $(2.2\pm 0.7)\times 10^9$ (Marty & Talstikhin, 1998). In addition, Sano & Marty applied the $C/{}^3\text{He}$ ratio of $10^{(13\pm 1)}$ for subducting material end-members (organic sediment and limestone) based on the compositions of crustal CO_2 -rich continental gases (O’Nions & Oxburgh, 1988), thus I also used the same $C/{}^3\text{He}$ ratio for an end-member value. Volcanic gas and end-member compositions are described in Table 2-4. Based on those values, respective contribution percentages of the three components in the ARC samples were calculated solving the following equations:

$$\delta^{13}\text{C}_V = \delta^{13}\text{C}_M M + \delta^{13}\text{C}_S S + \delta^{13}\text{C}_L L \quad (2-1)$$

$$1/(C/{}^3\text{He})_V = M/(C/{}^3\text{He})_M + S/(C/{}^3\text{He})_S + L/(C/{}^3\text{He})_L \quad (2-2)$$

$$M + S + L = 1 \quad (2-3)$$

Table 2-4. Sample and end-member compositions with carbon contributions.

Name	$\delta^{13}\text{C}$ (‰)	$\text{C}/^3\text{He}$	Carbon source contribution (%)		
			Upper mantle	Organic sediment	Limestone
(High temperature volcanic gases and steam wells)					
Klyuchevskoy	-11.6	1.1E+10	20.0	34.3	45.7
Koryak	-11.8	3.6E+10	6.1	38.0	55.9
Avacha	-5.7	2.3E+10	9.5	16.8	73.7
Mutnovsky	-9.9	1.3E+10	16.9	29.3	53.8
Chirpoy		5.9E+10	3.7		
Kudryavy	-7.2	9.0E+09	24.4	18.7	56.9
Usu	-4.4	1.0E+10	22.0	9.9	68.1
Kuju	-7.9	1.4E+10	16.0	22.9	61.1
Unzen	-6.1	8.1E+09	27.3	14.2	58.4
Satuma-Iwojima	-5.5	6.3E+09	34.9	10.8	54.3
Merapi	-3.9	1.4E+10	15.7	9.6	74.7
Lewoto	-3.9	1.3E+10	17.5	9.3	73.3
Ngawha	-8.7	2.8E+10	7.8	27.2	65.1
White Island	-2.0	3.6E+10	6.1	5.5	88.4
Ohaaki		6.9E+10	3.2		
Mokai		1.3E+10	16.6		
Ngauruhoe	-10.4	7.9E+09	27.7	28.7	43.6
La Primavera	-3.9	6.2E+09	6.6	7.0	86.4
Colima	-6.3	6.1E+09	13.7	6.2	80.1
Pacaya	-6.9	2.0E+10	11.2	20.7	68.1
Cerro Negro	-2.5	3.3E+10	14.4	22.2	63.3
Momotombo	-2.8	1.6E+10	18.8	12.3	68.9
Galeras	-7.6	1.5E+10	36.1	13.2	50.8
Cumbal	-4.9	1.2E+10	35.5	5.3	59.2
Average values	-6.4	2.0E+10	11.0	18.9	70.1
(End-members)					
Upper mantle	-6.5	2.2E+09	100.0		
Organic sediment	-30.0	1.0E+13		100.0	
Limestone with slab carbonate	0.0	1.0E+13			100.0

Data of subaerial volcanoes and three end-members are described here. See text for the calculations of end-member contributions.

where subscripts *M*, *S*, and *L* indicate contributions of the upper mantle component, organic sediment, and limestone, respectively. Subscripts V, M, S, and L of $\delta^{13}\text{C}$ values and $\text{C}/^3\text{He}$ ratios correspond to compositions of high temperature volcanic gases, the upper mantle, organic sediment, and limestone. Calculated contributions are described in Table 2-4. The contribution of the upper mantle carbon was 3.2%-36.1% with an average of $(11.0+6.5/-4.7)\%$. The uncertainty of the upper mantle contribution was calculated based on the highest and the lowest upper mantle contributions calculated based on extremely high or low values' sample and end-member compositions as follows: the upper mantle contribution of 17.5% derived from the case applying $\text{C}/^3\text{He}$ ratios of 1.7×10^{10} , 2.9×10^9 , 1.0×10^{14} , and 1.0×10^{14} for ARC samples, the upper mantle, organic sediment, and limestone; and the upper mantle contribution of 6.3% derived from the case applying $\text{C}/^3\text{He}$ ratios of 2.3×10^{10} , 1.5×10^9 , 1.0×10^{12} , and 1.0×10^{12} for ARC samples, the upper mantle, organic sediment, and limestone. This upper mantle contribution indicates that ~90% of carbon released at arc volcanoes is attributable to subducted materials, that is, carbonate and organic carbon. As discussed above, the global carbon flux at ARC is $(2.1 \pm 0.5) \times 10^{12}$ mol/y. The end-member deconvolution implies that 11% of carbon in high temperature volcanic gases is derived from the upper mantle component, providing carbon flux of $(2.3 \pm 1.5 / -1.2) \times 10^{11}$ mol/y from the mantle to atmosphere via arc volcanoes.

2.4. Contribution to global flux of carbon from present hot spot magmatism

$\text{C}/^3\text{He}$ ratios in hotspot areas have been well observed. Marty and Jambon (1987) calculated an average $\text{C}/^3\text{He}$ ratio of 5.3×10^9 in Loihi samples using already reported data (Kurz et al., 1983; Rison & Craig, 1983; Exley et al., 1986). They also determined the $\text{C}/^3\text{He}$ ratio in Kilauea gases as 3.4×10^9 based on observational datasets (Naughton et al., 1973; Craig & Lupton, 1976). In addition, $\text{C}/^3\text{He}$ ratios of 2.1×10^9 and 2.7×10^9 are reported for Yellowstone (Craig et al., 1978), and 2.0×10^9 and 7.9×10^9 are reported for Iceland gases (Sano et al., 1985; Mamyrin & Tolstikhin, 1984). These values are slightly higher than the MORB value. However expected hotspot $\text{C}/^3\text{He}$ ratios are lower than MORB because their deep sources are less degassed relative to the MORB mantle, so the observed data should be treated with caution (Marty & Jambon, 1987). In addition, ^3He flux at MOR is 200 times higher than that at hotspots, therefore the hotspot contribution to the global carbon flux is negligibly small.

2.5. Global carbon cycle

A summary of global carbon flux is depicted in Fig. 2-1. The total volcanic flux of carbon is $(3.3\pm 0.6)\times 10^{12}$ mol/y, which is two orders of magnitude smaller than anthropogenic emission of $(6.9\pm 0.6)\times 10^{14}$ mol/y by fossil fuel combustion and cement production (Ciais et al., 2013). The MOR flux combined with the wedge mantle flux is $(1.4\pm 0.4)\times 10^{12}$ mol/y. This value, if accumulated for 4.54×10^9 years, results in $(6.5\pm 1.9)\times 10^{21}$ mol of carbon, which is comparable to the surface inventory of 7.0×10^{21} mol (Hilton et al., 2002). If steady-state recycling of carbon is applied, then the total subduction flux becomes $(3.3\pm 0.6)\times 10^{12}$ mol/y. This estimate is consistent with the carbon subduction flux of 3.46×10^{12} mol/y (Hilton et al., 2002).

3. Sulfur cycle

3.1. How to assess upper mantle-derived compositions

One might estimate sulfur fluxes from the mantle to the surface based on ^3He fluxes in the same way as carbon discussed in the previous section. However, except for a very rough estimate (Kagoshima et al., 2012), no report in the literature has described an estimation of mantle sulfur flux at MOR as calibrated against the mantle ^3He flux because representative $\text{S}/^3\text{He}$ ratios released from the upper mantle into the ocean have never been reported.

In the case of the carbon and helium coupling, the representative material for the upper mantle is MORB glasses. They have $\text{C}/^3\text{He}$ ratios close to 2.0×10^9 both in CO_2 vesicles and glass matrix under the equilibria of helium in those two phases (Marty & Jambon, 1987), implying that degassing and volatile release from MORB does not cause significant fractionation of $\text{C}/^3\text{He}$ ratios therein. Therefore, $\text{C}/^3\text{He}$ ratios released from the upper mantle into the ocean can be represented by compositions of MORB glasses. It should be noted that the representative $\text{C}/^3\text{He}$ ratio in the upper mantle had been modified to be 2.2×10^9 (Marty & Talstikhin, 1998) as discussed in the previous section. On the other hand, it is much more complicated and difficult to determine $\text{S}/^3\text{He}$ ratios which represents the released components from the upper mantle into the ocean than representative $\text{C}/^3\text{He}$ ratios because $\text{S}/^3\text{He}$ ratios in MORB vesicles and glass matrix are much discrepant due to the difference between partition coefficients of sulfur and ^3He between $\text{CO}_2\text{-H}_2\text{O}$ vapor (vesicles) and basaltic melt (glass matrix). In MORB glasses, sulfur is mostly stored in glass matrix, while helium mostly stays in vesicles. This is why $\text{S}/^3\text{He}$ ratios in vesicles or matrix of MORB glasses are not representatives of components transferred from the upper mantle into the ocean, while they apparently reflect the upper mantle composition itself.

Namiki and Kagoshima (2014) suggested one dominant degassing process from magmas to surface reservoirs by decompression experiments of syrup including bubbles as an analogue of ascending magmas including voids in a volcanic conduit. They found appearance of large voids in the syrup during decompression. An expansion of one void deep in the syrup leads to another void expansion, which results in the propagation of voids upward to the syrup surface and significant outgassing. This upward propagation and degassing pathways are generated by bubble film-rupturing, causing efficient

degassing from syrup to the surface (Fig. 2-4). Here, syrup and involved voids can be also treated as analogues of basaltic melts and CO₂-H₂O bubbles in them at MOR which finally become matrix and vesicles of MORB glasses after chilling. Such process generating chilled margin indicates that vesicle components are much more dominant for degassing from magmas and fluxes from the upper mantle relative to glass matrix components which are not easily dissolved into the ocean like fluids in vesicles. Thus we will take vesicle components as a representative value injected from the upper mantle to the ocean, and another representative value should be derived from compositions of submarine hydrothermal fluids which are generated components through seawater-basalt interactions and degassing processes from the upper mantle.

In order to estimate representative components released from the upper mantle, I conducted two approaches below:

- 1) Measurement of sulfur and helium compositions in vesicles of MORB glasses.
- 2) Determination of representative sulfur and helium compositions in high temperature (>200C) submarine hydrothermal fluids compiling data already reported.

Representative S/³He ratios derived from the upper mantle is estimated comparing values obtained by approaches 1) and 2). For 1), MORB glasses were crushed *in vacuo* with alkaline solutions, and analyzed by appropriate conventional methods. As carbon, representative upper mantle-derived S/³He ratios and δ³⁴S values enable us to quantify sulfur and helium behavior at ARC systems and the global mass balance of sulfur.

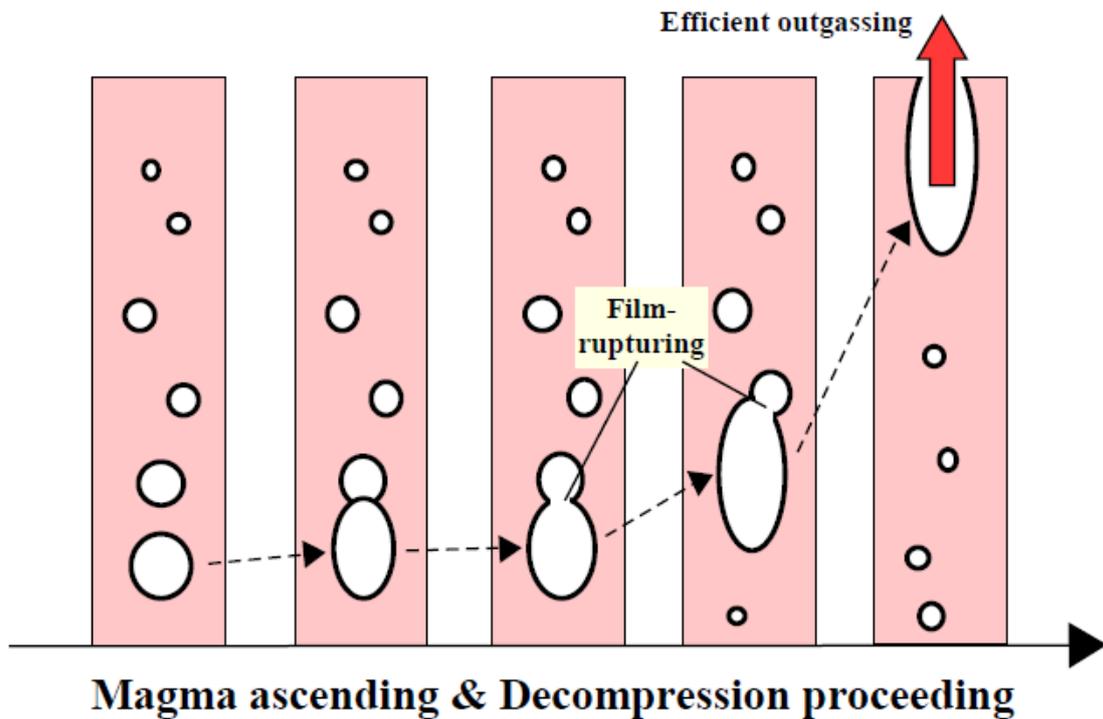


Figure 2-4. Expected bubble evolutions during magma ascending in volcanic conduits.

This figure was illustrated based on Figure 2 and Figure 4 of Namiki & Kagoshima (2014). Red squares and white circles indicate the same cell in a particular magma and voids in volcanic conduits, respectively. The magma is ascending and decompression is proceeding righter and righter. During magma ascent, voids are getting larger and rising in the cell, which results in the conflict among voids. Once conflicting bubble films rupture, the voids connect each other. These bubble rising and evolution associated with film-rupturing propagate from the deep magma to the surface as described in dotted vectors. Finally, evolved voids in the surface cause efficient outgassing from the magma to the atmosphere or the ocean as described in a red vector on the right. This efficient outgassing process may dominate volatile fluxes at MOR.

