Global Marine Environmental Studies
Department of Natural Environmental Studies
Graduate School of Frontier Sciences
The University of Tokyo

FY 2012
Master Thesis

Boron content and isotope of vent fluids from seafloor hydrothermal systems
海底熱水活動域から採取された熱水のホウ素濃度と同位体組成

24th, Jan. 2013 Submission
Mar. 2013 Completion

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1. Introduction

Seafloor hydrothermal system was firstly discovered in the Pacific by scientists diving in the submersible Alvin in 1977 (Corliss et al., 1979). They found not only hot, metal-rich fluids pouring from seafloor, but also organisms previously unknown. So far, many hydrothermal vent fields have been discovered in Pacific, Atlantic, and Indian Ocean (Figure 1). Hydrothermal system is defined by circulatory system where cold seawater sinks into seafloor through cracks of the crust and is heated whereupon it rises back to the rock-ocean interface due to the lower density (Figure 2). In this process, cold, alkaline and metal-depleted seawater changes into hot, acidic, Mg-free and metal-enriched vent fluid by water-rock interaction. When hot vent fluids encounter cold seawater, lots of metal elements precipitate as sulfides and generate ore deposits on the seafloor. Edmond et al. (1979) studied the elemental flux from hydrothermal systems to the ocean, and estimated that hydrothermal systems contributed amount of chemical substance only next to the rivers. Hydrothermal systems also transport heat from the interior of the earth to the surface efficiently.

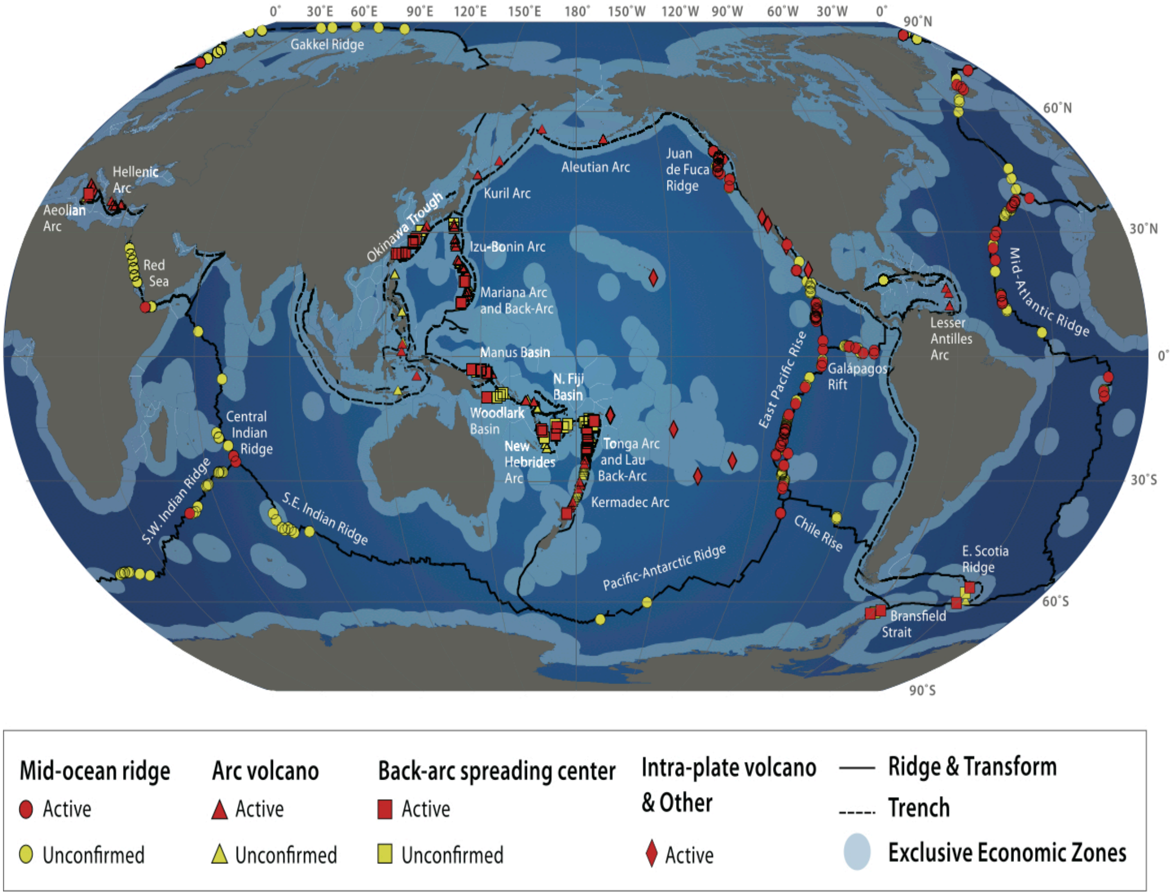

Figure 1. Global distribution of hydrothermal vent fields (Interridge vents database: http://www.interridge.org/irvents/maps)

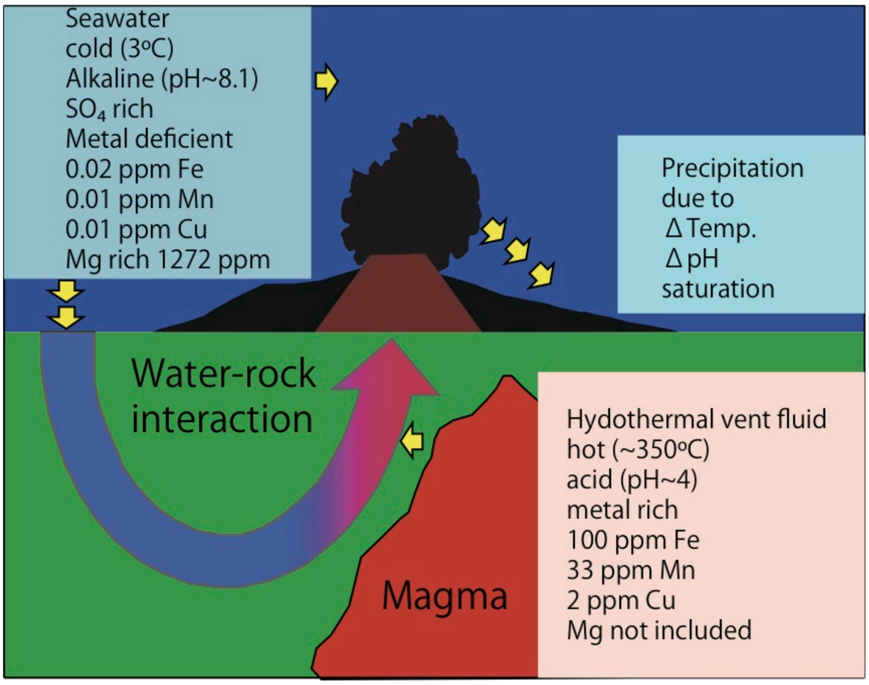

Figure 2. Mechanism of hydrothermal system: cold seawater (blue column): low temperature (~3ºC), alkalinity (pH~8.1), SO_4, Mg enriched, low heavy metal contents; hydrothermal fluid (red column): high temperature (~350ºC), acidity (pH~4), H_2S enriched, Mg free, high heavy metal contents (modified from Kawahata, 2008).

Geochemistry of hydrothermal vent fluids in mid-ocean ridge (MOR) site has been well studied. East Pacific Rise (EPR) is known as one of the fastest spreading ridge in the Pacific. The chemical compositions of vent fluids from EPR are broadly comparable to those of seawater-basalt experiments (Mottl and Holland, 1977), suggesting that EPR is a typical hydrothermal system dominated by seawater-basalt reaction. Von Damm et al. (1985a) reported that the chemical compositions of vent fluids from EPR 21ºN is extremely acid, hydrogen sulfide and metal enriched. pH in EPR 21ºN follows the range in 3.3 - 3.8. The H_2S value is 6.6 - 8.4 mmol/kg. Likewise, in Mid-Atlantic Ridge (MAR) of slow spreading center, chemical compositions of vent fluids are consistent with those in EPR. MARK site in MAR shows K content of 23.6 - 23.8 mmol/kg, relative to 23.5 mmol/kg in EPR 21ºN, while TAG site in MAR shows similar Mn (1000 µmol/kg) and Fe (1640 µmol/kg), compared to EPR 21ºN with Mn and Fe of 1024 µmol/kg and 1530µmol/kg, respectively (Campbell et al., 1988). It seems that there is no difference of hydrothermal systems between fast spreading centers and slow spreading centers. In arc and back-arc, major element components varied greatly. In sediment-starved hydrothermal systems, Manus Basin shows relatively low K content (14 - 20 mmol/kg) in Vienna Woods site hosted by basalt, while high K content (80 - 90 mmol/kg) in PACMANUS site hosted by dacite, relative to EPR 21ºN with 23 - 26 mmol/kg. Suiyo Seamount in Izu-Bonin Arc, which is hosted by dacite, shows low K content (30 mmol/kg), relative to PACMANUS (Chiba, 1995; Gamo et al., 1996; Reeves et al., 2011). Ca in Forecast Vent in Mariana Trough (61 mmol/kg) is high relative to those in Alice Springs (22 mmol/kg) in Mariana Trough, while similar with those in Suiyo Seamount (89 mmol/kg) in Izu-Bonin Arc and Vienna Woods (73 mmol/kg) in Manus Basin (Gamo, 1995; Gamo et al., 1997b). It reflects that vent fluid undergoes different water-rock reaction relative to that in MOR. Axial Seamount Hydrothermal Emissions Study (ASHES) of Juan de Fuca Ridge, which is supposed to undergo phase separation, exhibits great variation of chemical components. The dense brine was collected in Inferno site, and vapor-rich fluid was collected in Virgin Mound site. Inferno site shows high contents of major elements such as 638 mmol/kg of Cl, 47 mmol/kg of Ca and 26.8 mmol/kg of K, and high contents of trace elements such as 0.64 mmol/kg of Li, 1150 μmol/kg of Mn. While Virgin Mound site shows low contents of major elements such as 176 mmol/kg of Cl, 10 mmol/kg of Ca and 7 mmol/kg of K, and low contents of trace elements such as 0.18 mmol/kg of Li and 140 μmol/kg of Mn (Butterfield et al., 1990). It suggests that phase separation influences chemical compositions of vent fluids significantly. In sediment-hosted hydrothermal systems, it shows high NH_4 content in Guaymas Basin (11 - 16 mmol/kg) and Escanaba Trough (5.6 mmol/kg) in MOR, and Okinawa Trough (4.6 - 12 mmol/kg) in back-arc, relative to that in EPR 21°N, which is less than 0.01 mmol/kg, suggesting that chemical components of vent fluids are also derived from sediments (Gamo, 1995). In sediment-hosted hydrothermal systems in arc and back-arc, Sr content is high in Minami-Ensei (215 - 227 μmol/kg) relative to JADE site (94 mmol/kg) in Okinawa Trough, while similar with that in Suiyo Seamount (303 mmol/kg) in Izu-Bonin Arc. CLAM site has relatively thick sediment and shows highest NH_4 content (8.0 - 12.0 mmol/kg) and H_2S content (15 - 25 mmol/kg), suggesting significant contribution of sediment (Gamo, 1995).