3.2. Methods

3.2.1. Glass vesicle

It is difficult to measure the abundance of sulfur species such as H₂S and SO₂ in vesicles of MORB glass together with ³He because such sulfur species are highly reactive and so sticky that they easily adhere to the inner wall of a vacuum crushing vessel and purification lines, which makes impossible to collect and measure them in a high yield enough to ignore decrease in concentrations and isotope fractionations, especially in static gas-MS systems. This is why I developed a gas-extraction method called as “Frozen Crushing Method” (FCM; see experimental details in *Appendix A*; Kagoshima et al., 2012). Sulfur and ³He concentrations in vesicles of MORB glasses were determined using this method. Subsequently, collected sulfate ion in the alkaline solution was converted into BaSO₄ precipitations by adding BaCl₂ solutions, and δ³⁴S values derived from vesicles were obtained with an elemental analyzer (vario PYRO cube; Elementar Analysensysteme, GmbH) coupled to an isotope-ratio mass spectrometer (Delta XP; Thermo Fisher Scientific Inc.) via an interface (ConFlo IV; Thermo Fisher Scientific Inc.) at the University of Ottawa.

3.2.2. Glass matrix

For some MORB glasses, finely crushed powders (<212μm) were combusted at the temperature of 1800C *in vacuo* with a tantalum oven, and volatiles including noble gases were extracted into the vacuum line. Thus the abundance of helium and ³He/⁴He ratios in powders were determined with a noble gas mass spectrometer (VG5400; Waters Corp.) at the Atmosphere and Ocean Research Institute (AORI), the University of Tokyo, in the same way as helium extracted from vesicles. Sulfur contents in glass matrix were measured with a secondary ion mass spectrometer (NanoSIMS; Cameca SAS, Gennevilliers, France) at AORI, whereas δ³⁴S values of some samples were obtained using an elemental analyzer isotope-ratio mass spectrometer system (Isoprime-EA; Isoprime Ltd.) at the University of Tsukuba (Maruoka et al., 2003).

3.3. Results

3.3.1. Vesicles

I analyzed MORB glass samples collected at eight sites on East Pacific Rise, Mid-Atlantic Ridge, and Central Indian Ridge (Fig. 2-2). The $^3\text{He}/^4\text{He}$ ratios and ^3He contents of vesicles in MORB glasses range from 7.96 R_a to 9.57 R_a (where R_a is the atmospheric ratio of 1.382×10^{-6} (Sano et al., 2013)), and from 5.8×10^{-16} mol/g to 5.1×10^{-15} mol/g (Table 2-5), respectively. The values agree well with data presented in an earlier report (Graham et al., 2002). The samples show similar sulfur contents ranging from 3.3×10^{-8} mol/g to 1.7×10^{-7} mol/g in vesicles. The S/ ^3He molar ratios in vesicles range from 1.8×10^7 to 1.3×10^8 with an average of $(4.6 \pm 1.3) \times 10^7$ (1σ), which is a little more variable relative to sulfur contents, but similar in the order. This S/ ^3He ratio will be used for assessing representative components released from the upper mantle. Evaluating $\delta^{34}\text{S}$ values of vesicle sulfur was impossible due to their low abundance less than the blank contribution from the filtering system inevitable for converting sulfur into BaSO_4 precipitations for gas-MS analyses. Thus I assume that the initial $\delta^{34}\text{S}$ value of 0‰ derived from the upper mantle (Marini et al., 2011) is also retained in vesicles. This value is also equivalent to the typical $\delta^{34}\text{S}$ value of $(+0.3 \pm 0.5)\%$ found in submarine glasses (Sakai et al., 1984). When uncertainty of $\delta^{34}\text{S}$ value in vesicles is similar to that obtained by bulk analyses, a $\delta^{34}\text{S}$ value of $(0 \pm 0.5)\%$ can be applied for the vesicle value.

3.3.2. Glass matrix

^3He concentrations in MORB glass matrix are listed in Table 2-6. ^3He concentrations in RY380-R03b and 418R002 were taken from my own earlier study (Kagoshima et al., 2012). ^3He concentrations in glass matrix of other samples were estimated multiplying those in vesicles and glass/vesicle content ratios of ^3He in RY380-R03b and 418R002 which had been calculated to be 1.43 as an average of 2.48 and 0.37 for RY380-R03b and 418R002, respectively. The ^3He concentrations in glass matrix have the range of $(9-57) \times 10^{-16}$ mol/g. The sulfur contents of MORB glass matrix measured with a NanoSIMS listed in Table 2-6 are well within the variation of sulfur contents in MOR glass obtained using a conventional method (Sakai et al., 1984). The average value of S/ ^3He ratios in the glass matrix was $(1.8 \pm 0.5) \times 10^{10}$ (1σ). Observed $\delta^{34}\text{S}$ values are consistent with those of

Table 2-5. Helium isotopic compositions, sulfur concentrations, and S/³He ratios in MORB glass vesicles.

Sample name	Number of analyses	³ He/ ⁴ He (R _a)	³ He concentration (10 ⁻¹⁶ mol/g)	S concentration (10 ⁻⁹ mol/g)	S/ ³ He (10 ⁶)
(East Pacific Rise)					
RY380-R03b	4	9.49 ± 0.16	23 ± 1	41 ± 6	18 ± 3
ND 18-1	2	9.57 ± 0.28	6 ± 1	33 ± 2	58 ± 8
CL DR01	3	8.02 ± 0.17	37 ± 6	88 ± 19	27 ± 11
(Mid-Atlantic Ridge)					
418R002	4	8.29 ± 0.13	51 ± 4	173 ± 21	34 ± 5
CH98 DR12	2	9.22 ± 0.24	10 ± 1	48 ± 0.4	48 ± 4
CH31 DR12	2	8.82 ± 0.70	13 ± 6	146 ± 42	129 ± 30
(Central Indian Ridge)					
KH10-6 DR15-glass	7	8.13 ± 0.07 *	37 ± 5 *	140 ± 14	36 ± 3 **
KH10-6 DR16-glass	4	7.96 ± 0.09	28 ± 1	55 ± 4	20 ± 2
Average		8.69 ± 0.24	25 ± 5	90 ± 19	46 ± 13

Uncertainty: 1σ

Blank contributions have been already subtracted from all values listed in this table.

Numbers of datasets used for calculations of values with superscripts * and ** are five and six, respectively. They are different from “7” listed in the “Number of analyses” column. These data reductions were caused by mistakes during helium isotope analyses.

Table 2-6. ^3He and sulfur concentrations, $\text{S}/^3\text{He}$ ratios, and $\delta^{34}\text{S}$ values of MORB glass matrix.

Sample name	^3He concentration (10^{-16}mol/g)	Number of SIMS analyses	S concentration (10^{-6}mol/g)	$\text{S}/^3\text{He}$ (10^8)	Number of IRMS analyses	$\delta^{34}\text{S}$ (‰)
(East Pacific Rise)						
RY380-R03b	57 *	18	43	76	3	0.45
ND 18-1	9 **	10	42	472		
CL DR01	53 **	15	39	73	1	1.26
(Mid-Atlantic Ridge)						
418R002	19 *	18	34	181	3	0.53
CH98 DR12	14 **	15	41	290		
CH31 DR12	19 **	15	33	176	1	0.78
(Central Indian Ridge)						
KH10-6 DR15-glass	53 **	10	26	49	1	-0.19
KH10-6 DR16-glass	40 **	10	38	94	1	0.11
Average	33		37	176		0.49

*: ^3He concentrations reported by Kagoshima et al. (2012).

** : ^3He concentrations estimated based on those in vesicles and glass/vesicle content ratios of ^3He in RY380-R03b and 418R002. See text for the calculations.

MOR basalt and mantle values (Sakai et al., 1984; Marini et al., 2011), suggesting the typical upper mantle-derived sulfur signature.

3.4. Discussion

3.4.1. Representative components derived from the upper mantle at mid-ocean ridges

The representative S/³He ratio and the ³He flux derived from the upper mantle at MOR are needed for sulfur flux calculations. The observed S/³He ratios of vesicles in MORB glass range from 1.8x10⁷ to 1.3x10⁸ (Table 2-5). These values are lower than 4.9x10⁹ - 4.7x10¹⁰ found in the glass matrix (Table 2-6). This observation suggests higher solubility of sulfur than of helium in basaltic melt, which is also supported by recent laboratory experiments (Webster & Botcharnikov, 2011). The average S/³He ratio in MORB glass vesicles is (4.6±1.3)x10⁷. Although vesicle components are preferentially released from magmas by propagations of film-rupturing as discussed above, some parts of sulfur in voids are thought to be finally trapped as sulfide spherules on vesicle walls (Moore & Calk, 1991). Such sulfide spherules are not dissolved into alkaline solutions those I used for experiments, thus the average vesicle S/³He ratio may be considered as the minimum value derived from the upper mantle at MOR. Another possible way to determine a representative S/³He ratio at MOR is to study chemistry of submarine hydrothermal fluids. The average S/³He ratio is (3.4±0.7)x10⁸ (1σ) among 10 high-temperature (>200C) hydrothermal sites worldwide (Table 2-7). The δ³⁴S value of H₂S in hot vent fluids is variable (Marini et al., 2011), but the original value before the incursion of seawater is similar to the MOR basalt values (Alt, 1995; Gamo, 1995). A small part of H₂S might be generated from the reduction of seawater SO₄ from the recharge zone (Alt, 1995), although it is difficult to deconvolve the contribution from the mantle and seawater precisely. Therefore the vent S/³He ratio of (3.4±0.7)x10⁸ is expected to be the maximum estimate at MOR. One might take an average of these two independent estimates (1.9±1.5)x10⁸ as the representative value derived from the upper mantle at MOR. S/³He ratios in MORB glass matrix are higher than this upper mantle value (Table 2-6), implying that helium has degassed from the melt before it was quenched to glasses and therefore these ratios are not appropriate to be considered for sulfur flux calculations.

Table 2-7. Helium isotopic compositions, H₂S concentrations, and δ³⁴S values of H₂S in high-temperature (>200C) hydrothermal fluids from mid-ocean ridges.

Hydrothermal fluids	Temperature (C)	³ He/ ⁴ He (R _o)	³ He (pM)	H ₂ S (mM)	δ ³⁴ S (‰)	S ³ /He (10 ⁷)	Reference
(Eastern Pacific)							
Juan de Fuca (47-48°N)	370	8.0	17.4	4.4		25.3	Butterfield et al. (1994)
East Pacific Rise (21°N)	340	7.8	17.3	7.5	3.1	43.4	Woodruff & Shanks (1988); Welhan & Craig (1983); Kim et al. (1984); Campbell et al. (1988a)
East Pacific Rise (13°N)	380	7.5	24.7	5.2		21.0	Kim et al. (1984); Merlivat et al. (1987); Bowers et al. (1988)
East Pacific Rise (11°N)	347	8.3	18.2	8.2	4.7	45.1	Kim et al. (1984); Bowers et al. (1988); Bluth & Ohmoto (1988)
East Pacific Rise (17-19°S)	382	8.3	9.2	7.0	6.2	75.4	Shanks (2001); Jean-Baptiste et al. (1997)
(Mid-Atlantic Ridge)							
Menez Gwen (38°N)	284	8.7	17.6	1.6		9.1	Charlou et al. (2000)
Lucky Strike (37°N)	324	8.1	4.5	2.7		61.0	Charlou et al. (2000)
Rainbow (36°N)	365	7.5	25.0	1.2		4.8	Charlou et al. (2002); Jean-Baptiste et al. (2004)
TAG (26°N)	358	7.5	15.8	4.0	8.5	25.4	Charlou et al. (1996); Rudnicki & Elderfield (1992); Chiba et al. (2001)
Snake Pit (23°N) MARK	350	7.9	19.4	5.9	5.0	30.5	Rudnicki & Elderfield (1992); Campbell et al. (1988b)
Average		8.0	16.9	4.8	5.5	34.1	

3.4.2. Sulfur flux at mid-ocean ridges

As described earlier, based on the saturation anomaly of ^3He in deep seawater of the eastern Pacific, a value of (1070 ± 270) mol/y was calculated for the ^3He flux at MOR (Craig et al., 1975), but a more recent estimate of the MOR ^3He flux is (527 ± 102) mol/y derived from an ocean circulation model which also considers radiocarbons and chlorofluorocarbons together with ^3He anomaly in deep seawater (Bianchi et al., 2010). The combination of this MOR ^3He flux of (527 ± 102) mol/y and the average S/ ^3He ratio of $(1.9\pm 1.5)\times 10^8$ obtained in this study provides MOR sulfur flux of $(1.0\pm 0.8)\times 10^{11}$ mol/y (Fig. 2-5). This flux is depicted in Fig. 2-6 together with previously reported fluxes. This mantle flux is consistent with the estimate based on seawater-basalt sulfur isotopic exchange during hydrothermal alteration (Alt, 1995), but it is about an order of magnitude smaller than the value calculated by the production rate of the oceanic crust and sulfur contents therein (Hansen & Wallmann, 2003). This difference suggests that most sulfur remains in the silicate melt and finally solidifies as sulfide in the oceanic crust, and does not contribute to the MOR flux that dissolves and discharges into the ocean. This is consistent with suggestions by Sakai & Matsuhisa (1996) and Tajika (1998), indicating a small part of sulfur in the oceanic crust is released into the ocean, while the most part remains in the oceanic crust. When we consider the mass balance of sulfur in global ocean water, the mantle sulfur flux of $(1.0\pm 0.8)\times 10^{11}$ mol/y is a second-order flux compared with the riverine input of 8.9×10^{11} mol/y into the ocean and the output of 5.5×10^{11} mol/y as sedimentary pyrite and evaporitic sulfate (Holser et al., 1988). However, the sulfur flux from the upper mantle into the ocean represents a deep Earth contribution and is therefore distinct from riverine sulfur input that is continent-derived and may be strongly related to return from subducting materials.