Boron is metalloid in the periodic table, with the symbol of B and the atomic number 5. Boron has two natural stable isotopes: ^{11}B and ^{10}B, whose relative abundances are 80.18% and 19.82%, respectively. For the significant isotopic fractionation, boron isotopic geochemistry has been developed rapidly along with the technical improvement and innovation. Recently, boron isotopic application has been attracting attentions since it can provide valuable information about geological and environmental processes. Boron usually combines with oxygen in nature, constituting the B-O bond. Boron has only two existential states, which are trigonal $B(OH)_3$ and tetrahedral $B(OH)_4^-$ anion. The heavy isotope ^{11}B is enriched in trigonal species, while the light isotope ^{10}B is enriched in tetrahedral species. Since the different boron isotopic composition ($\delta^{11}B$) in different ion species, boron isotopic application is widely used in global environmental analyses, such as nebula formation process and solar cosmic ray event, the formation of seafloor ore deposits, presumption of pH of seawater, derivation of seafloor sediment, process of crust-mantle and subduction evolution (Jiang, 2000). Due to high solubility and significant difference of δ^{11}B between seawater (+39.6‰) and mid-ocean ridge basalt (MORB, -4‰), boron is also applied to seafloor hydrothermal systems as a tracer during water-rock reaction.

Spivack and Edmond (1987) reported the boron isotope exchange between seawater and the oceanic crust based on analyzing B content and δ^{11}B of vent fluids from the East Pacific Rise (EPR). The B contents of the vent fluids were between 0.43 - 0.51 mmol/kg, δ^{11}B of the vent fluids were between 30.0 - 36.8‰, which were considered as that boron was extracted from rock during seawater and basalt reaction at high temperature (Spivack and Edmond, 1987). Butterfield et al. (1990) reported the chemistry of the vent fluids from ASHES. Although the contents of major elements showed great difference between Inferno field and Virgin Mound field, boron contents were measured as 0.59 mmol/kg in Inferno field and 0.45 mmol/kg in Virgin Mound field (Butterfield et al., 1990). Both of the concentrations were elevated over seawater. The δ^{11}B value was 32.5‰ in Inferno field and 34.5‰ in Virgin Mound field. Although Virgin Mound is supposed to undergo a substantial water-rock reaction after becoming segregated (Massoth et al., 1989; Butterfield et al., 1990), how phase separation influences boron compositions needs a further study. Sediment-hosted hydrothermal systems were discovered in Guaymas Basin and Escanaba Trough. Guaymas Basin had 1.6 - 1.7 mmol/kg of boron content and 17.5 - 23.2‰ of δ^{11}B (Spivack et al., 1987), while Escanaba Trough had 1.7 - 2.2 mmol/kg of B content and 10.1 - 11.5‰ of δ^{11}B (Palmer, 1991; Campbell et al., 1994). It showed high B contents and low δ^{11}B in sediment-hosted vent fluids relative to sediment-starved MOR. The vent fluid from Mariana Trough in arc and back-arc was also studied. It showed high B contents (0.7 - 0.8 mmol/kg) and low δ^{11}B (22.5 - 29.8‰) relative to those in MOR. It was thought that the contribution of slab subducting in arc and back-arc influenced the component of boron during water-rock reaction (Palmer, 1991). However, one site in Mariana Trough can hardly indicate the difference between arc, back-arc hydrothermal systems and MORB-type hydrothermal systems. Several hydrothermal systems have been discovered in arc and back-arc following the discoveries of MORB-type hydrothermal systems including sediment-starved hydrothermal systems, phase separated hydrothermal systems and sediment-hosted hydrothermal systems. In this study, vent fluids collected from sediment-starved Manus Basin (Vienna Woods, PACMANUS), Izu-Bonin Arc (Suiyo Seamount), Mariana Trough (Alice Springs, Forecast Vent), North Fiji Basin (White Lady, Kaiyo, LHOS); sediment-hosted Okinawa Trough (JADE, Minami-Ensei, CLAM) in arc and back-arc in the western Pacific were studied. The purposes of this study are to investigate water-rock reaction in (1) sediment-starved hydrothermal systems with various host rocks; (2) phase separated hydrothermal systems; (3) sediment-hosted hydrothermal systems, using boron contents and isotopic compositions.

2. Geological settings

Samples for this study were provided by Professor Toshitaka Gamo in Atmosphere Ocean Research Institute of the University of Tokyo, and mapped in Figure 3. The geological settings are summarized as follows (Table 1).

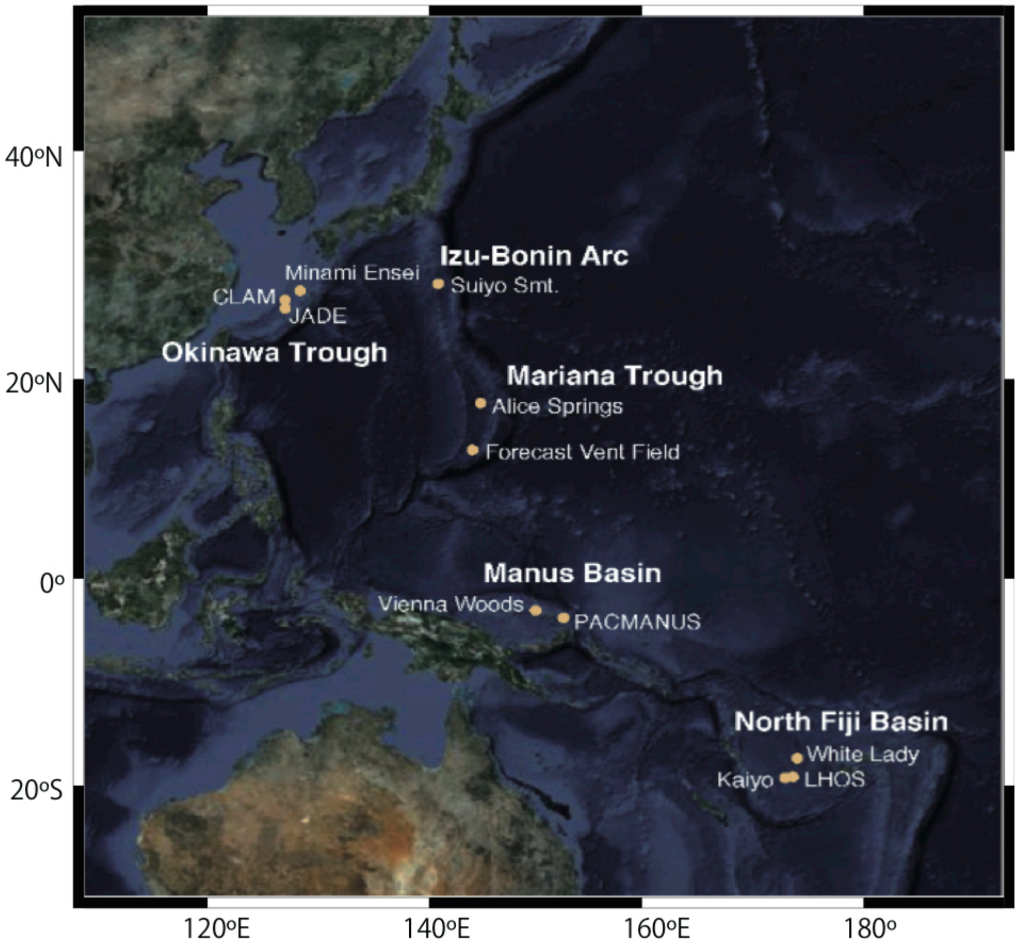

Figure 3. Locations of hydrothermal systems in this study

2.1 Manus Basin (Vienna Woods, PACMANUS)

The Manus Basin (150°E - 152°E, 3°S - 4°S) is located in the southwest of the Pacific, behind the New Britain arc-trench system (Figure 4). It is a back-arc basin where the spreading is thought to occur on three successive ridge segments, which are western Manus spreading center (WMSC), Manus spreading center (MSC), and southeastern ridges (SER) (Taylor et al., 1994; Taylor and Martinez, 1996). The southern part of the Manus spreading center has the fastest spreading rate (10 cm/yr) among back-arc basins (Taylor, 1979; Taylor et al., 1994; Martinez and Taylor, 1996). Hydrothermal activity in the Manus Basin was firstly found at Vienna Woods site (3°09.8′S, 150°16.7′E) along the Manus spreading center (Both et al., 1986; Tufar, 1990; Lisitsyn et al., 1993). PACMANUS site was observed along the southeastern ridges (Gamo et al., 1993).

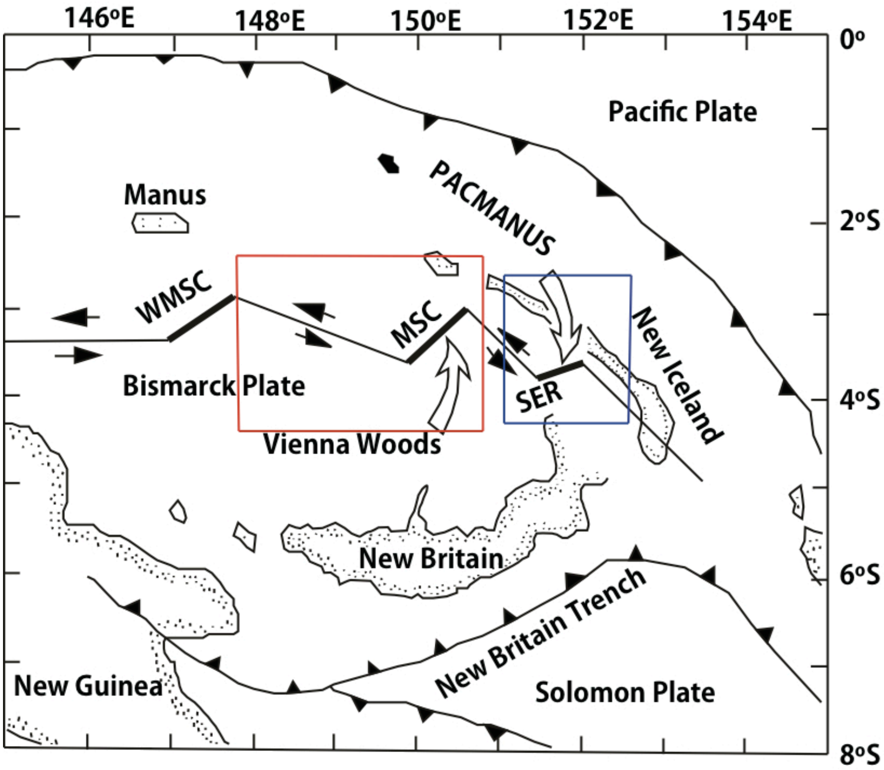

Figure 4. Topographic map of Manus Basin: Red rectangle: Vienna Woods site; Blue rectangle: PACMANUS site; WMSC: western Manus spreading center; MSC: Manus spreading center; SER: southeastern ridges (Taylor et al., 1979)

The Vienna Woods site has a depth of approximately 2500 m. It consists of basaltic rocks and has a lot of anhydrite-sulfide chimneys with a height of 10 - 15 m from the seafloor. Opaque fluids erupting from the chimneys are observed. The maximum temperature of the fluid in the Vienna Woods was measured at 302°C in 1995 and 292°C in 2000 (Lisitsyn et al., 1993; Auzende et al., 1996; Gamo et al., 1997a; Douville et al., 1999; Fourre et al., 2006). The pH of the fluid is 4 - 4.5. The fluid chemistry is reported to be similar to observations from basalt-hosted hydrothermal systems in mid-oceanic ridge settings (Von Damm, 1995; German and Von Damm, 2003). Sr concentration in the Vienna Woods is more than 200 μmol/kg, which is considered as being controlled by the reactions involving plagioclase minerals (Reeves et al., 2011). Potassium concentration in the Vienna Woods is low (14 - 20 mmol/kg), suggesting low K concentration in the host rock of Manus Basin Center (Reeves et al., 2011). SiO_2 concentration in the Vienna Woods was observed in 1995, approximately 15 mmol/kg (Gamo et al., 1997a). Including the low Fe concentration (0.12 - 0.17 mmol/kg) and the high Mn concentration (0.21 - 0.37 mmol/kg), it is suggested that the Vienna Woods fluid may be experiencing great extend of conductive cooling with time (Reeves et al., 2011).

The PACMANUS site has a depth of approximately 1710 m. It consists of dacitic rocks and has sulfide chimneys where the black smokers are observed. The temperature of the PACMANUS fluid has a large range, the maximum temperature was measured at 268°C in 1995 (Gamo et al., 1996). The pH of the fluid is 2.5, lower than that in the Vienna Woods. The concentrations of some components in the fluid such as total carbon and trace elements are higher than those of vent fluid in Vienna Woods due to the dacitic host rock (Shitashima et al., 1997). It shows higher K concentration (80 - 90 mmol/kg) and lower Ca concentration (10 - 20 mmol/kg) relative to those in the Vienna Woods fluid, which are 14 - 20 mmol/kg and 75 - 80 mmol/kg, respectively. It reflects interaction between the seawater and the host rock of dacite (Chiba, 1995; Gamo et al., 1996). The Sr concentration in the PACMANUS is similar to that in the seawater (89.6 μmol/kg), lower than that in Vienna Woods (225 - 247 μmol/kg). The $^{87}Sr/^{86}Sr$ ratios range at 0.70394 - 0.70428, which are consistent with a predominantly rock-derived source of Sr (Reeves et al., 2011).

2.2 Izu-Bonin Arc (Suiyo Seamount)

The Suiyo Seamount (Suiyo Smt.) (140º39'E, 28º33'N) is a submarine volcano in the Izu-Bonin (Ogasawara) Arc, which is an intraoceanic island arc in conjunction with the Izu-Ogasawara Trench (Figure 5). It consists of low-K dacitic rocks (Nagaoka et al., 1992) and has a height of approximately 1600 m and basal dimensions of 31.5 km in an E-W direction, and 15 km in a N-S direction (Nagaoka et al., 1991). It has a summit caldera measuring 1.5 km in diameter and 500 m

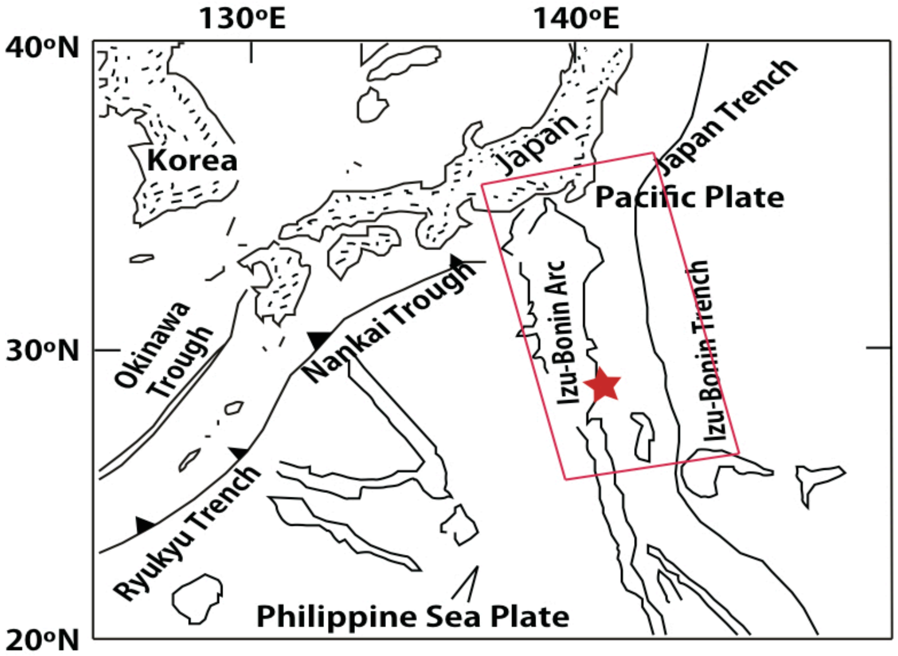

Figure 5. Topographic map of Izu-Bonin Arc: Red rectangle zone: Izu-Bonin Arc (Taylor et al., 1990); Red star mark: Suiyo Seamount

in depth. The active hydrothermal vent at the bottom of the caldera was discovered in 1991 during dive of the Shinkai 2000 (Kasuga and Kato, 1992). The chimneys contain the mixture of chalcopyrite, anhydrite, sphalerite and barite (Kasuga and Kato, 1992).

The vent fluids collected from Suiyo Seamount show high temperature of 226 - 311ºC (Ishibashi et al., 1994a), and low pH about 3.7 (Tsunogai et al., 1994; Gamo et al., 1995). Ishibashi et al. (1994a) reported the fluid chemistry of Suiyo Seamount. The fluid chemistry is common to other hydrothermal systems: 1) lack of Mg and SO_4; 2) enrichment in cations relative to seawater; 3) reducing property due to H_2S. On the other hand, the vent fluids from Suiyo Seamount show some unique characteristics. First, Si concentration of the fluid is lower than that from East Pacific Rise 21ºN (EPR 21ºN). This is due to low solubility of SiO_2 in the fluid because of low pressure and low temperature (311ºC) in Suiyo Seamount relative to EPR 21ºN (350ºC). For Ca enrichment (and Na depletion) in the fluids, Ishibashi et al. (1994a) proposed some hypotheses as follows: 1) phase separation due to boiling, 2) complex formation as $CaCO_3$ in CO_2 enriched fluid, 3) difference in compositions of altered mineral. Tsunogai et al. (1994) analyzed chemical and isotopic compositions of dissolved gas in the fluids from Suiyo Seamount. The $CO_2/^3He$ ratio is comparable to typical value of island-arc volcanic gases. On the other hand, helium isotope ratio ($^3He/^4He$) is close to the value of the mid-ocean ridge helium. $^3He/^4He$ ratio is a very strong indicator for the study about the origin of volcanic gases due to lack of chemical reactivity of He. The $\delta^{13}C$ values of CO_2 are quite high compared to other subaerial arc volcanic gases and those from mid-ocean ridges. These results are unlikely to result from fractionation process or crustal contribution, but are regarded as the intrinsic value of the magma source of Suiyo Seamount (Tsunogai et al, 1994).

2.3 Mariana Trough (Alice Springs, Forecast Vent)

Mariana Trough is an extending back-arc basin behind the Mariana Trench, where the Pacific plate subducts under the Philippine Sea plate (Gamo et al., 1997b) (Figure 6). There are two hydrothermal active sites with hot fluid venting in the Mariana arc and back-arc system: one is sediment-starved back-arc type at the mid-Mariana Trough (Alice Springs), the other is sediment-starved arc type at the southern Mariana Trough (Forecast Vent). The Mariana Trough consists of basaltic rock having transitional composition between normal MORB and Mariana Island Arc basalt (Volpe et al., 1987).

The hydrothermal fluids taken from the Alice Springs (18º12'N, 143º30'E; depth: 3600 m) in 1992 showed the maximum temperature of 280ºC and pH of 3.9 (25ºC), which was similar to those taken in 1987 (287ºC and pH of 4.4) (Gamo et al., 1997b). The similarity in fluid chemistry between 1987 and 1992 showed that there was little variation in hydrothermal activity during five years. Gamo (1995) concluded the fluid chemical characteristics of the Mariana Trough in comparison with those of other submarine hydrothermal active sites. The fluid in mid-Mariana Trough shows the common characteristics with those in arc and back-arc basin. High CO_2 concentration in the Mariana Trough is reported as that it is likely derived from the subducting slab materials below the Mariana Trough (Gamo et al., 1997b). The fluid shows almost no NH_4 and I, which are strongly enriched in fluids that have a marine sedimentary input (Von Damm et al., 1985b; Campbell and Edmond, 1989). Therefore, it could be known that there is no sediment in Alice Springs. The $^{87}Sr/^{86}Sr$ ratio (0.7038) in the fluid is similar to that in sediment-starved MOR site (East Pacific Rise 21ºN: 0.7030~0.7036) (Gamo, 1995).

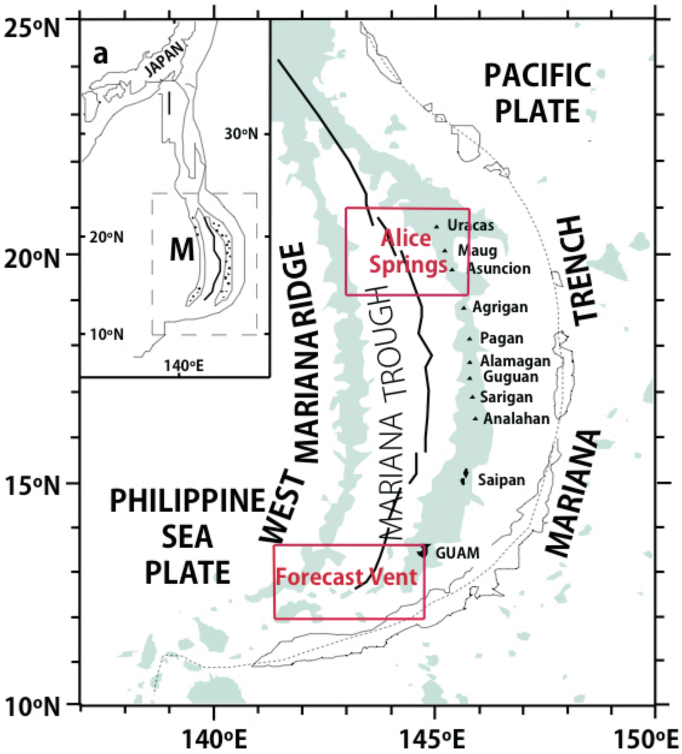

Figure 6. Topographic map of Mariana Trough: Alice Springs is in back-arc while Forecast Vent is in arc (Stern et al., 2003; Shaw et al., 2008).