3.4.3. Sulfur flux at arc volcanoes

ARC ^3He flux was estimated from the MOR flux, given the assumption that the magma production rate of ARC is 20% of that of MOR. This portion is consistent with the estimate of global magma emplacement and volcanic output averaged over the last 180 m.y. (Crisp, 1984). Currently accepted MOR ^3He flux of (527 ± 102) mol/y (Bianchi et al., 2010) would result in an ARC ^3He flux of (105 ± 20) mol/y which is consistent with the value obtained by summation of ^3He flux at arc volcanoes worldwide (Hilton et

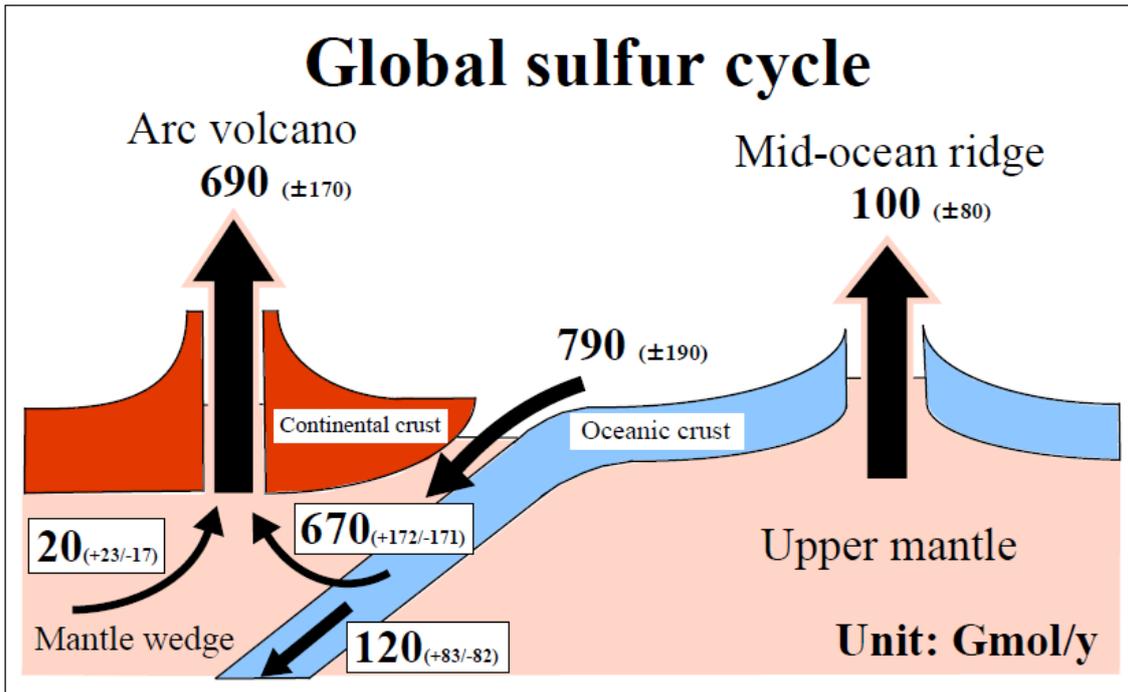


Figure 2-5. Global sulfur fluxes among the Earth's interior and surface reservoir.

Numbers are sulfur fluxes in the unit of Gmol/y among reservoirs with errors as subscripts. See text for calculations of fluxes at mid-ocean ridges (100 Gmol/y) and arc volcanoes (680 Gmol/y), and the mantle contribution to the ARC flux (21 Gmol/y). Other fluxes related to recycle and return processes were calculated under the assumption of the steady-state surface reservoir of sulfur.

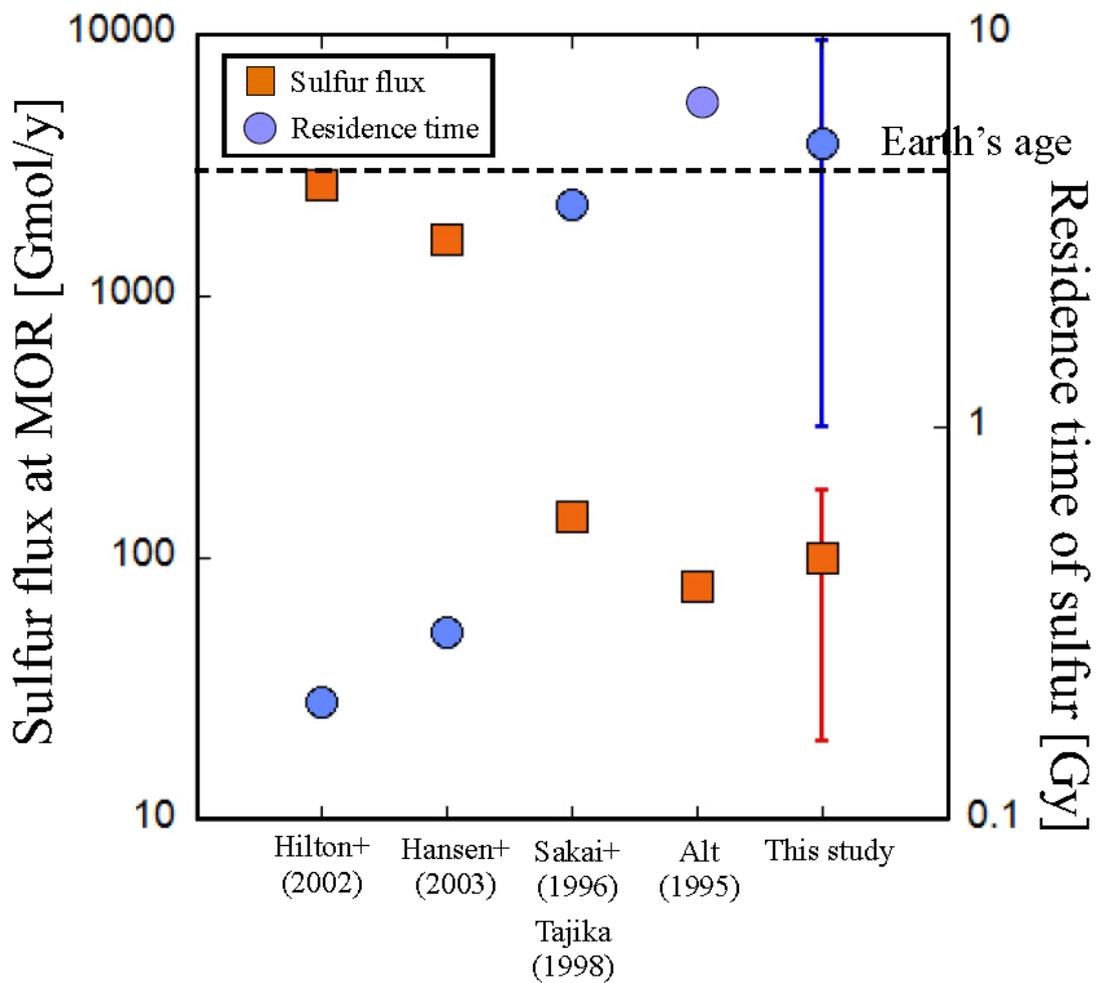


Figure 2-6. Sulfur fluxes at mid-ocean ridges.

Sulfur fluxes at MOR are from this study, Hilton et al. (2002), Hansen & Wallmann (2003), Sakai & Matsuhisa (1996), Tajika (1998), and Alt (1995). The residence times were calculated using sulfur fluxes and sulfur surface inventory of 5.3×10^{20} mol/y reported by Hilton et al. (2002). The Earth's age of 4.54×10^9 years (Tera, 1981) is depicted as the dashed line. The residence time longer than the Earth's age obtained in this study allows a catastrophic degassing history of sulfur. See text for the errors.

Table 2-8. Helium isotopic ratios, $\delta^{34}\text{S}$ values, and $\text{S}/^3\text{He}$ ratios in high temperature ($>200\text{C}$) volcanic gases.

Name	Lat.	Lon.	Location	Temp. ($^{\circ}\text{C}$)	$^3\text{He}/^4\text{He}$ (R_{∞})	$\delta^{34}\text{S}$ (‰)	$\text{S}/^3\text{He}$ (10^6)	Reference
Koryak	53.32N	158.69E	Kamchatka	215	5.3		8.0	Taran (2009)
Avacha	53.26N	158.83E	Kamchatka	473	7.1	6.4	2.3	Taran (2009); Taran et al. (1997)
Mutnovsky	52.45N	158.2E	Kamchatka	543	8.2	7.7	10.8	Taran (2009); Taran et al. (1992)
Kudryavy	46N	148E	Kuril	912	6.8	4.7	1.6	Taran (2009); Taran et al. (1995)
Usu	42.53N	140.83E	Japan	750	5.4	7.0	3.4	Fischer (2008); Marty et al. (1989); Kasasaku et al. (1999)
Kuju	33.1N	131.3E	Japan	580	7.6	4.2	7.8	Mizutani et al. (1986); Nagao et al. (1981); Saito et al. (2002)
Unzen	32.75N	130.3E	Japan	818	7.3		2.1	Fischer (2008); Sano & Williams (1996)
Satsuma-Iwojima	30.8N	130.3E	Japan	885	7.9	11.7	12.6	Taran (2009); Kasasaku et al. (1999)
Merapi	7.52S	110.43E	Indonesia	803	7.4		3.1	Taran (2009)
Lewotolo	8.27S	123.5E	Indonesia	490	3.6	5.2	11.6	Poorter et al. (1991); Varekamp et al. (1992)
White Island	37.52S	177.18E	New Zealand	495	6.1	4.0	8.4	Marty & Giggenbach (1990); Giggenbach (1982)
Ngauruhoe	39.15S	175.63E	New Zealand	640	6.7	4.4	8.4	Fischer (2008); Giggenbach (1982); Giggenbach et al. (1993); Giggenbach (1996)
Momotombo	12.41N	86.52E	Nicaragua	747	7.1	5.9	4.6	Taran (2009); Menyailov et al. (1986)
Galeras	1.22N	77.37W	Colombia	642	8.4	-8.9	1.0	Marini et al. (2011); Fischer (2008); Sano & Williams (1996)
Colima	0.95N	77.89W	Mexico	814	6.6	3.4	12.2	Taran (2009); Taran et al. (2001)
Average					6.8	4.6	6.5	

al., 2002). I selected 15 high-temperature (>200C) volcanic gases around the world and compiled their helium and sulfur compositions in Table 2-8. Their $^3\text{He}/^4\text{He}$ ratios range from 3.6 R_a to 8.4 R_a which are consistent with the range of subduction-type helium signature (Hilton et al., 2002; Sano & Fischer, 2013). $S/^3\text{He}$ ratios in volcanic gases range from 1.0×10^9 to 1.3×10^{10} with an average value of $(6.5 \pm 1.1) \times 10^9$ (1σ). Therefore, the ARC sulfur flux is estimated to be $(6.9 \pm 1.7) \times 10^{11}$ mol/y multiplying this volcanic gas ratio and the ARC ^3He flux of 105 ± 20 mol/y.

3.4.4. Deconvolution of sulfur flux at ARC

In order to estimate the sulfur flux from the mantle to the surface through arc volcanisms, I deconvolved magmatic sulfur into the mantle component and other end-members. As discussed for carbon, sulfur and helium isotopic compositions are also useful for investigating the origin of sulfur at arc volcanoes. The thermodynamic equilibrium between SO_2 and H_2S together with their $\delta^{34}\text{S}$ values might provide constraints on the evolution of volcanic gases, such as an isochemical cooling path, under the assumption that the initial $\delta^{34}\text{S}_{\Sigma\text{S}}$ value is $(0 \pm 0.5)\%$ as discussed for the results of vesicle analyses, where $\delta^{34}\text{S}_{\Sigma\text{S}}$ denotes the total sulfur isotopic ratio of SO_2 and H_2S . In addition, the $\delta^{34}\text{S}_{\Sigma\text{S}}$ values might provide information related to the origin of sulfur in ARC volcanic gases, even though they might be affected by a gas-melt separation and related fractionation processes (Marini et al., 2011; de Moor et al., 2013). Available data of ^3He and total sulfur contents, and $\delta^{34}\text{S}_{\Sigma\text{S}}$ values for high-temperature volcanic gases (>200C) in subduction zones were compiled from the literature and listed in Table 2-8. The $\delta^{34}\text{S}_{\Sigma\text{S}}$ values are generally positive, except for one outlier from Galeras. This similarity suggests that the sulfur signature of an ARC magma source is due to incorporation of subducted sulfate partly derived from a seawater component (de Moor et al., 2013; Sakai & Matsubaya, 1977; Alt et al., 1993) with high $\delta^{34}\text{S}$ values. The average $S/^3\text{He}$ ratio of $(6.5 \pm 1.1) \times 10^9$ among these high-temperature ARC gases is significantly high value relative to that of the upper mantle, suggesting enrichment of sulfur in the ARC mantle source by subduction processes.

As discussed for carbon, following Sano & Marty (1995), sulfur and helium isotopic compositions in arc volcanic gases can be explained by some-component mixing because

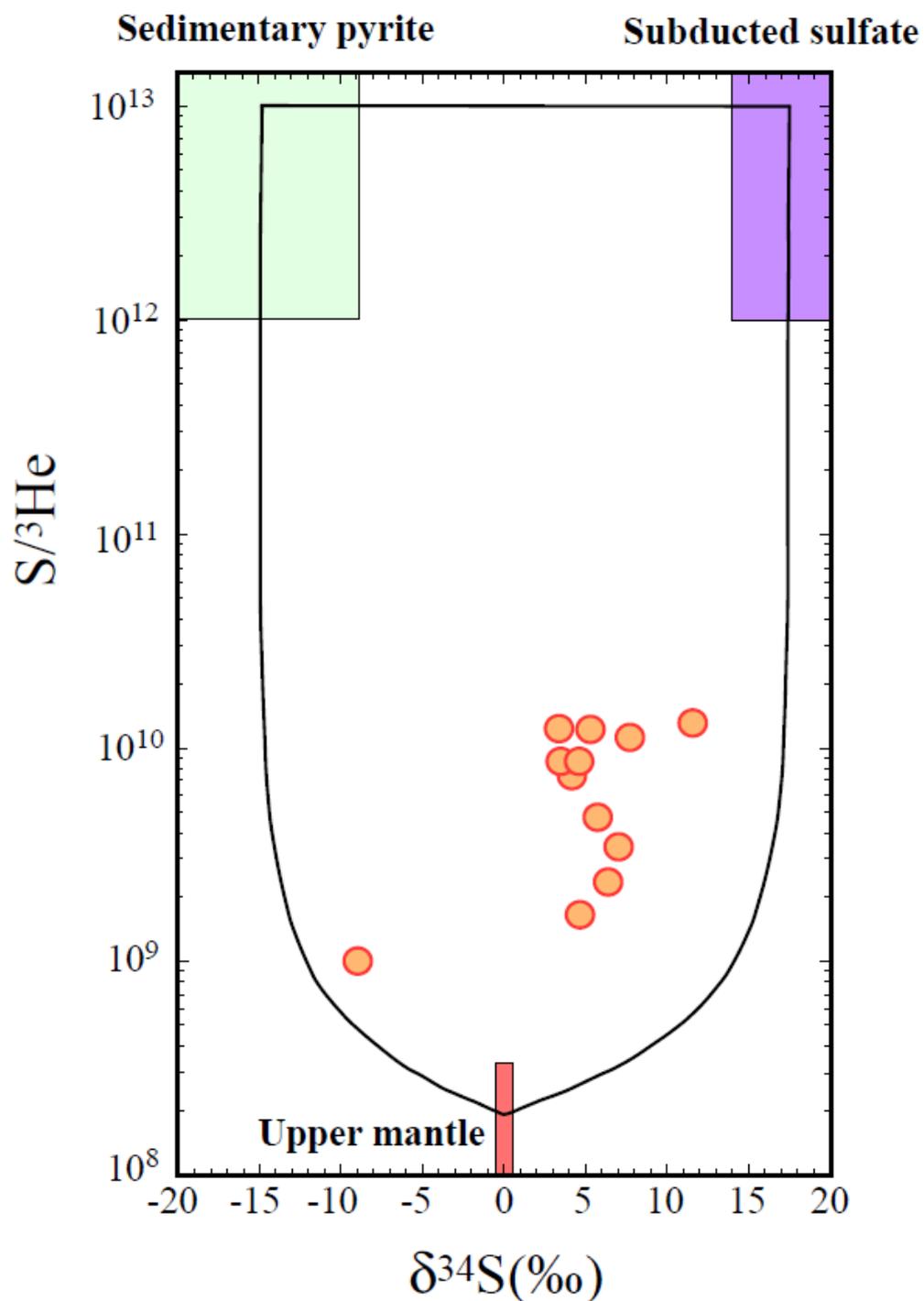


Figure 2-7. Sulfur and helium compositions in volcanic gases and their end-members.