At the Forecast Vent (13º24'N, 143º55'E; depth: 1470 m), clear solution (maximum temperature of 202ºC) was emanating from white chimneys. Gamo et al. (1997b) concluded the Forecast Vent chemical components compared to those of Suiyo Seamount. It seems to be more similar to those of Suiyo Seamount, a typical island-arc hydrothermal site, than those of Alice Springs, which is back-arc hydrothermal site. The fluid also shows high Cl concentration (593 mM) in the Forecast Vent. The fluid of Forecast Vent has lower SiO_2 concentration than that in other arc or back-arc site. It is likely due to the low temperature (maximum in 202ºC) relative to that in Suiyo Seamount, according to the relationship between SiO_2 concentration and equilibrium condition with quartz (Von Damm et al., 1991). Ca concentration in the Forecast Vent (61 mmol/kg) is close to that in the Suiyo Seamount (89 mmol/kg), while higher than that in Alice Springs (22 mmol/kg) (Gamo, 1995; Gamo et al., 1997b). The $\delta^{13}C(CO_2)$ and $\delta^{13}C(CH_4)$ values of the Forecast Vent fluid (-1‰ and -11‰) were almost equal to those of Suiyo Seamount fluid, significantly higher than those of the back-arc and mid-ocean ridge hydrothermal fluids (Tsunogai et al., 1994; Tsunogai, 1996). Tsunogai (1996) stated that the $\delta^{13}C(CO_2)$ and $\delta^{13}C(CH_4)$ values should be explained by original characteristics of the magma source, several percents of which might be the slab subducting material. This explanation is consistent with the fact that the $^3He/^4He$ ratio of the Forecast Vent as well as that of the Suiyo Seamount is almost the same with those observed at mid-ocean ridges (Tsunogai, 1996).

2.4 North Fiji Basin (White Lady, Kaiyo, LHOS)

The North Fiji Basin located at the boundary of the Pacific and Indo-Australian plates is observed to be an active marginal basin (Figure 7). It started to spread at 10 - 12 Ma ago having a complex, multi-stage tectonic story and the present spreading began about 1 Ma ago (Auzenda et al., 1988; Tanahashi et al., 1991). The main tectonic structures in the North Fiji Basin were considered as rifts in the New Hebrides back-arc, a main spreading system and triple junction in the central part of the basin (Johnson et al., 1992), and the Fiji Transform Fault (Clarke et al., 1993). The Indo-Australia Plate is subducting eastward at the New Hebrides Trench beneath the New Hebrides Arc. Lava tubes, pillows, lava lakes and massive flows are observed over the entire area, showing the morphologic features of oceanic ridge basalts. Vent fluid samples were taken from three vent fields, White Lady, Kaiyo, and Long-term Hydrothermalism Observation System (LHOS).

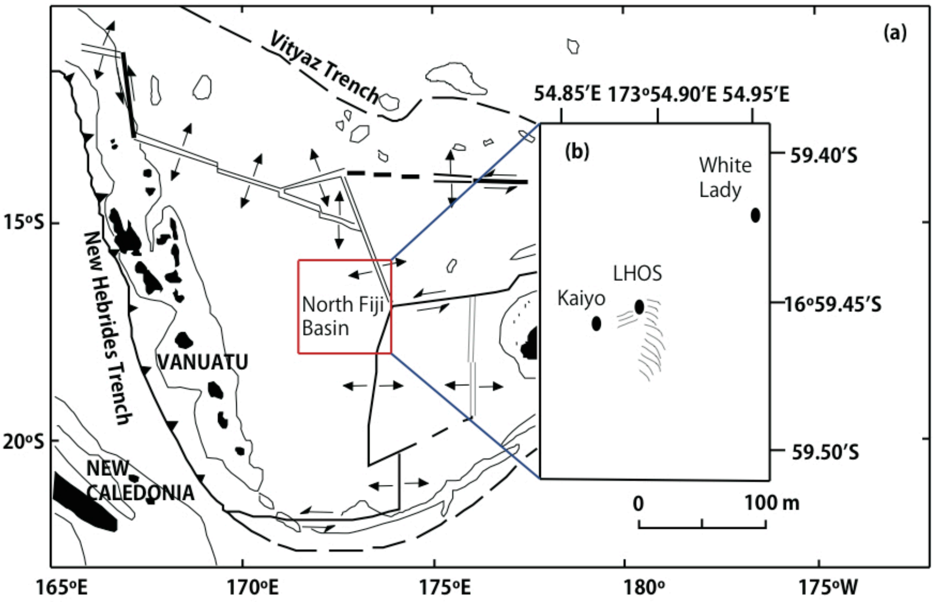

Figure 7. Topographic map of North Fiji Basin: (a) North Fiji Basin (Stratford and Rodda, 2000); (b) Hydrothermal systems (White Lady, Kaiyo, LHOS) in North Fiji Basin (Ishibashi et al., 1994b).

The highest fluid temperature in the White Lady was measured as 285ºC and the pH was less than 4.7 (Grimaud et al., 1991). Grimaud et al. (1991) reported the fluid chemistry of White Lady. The concentration end members of all major elements are significantly lower than those of most other hydrothermal systems. Cl and Na have especially low concentrations. White Lady fluids showed similar characteristics to the vapor-rich fluid in the ASHES vent field and strongly supported that the fluids experienced phase separation and segregation during hydrothermal circulation (Ishibashi et al., 1994b). Si concentration (14 mmol/kg) in the fluid is close to those in AHSES of Juan de Fuca Ridge, while is lower than those in many previously studied hydrothermal systems (Grimaud et al., 1991). Ishibashi et al. (1994c) reported the gas contents in the North Fiji Basin. The vent fluid of White Lady did not show a high CO_2 concentration, with comparison to the CO_2-rich fluid in ASHES, with 14.4 mmol/kg in CO_2.

The Kaiyo and LHOS vents are in the southwest of the White Lady. Ishibashi et al. (1994b) reported the Kaiyo-LHOS fluid chemistry, which showed common characteristic with the White Lady fluid. The Cl-Mg linear correlation of the Kaiyo-LHOS did not show clear difference from that of the White Lady. Sodium (Na) concentration in the Kaiyo-LHOS (239 mmol/kg) is a little higher than that in the White Lady (210 mmol/kg). Potassium (K) concentration is 14.5 mmol/kg relative to 10.5 mmol/kg in the White Lady, which might result from the K-rich basaltic rock in the Kaiyo-LHOS site. It also suggested that the fluid in the Kaiyo-LHOS experienced phase separation process. CO_2 concentration was measured as 11.0 mmol/kg and CH_4 as 43.5 μmol/kg (Ishibashi et al., 1994c), relative to the White Lady with 14.5 mmol/kg and 30.4 μmol/kg, respectively. It showed that the gas geochemistry of the fluid from the Kaiyo-LHOS had several similar characteristics to that of the White Lady. In the North Fiji Basin, CH_4 is in the range of 30 - 120 μmol/kg, while He is in the range of $2 - 5\times10^{-5}$ cm^3/g. This signature suggested that magma beneath White Lady and Kaiyo-LHOS hydrothermal systems had the similar gas abundances and that the mechanism of the process that introduce the gas species into the circulation of these hydrothermal systems was common. Both the gas contents and isotopic compositions of the vent fluids from the North Fiji Basin revealed several similar characteristics to the mid-ocean ridge hydrothermal systems and no apparent derivation from slab subducting.

2.5 Okinawa Trough (JADE, Minami-Ensei, CLAM)

The Okinawa Trough (24ºN-32ºN, 122ºE-130ºE) behind the Ryukyu arc-trench system is considered to be an intra-continental plate back-arc basin in the initial stage of rifting (Kimura et al., 1986; Sibuet et al., 1987) (Figure 8). It is an elongated trough with length at approximately 1000 km, width at approximately 100 km, maximal depth at approximately 2.7 km. The mid-Okinawa Trough is considered as a transitional region between the northern trough with a thin continental crust and the southern trough characterized by echelon graben depressions (Sibuet et al., 1987). The graben system along the central axis consists of five segments with elongated basaltic ridges, which are composed of a bimodal assemblage of young volcanic rocks (Chiba et al., 1997). High temperature hydrothermal fluids are found in the mid-Okinawa Trough: JADE site at the Izena Cauldron (27º16'N, 127º05'E) in 1988 (Halbach et al., 1989) with a depth of 1400 m; CLAM site at the Iheya ridge (27º33'N, 126º58'E) in 1988 (Tanaka et al., 1989); Minami-Ensei at the Minami-Ensei Knoll (28º24'N, 127º39'E) in 1990 (Hashimoto et al., 1990).

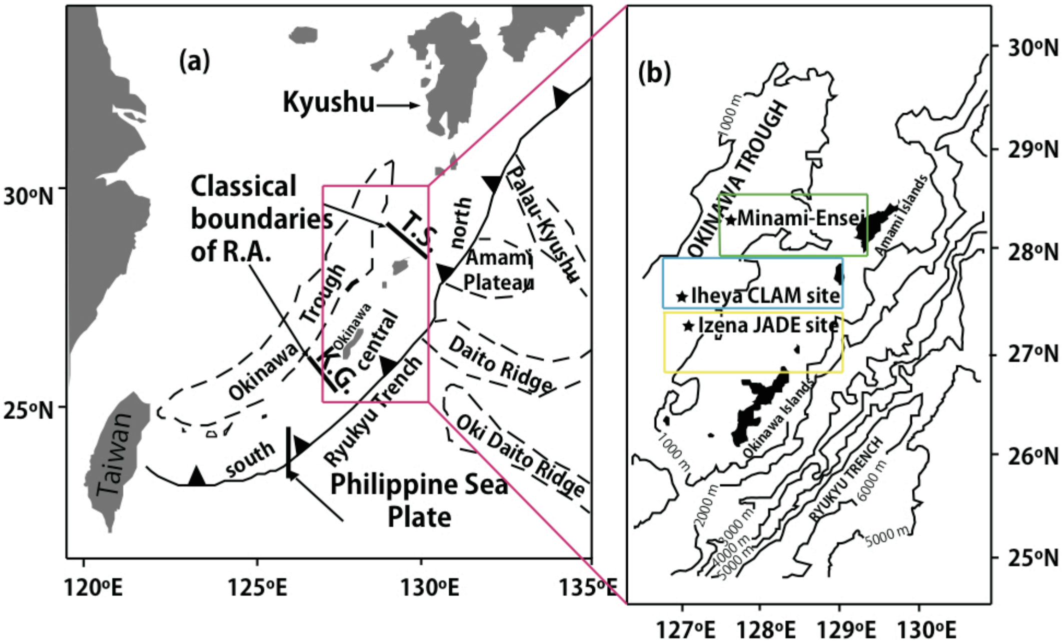

Figure 8. Topographic map of Okinawa Trough: (a) Red rectangle: topographic map of Okinawa Trough (Wang et al., 2008); (b) Hydrothermal sites in Okinawa Trough (Chiba, 1997): Yellow rectangle: Izena cauldron (JADE site); Green rectangle: Minami-Ensei; Blue rectangle: Iheya Ridge (CLAM site).

The fluid from JADE site shows high temperature of approximately 320ºC (Shitashima et al., 1994) and pH of 4.7 (Gamo, 1995). Besides the common characteristic hydrothermal fluids, JADE site shows some unique characteristics. Compared to the fluid from MOR, Li and K concentrations are high, and Ca concentration is relatively low at 22.3 mmol/kg. It is considered as the contribution of the distinctive andesite-rhyolite rock in back-arc compared to the basalt in MOR (Gamo et al., 1990). The fluid shows similar Cl concentration with the ambient seawater, and is supposed not undergoing phase separation process (Gamo et al., 1990). Zn concentration in JADE site is high (7.6 μmol/kg), approximately 20 times than that in CLAM site. It suggests that the hydrothermal circulation in JADE site occurs more pronounced (Shitashima, 1994). Mn in JADE site shows high concentration (110 μmol/kg) compared to Fe (2.8 μmol/kg). It is reported that Mn will not precipitate while Fe precipitates as sulfide. Ni, Cu and Pb show extremely low concentrations due to the precipitation later than Fe, and removed after eruption (Shitashima, 1994). JADE site shows high CO_2 and CH_4 contents. The carbon, helium isotopic compositions and $CO_2/^3He$ ratio are within the range of island arc magmatic gases, suggesting that both CO_2 and He are dominantly derived from a magmatic source beneath the system (Ishibashi et al., 1995).

The fluid from Minami-Ensei shows a temperature range of 265 - 278 ºC and pH of 4.90 - 5.08 (Chiba et al., 1993). The fluid from Minami-Ensei shows similar metal contents to the fluid from JADE site. The high alkalinity (3.02 - 3.15 mmol/kg) and NH_4 (4.56 - 4.70 mmol/kg) contents suggest that the fluid also undergoes the interaction with sediment. $^{87}Sr/^{86}Sr$ (0.7100) ratio in Minami-Ensei is higher than that in seawater (0.709), suggesting that the fluid interacts with sediment having higher $^{87}Sr/^{86}Sr$ ratio (Chiba et al., 1992). Although CO_2 content (63.9 - 95.7 mmol/kg) from the Minami-Ensei is higher than other fluids from MOR, it is lower than half of that from JADE site (209 mmol/kg). It is considered that there is a gradual boiling under the Minami-Ensei vent, rather than a large scale boiling (Chiba et al., 1993), suggesting that CO_2 in Minami-Ensei is also derived from magma activity according to the C isotopic composition following in the range of -0.4 - -5.3‰, which is similar to that in JADE site. $^3He/^4He$ ratio (6.97 - 7.51) is higher than that from JADE site. It is suggested that He is derived from mantle, not radioactive decay from continental crust (Chiba et al., 1993).

The fluid from CLAM site shows a maximum temperature of 220ºC and high pH of 5.3 (Chiba, 1997). It is reported that there is thicker sediment on the CLAM site than that on the JADE site (Shitashima, 1994). Therefore, NH_4 and H_2S contents are higher than those in JADE site. Metal concentrations such as V, Mo, and Cd, are low because of increased precipitation of sulfides in sediment (Shitashima, 1994). Normal Cl concentration was also reported in CLAM site and suggested that the fluid did not undergo phase separation process (Gamo et al., 1990). The $\delta^{34}S$ value shows various range of -0.2‰ - +3.0‰. It is considered as the attribution to multiple evolutionary stages of sulfate reduction among the CLAM vents. The fluid shows higher $CO_2/^3He$ (120) and $CH_4/^3He$ (4200) than those in the JADE site, which are 26 and 920, respectively. A substantial part of the CLAM gas species is considered as deriving from an additional shallow source during hydrothermal water-sediment reaction, though the mechanisms are somewhat unclear (Ishibashi et al., 1995).

3. Methods

Major elements of the fluid samples were measured by ICP-AES at the department of Geological Survey of Japan. The samples whose major elements were consistent with those from reference data were selected for further boron experiments. The experiments for dating boron contents and isotopic compositions were conducted in the Kochi Core Center. The experimental pretreatments were carried out in clean room to minimize the contamination by boron from the experiment environment.

3.1 Boron contents

The procedure used in this study was reported in Nagaishi and Ishikawa (2009) in detail. Each sample was transferred by 10 μl into 7-mL PFA Teflon vial and dissolved by 5 mL internal solution (400 ng/mL Be and 10 ng/mL In and Re). The dilution rates of samples were calculated by weight that was measured in each step. The quadrupole ICP-MS, ELAN DRC II (Parkin Elmer, USA) was used in this study. The analytical error was <±5% RSD. Sample measurements were followed by sample-washout with 0.015 M HF/0.15 M HNO_3, which can not only stabilize the signals of boron, but also enable effective washout of boron and beryllium (Nagaishi and Ishikawa, 2009).

3.2 Boron isotopic compositions

Each sample was transferred into 7-mL PFA Teflon vial by the volume that contain 200 ng boron calculated by the measured boron concentration. Then, 0.1 mol/L HCl was added to each vial to 1 mL. The sample solutions passed through a centrifuge ultrafiltration device (Centricut V-10, MWCO 10000, Kurabo, Japan) were prepared for the further step. In pretreatment, ion-exchange chromatography was used to obtain the eluates that contain the boron ion in the shape of $Cs_2BO_2^+$. Measuring $Cs_2BO_2^+$ by positive ion thermal ionization mass spectrometry (P-TIMS) is supposed to be one of the most precise and accurate techniques for boron isotope analysis (Ishikawa and Nagaishi, 2011).

Firstly, samples were passed through 0.6 mL of cation-exchange resin column (Bio-Rad, USA, AG 50W - X12^{R}, 200 - 400 mesh), which had been cleaned with 1.5 mL of 6 mol/L HCl three times and 1.0 mL of H_2O twice. Then, 0.2 mL H_2O and 60 μL 38%-HF (AA - 100) were added in sequence to remove major cations completely and yield a HF concentration of 1 mol/L of the eluate. Secondly, the solutions were passed through 30 μL anion-exchange resin column (Bio-Rad, USA, AG 1-X4^{R}, 200 - 400 mesh), which had been cleaned with 1.0 mL of 6 mol/L HCl three times and 0.1 mL of H_2O twice and conditioned by 0.1 mL of 1 mol/L HF. Then, 120 μL of acid mixture (0.5 mol/L HF + 2 mol/L HCl) were added and result in the absorption of boron in anion-exchange resin column. The solution catchers were changed with concave-bottom 5 mL Teflon beaker containing

Cs solution and mannitol solution. 150 μL of 6 mol/L HCl were added to collect the final boron fraction resulting in a B/Cs mole ratio of 2 and a ratio of 50 μL mannitol per 100 ng B. The resulting boron fraction was then evaporated to dryness at 60ºC overnight.

The dried sample was dissolved with 1.6 μL of milli-Q, and 0.8 μL of the solution was loaded on a degassed Ta filament (single filament configuration) after loading of 1.5 μL acetone solution and 1.2 μL of graphite slurry in turn. The filament was dried with the current to 0.7 A. The filaments were then fixed up to a sample magazine and placed into an oven at 260ºC for 40 min. The temperature of filaments were raised to 240ºC rapidly and kept for another 40 min. Then, the sample magazine was introduced to a vacuum flowing N_2 gas for 30 min to cool down to room temperature. After that, the sample magazine was loaded to the TRITON thermal ionization mass spectrometer (Thermal Finnigan, Germany) at Kochi Core Center, and $Cs_2BO_2^+$ ions (m/z = 308 and 309) were detected to calculate the boron isotope ratio.

Boron isotope ratio was calculated as per mil deviation relative to boron isotopic reference material NIST SRM 951 boric acid by natural boron isotope (^{10}B and ^{11}B).

$$\delta^{11}B(‰) = [\{(^{11}B/^{10}B)_{\text{sample}} - 0.00079\}/\{(^{11}B/^{10}B)_{\text{SRM951}} - 0.00079\}\text{-}1]\text{x}1000‰$$

where 0.00079 is a correction term for the ^{17}O interference.

In this study, four separate analysis of SRM 951 showed a mean value of $^{11}B/^{10}B = 4.05418 \pm 0.00064$ (2SD), which is indistinguishable from the value of SRM951 reported by Ishikawa and Nagaishi (2011), which is 4.05291±0.00031 (2SD, N = 31). The analytical reproducibility is less than 0.1% (2SD). The procedural blank of boron was negligible with regard to the δ^{11}B.

4. Results

The result data of boron contents and $\delta^{11}B$ are listed with geological setting of each hydrothermal site in Table 1.

4.1 Manus Basin

Vienna Woods shows vent fluid components similar with EPR 21°N in B content and $\delta^{11}B$, which are 0.41 - 0.53 mmol/kg and 30.1 - 38.0‰, respectively. Although in the same Manus Basin, different B content and $\delta^{11}B$ were observed in PACMANUS. The B content of PACMANUS is 0.52 - 1.04 mmol/kg, which is higher than that of Vienna Woods. The $\delta^{11}B$ value of PACMANUS reaches the range in 17.8 - 31.0‰, which is lower than that of Vienna Woods.

4.2 Izu-Bonin Arc

Suiyo Seamount follows the similar pattern with PACMANUS, shows B content of 1.15 - 1.64 mmol/kg, $\delta^{11}B$ of 18.6 - 21.2‰.

4.3 Mariana Trough

Alice Springs shows 0.62 - 0.82 mmol/kg of B content and ~20.3‰ of $\delta^{11}B$, which are consistent with the data conducted by Palmer (1991). Forecast Vent has the range of B content in 0.42 - 0.53 mmol/kg, while the $\delta^{11}B$ is 28.9 - 35.5‰.

4.4 North Fiji Basin

White Lady exhibits a range of 0.42 - 0.44 mmol/kg and $\delta^{11}B$ of 36.3 - 37.5‰. The B content and $\delta^{11}B$ values of Kaiyo are measured as 0.47 - 0.53 mmol/kg and 34.9 - 37.5‰, respectively, while LHOS has ~0.44 mmol/kg of B content and 36.7 - 37.9‰ of $\delta^{11}B$. Three sites of North Fiji Basin show low B contents and high $\delta^{11}B$ relative to those in arc and back-arc hydrothermal fluids, and similar to those in EPR 21°N.