Volcanic gas data described in Table 2-8 and 2-9 are shown as red circles. Three square zones are end-members of volcanic gases: the upper mantle-derived component, sedimentary pyrite with reduced sulfur derived from slab abbreviated as “sedimentary pyrite”, and subducted sulfate. Mixing lines of three end-members are depicted as solid curves.

Table 2-9. Sample and end-member compositions with sulfur contributions.

Name	$\delta^{34}\text{S}$ (‰)	$\text{S}/^3\text{He}$	Sulfur source contribution		
			Upper mantle	Sedimentary pyrite	Subducted sulphate
Koryak		8.0E+09	2.4%		
Avacha	6.4	2.3E+09	8.4%	29.9%	61.7%
Mutnovsky	7.7	1.1E+10	1.8%	29.3%	68.9%
Kudryavy	4.7	1.6E+09	11.9%	33.1%	55.0%
Usu	7.0	3.4E+09	5.7%	29.3%	65.0%
Kuju	4.2	7.8E+09	2.4%	39.7%	57.9%
Unzen		2.1E+09	9.1%		
Satsuma-Iwojima	11.7	1.3E+10	1.5%	17.1%	81.4%
Merapi		3.1E+09	6.1%		
Lewotolo	5.2	1.2E+10	1.6%	37.1%	61.3%
White Island	4.0	8.4E+09	2.2%	40.5%	57.3%
Ngauruhoe	4.4	8.4E+09	2.3%	39.3%	58.4%
Momotombo	5.9	4.6E+09	4.2%	33.5%	62.4%
Galeras	-8.9	1.0E+09	18.8%	71.4%	9.8%
Colima	3.4	1.2E+10	1.6%	42.6%	55.9%
Average values	4.6	6.5E+09	2.9%	38.1%	59.0%

(End-members)					
Upper mantle	0.0	1.9E+08	100.0%		
Sedimentary pyrite	-14.9	1.0E+13		100.0%	
Subducted sulfate	17.5	1.0E+13			100.0%

Data of subaerial volcanoes and three end-members are described here. See text for the calculations of end-member contributions.

sources of volcanic gases are mixtures of the upper mantle component and subducting materials. I apply here the upper mantle-derived component, sedimentary pyrite with reduced sulfur derived from slab (abbreviated as sedimentary pyrite hereafter), and subducted sulfate as end-members producing volcanic gas compositions (Fig. 2-7; Table 2-9). The $S/^3\text{He}$ ratio derived from the upper mantle is $(1.9\pm 1.5)\times 10^8$ determined by compositions of MORB vesicles and submarine hydrothermal fluids in the current study. As carbon, one would apply a fixed $S/^3\text{He}$ ratio of $10^{(13\pm 1)}$ for subducting materials such as sedimentary pyrite, slab components, and subducted sulfate because pyrite and slab are depleted in the primordial ^3He injected from the mantle (Hiyagon, 1994), and the seawater $\text{SO}_4/^3\text{He}$ of 1.0×10^{14} is almost equivalent to the value suggested here for subducting materials. The $\delta^{34}\text{S}$ values of sedimentary pyrite vary considerably as a result of bacterial reduction of seawater sulfate, and have a mean value of -20.9‰ in the Western Pacific (Alt & Burdett, 1992). Results of a recent study (Alt et al., 2012) of the oceanic basement in northern Italy suggest that low-temperature serpentinization produces a negative $\delta^{34}\text{S}_{\text{SS}}$ value with $(-8.9\pm 8.0)\text{‰}$. An average of the two components, $(-14.9\pm 6.0)\text{‰}$, can be regarded as a representative $\delta^{34}\text{S}$ value of sedimentary pyrite. On the other hand, subducted sulfate is mostly derived from sulfate dissolved in seawater with a $\delta^{34}\text{S}$ value of $+21.0\text{‰}$ (Rees, 1978). Metasomatic fluids released from sediment, of which the sulfur is mostly in the form of sulfate, have a $\delta^{34}\text{S}$ value of $+14\text{‰}$ when their sulfur compositions resemble the bulk sediment composition (Alt et al., 1993). Using these values, the $\delta^{34}\text{S}$ value of subducted sulfate is defined as $(+17.5\pm 3.5)\text{‰}$ as an average of the two components. Figure 2-7 presents the relation between $S/^3\text{He}$ ratios and $\delta^{34}\text{S}_{\text{SS}}$ values in arc volcanic gases, indicating that their sulfur and helium compositions can be exactly explained by mixing of three components applied here.

When sulfur in volcanic gases are mixtures of the upper mantle, sedimentary pyrite, and subducted sulfate having respective masses M , P , and S , contribution percentages of the three components in the ARC samples can be deconvolved solving the following equations:

$$\delta^{34}\text{S}_V = \delta^{34}\text{S}_M M + \delta^{34}\text{S}_P P + \delta^{34}\text{S}_S S \quad (2-4)$$

$$1/(S/^3\text{He})_V = M/(S/^3\text{He})_M + P/(S/^3\text{He})_P + S/(S/^3\text{He})_S \quad (2-5)$$

$$M + P + S = 1 \quad (2-6)$$

In those equations, subscripts V, M, P and S denote the volcanic gases (ARC samples), the upper mantle, sedimentary pyrite, and subducted sulfate, respectively. As discussed above, $\delta^{34}\text{S}_M = (0\pm 0.5)\%$, $\delta^{34}\text{S}_P = (-14.9\pm 6.0)\%$, $\delta^{34}\text{S}_S = (+17.5\pm 3.5)\%$, $(\text{S}/^3\text{He})_M = (1.9\pm 1.5)\times 10^8$, $(\text{S}/^3\text{He})_P = 1.0\times 10^{(13\pm 1)}$, and $(\text{S}/^3\text{He})_S = 1.0\times 10^{(13\pm 1)}$ are applied for contribution calculations. The contribution of mantle sulfur is 1.5%-19% (2.9% average) in ARC samples, and the main contribution derives from subducted sulfate and sedimentary pyrite (Table 2-9). The volcanic gas from Satsuma-Iwojima shows the highest subducted sulfate contribution of 81.4% with the highest $\delta^{34}\text{S}_{\Sigma\text{S}}$ value of 11.7%. In order to explain the heavy $\delta^{34}\text{S}_{\Sigma\text{S}}$ values of ARC volcanic gases, incorporation of a seawater component in the magma source has been inferred since the 1970s (Sakai & Matsubaya, 1977). Here we first provide a quantification of the relative amount of the subducted seawater sulfate contribution to ARC gases, which allows us to evaluate the recycling capacity of ARC volcanoes within the global sulfur cycle.

The ARC sulfur flux was calculated to be $(6.9\pm 1.7)\times 10^{11}$ mol/y as discussed in the previous section. This value is significantly higher than MOR sulfur flux of $(1.0\pm 0.8)\times 10^{11}$ mol/y also estimated in this study. However the upper mantle contribution to ARC volcanic gases is only $(2.9\pm 3.3\pm 2.4)\%$ of total sulfur, on average. The uncertainty of the upper mantle contribution was calculated based on the highest and the lowest upper mantle contributions calculated from extremely high or low values' sample and end-member compositions as follows: the upper mantle contribution of 6.2% derived from the case applying $\text{S}/^3\text{He}$ ratios of 5.4×10^9 , 3.4×10^8 , 1.0×10^{14} , and 1.0×10^{14} for ARC samples, the upper mantle, sedimentary pyrite, and subducted sulfate; and the upper mantle contribution of 0.5% derived from the case applying $\text{S}/^3\text{He}$ ratios of 7.6×10^9 , 4.0×10^7 , 1.0×10^{12} , and 1.0×10^{12} for ARC samples, the upper mantle, sedimentary pyrite, and subducted sulfate. The sulfur flux from the wedge mantle at ARC then becomes $(2.0\pm 2.3\pm 1.7)\times 10^{10}$ mol/y, which is less than the mantle sulfur flux discharging into the ocean at MOR. The major contribution of the ARC sulfur flux is derived from subducted sedimentary pyrite and subducted sulfate partly derived from the seawater component.

3.4.5. Contribution to global flux of sulfur from present hot spot magmatism

Intra-plate volcanism such as that at Hawaii or Yellowstone might release large amounts of sulfur, but no study for that has been reported in the literature. The global hot spot ^3He flux of 2.5 mol/y was reported based on Hawaiian magma (Torgersen, 1989), which was not scaled to MOR flux as for ARC. It is not necessary to revise the value according to the new MOR flux (Bianchi et al., 2010). The S/ ^3He ratio of Kilauea volcanic gas is 5.6×10^8 , where the S/He ratio and $^3\text{He}/^4\text{He}$ ratio were referred from the literature (Craig & Lupton, 1976; Fischer, 2008). Yellowstone and Iceland fluid samples (Hearn et al., 1990; Sano et al., 1985) show ratios of 5.0×10^7 and 1.1×10^8 , which are both smaller than the Hawaiian value, although their temperatures are lower than 200C. Then the global sulfur flux at hot spot regions might not exceed the value of 1.4×10^9 mol/y, which is almost two orders of magnitude smaller than the MOR flux of 1.0×10^{11} mol/y. Therefore the hot spot magmatism does not strongly affect the global sulfur cycle and is ignored for discussion of geochemical sulfur cycles in this study.

3.4.6. Global sulfur cycle

A summary of the global sulfur flux is depicted in Fig. 2-5. Present hot spot magmatism does not likely contribute substantially to the global flux of sulfur as discussed in the previous section. The total volcanic flux of sulfur is estimated as $(7.9 \pm 1.9) \times 10^{11}$ mol/y and represents about one-third of the anthropogenic emissions due to coal burning and sulfide ore smelting (Moller, 1984). This natural flux, if it has remained constant over 4.54 billion years of geological time (Tera, 1981), engenders an accumulation of $(3.6 \pm 0.9) \times 10^{21}$ mol. This value is greater than the surface inventory of 5.3×10^{20} mol (Hilton et al., 2002). If we take the MOR flux together only with the mantle wedge flux of $(2.0 \pm 2.3 \pm 1.7) \times 10^{10}$ mol/y, then the accumulation becomes $(5.4 \pm 3.8) \times 10^{20}$ mol in total, which is comparable to the surface inventory. When steady-state recycling of sulfur is applied, the total subducting flux becomes $(7.9 \pm 1.9) \times 10^{11}$ mol/y. This value is lower than 4.11×10^{12} mol/y reported by Hilton et al. (2002). Such contradiction may be derived by the difference in estimation methods of sulfur fluxes, that is, Hilton's flux includes components staying in the oceanic crust and subducted which is not considered as fluxes in this study because such components does not contribute to the global flux from the mantle to the surface.

4. Conclusions

Sulfur and helium compositions in MORB vesicles were determined by the currently established crushing technique based on the conventional noble gas analyses. The advantage of this technique is that sulfur fluxes could be calibrated against the well-determined ^3He fluxes because sulfur is extracted simultaneously with helium isotopes. The data obtained by the crushing method was applied to constrain the sulfur flux at MOR. In conclusion, the best estimates of MOR sulfur and carbon flux are $(1.0\pm 0.8)\times 10^{11}$ mol/y and $(1.2\pm 0.4)\times 10^{12}$ mol/y, respectively at present, which are less than their volcanic fluxes at ARC. Sulfur and carbon fluxes from only the mantle wedge to the surface environment at ARC were calculated to be $(2.0\pm 2.3\text{--}1.7)\times 10^{10}$ mol/y and $(2.3\pm 1.5\text{--}1.2)\times 10^{11}$ mol/y, respectively. Summations of MOR fluxes and mantle contributions to ARC fluxes provided mantle-derived sulfur and carbon fluxes of $(1.2\pm 0.8)\times 10^{11}$ mol/y and $(1.4\pm 0.4)\times 10^{12}$ mol/y, respectively. These data provide a C/S flux ratio of (12 ± 8) which is similar to the C/S ratio in the surface inventory of 13 (Hilton et al., 2002). The results suggest that the main source of sulfur and carbon is the upper mantle. To balance the mass between the crust and the mantle, the sulfur subducted into the mantle and not immediately recycled to the surface is expected to be equivalent to $(1.2\pm 0.8)\times 10^{11}$ mol/y, which is about $(15\pm 11)\%$ of the subducted sulfur of $(7.9\pm 1.9)\times 10^{11}$ mol/y. We calculated sulfur and carbon fluxes from the mantle based on the plausible S/ ^3He and C/ ^3He ratios and the recently reported ^3He flux at MOR, which constrained geochemical cycles of sulfur and carbon, and evolutionary histories of the atmosphere and hydrosphere.

Chapter 3

Geochemical cycles of halogens

Contents in this chapter will be published in five years.

本章については、5年以内に雑誌等で刊行予定のため非公開。

Chapter 4

Summary and general conclusions

Earth's atmosphere and ocean have been produced by accumulation of volatile species injected from the mantle through volcanic and hydrothermal activity. Sulfur and carbon are major components of volcanic gases which are injected into surface environment in forms of SO₂, H₂S, CO₂, CH₄, and they significantly affect atmospheric and oceanic chemistry and their evolution. Therefore their fluxes are important to reveal Earth's evolution and to assess how much volcanic activity affects chemistry of surface environment. Halogens are also important volatile elements for elucidating evolutionary histories of Earth's atmosphere and ocean because they form variable chemical compounds in surface environments due to their high chemical activity. In addition, they are concentrated in fluids and have been used as hydrogeological tracers. In order to constrain their evolution on Earth, I have assessed their behavior between the mantle and surface environments in this study. For sulfur and halogen fluxes, an approach using calibration against the reliable ³He flux was applied for elucidating their cycles.