4.5 Okinawa Trough

JADE site has a range of B content in 0.68 - 4.70 mmol/kg and $\delta^{11}B$ in 4.1 - 19.1‰. Minami-Ensei is observed 3.43 - 4.25 mmol/kg of B content and 2.3 - 4.4‰ of $\delta^{11}B$. CLAM site is measured 1.74 - 2.49 mmol/kg of B content and 6.3 - 7.2‰ of $\delta^{11}B$. All of the fluids from Okinawa Trough show high B contents and low $\delta^{11}B$ relative to those in sediment-starved sites.

Table 1. Results of B contents and δ^{11}B values of vent fluids

Sites		Sample	Type	Sediment	Host rock	Depth (m)	Temp. (ºC)	pH (25ºC)	Mg (mM)	B (mM)[5]	δ^{11}B (‰)[5]
Manus Basin[1]	Vienna Woods		Back-arc	Starved	Basalt	2500	285 - 300	4.5			
		303-TS1							46.3	0.41	38.0
		307-1							20.3	0.47	33.0
		307-2							2.5	0.53	30.1
	PACMAN US		Back-arc	Starved	Dacite	1650 - 1700	260	2.7 - 3.1			
		301-6							21.7	1.04	17.8
		304-1							42.0	0.52	31.0
Izu-Bonin[2]	Suiyo Seamount		Arc	Starved	Dacite	1380	296 - 311	3.7			
		D630-3							17.7	1.15	21.2
		D631-2							0.8	1.64	18.6
		D631-6							3.7	1.30	18.9
Mariana Trough[2]	Alice Springs		Back-arc	Starved	Basalt	3600	280	3.9			
		D154-2							0.9	0.62	20.3
		D154-5							1.0	0.82	20.3
	Forecast Vent		Arc	Starved	Basalt	1490	202	-			
		D182-4							43.2	0.42	35.5
		D187-2							25.3	0.53	28.9
North Fiji Basin[3]	White Lady		Back-arc	Starved	Basalt	1970	350 - 400	4.7			
		1ST5-2							8.6	0.44	36.3
		1ST6-1							25.7	0.42	37.5
	Kaiyo		Back-arc	Starved	Basalt	2000	291	4.7			
		D80-3							31.5	0.47	37.5
		D80-4							8.5	0.53	34.9
	LHOS		Back-arc	Starved	Basalt	2000	291	4.7			
		D93-3							24.4	0.44	36.7
		D93-4							33.5	0.44	37.9
Okinawa Trough[4]	JADE		Back-arc	hosted	Andesite -rhyolite	1340	320	4.7			
		D423-3							1.0	4.70	4.1
		D423-5							45.2	0.68	19.1
	Minami-Ensei		Back-arc	hosted	-	710	267 - 278	4.9 - 5.1			
		D621-5							27.2	3.43	4.4
		D622-1							4.9	4.25	2.3
		D622-2							1.4	3.73	2.6
	CLAM		Back-arc	hosted	Basalt	1400	100 - 216	5.4			
		D426-6							39.5	1.74	7.2
		D427-6							33.4	2.49	6.3
SW									53.3	0.41	39.6

1. Gamo et al., 1996; 2. Gamo et al., 1997b; 3. Ishibashi et al., 1994b; 4. Chiba, 1997; 5. this study.
Mg refers to 1, 2, 3, 4; SW is seawater.

5. Discussions

5.1 Sediment-starved hydrothermal systems

During water-rock reaction, Mg concentration becomes zero due to the formation of magnesium silicates (Bischoff and Dickson, 1975; Mottl and Seyfried, 1980). The Mg contents measured in the samples are considered as the contribution from seawater during the mixing with the vent fluids. Therefore, Boron content of end member fluid is calculated by extrapolating to Mg=0 (Figure 9a). The B contents and $\delta^{11}B$ are calculated with mass balance calculations:

$$R_m C_m = R_h C_h f + R_{sw} C_{sw} (1-f) \qquad (1)$$

$$C_m = C_h f + C_{sw} (1-f) \qquad (2)$$

where R_h, R_{sw} and R_m are $\delta^{11}B$ of hydrothermal fluid, seawater and mixture, respectively. C_h, C_{sw} and C_m are B contents of hydrothermal fluid, seawater and mixture, respectively. f is the mixing ratio of hydrothermal fluid. Therefore,

$$R_m = \alpha / C_m + \beta \qquad (3)$$

where, $\alpha = C_h C_{sw} (R_{sw} - R_h)/(C_h - C_{sw})$, $\beta = (R_h C_h - R_{sw} C_{sw})/(C_h - C_{sw})$

It means the $\delta^{11}B$ value and 1/B play a linear correlation. By this linear correlation, end member $\delta^{11}B$ values can be computed by B content end members (Figure 9b). The end members of 1/B and $\delta^{11}B$ are summarized in Figure 10.

In this section, sediment-starved sites are discussed except North Fiji Basin, which are discussed in the later section. The end member fluid of the Vienna Woods shows 0.53 mmol/kg of B content and 29.8‰ of $\delta^{11}B$, which are similar with those in EPR 21ºN, which are 0.53 mmol/kg of B content and 31.0‰ of $\delta^{11}B$, respectively. Low K concentration in the Vienna Woods (14 - 20 mmol/kg) (Reeves et al., 2011) is similar to those in MOR (Gamo, 1995). The Ca/Cl and Na/Cl, end member Sr/Cl and Sr/Ca ratios in the Vienna Woods are in the range of MOR hydrothermal systems (Berndt et al., 1988). Combined with major elements, Vienna Woods shows high degree of uniformity and compositionally similar with those in MOR, indicating the MORB-like property (Reeves et al., 2011).

In the Mariana Trough, B content and $\delta^{11}B$ of vent fluid from the Alice Springs obtained in this study are consistent with the previous reported values (Palmer, 1991). The $\delta^{11}B$ value of Alice Springs is 19.9‰, the B content is 0.72 mmol/kg, while the Forecast Vent shows $\delta^{11}B$ of 24.0‰ and B content of 0.63 mmol/kg. The B contents in Mariana Trough exhibit higher than those in Vienna Woods in Manus Basin and EPR 21ºN in MOR, and the $\delta^{11}B$ values in the Mariana Trough are low relative to those in Vienna Woods and EPR 21ºN. High CO_2 from the Alice Springs and the Forecast Vent are observed, which are 43.4 mmol/kg and 42.1 mmol/kg, respectively, relative to that of EPR 21ºN, reflecting the contribution from slab subducting (Palmer, 1991). In the Mariana

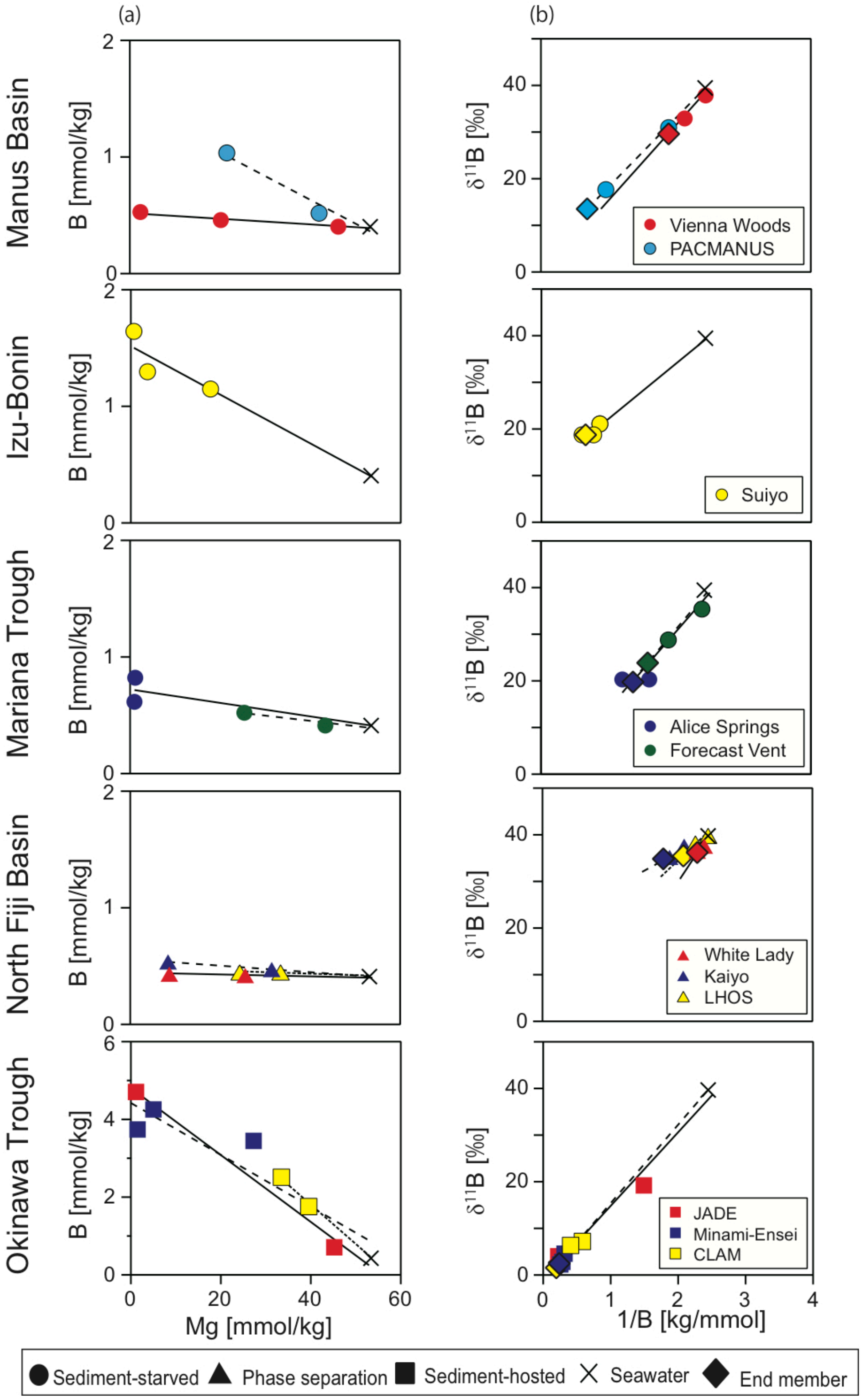

Figure 9. Results of B contents and δ^{11}B: boron (B) contents are plotted with Mg. (a) The B values extrapolate to end members while Mg contents fall to zero. The end members are considered as the values of the vent fluids since Mg is completely removed from fluid during water-rock reaction (Bischoff and Dickson, 1975; Mottl and Seyfrid, 1980). (b) The δ^{11}B values are plotted with 1/B due to mass balance calculation, and the B content end members are used to calculate the δ^{11}B values of the vent fluids.

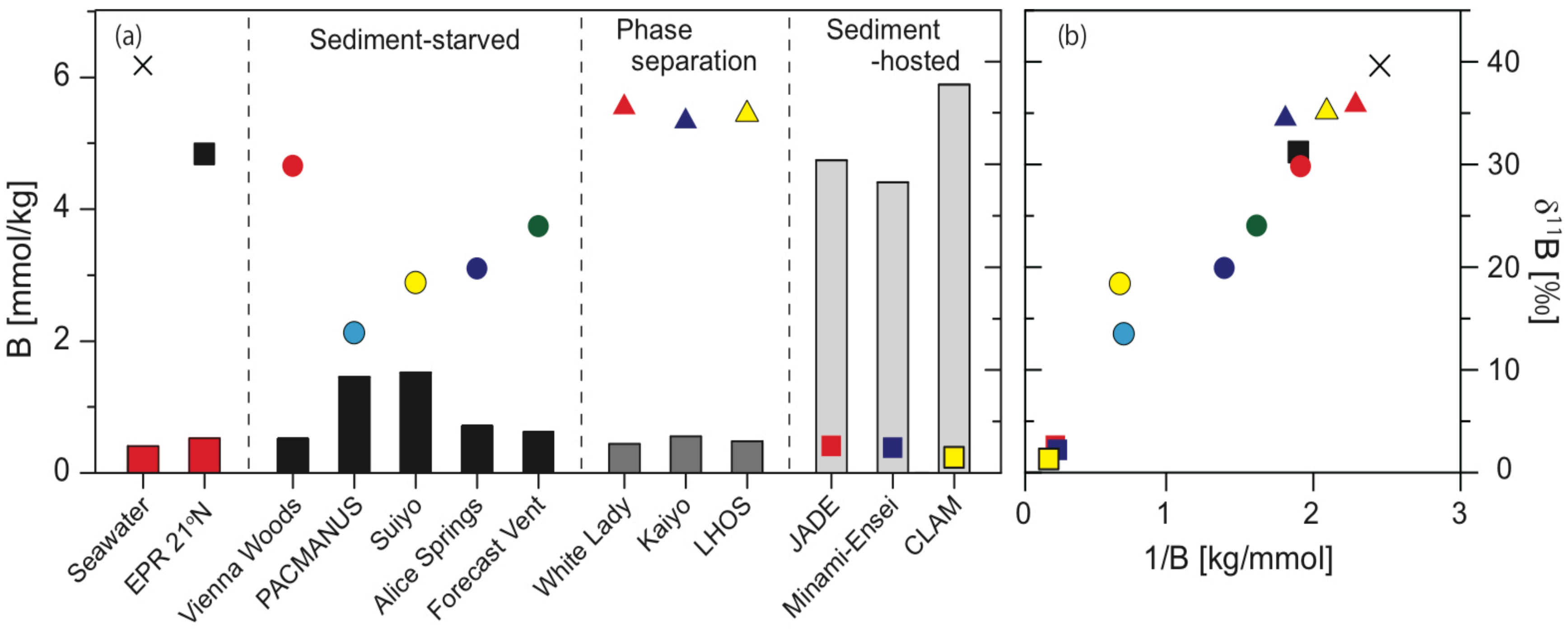

Figure 10. End members of B contents and $\delta^{11}B$: (a) End members of Boron (B) contents are showed as the bar graph, and end members of boron isotopic compositions ($\delta^{11}B$) are also plotted. The vent fluid sites in this study are divided into three parts, which are sediment-starved sites, phase separation sites and sediment-hosted sites. (b) $\delta^{11}B$ end members are plotted with 1/B end members. The positive correlation means higher boron contents derived from host rock or sediment can result in higher boron contents and lower boron isotopic compositions of vent fluids during water-rock or water-sediment reaction.

Table 2. B content and δ^{11}B end members of vent fluids with other chemical components

Sites	Manus Basin		Izu-Bonin	Mariana Trough		North Fiji Basin			Okinawa Trough			MORB
end members	Vienna Woods	PAC MANUS	Suiyo Seamount	Alice Springs	Forecast Vent	White Lady	Kaiyo	LHOS	JADE	Minami-Ensei	CLAM	EPR 21ºN
Reference	1,4	4	1	1,3	1	5	6		1	1,2	1	1,7
Li (mM)	0.7	-	0.6	0.59-0.83	0.3	0.20-0.28	0.28		2.48	5.4-5.8	3-4	0.89-1.48
K (mM)	23	89	30	31-48	26	10.5	14.5		72	49-51	50-60	23-26
Na (mM)	512	487	446	438	438	210	239		425	410-431	-	432-510
Ca (mM)	73	18	89	22	61	6.5	9		22	21-22	~20	11.7-20.8
Sr (mM)	312	102	303	72-90	165	30	43		94	215-227	-	65-97
^{87}Sr/^{86}Sr	-	-	-	0.7036	0.7038	0.7046	-		0.7089	0.7100	-	0.7030 - 0.7036
Cl (mM)	640	639	658	544-557	593	255	267		550	501-527	550	489-579
Rb (μM)	-	-	-	30	-	8.8	17.1		360	-	180 - 220	23 - 28
Mn (μM)	297	3221	587	295	300	12	26		110	88 - 94	400 - 500	700 - 1020
Fe (μM)	77	4337	435	6.4	11	13	8.8		2.8	-	-	650 - 2430
NH_4^+ (mM)	-	<0.1	<0.1	0	<0.1	-	-		5.0	4.6 - 4.7	8.0 - 12..0	<0.01
CO_2 (mM)	-	-	34-42	43.4	42.1	14.4	11.1		209	64-96	160-200	5.7-8.0
H_2S (mM)	-	-	1.2-1.6	2.5	0.4	2.0	4.0		12.4	1.6-2.4	15-25	6.6-8.4
Alkalinity (mM)	-0.1	-4.0	-0.2	0.1 - 0.4	0.18	0.12	-0.87		1.9	3.0 - 3.5	10 – 20	-0.2 - -0.5
B (mM)	0.54	1.93	1.4	0.71-0.83	-	0.47	0.48		3.4	3.7-4.0	5-6	0.50-0.55
δ^{11}B (‰)	-	-	-	20-30	-	-	-		-1.0	-	7-9	29.0-33.0
This study												
B (mM)	0.53	1.45	1.52	0.72	0.63	0.44	0.56	0.48	4.74	4.41	5.89	-
δ^{11}B (‰)	29.8	13.6	18.5	19.9	24.0	35.9	34.5	35.2	2.6	2.4	1.5	-
Cs (mM)	0.0003	0.0026	0.0018	0.0007	0.0005	0.0001	0.0002	0.0002	0.0241	0.0267	0.0225	-
Cs/B*1000	0.6	1.8	1.2	1.0	0.8	0.2	0.4	0.4	5.1	6.1	3.8	-

1. Gamo et al., 1995; 2. Chiba et al., 1993; 3. Gamo et al., 1994; 4. Gamo (pers. comm.); 5. Grimaud et al., 1991; 6. Ishibashi et al., 1994b; 7. Von Damn et al., 1985a.

Trough, it can be considered that boron is also contributed from slab subducting since boron is easily extracted into melt and increase the host rock boron content. The slightly high δ^{11}B in the Forecast Vent relative to the Alice Springs might reflect that the basaltic host rock of the Forecast Vent contains slightly higher δ^{11}B than the basaltic host rock of the Alice Springs due to the arc geological setting. Meanwhile, the Forecast Vent has maximum temperature of 202ºC, lower than the Alice Springs that has maximum temperature of 280ºC. This temperature difference is supported by SiO_2 in vent fluids. In fact, SiO_2 in the vent fluid of the Forecast Vent (7.7 mmol/kg) is lower than that of the Alice Springs (12.3 - 14 mmol/kg). $\delta^{11}B_{\text{solid-fluid}}$ fractionation, which is a function of temperature, has been established (Wunder et al., 2005) as follow: $\delta^{11}B_{\text{solid-fluid}} = -10.69(1000/T[K]) + 3.88$. Based on this calculation, -18.6‰ difference between vent fluid and host rock in δ^{11}B at 202ºC in Forecast Vent is calculated. In the contrast, in the Alice Springs, the difference is -15.4‰. Thus the difference of reaction temperature causes 3.2‰ difference in vent fluid, if basalt in Forecast Vent is quite similar to Alice Springs in terms of δ^{11}B. It is consistent with the result in this study. Therefore, it is possible that the different δ^{11}B composition between Alice Springs and Forecast Vent is mainly controlled by temperature.

B content (1.45 mmol/kg) is high and δ^{11}B (13.6‰) is low in PACMANUS in Manus Basin relative to those in Vienna Woods and EPR 21ºN. Suiyo Seamount in Izu-Bonin Arc also shows high B content (1.52 mmol/kg) and low δ^{11}B (18.5‰), which are similar to those in PACMANUS. It can be also considered that the host rocks of PACMANUS and Suiyo Seamount are influenced by slab subducting and the host rock boron contents increase as in Mariana Trough. Compared to those of Mariana Trough, PACMANUS and Suiyo Seamount also show high B contents and low δ^{11}B of vent fluids. Therefore, as well as the contribution from slab subducting, boron compositions in the host rocks of PACMANUS and Suiyo Seamount may also derived from another materials. It is known that host rocks in PACMANUS and Suiyo Seamount are dacite (Gamo et al., 1996; Nagaoka et al., 1992). Dacitic rocks are generally enriched in boron due to derivation from boron-rich dacitic magma resulting from the magma differentiation in subduction zone and slab subducting (Gurenko et al., 2005; Gross, 2012). Izu-arc has boron contents in the range of 0.4 - 2.3 mmol/kg (Ryan and Langmuir, 1993), while mid-ocean ridge basalt (MORB) has typical range in 0.02 - 0.04 mmol/kg (Spivack and Edmond, 1987). High B content leached from dacite can result in high B content of vent fluid during water-rock reaction. In this study lower δ^{11}B of vent fluids from dacite compared to basalt are measured, although the dacitic rock is supposed containing higher δ^{11}B, such as Izu-arc dacitic rock exhibits the δ^{11}B value in the range of +1 - +7‰ (Barth, 1993; Ishikawa and Nakamura, 1994), than those in MORB (-4‰). Reaction with ^{11}B-enriched rock might result in high δ^{11}B of vent fluid. However, the low δ^{11}B values of the vent fluids from dacite-hosted hydrothermal systems strongly suggest that the amount of boron originated from rock dominates the boron isotopic composition of vent fluid. Although boron is efficiently leached from rock during water-rock reaction at high temperature, fluid-rock distribution coefficient of boron (D) depend on the secondary mineral assemblage and alteration temperature (Yamaoka et al., 2012). Assuming same water/rock ratio and D, higher boron content of host rock results in larger amount of boron leached from rock during seawater-rock interaction. Differences in δ^{11}B value in host rock and isotopic fractionation between fluid and rock would have relatively small effect since the possible δ^{11}B values of dacitic rocks (+1 to +7‰) are much lower than the δ^{11}B value of seawater (+39.6‰).