In *Chapter 2*, in order to estimate sulfur flux at mid-ocean ridges (MOR), I focused on the volatile components preferentially released from magmas through film rupturing processes in ascending magmas. Such components are expected to be retained in vesicles of MORB glasses, and they are analyzed with the currently established crushing technique based on the conventional noble gas analyses. Sulfur is extracted into the solution and measured using ion chromatography, while helium isotopes are measured using a noble gas mass spectrometer in the protocol. The advantage of this technique is that sulfur fluxes could be calibrated against the well-determined ³He fluxes because sulfur is extracted simultaneously with helium isotopes. The data obtained by the crushing method was applied to constrain the sulfur flux at MOR. Carbon flux was also calibrated against the ³He flux. In conclusion, the best estimates of MOR sulfur and carbon fluxes are $(1.0 \pm 0.8) \times 10^{11}$ mol/y and $(1.2 \pm 0.4) \times 10^{12}$ mol/y, respectively at present, which are less than their volcanic fluxes at arc volcanoes (ARC). Wedge mantle contributions to ARC fluxes have been deconvolved, providing total mantle fluxes combined with MOR

results. I calculated the mantle C/S flux ratio as (12+/-8) which is similar to the C/S ratio in the surface inventory of 13. The results suggest that the main source of sulfur and carbon is the upper mantle.

In *Chapter 3*, in order to estimate halogen fluxes at MOR, I focused on the volatile components preferentially released from magmas as sulfur, and analyzed MORB glasses. The complete halogens and helium datasets in MORB vesicles were obtained by combinations of some independent analyses. Helium, fluorine, and chlorine data were obtained by crushing experiment followed by noble gas mass spectrometry and ion chromatography, which is the similar way as sulfur. Chlorine, bromine, and iodine contents in vesicles were determined by the noble gas method which converts halogens into proxy noble gas isotopes. Combinations of data enabled me to estimate halogen fluxes at MOR by calibrating against the well documented ^3He flux.

This part will be published in five years.

この部分については、5年以内に雑誌等で刊行予定のため非公開。

In conclusions, I have determined sulfur, carbon, and halogen fluxes between the mantle and surface environment by calibrating against the reliable ^3He fluxes. Simultaneous analyses of helium and other highly reactive volatile elements, when combined with other conventional analytical techniques, provided complete datasets of sulfur, halogens and helium.

This part will be published in five years.

この部分については、5年以内に雑誌等で刊行予定のため非公開。

I have investigated geochemical cycles of variable volatile elements in my Ph.D. course followed by a half year as a research associate in Atmosphere and Ocean Research Institute. In the future, research focusing on behaviors of volatile elements including helium at individual volcano is needed in order to elucidate volatile cycles in subduction zones more precisely. This is also important to assess volcanic hazards such as enormous eruptions. A case study has been conducted at Ontake volcano for revealing helium and carbon behaviors related to eruptions (see *Appendix C*), indicating that helium isotopes are the most sensitive magmatic tracers and useful to assess volcanic activity. Chlorine isotopes could be also useful tracers for investigating volatile cycles at subduction zones. Chlorine isotope analyses with reasonably high resolution using NanoSIMS have been conducted (see *Appendix B*), and the results showed that the NanoSIMS technique is useful for assessing aqueous alteration. The precision should be enhanced to trace magmatic chlorine for elucidating geochemical cycles of halogens and water.

Appendix A

Frozen Crushing Method

Sulfur and halogen concentrations in MORB glasses were measured for estimating their mantle fluxes and geochemical cycles in this study. The detail of the crushing method (Frozen Crushing Method, abbreviated as FCM hereafter; Kagoshima et al., 2012) applied to extract sulfur, fluorine, chlorine, and noble gases from MORB vesicles simultaneously in *Chapter 2* and *3* is described below. Applying FCM, MORB vesicle compositions are determined by crushing with frozen alkaline solutions followed by analyses using a noble gas mass spectrometer and an anion chromatography system.

FCM is a modified version of the conventional *in vacuo* crushing method for solid samples. A difference is that samples are loaded in the vacuum crushing vessel with alkaline solutions such as NaOH solution and NH₃ solution. 0.5g to 1.0g of fresh submarine glass aliquots were selected by eyes and washed by ultra-sonic bath with Milli-Q water (>18 MΩ cm; Millipore Co.) for five minutes followed by ethanol for five minutes. After that, ultra-sonicated samples were loaded into a stainless-steel crusher with 1-2 cm³ of alkaline solution (diluted NaOH or NH₃ solutions whose concentrations were 0.2-4.0 mol/L and 5.6 mol/L (10%), respectively) and a stainless-steel ball for crushing (Fig. A-1b). In the conventional way, air fraction is removed by vacuum before crushing because atmospheric noble gases can easily mask sample noble gas signatures. However, FCM does not allow us to pump out air in the room temperature because the vessel contains liquid water inside. This problem can be solved by pumping out after freezing solutions at liquid nitrogen temperature (77K). Closing the crusher, the alkaline solution was frozen by cooling the crusher itself in liquid nitrogen, and the air in the crusher were removed using a rotary pump (Fig. A-1c). Once the frozen solution was melted at the room temperature using hot water, it was frozen again using liquid nitrogen and evacuated with a turbo molecular pump (TMP) for five minutes. Applying this TMP evacuation procedure to the solution for two times, the atmospheric noble gases dissolved in the solution and on the sample surface were removed, and blanks of helium were resulted to be negligibly small compared with actual samples. The blank contribution to ³He concentrations in samples were calculated as less than 1%. After the TMP procedure, sample aliquots were crushed by 1500 to 2000-time strokes of the vessel at around liquid

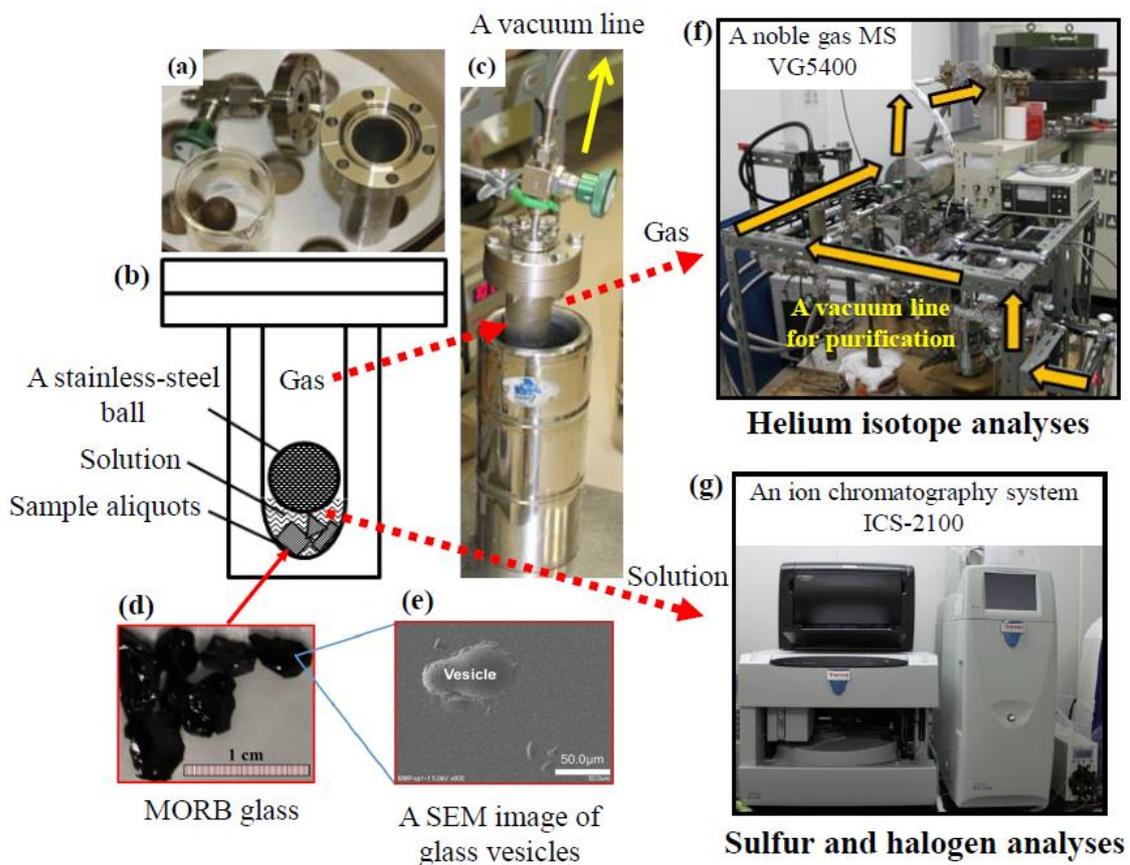


Figure A-1. Frozen Crushing Method.

(a) A stainless-steel crusher and a stainless-steel ball used for FCM; (b) a schematic view of inside of the crusher; (c) the crusher attached to a vacuum line being cooled at the temperature of 77K by liquid nitrogen; (d) MORB glass aliquots loaded into the crusher; (e) a SEM image of glass vesicles where volatiles are extracted from; (f) a noble gas mass spectrometer (VG5400) used for helium isotope analyses and the vacuum line for purification of gases transferred from the crusher with vectors indicating flows of purification; and (g) an ion chromatography system (ICS-2100) used for sulfur and halogen analyses of solutions extracted from the crusher.

nitrogen temperature which keeps the solution mostly frozen. The glass aliquots were crushed with the frozen solution by the stainless-steel ball in the crusher, and volatiles were extracted from the glass vesicles by mechanical fracturing. Within the extracted volatiles, sulfur and halogen species, which are highly reactive ones, are fixed immediately in the semi-frozen alkaline solution. On the other hand, noble gases including helium isotopes are extracted into the gaseous phase in the crushing vessel. Adsorption of much amount of the solution on the inner wall of the crushing vessel was avoided by the low temperature keeping the solution mostly frozen.

After the crushing procedures, the solution was frozen again and the gaseous phase in the crusher was introduced into a vacuum line for purification followed by noble gas analyses (Fig. A-1f). At first, H₂O and CO₂ were trapped by a U-tube with the liquid nitrogen temperature (77K) for 1-2 minutes. Subsequently, other major components such as N₂ and O₂ were removed using an activated charcoal also at the liquid nitrogen temperature of 77K for 20 minutes. Next, H₂ and heavy noble gases were removed by a heated Ti-getter and another activated charcoal kept at 77K for 20 minutes. After that, I measured ⁴He/²⁰Ne ratios of the purified gas with a quadrupole mass spectrometer in order to evaluate contamination from air fractions. At last, neon was removed by a cryogenic charcoal kept at 40K. The purified helium gas was introduced into a noble gas mass spectrometer (VG5400; Waters Corp.) at the Atmosphere and Ocean Research Institute (AORI), the University of Tokyo for helium isotope analyses. Using VG5400, the ⁴He amount and the ³He/⁴He ratio in the gas was measured (Sano & Wakita, 1988), and they were calibrated against air and our in-house standard gas which has a particular ³He/⁴He ratio of 20.4 R_a (Helium standard of Japan; Matsuda et al., 2002).

Subsequently, the vacuum in the crusher was broken and the alkaline solution was filtered to remove glass fragments whose diameters are longer than 0.2 μm. After that, all the sulfur compounds were converted into sulfate ions by oxidation with 1-2 cm³ of hydrogen peroxide (30%). Sulfur, fluorine, and chlorine concentrations in the solution were measured using an ion chromatography system (ICS-2100; Thermo Fisher Scientific Inc.; Fig. A-1g) at AORI. The anions (F⁻, Cl⁻, and SO₄²⁻) were analyzed using an AS11-HC anion exchange column with an AG11-HC guard column (Thermo Fisher Scientific Inc.). An EGCIII-KOH cartridge (Thermo Fisher Scientific Inc.) was used to produce potassium hydroxide eluent. In addition, a CRD-200 carbonate removal devise (Thermo

Fisher Scientific Inc.) was used to remove carbonate ions which interfere sulfate peaks. Blank solutions were prepared by the same concentrations of the alkaline solutions and times of stroking as actual samples. After noble gas, sulfur, and halogen analyses, finely crushed sample glass powders whose diameters are shorter than 212 μm were weighed in order to determine weights of samples crushed and concentrations of volatile elements originally in the samples. More details about FCM are presented in an earlier report (Kagoshima et al., 2012).

Appendix B

Chlorine isotope analyses using NanoSIMS

Contents in this appendix will be published in five years.

本補遺の内容については、5年以内に雑誌等で刊行予定のため非公開。

Appendix C

Helium and carbon isotope variations at Ontake volcano, Japan

Contents in this appendix will be published in five years.

本補遺の内容については、5年以内に雑誌等で刊行予定のため非公開。

References

- Alt, J.C. Sulfur isotopic profile through the oceanic crust: Sulfur mobility and seawater-crustal sulfur exchange during hydrothermal alteration. *Geology* **23**, 585-588 (1995).
- Alt, J.C. & Burdett, J.W. Sulfur in Pacific deep-sediments (Leg 129) and implications for cycling of sediment in subduction zones. *Proc. ODP, Sci. Results* **129**, 283-294 (1992).
- Alt, J.C., Shanks III, W.C., Crispini, L., Gaggero, L., Schwarzenbach, E.M., Fruh-Green, G.L. & Bernasconi, S.M. Uptake of carbon and sulfur during seafloor serpentinization and effects of subduction metamorphism in Ligurian peridotites. *Chem. Geol.* **322-323**, 268-277 (2012).
- Alt, J.C., Shanks III, W.C. & Jackson, M.C. Cycling of sulfur in subduction zones: The geochemistry of sulfur in the Mariana Island Arc and back-arc trough. *Earth Planet. Sci. Lett.* **119**, 477-494 (1993).
- Barnes, J.D. & Sharp, Z.D. A chlorine isotope study of DSDP/ODP serpentinized ultramafic rocks: insights into the serpentinization process. *Chem. Geol.* **228**, 246-265 (2006).
- Barnes, J.D., Sharp, Z.D., Fischer, T.P., Hilton, D.R. & Carr, M.J. Chlorine isotope variations along the Central American volcanic front and back arc. *Geochem. Geophys. Geosyst.* **10**, Q11S17 (2009).
- Bianchi, D., Sarmiento, J.L., Gnanadesikan, A., Key, R.M., Schlosser, P. & Newton, R. Low helium flux from the mantle inferred from simulations of oceanic helium isotope data. *Earth Planet. Sci. Lett.* **297**, 379-386 (2010).
- Bluth, G.J. & Ohmoto, H. Sulfide-sulfate chimneys on the East Pacific Rise, 11° and 13°N latitudes. Part II: Sulfur isotopes. *Can. Mineral.* **26**, 505-515 (1988).
- Bluth, G.J.S., Schnetzler, C.C., Krueger, A.J. & Walter, L.S. The contribution of explosive volcanism to global atmospheric sulphur dioxide concentrations. *Nature* **366**, 327-329 (1993).
- Böhlke, J.K. & Irwin, J.J. Laserprobe analyses of Cl, Br, I, and K in fluid inclusions: Implications for the sources of salinity in some ancient hydrothermal fluids. *Geochim. Cosmochim. Acta* **56**, 203-225 (1992).
- Bonifacie, M., Jendrzewski, N., Agrinier, P., Coleman, M., Pineau, F. & Javoy, M.

- Pyrohydrolysis-IRMS determination of silicate chlorine stable isotope compositions. Application to oceanic crust and meteorite samples. *Chem. Geol.* **242**, 187-201 (2007a).
- Bonifacie, M., Monnin, C., Jendrzewski, N., Agrinier, P. & Javoy, M. Chlorine stable isotopic composition of basement fluids of the eastern flank of the Juan de Fuca Ridge (ODP Leg 168). *Earth Planet. Sci. Lett.* **260**, 10-22 (2007b).
- Bonifacie, M., Jendrzewski, N., Agrinier, P., Humler, E., Coleman, M. & Javoy, M. The chlorine isotope composition of Earth's mantle. *Science* **319**, 1518-1520 (2008).
- Bowers, T.S., Campbell, A.C., Measures, C.I., Spivack, A.J., Khadem, M., Edmond, J.M. Chemical controls on the composition of vent fluids at 13°N-11°N and 21°N, East Pacific Rise. *J. Geophys. Res.* **93**, 4522-4536 (1988).
- Butterfield, D.A., McDuff, R.E., Mottl, M.J., Lilley, M.D., Lupton, J.E. & Massoth, G.J. Gradients in the composition of hydrothermal fluids from the Endeavour segment vent field: Phase separation and brine loss. *J. Geophys. Res.* **99**, 9561-9583 (1994).
- Campbell, A.C., Bowers, T.S., Measures, C.I., Falkner, K.K., Khadem, M. & Edmond, J.M. 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). *J. Geophys. Res.* **93**, 4537-4549 (1988a).
- Campbell, A.C. & Edmond, J.M. Halide systematics of submarine hydrothermal vents. *Nature* **342**, 168-170 (1989).
- Campbell, A.C., Palmer, M.R., Klinkhammer, G.P., Bowers, T.S., Edmond, J.M., Lawrence, J.R., Casey, J.F., Thompson, G., Humphris, S., Rona, P. & Karson, J.A. Chemistry of hot springs on the Mid-Atlantic Ridge. *Nature* **335**, 514-519 (1988b).
- Capasso, G., Carapezza, M.L., Federico, C., Inguaggiato, S. & Rizzo, A. Geochemical monitoring of the 2002-2003 eruption at Stromboli volcano (Italy): precursory changes in the carbon and helium isotopic composition of fumarole gases and thermal waters. *Bull. Volcanol.* **68**, 118-134 (2005).
- Cartigny, P., Pineau, F., Aubaud, C., Javoy, M. Towards a consistent mantle carbon flux estimate: insights from volatile systematics (H₂O/Ce, δD, CO₂/Nb) in the North Atlantic mantle (14°N and 34°N). *Earth Planet. Sci. Lett.* **265**, 672-685 (2008).
- Charlou, J.L., Donval, J.P., Douville, E., Jean-Baptiste, P., Radford-Knoery, J., Fouquet, Y., Dapoigny, A. & Stievenard, M. Compared geochemical signatures and the

- evolution of Menez Gwen (37°50'N) and Lucky Strike (37°17'N) hydrothermal fluids, south of the Azores Triple Junction on the Mid-Atlantic Ridge. *Chem. Geol.* **171**, 49-75 (2000).
- Charlou, J.L., Donval, J.P., Fouquet, Y., Jean-Baptiste, P. & Holm, N. Geochemistry of high H₂ and CH₄ vent fluids issuing from ultramafic rocks at the Rainbow hydrothermal field (36°14'N, MAR). *Chem. Geol.* **191**, 345-359 (2002).
- Charlou, J.L., Donval, J.P., Jean-Baptiste, P., Dapoigny, A. & Rona, P.A. Gases and helium isotopes in high temperature solutions sampled before and after ODP Leg 158 drilling at TAG hydrothermal field (26°N, MAR). *Geophys. Res. Lett.* **23**, 3491-3494 (1996).
- Chiba, H., Masuda, H., Lee, S.-Y. & Fujioka, K. Chemistry of hydrothermal fluids at the TAG active mound, MAR 26°N, in 1998. *Geophys. Res. Lett.* **28**, 2919-2922 (2001).
- Ciais, P., Sabine, C., Bala, G., Bopp, L., Brovkin, V., Canadell, J., et al. Carbon and Other Biogeochemical Cycles. In: *Climate Change 2013: The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change* (eds Stocker, T.F., Qin, D., Plattner, G.-K., Tignor, M., Allen, S.K., Boschung, J., et al.) 465-570 (Cambridge University Press, 2013).
- Coogan, L.A. & Dosso, S. An internally consistent, probabilistic, determination of ridge-axis hydrothermal fluxes from basalt-hosted systems. *Earth Planet. Sci. Lett.* **323-324**, 92-101 (2012).
- Coplen, T.B., Böhlke, J.K., De Bièvre, P., Ding, T., Holden, N.E. et al. Isotope-abundance variations of selected elements (IUPAC Technical Report). *Pure Appl. Chem.* **74**, 1987-2017 (2002).
- Craig, H., Clarke, W.B. & Beg, M.A. Excess ³He in deep water on the East Pacific Rise. *Earth Planet. Sci. Lett.* **26**, 125-132 (1975).
- Craig, H. & Lupton, J.E. Primordial neon, helium and hydrogen in oceanic basalts. *Earth Planet. Sci. Lett.* **31**, 369-385 (1976).
- Craig, H., Lupton, J.E., Welhan, J.A. & Poreda, R. Helium isotope ratios in Yellowstone and Lassen Park volcanic gases. *Geophys. Res. Lett.* **31**, 369-372 (1978).
- Crisp, J.A. Rates of magma emplacement and volcanic output. *J. Volcanol. Geotherm. Res.* **20**, 177-211 (1984).

- de Moor, J.M., Fischer, T.P., Sharp, Z.D., King, P.L., Wilke, M., Botcharnikov, R.E., Cottrell, E., Zelenski, M., Marty, B., Klimm, K., Rivard, C., Ayalew, D. Ramirez, C. & Kelley, K.A. Sulfur degassing at Erta Ale (Ethiopia) and Masaya (Nicaragua) volcanoes: Implications for degassing processes and oxygen fugacities of basaltic systems. *Geochem. Geophys. Geosyst.* **14**, 4076-4108 (2013).
- Déruelle, B., Dreibus, G. & Jambon, A. Iodine abundances in oceanic basalts: implications for Earth dynamics. *Earth Planet. Sci. Lett.* **108**, 217-227 (1992).
- Earthquake Research Institute, University of Tokyo. Ontake Volcano. *Material presented at Coord. Comm. Prediction of Volcanic Eruption 130th, (Part 1) Ontake volcano.* <http://www.data.jma.go.jp/svd/vois/data/tokyo/STOCK/kaisetsu/CCPVE/shiryo/130/130_no01.pdf>, (2014) (Date of access: January 28, 2015).
- Eggenkamp, H.G.M. & Coleman, M.L. Heterogeneity of formation waters within and between oil fields by halogen isotopes. In: *Water Rock Interaction Proceedings* (eds. Arehart, G.B. & Hulston, J.R.), 309-312 (Taylor and Francis, Rotterdam, 1998).
- Exley, R.A., Matthey, D.P., Clague, D.A. & Pillinger, C.T. Carbon systematics of a mantle "hot spot": a comparison of Loihi Seamount and MORB glasses. *Earth Planet. Sci. Lett.* **78**, 189-199 (1986).
- Fehn, U., Moran, J.E., Snyder, G.T. & Muramatsu, Y. The initial $^{129}\text{I}/\text{I}$ ratio and the presence of 'old' iodine in continental margins. *Nucl. Instrum. Methods Phys. Res. Sect. B.* **259**, 496-502 (2007).
- Fischer, T.P. Fluxes of volatiles (H_2O , CO_2 , N_2 , Cl , F) from arc volcanoes. *Geochem. J.* **42**, 21-38 (2008).
- Fischer, T.P., Giggenbach, W.F., Sano, Y. & Williams, S.N. Fluxes and sources of volatiles discharged from Kudryavy, a subduction zone volcano, Kurile Islands. *Earth Planet. Sci. Lett.* **160**, 81-96 (1998).
- Fuge, R. & Johnson, C.C. The geochemistry of iodine—a review. *Environ. Geochem. Health* **8**, 31-54 (1986).
- Gamo, T. Wide variation of chemical characteristics of submarine hydrothermal fluids due to secondary modification processes after high temperature water-rock interaction: a review. In: *Biogeochemical processes and ocean flux in the Western Pacific* (eds Sakai, H. & Nozaki, Y.) 425-451 (Terrapub, 1995).
- German, C.R. & Von Damm, K.L. Hydrothermal processes. In: *Treatise on Geochemistry.*

- (eds Holland, H.D. & Turekian, K.K.), 181-222 (Elsevier, 2004).
- Giggenbach, W. The chemical and isotopic composition of gas discharges from New Zealand andesitic volcanoes. *Bull. Volcanol.* **45**, 253-255 (1982).
- Giggenbach, W. Are Tokaanu chloride waters the outflow from Ketetahi or Hipaua? *Proceedings of the 18th New Zealand Geothermal Workshop. University of Auckland.* **18**, 175-182 (1996).
- Giggenbach, W.F., Sano, Y. & Wakita, H. Isotopic composition of helium, and CO₂ and CH₄, contents in gases produced along the New Zealand part of a convergent plate boundary. *Geochim. Cosmochim. Acta* **57**, 3427-3455 (1993).
- Gilmour, J.D., Pravdivtseva, O.V., Busfield, A. & Hohenberg, C.M. The I-Xe chronometer and the early solar system. *Meteorit. Planet. Sci.* **41**, 19-31 (2006).
- Godon, A., Jendrzewski, N., Castrec-Rouelle, M., Dia, A., Pineau, F., Boulègue, J. & Javoy, M. Origin and evolution of fluids from mud volcanos in the Barbados accretionary complex. *Geochim. Cosmochim. Acta* **68**, 2153-2165 (2004).
- Graham, D.W. Noble gas isotope geochemistry of mid-ocean ridge and ocean island basalts: characterization of mantle source reservoirs. In: *Noble Gases in Geochemistry and Cosmochemistry. Reviews in Mineralogy and Geochemistry 47* (eds Porcelli, D., Ballentine, C.J. & Wieler, R.) 247-317 (Mineralogical Society of America, 2002).
- Grimaud, D., Michard, A. & Michard, G. Composition chimique et composition isotopique du strontium dans les eaux hydrothermales sous-marines de la dorsale Est Pacifique à 13° Nord. *C.R. Acad. Sc. Paris* **299**, Série II, 865-870 (1984).
- Hamano, Y. & Ozima, M. Earth-atmosphere evolution model based on Ar isotopic data. In: *Terrestrial Rare Gases* (eds Alexander, E.C., Jr. & Ozima, M.), 155-171 (Japan Scientific Societies Press, 1978).
- Hansen, K.W. & Wallmann, K. Cretaceous and Cenozoic evolution of seawater composition, atmospheric O₂ and CO₂: A model perspective. *Am. J. Sci.* **303**, 94-148 (2003).
- Hearn, E.H., Kennedy, B.M. & Truesdell, A.H. Coupled variations in helium isotopes and fluid chemistry: Shoshone Geysers Basin, Yellowstone National Park. *Geochim. Cosmochim. Acta* **54**, 3103-3113 (1990).
- Hilton, D.R., Fischer, T.P. & Marty, B. Noble gases and volatile recycling at subduction zone. In: *Noble Gases in Geochemistry and Cosmochemistry. Reviews in Mineralogy*

- and Geochemistry 47* (eds Porcelli, D., Ballentine, C.J. & Wieler, R.), 319-370 (Mineralogical Society of America, 2002).
- Hiyagon, H. Retention of solar helium and neon in IDPs in deep sea sediment. *Science* **263**, 1257-1259 (1994).
- Hohenberg, C.M. & Kennedy, B.M. I-Xe dating: intercomparisons of neutron irradiations and reproducibility of the Bjurbole standard. *Geochim. Cosmochim. Acta* **45**, 251-256 (1981).
- Holland, H. D. *The Chemistry of the Atmosphere and Oceans*, 351 pp. (Wiley, New York, 1978).
- Holser, W.T., Schidlowski, M., Mackenzie, F.T. & Maynard, J.B. Biogeochemical cycles of carbon and sulfur. In: *Chemical cycles in the evolution of the earth* (eds Gregor, B.C., Garrels, R.M., Mackenzie, F.T. & Maynard B.J.) 105-174 (John Wiley & Sons, 1988).
- Ito, E., Harris, D.M. & Anderson, A.T., Jr. Alteration of oceanic crust and geologic cycling of chlorine and water. *Geochim. Cosmochim. Acta* **47**, 1613-1624 (1983).
- Japan Meteorological Agency. *Material presented at Coord. Comm. Prediction of Volcanic Eruption 130th, (Part 1) Ontake volcano*.
 <http://www.data.jma.go.jp/svd/vois/data/tokyo/STOCK/kaisetsu/CCPVE/shiryu/130/130_no01.pdf>, (2014) (Date of access: January 28, 2016.).
- Japan Meteorological Agency. Ontake volcano. *Bull. Volcanol. Soc. Japan* **38**, 33-34 (1993).
- Japan Meteorological Agency. The western Nagano Prefecture earthquake, 1984. *Rep. Coord. Comm. Earthquake Predict* **33**, 116-122 (1985).
- Japan Meteorological Agency. Volcanic activity of Ontake volcano. *Rep. Coord. Comm. Pred. Volcanic Erup.* **50**, 10-12 (1991).
- Japan Meteorological Agency. Volcanic activity of Ontake volcano. *Rep. Coord. Comm. Pred. Volcanic Erup.* **97**, 14-29 (2007).
- Javoy, M. Pineau, F. & Delorme, H. Carbon and nitrogen isotopes in the mantle. *Chem. Geol.* **57**, 41-62 (1986)
- Jean-Baptiste, P. Helium-3 distribution in the DeepWorld Ocean. In: *Isotopes of Noble Gases as Tracers in Environmental Studies* (ed Rozanski, K.), 219-240 (International Atomic Energy Agency, Vienna, 1992).

- Jean-Baptiste, P., Dapoigny, A., Stievenard, M., Charlou, J. L., Fouquet, Y., Donval, J.P. & Auzende, J.M. Helium and oxygen isotope analyses of hydrothermal fluids from the East Pacific Rise between 17°S and 19°S. *Geo-Mar. Lett.* **17**, 213-219 (1997).
- Jean-Baptiste, P., Fourré, E., Charlou, J.L., German, C.R. & Radford-Knoery, J. Helium isotopes at the Rainbow hydrothermal site (Mid-Atlantic Ridge, 36°14'N). *Earth Planet. Sci. Lett.* **221**, 325-335 (2004).
- Johnson, L., Burgess, R., Turner, G., Milledge, J.H. & Harris, J.W. Noble gas and halogen geochemistry of mantle fluids: comparison of African and Canadian diamonds. *Geochim. Cosmochim. Acta* **64**, 717-732 (2000).
- Kagoshima, T., Takahata, N., Jung, J., Amakawa, H., Kumagai, H. & Sano, Y. Estimation of sulfur, fluorine, chlorine and bromine fluxes at Mid Ocean Ridges using a new experimental crushing and extraction method. *Geochem. J.* **46**, e21-e26 (2012).
- Kasasaku, K., Minari, T., Mukai, H. & Murano, K. Stable sulfur isotope ratios of the gases from Mt. Sakurajima and Satsuma-Iwojima volcanoes –Assessment of volcanic sulfur on rainfall sulfate in Kagoshima Prefecture. *Nippon Kagaku Kaishi* **7**, 479-486 (1999).
- Kawamoto, T., Mibe, K., Bureau, H., Reguer, S., Mocuta, C., Kubsky, S., Thiaudiere, D., Ono, S. & Kogiso, T. Large-ion lithophile elements delivered by saline fluids to the sub-arc mantle. *Earth Planets Space* **66**, 61 (2014).
- Kendrick, M.A. High precision Cl, Br and I determinations in mineral standards using the noble gas method. *Chem. Geol.* **292-293**, 116-126 (2012).
- Kendrick, M.A., Arculus, R., Burnard, P. & Honda, M. Quantifying brine assimilation by submarine magmas: Examples from the Galápagos Spreading Centre and Lau Basin. *Geochim. Cosmochim. Acta* **123**, 150-165 (2013a).
- Kendrick, M.A., Honda, M., Pettke, T., Scambelluri, M., Phillips, D. & Giuliani, A. Subduction zone fluxes of halogens and noble gases in seafloor and forearc serpentinites. *Earth Planet. Sci. Lett.* **365**, 86-96 (2013b).
- Kendrick, M.A., Kamenetsky, V.S., Phillips, D. & Honda, M. Halogen systematics (Cl, Br, I) in Mid-Ocean Ridge Basalts: A Macquarie Island case study. *Geochim. Cosmochim. Acta* **81**, 82-93 (2012).
- Kendrick, M.A., Scambelluri, M., Honda, M. & Phillips, D. High abundances of noble gas and chlorine delivered to the mantle by serpentinite subduction. *Nat. Geosci.* **4**,

807-812.

- Kim, K-R., Welhan, J.A. & Craig, H. The hydrothermal vent fields at 13°N and 11°N on the East Pacific Rise: ALVIN 1984 results. *EOS*, **65**, 973 (abstract, 1984).
- Kimata, F., Miyajima, R., Murase, M., Darwaman, D., Ito, T. et al. Ground uplift detected by precise leveling in the Ontake earthquake swarm area, central Japan in 2002-2004. *Earth Planet. Space* **56**, e45-e48 (2004).
- Konno, U., Takai, K. & Kawagucci, S. Stable chlorine isotope ratio analysis of subnanomolar level methyl chloride by continuous-flow isotope ratio mass spectrometry. *Geochem. J.* **47**, 469-473 (2013).
- Kurz, M.D., Jenkins, W.J., Hart, S.R. & Clague, D. Helium isotopic variations in volcanic rocks from Loihi seamount and the island of Hawaii. *Earth Planet. Sci. Lett.* **66**, 388-406 (1983).
- Kutterolf, S., Hansteen, T.H., Freundt, A., Wehrmann, H., Appel, K., Krüger, K. & Pérez, W. Bromine and chlorine emissions from Plinian eruptions along the Central American Volcanic Arc: From source to atmosphere. *Earth Planet. Sci. Lett.* **429**, 234-246 (2015).
- Long, A., Eastoe, C.J., Kaufmann, R.S., Martin, J.G., Wirt, L. & Finley, J.B. High-precision measurement of chlorine stable isotope ratios. *Geochim. Cosmochim. Acta* **57**, 2907-2912 (1993).
- Lu, Z., Hensen, C., Fehn, U. & Wallmann, K. Halogen and ¹²⁹I systematics in gas hydrate fields at the northern Cascadia margin (IODP Expedition 311): Insights from numerical modeling. *Geochem. Geophys. Geosyst.* **9**, Q10006 (2008).
- Lyon, G.L. & Hulston, J.R. Carbon and hydrogen isotope compositions of New Zealand geothermal gases. *Geochim. Cosmochim. Acta* **48**, 1161-1171 (1983).
- Mamyrin, B.A., & Tolstikin, I.N. Chapter 8 in *Helium Isotopes in Nature*, 267 pp (Elsevier, Amsterdam, 1984).
- Marini, L., Moretti, R. & Accornero, M. Sulfur isotopes in magmatic-hydrothermal systems, melts, and magma. In: *Sulfur in magmas and melts: Its importance for natural and technical processes. Reviews in Mineralogy and Geochemistry* 73 (eds Behren, H. & Webster, J.D.) 423-492 (Mineralogical Society of America, 2011).
- Martin, J.B., Gieskes, J.M., Torres, M. & Kastner, M. Bromine and iodine in Peru margin sediments and pore fluids: implications for fluid origins. *Geochim. Cosmochim. Acta*

- 57, 4377-4389 (1993).
- Marty, B. & Giggenbach, W.F. Major and rare gases at White Island volcano, New Zealand: Origin and flux of volatiles. *Geophys. Res. Lett.* **17**, 247-250 (1990).
- Marty, B. & Jambon, A. C/³He in volatile fluxes from the solid Earth: Implications for carbon geodynamics. *Earth Planet. Sci. Lett.* **83**, 16-26 (1987).
- Marty, B., Jambon, A. & Sano, Y. Helium isotopes and CO₂ in volcanic gases of Japan. *Chem. Geol.* **76**, 25-40 (1989).
- Marty, B. & Tolstikhin, I.N. CO₂ fluxes from mid-ocean ridges, arcs and plumes. *Chem. Geol.* **145**, 233-248 (1998).
- Maruoka, T., Koeberl, C., Hancox, P.J. & Reimold, W.U. Sulfur geochemistry across a terrestrial Permian-Triassic boundary section in the Karoo Basin, South Africa. *Earth Planet. Sci. Lett.* **206**, 101-117 (2003).
- Matsuda, J., Matsumoto, T., Sumino, H., Nagao, K., Yamamoto, J., Miura, Y., Kaneoka, I., Takahata, N. & Sano, Y. The ³He/⁴He ratio of the new internal He standard of Japan (HESJ). *Geochem. J.* **36**, 191-195 (2002).
- McDougall, I. & Harrison, T.M. *Geochronology and Thermochronology by the ⁴⁰Ar/³⁹Ar Method.*, 212 pp (Oxford University Press, New York, 1999).
- Menyailov, I.A., Nikitina, L.P., Shapar, V.N. & Pilipenko, V.P. Temperature increase and chemical change of fumarolic gases at Momotombo volcano, Nicaragua, in 1982-1985: Are these indicators of a possible eruption? *J. Geophys. Res.* **91**, 12, 199-212, 214 (1986).
- Merlivat, L., Pineau, F. & Javoy, M. Hydrothermal vent waters at 13°N on the East Pacific Rise: Isotopic composition and gas concentration. *Earth Planet. Sci. Lett.* **84**, 100-108 (1987).
- Michard, G., Albarède, F., Michard, A., Minster, J.F., Charlou, J.L. & Tan, N. Chemistry of solutions from the 13°N East Pacific Rise hydrothermal site. *Earth Planet. Sci. Lett.* **67**, 297-307 (1984).
- Mizoue, M., Nakamura, M., Seto, N., Sakai, K., Kobayashi, M., Haneda, T. & Hashimoto, S. A concealed fault system as inferred from the aftershock activity accompanying the 1984 western Nagano Prefecture earthquake of M6.8. *Bull. Earthquake Res. Inst.* **60**, 199-220 (1985).
- Mizutani, Y., Hayashi, S. & Sugiura, T. Chemical and isotopic compositions of fumarolic

- gases from Kuju-Iwoyama, Kyushu, Japan. *Geochem. J.* **20**, 273-285 (1986).
- Moller, D. Estimation of the global man-made sulphur emission. *Atoms. Environ.* **18**, 19-27 (1984).
- Moore, J.G. & Calk, L.C. Degassing and differentiation in subglacial volcanoes, Iceland. *J. Volcanol. Geotherm. Res.* **46**, 157-180 (1991).
- Morikawa, N., Kazahaya, K., Fourre, E., Takahashi, H.A., Jean-Baptiste, P., Ohwada, M., LeGuern, F.J. & Nakama, A. Magmatic He distribution around Unzen volcano inferred from intensive investigation of helium isotopes in groundwater. *J. Volcanol. Geotherm. Res.* **175**, 218-230 (2008).
- Muenow, D.W., Liu, N.W.K., Gracia, M.O. & Saunders, A.D. Volatiles in submarine volcanic rocks from the spreading axis of the East Scotia Sea back-arc basin. *Earth Planet. Sci. Lett.* **47**, 272-278 (1980).
- Muramatsu, Y., Doi, T., Tomaru, H., Fehn, U., Takeuchi, R. & Matsumoto, R. Halogen concentrations in pore waters and sediments of the Nankai Trough, Japan: implications for the origin of gas hydrates. *Appl. Geochem.* **22**, 534-556 (2007).
- Muramatsu, Y., Fehn, U. & Yoshida, S. Recycling of iodine in fore-arc areas: evidence from the iodine brines in Chiba, Japan. *Earth Planet. Sci. Lett.* **192**, 583-593 (2001).
- Muramatsu, Y. & Wedepohl, K.H. The distribution of iodine in the earth's crust. *Chem. Geol.* **147**, 201-216 (1998).
- Nagao, K., Takaoka, N. & Matsubayashi, O. Rare gas isotopic compositions in natural gases of Japan. *Earth Planet. Sci. Lett.* **53**, 175-188 (1981).
- Nagoya University. The 1993 seismic activity in the south-eastern foot of Mt. Ontake. *Rep. 50*, 132-140, Coord. Comm. On Earthquake Predict., Tokyo, Japan (1993).
- Nakamichi, H., Kimata, F., Yamazaki, F., Okubo, M., Yamada, M. & Watanabe, T. Precise hypocenter distribution and very-long-period events of Ontake volcano, central Japan. *Cities on Volcanoes 5 conference*, Shimabara, 12-P-10 (2007).
- Namiki, A. & Kagoshima, T. Intermittent and efficient outgassing by the upward propagation of film ruptures in a bubbly magma. *J. Geophys. Res. Solid Earth* **119**, 919-935 (2014).
- Naughton, J.J., Lee, J.H., Keeling, D., Finlayson, J.B., & Dority, G. Helium flux from the earth's mantle as estimated from Hawaiian fumarolic degassing. *Science* **180**, 55-57, (1973).

- Nishio, Y., Tsutsumi, M., Gamo, T. & Sano, Y. Hydrogen effect on the $\delta^{13}\text{C}$ value of CO_2 measured by mass spectrometry with electron-impact ionization. *Anal. Sci.* **11**, 9-12 (1995).
- O'Nions, R.K. and Oxburgh, E.R. Helium, volatile fluxes and the development of continental crust. *Earth Planet. Sci. Lett.* **90**, 331-347 (1988).
- Ozima, M. & Podosek, F. A. *Noble Gas Geochemistry*. 2nd ed., 286 pp (Cambridge Univ. Press, 2002).
- Poorter, R.P.E., Varekamp, J.C., Poreda, R.J., Van Bergen, M.J. & Kreulen, R. Chemical and isotopic compositions of volcanic gases from the east Sunda and Banda arcs, Indonesia. *Geochim. Cosmochim. Acta* **55**, 3795-3807 (1991).
- Pujol, M., Marty, B., Burgess, R., Turner, G. & Philippot, P. Argon isotopic composition of Archaean atmosphere probes early Earth geodynamics. *Nature* **498**, 87-92 (2013).
- Pyle, D.M. & Mather, T.A. Halogens in igneous processes and their fluxes to the atmosphere and oceans from volcanic activity: A review. *Chem. Geol.* **263**, 110-121 (2009).
- Ransom, B., Spivack, A.J. & Kastner, M. Stable Cl isotopes in subduction-zone pore waters: implications for fluid-rock reaction and the cycling of chlorine. *Geology* **23**, 715-718 (1995).
- Rees, C.E., Jenkins, W.J. & Monster, J. The sulfur isotopic composition of ocean water sulphate. *Geochim. Cosmochim. Acta* **42**, 337-381 (1978).
- Rison, W. & Craig, H. Helium isotopes and mantle volatiles in Loihi seamount and Hawaiian Island basalts and xenoliths. *Earth Planet. Sci. Lett.* **66**, 407-426 (1983).
- Ronov, A.B. & Yaroshevsky, A.A. A new model for the chemical structure of the Earth's crust. *Geokhimiya* **12**, 1761-1795 (1976).
- Rouilleau, E., Sano, Y., Takahata, N., Kawagucci, S. & Takahashi, H. He, N and C isotopes and fluxes in Aira caldera: Comparative study of hydrothermal activity in Sakurajima volcano and Wakamiko crater, Kyushu, Japan. *J. Volcanol. Geotherm. Res.* **258**, 163-175 (2013).
- Rouilleau, E., Sano, Y., Takahata, N., Yang, F.T. & Takahashi, H.A. He, Ar, N and C isotope compositions in Tatun Volcanic Group (TVG), Taiwan: Evidence for an important contribution of pelagic carbonates in the magmatic source. *J. Volcanol. Geotherm. Res.* **303**, 7-15 (2015a).

- Rouilleau, E., Vinet, N., Sano, Y., Takahata, N., Shinohara, H., Ooki, M., Takahashi, H.A. & Furukawa, R. Effect of the volcanic front migration on helium, nitrogen, argon, and carbon geochemistry of hydrothermal/magmatic fluids from Hokkaido volcanoes, Japan. *Chem. Geol.* **414**, 42-58 (2015b).
- Rudnicki, M.D. & Elderfield, H. Helium, radon and manganese at the TAG and Snakepit hydrothermal vent fields, 26° and 23°N, Mid-Atlantic Ridge. *Earth Planet. Sci. Lett.* **113**, 307-321 (1992).
- Saal, A.L., Hauri, E.H., Langmuir, C.H., Perfit, M.R. Vapour undersaturation in primitive mid-ocean-ridge basalt and the volatile content of Earth's upper mantle. *Nature* **419**, 451-455 (2002).
- Saito, G., Shinohara, H. & Kazahaya, K. Successive sampling of fumarolic gases at Satsuma-Iwojima and Kuju volcanoes, southwest Japan: Evaluation of short-term variations and precision of the gas sampling and analytical techniques. *Geochem. J.* **36**, 1-20 (2002).
- Sakai, H., DesMaraise, D.J., Ueda, A. & Moore, J.G. Concentrations and isotope ratios of carbon, nitrogen and sulfur in ocean-floor basalts. *Geochim. Cosmochim. Acta* **48**, 2433-2441 (1984).
- Sakai, H. & Matsubaya, O. Stable isotopic studies of Japanese geothermal systems. *Geothermics* **5**, 97-124 (1977).
- Sakai, H. & Matsuhisa, Y. *Stable Isotope Geochemistry* (in Japanese), 403pp (University of Tokyo Press, 1996).
- Sakamoto, M., Sano, Y. & Wakita, H. $^3\text{He}/^4\text{He}$ ratio distribution in and around the Hakone volcano. *Geochem. J.* **26**, 189-195 (1992).
- Sano, Y. & Fishcer, T.P. The analysis and interpretation of noble gases in modern hydrothermal systems. In: *The Noble Gases as Geochemical Tracers. Advances in Isotope Geochemistry*. (ed Burnard, P.) 249-317 (Springer-Verlag, 2013).
- Sano, Y., Gamo, T., Notsu, K. & Wakita, H. Secular variations of carbon and helium isotopes at Izu-Oshima Volcano, Japan. *J. Volcanol. Geotherm. Res.* **64**, 83-94 (1995).
- Sano, Y., Gamo, T. & Williams, S.N. Secular variations of helium and carbon isotopes at Galeras volcano, Colombia. *J. Volcanol. Geotherm. Res.* **77**, 255-265 (1997).
- Sano, Y., Hirabayashi, J. & Oba, T. Carbon and helium isotopic ratios at Kusatsu-Shirane Volcano, Japan. *Appl. Geochem.* **9**, 371-377 (1994).

- Sano, Y. & Marty, B. Origin of carbon in fumarolic gas from island arcs. *Chem. Geol.* **119**, 265-274 (1995).
- Sano, Y., Marty, B. & Burnard, P. Noble gases in the atmosphere. In: *The Noble Gases as Geochemical Tracers. Advances in Isotope Geochemistry.* (ed Burnard, P.) 17-31 (Springer-Verlag, 2013).
- Sano, Y., Sakamoto, M., Ishibashi, J., Wakita, H. & Matsumoto, R. Helium isotope ratios of pore gases in deep-sea sediments, Leg 128. *Proc. Ocean Drill. Program. Sci. Results.* **127/128**, 747-751 (1992).
- Sano, Y., Nakamura, Y., Wakita, H., Urabe, A. & Tominaga, T. Helium-3 emission related to volcanic activity. *Science* **224**, 150-151 (1984).
- Sano, Y., Nishio, Y., Sasaki, S., Gamo, T. & Nagao, K. Helium and carbon isotope systematics at Ontake volcano, Japan. *J. Geophys. Res.* **103**, 23863-23873 (1998).
- Sano, Y. & Terada, K. In situ ion microprobe U-Pb dating and REE abundances of a Carboniferous conodont. *Geophys. Res. Lett.* **28**, 831-834 (2001).
- Sano, Y., Tsutsumi, Y., Terada, K. & Kaneoka, I. Ion microprobe U-Pb dating of Quaternary zircon: implication for magma cooling and residence time. *J. Volcanol. Geotherm. Res.* **117**, 285-296 (2002).
- Sano, Y., Urabe, A., Wakita, H., Cita, H. & Sakai, H. Chemical and isotopic composition of gas in geothermal fluids in Iceland. *Geochem. J.* **19**, 135-148 (1985).
- Sano, Y. & Wakita, H. Geographical distribution of $^3\text{He}/^4\text{He}$ ratios in Japan: Implications for arc tectonics and incipient magmatism. *J. Geophys. Res.* **90**, 8729-8741 (1985).
- Sano, Y. & Wakita, H. Precise measurement of helium isotopes in terrestrial gases. *Bull. Chem. Soc. Japan* **61**, 1153-1157 (1988).
- Sano, Y., Wakita, H. & Williams, S.N. Helium-isotope systematics at Nevado del Ruiz volcano, Colombia: implications for the volcanic hydrothermal system. *J. Volcanol. Geotherm. Res.* **42**, 41-52 (1990).
- Sano, Y. & Williams, S.N. Fluxes of mantle and subducted carbon along convergent plate boundaries. *Geophys. Res. Lett.* **23**, 2749-2752 (1996).
- Sawada, Y. Ontake volcano. *Bull. Volcanic Erup.* **19**, 49-51 (1981).
- Schilling, J.-G., Bergeron, M.B. & Evans, R. Volatiles in the mantle beneath the North Atlantic. *Trans. Roy. Soc. Land.* **A297**, 147-178 (1980).
- Schilling, J.-G., Unni, C.K. & Bender, M.L. Origin of chlorine and bromine in the oceans.

- Nature* **273**, 631-636 (1978).
- Schlitzer, R. Ocean Data View, <http://odv.awi.de> (2013).
- Selverstone, J. & Sharp, Z.D. Chlorine isotope evidence for multicomponent mantle metasomatism in the Ivrea Zone. *Earth Planet. Sci. Lett.* **310**, 429-440 (2011).
- Shanks III, W.C. Stable isotopes in seafloor hydrothermal systems: Vent fluids, hydrothermal deposits, hydrothermal alteration, and microbial processes. In: *Stable Isotope Geochemistry. Reviews in Mineralogy and Geochemistry 43* (eds Valley, J.W. & Cole, D.R.) 469-525 (Mineralogical Society of America, 2001).
- Sharp, Z.D., Barnes, J.D., Brearley, A.J., Fischer, T.P., Chaussidon, M. & Kamenetsky, V.S. Chlorine isotope homogeneity of the mantle, crust and carbonaceous chondrites. *Nature* **446**, 1062-1065 (2007).
- Sharp, Z.D., Mercer, J.A., Jones, R.H., Brearly, A.J., Selverstone, J., Bekker, A. & Stachel, T. The chlorine isotope composition of chondrites and Earth. *Geochim. Cosmochim. Acta* **107**, 189-204 (2013).
- Sharp, Z.D., Shearer, C.K.J. & Barnes, J.D. The chlorine isotope composition of the Moon. *Lunar Planet. Sci. Conf.* **40**, 604.pdf (2009).
- Stoiber, R.E. & Jepsen, A. Sulfur dioxide contributions to the atmosphere by volcanoes. *Science* **182**, 577-578 (1973).
- Stettler, A. & Bochsler, P. He, Ne and Ar composition in a neutron activated sea-floor basalt glass. *Geochim. Cosmochim. Acta* **43**, 157-169 (1979).
- Sturchio, N.C., Williams, S.N. & Sano, Y. The hydrothermal system of Volcan Puracé Colombia. *Bull. Volcanol.* **55**, 289-296 (1993).
- Sumino, H., Burgess, R., Mizukami, T., Wallis, S.R., Holland, G. & Ballentine, C.J. Seawater-derived noble gases and halogens preserved in exhumed mantle wedge peridotite. *Earth Planet. Sci. Lett.* **294**, 163-172 (2010).
- Tajika, E. Mantle degassing of major and minor volatile elements during the Earth's history. *Geophys. Res. Lett.* **25**, 3991-3994 (1998).
- Takahata, N., Yokochi, R., Nishio, Y. & Sano, Y. Volatile element isotope systematics at Ontake volcano, Japan. *Geochem. J.* **37**, 299-310 (2003).
- Taran, Y.A. Geochemistry of volcanic and hydrothermal fluids and volatile budget of the Kamchatka-Kuril subduction zone. *Geochim. Cosmochim. Acta* **73**, 1067-1094 (2009).

- Taran, Y.A., Bernard, A., Gavilanes, J.-C., Lunezheva, E., Cortés, A. & Armienta, M.A. Chemistry and mineralogy of high-temperature gas discharges from Colima volcano, Mexico. Implications for magmatic gas-atmosphere interaction. *J. Volcanol. Geotherm. Res.* **108**, 245-264 (2001).
- Taran, Y.A., Connor, C.B., Shapar, V.N., Ovsyannikov, A.A. & Bilichenko, A.A. Fumarolic activity of Avachinsky and Koryaksky volcanoes, Kamchatka, from 1993 to 1994. *Bull. Volcanol.* **58**, 441-448 (1997).
- Taran, Y.A., Hedenquist, J.W., Korzhinsky, M.A., Tkachenko, S.I. & Shmulovich, K.I. Geochemistry of magmatic gases from Kudryavy volcano, Iturup, Kuril Islands. *Geochim. Cosmochim. Acta* **59**, 1749-1761 (1995).
- Taran, Y., Inguaggiato, S., Varley, N., Capasso, G. & Favara, R. Helium and carbon isotopes in thermal waters of the Jalisco block, Mexico. *Geofis. Int.* **41**, 459-466 (2002).
- Taran, Y.A., Pilipenko, V.P., Rozhkov, A.M. & Vakin, E.A. A geochemical model for fumaroles of the Mutnovsky volcano, Kamchatka, USSR. *J. Volcanol. Geotherm. Res.* **49**, 269-283 (1992).
- Taran, Y.A., Rozhkov, A.M., Serafimova, E.K. & Esikov, A.D. Chemical and isotopic composition of magmatic gases from the 1988 eruption of Klyuchevskoy volcano, Kamchatka. *J. Volcanol. Geotherm. Res.* **46**, 255-263 (1991).
- Tedesco, D. & Scarsi, P. Intensive gas sampling of noble gases and carbon at Vulcano Island (southern Italy). *J. Geophys. Res.* **104**, 10499-10510 (1999).
- Tera, F. Aspects of isochronism in Pb isotope systematics-application to planetary evolution. *Geochim. Cosmochim. Acta* **45**, 1439-1448 (1981).
- Tomaru, H., Fehn, U., Lu, Z.L., Takeuchi, R., Inagaki, F., Imachi, H., Kotani, R., Matsumoto, R. & Aoike, K. Dating of dissolved iodine in pore waters from the gas hydrate occurrence offshore Shimokita Peninsula, Japan: ¹²⁹I results from the D/V Chikyū shakedown Cruise. *Resour. Geol.* **59**, 359-373 (2009).
- Torgersen, T. Terrestrial helium degassing fluxes and the atmospheric helium budget: Implications with respect to the degassing processes of continental crust. *Chem. Geol.* **79**, 1-14 (1989).
- Turner, G. Extinct iodine 129 and trace elements in chondrites. *J. Geophys. Res.* **70**, 5433-5445 (1965).

- Ueki, S. & Sano, Y. In situ ion microprobe Th-Pb dating of Silurian conodonts. *Geochem. J.* **35**, 307-314 (2001).
- Unni, C.K. Cl/Br degassing during submarine and subaerial volcanism. (Ph.D. dissertation, University of Rhode Island, 1976).
- Unni, C.K. & Schilling, J.-G. Cl and Br degassing by volcanism along the Reykjanes Ridge and Iceland. *Nature* **272**, 19-23 (1978).
- Urabe, A., Tominaga, T., Nakamura, Y. & Wakita, H. Chemical compositions of natural gases in Japan. *Geochem. J.* **19**, 11-25 (1985).
- Uyeda, S. & Kanamori, H. Back-arc opening and the mode of subduction. *J. Geophys. Res.* **84**, 1049-1061 (1979).
- Van Soest, M.C., Hilton, D.R. & Kreulen, R. Tracing crustal and slab contributions to arc magmatism in the Lesser Antilles island arc using helium and carbon relationships in geothermal fluids. *Geochim. Cosmochim. Acta* **62**, 3323-3335 (1998).
- Varekamp, J.C., Kreulen, R., Poorter, R.P.E. & Van Bergen, M.J. Carbon sources in arc volcanism, with implications for the carbon cycle. *Terra Nova* **4**, 363-373 (1992).
- Wallace, P.J. Volatiles in subduction zone magmas: concentrations and fluxes based on melt inclusion and volcanic gas data. *J. Volcanol. Geotherm. Res.* **140**, 217-240 (2005).
- Webster, J.D. & Botcharnikov, R.E. Distribution of sulfur between melt and fluid in S–O–H–C–Cl-bearing magmatic systems at shallow crustal pressures and temperatures. In: *Sulfur in magmas and melts: Its importance for natural and technical processes. Reviews in Mineralogy and Geochemistry* 73 (eds Behren, H. & Webster, J.D.) 247-283 (Mineralogical Society of America, 2011).
- Weiss, Y., McNeill, J., Pearson, D.G., Nowell, G.M. & Ottley, C.J. Highly saline fluids from a subducting slab as the source for fluid-rich diamonds. *Nature* **524**, 339-349 (2015).
- Welhan, J.A. & Craig, H. Methane, hydrogen and helium in hydrothermal fluids at 21°N on the East Pacific Rise. In: *Hydrothermal Processes at Seafloor Spreading Centers* (eds Rona, P.A., Boström, K., Laubier, L. & Smith, K.L., Jr.) 391-409 (Plenum Press, 1983).
- Williams, S.N., Sano, Y. & Wakita, H. Helium-3 emission from Nevado del Ruiz volcano, Colombia. *Geophys. Res. Lett.* **14**, 1035-1038 (1987).

Woodruff, L.G. & Shanks III, W.C. Sulfur isotope study of chimney minerals and vent fluids from 21°N, East Pacific Rise: Hydrothermal sulfur sources and disequilibrium sulfate reduction. *J. Geophys. Res.* **93**, 4562-4572 (1988).