The B contents and δ^{11}B of vent fluid that generated during water-rock reaction can be estimated based on closed system according to the mass balance equations, if the initial values of host rocks are given:

$$C^i_r+(W/R)C^i_f=C^f_r+(W/R)C^f_f \tag{4}$$

$$\{R^i_rC^i_r+(W/R)R^i_fC^i_f\} \;/\; \{C^i_r+(W/R)C^i_f\} =\{R^f_rC^f_r+(W/R)\,R^f_fC^f_f\}/\{C^f_r+(W/R)C^f_f\} \tag{5}$$

where C^i_r and C^i_f are initial B contents of host rock and fluid (seawater), respectively. C^f_r and C^f_f are final B contents of host rock and fluid, respectively. R^i_r and R^i_f are initial ^{11}B/^{10}B of host rock and fluid, respectively. R^f_r and R^f_f are final ^{11}B/^{10}B of host rock and fluid, respectively. W/R is water-rock ratio. $R^f_r/R^f_f = \alpha$ is introduced for the isotope fractionation factor, which is 0.986 in 300°C and 0.981 in 200°C (Wunder et al., 2005). C^f_r/C^f_f=Kd is for concentration fractionation factor. In Vienna Woods of Manus Basin, since it has MORB-like feature, the B content of initial host rock is supposed as 0.26 mmol/kg, which is in the boron content range of Sumisu rift back-arc basin (0.26 - 1.1 mmol/kg) (Ryan and Langmuir, 1993), while the δ^{11}B value is -4‰, which is typical value in MORB. In PACMANUS and Suiyo Seamount, the B contents of initial host rocks are supposed as 2 mmol/kg, which is in the range of boron content of Izu-arc (0.4 - 2.3 mmol/kg) (Ryan and Langmuir, 1993), while the δ^{11}B are 4‰, which is the average of +1 - +7‰ (Barth, 1993; Ishikawa and Nakamura, 1994). In Alice Springs and Forecast Vent of Mariana Trough, the B contents are supposed as 0.68 mmol/kg, which is the average value in Sumisu rift back-arc basin (0.26 - 1.1 mmol/kg) (Ryan and Langmuir, 1993), while the δ^{11}B values are -4‰, which is the average δ^{11}B value of Mariana Trough (-6.7 - -1.4‰) (Barth, 1993). Given that W/R=2, α=0.986, Kd= 0.1 which is common in water-rock reaction (Yamaoka et al., 2012). The B contents and δ^{11}B of vent fluids are quite similar to the results in this study (Table 3).

Table 3. The presumption of B contents and δ^{11}B of vent fluids during water-rock reaction

Sites		Host rock		Vent fluid	
		B (mmol/kg)	δ^{11}B (‰)	B (mmol/kg)	δ^{11}B (‰)
Manus Basin	Vienna Woods	0.26	-4.0	0.55	29.8
	PACMANUS	2.0	4.0	1.38	15.0
Izu-Bonin Arc	Suiyo Seamount	2.0	4.0	1.38	15.0
Mariana Trough	Alice Springs	0.68	-4.0	0.75	20.5
	Forecast Vent	0.68	-4.0	0.75	20.5
EPR 21°N[1]		0.04	-4	0.50 - 0.55	29.0 - 33.0
Seawater				0.41	39.6

1. Spivack and Edmond (1987). The B contents and δ^{11}B of host rock are supposed by references. The B contents and δ^{11}B of vent fluids are presumed based on the mass balance equations, and quite similar to the result of experimental data in this study (Table 2), given that water-rock ratio (W/R) is 2, isotope fractionation factor (α) is 0.986 (300°C), concentration fractionation factor (Kd) is 0.1 (Yamaoka et al., 2012).

5.2 Phase separated hydrothermal systems

Phase relation of seawater was experimented by Bischoff and Rosenbauer (1988), indicating that phase-boundary of seawater exists in 3.2%wt of NaCl in H_2O system. Many evidences were given, especially wide chlorinity (Cl) variation, to support the experience of phase separation of vent fluids. Butterfield et al. (1990) reported the phase separation hydrothermal system in Axial

Seamount Hydrothermal Emissions Study (ASHES) vent field of Juan de Fuca Ridge in the eastern Pacific. It clarified the variety of chemical compositions between saline brine and vapor-like fluid. The unique characteristics of phase separated fluid was concluded as (1) variation of Cl and most major element contents, (2) gas contents has negative correlation with Cl, (3) Fe depletes in vapor-rich fluids (Butterfield et al., 1990; Ishibashi et al., 1994b). In ASHES vent field, vent fluid of Inferno site was observed as brine with high Cl content (631 mol/kg), including high Fe (1065 μmol/kg) and low CO_2 content (50 mmol/kg), while vent fluid of Virgin Mound was identified as vapor-like fluid with low Cl content (220 mmol/kg), low Fe (12μmol/kg) and high CO_2 (285 mmol/kg). Besides, the major elements such as Na, Ca and K, and halide elements such as Br, and trace elements such as Li also have high separated degree (Butterfield et al., 1990). Nevertheless, B contents in Inferno (0.59 mmol/kg) and Virgin Mound (0.45 mmol/kg) did not behave high separation (Butterfield et al., 1990), as well as the $\delta^{11}B$ values.

In North Fiji Basin, major elements and gas contents are listed in Table 2. It shows low concentrations of vent fluid in White Lady, Kaiyo and LHOS in North Fiji Basin, similar with those in Virgin Mound of ASHES, indicating vapor-like characteristic except low gas contents. Gas contents in vapor-like fluid should be highly concentrated described by Butterfield et al. (1990), while CO_2 (11.1 - 14.4 mmol/kg) and H_2S contents (2 - 4 mmol/kg) are depleted when Cl content is depleted in North Fiji Basin (Grimaud et al., 1991; Ishibashi et al., 1994b). It responds to the suggestion that the vent fluid in ASHES might contain high gas contents originally, and gas contents in North Fiji Basin system would properly result from a vapor-like fluid (Ishibashi et al., 1994b).

B contents of North Fiji Basin measured in this study are especially low, approaching to seawater, but still higher than seawater. All the $\delta^{11}B$ values in North Fiji Basin are high, approaching to seawater. To investigate boron behavior in phase separation in North Fiji Basin, B contents and $\delta^{11}B$ are plotted with Cl in Figure 11, compared to those in ASHES. In Figure 11(a), although there is a positive linear correlation between B and Cl contents of vent fluids in ASHES, and B contents of fluid samples in North Fiji Basin entirely plot in Cl-depleted site of ASHES, resulting in low B content end members, the gradient of the correlation line is too small to judge whether B contents vary with Cl contents. In Figure 11b, both of ASHES and North Fiji Basin reveal high $\delta^{11}B$ irrespective of Cl variation. It suggests that there is just a feeble separation for boron in vent fluid. For further study about boron in phase separation, Liebscher et al. (2005) carried out an experiment of liquid-vapor fractionation of boron contents and boron isotopes, indicating that boron would behave different between closed system and open system. For closed system that the bulk compositions of NaCl, B content and $\delta^{11}B$ remain constant, B content slightly reduces in vapor-like fluid and slightly increases in brine while $\delta^{11}B$ is almost unchanged. For open system that the bulk compositions continuously change, B content slightly increases in brine as in closed system, while reduces significantly with the fluid dilution. $\delta^{11}B$ in open system behaves similar with closed system in condensed fluid, while increases slightly when the fluid dilutes and increases significantly when the fluid is highly diluted (Liebscher et al., 2005). Since the B contents and $\delta^{11}B$ values of vent fluids in North Fiji Basin and in ASHES are approached to those in seawater, phase separation can be hardly detected in boron component, and it responds to the suggestion that phase separated fractionation is negligible in boron component (Berndt and Seyfried, 1990; Spivack et al., 1990).

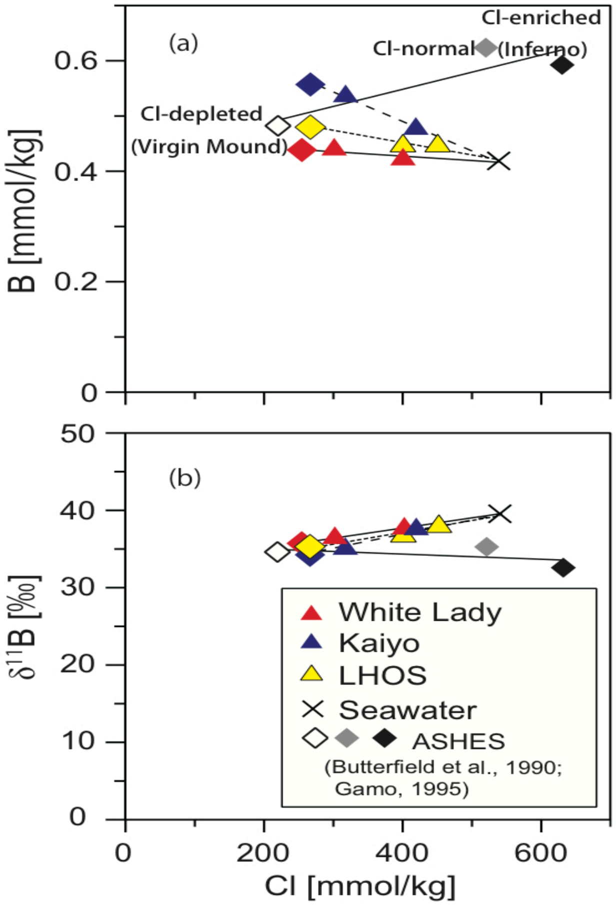

Figure 11. Boron (B) vs chlorine (Cl) in phase separated hydrothermal systems: (a) Correlation of Cl and B contents in ASHES vent field and North Fiji Basin (White Lady, Kaiyo and Forecast Vent); (b) Correlation of Cl contents and $\delta^{11}B$ in ASHES vent field and North Fiji Basin (White Lady, Kaiyo and Forecast Vent): the diamond shows the end member value, black to white diamonds show B contents and $\delta^{11}B$ from brine (Cl-enriched) to vapor-like fluid (Cl-depleted). Triangles show the values of samples collected from North Fiji Basin in this study, and the different colors show different sites. The values of Cl, B and $\delta^{11}B$ in ASHES were reported by Butterfield et al. (1990) and Gamo (1995). The values of Cl in White Lady were reported by Grimaud et al. (1991), while the values of Cl in Kaiyo and LHOS were reported by Ishibashi et al. (1994b).

Other process than fluid phase separation should be considered as the domination of boron chemistry in North Fiji Basin. Ignoring the phase separation process, the B content and δ^{11}B of vent fluid can straightly reflect the water-rock reaction in sediment-starved hydrothermal systems because there is no other process can vary boron chemistry of fluid so widely. Compared to those in EPR 21ºN and Vienna Woods, the B contents and δ^{11}B of vent fluids in North Fiji Basin in this study can be considered as the result of water-rock reaction and respond to the suggestion that North Fiji Basin is hosted by basalt with MORB-like feature (Eissen et al., 1991, 1994; Nohara et al., 1994).

5.3 Sediment-hosted hydrothermal systems

Significantly high B contents and low δ^{11}B are detected in the vent fluids in sediment-hosted Okinawa Trough (Table 1). At JADE site, 4.74 mmol/kg of B content was found in the vent fluid. At Minami-Ensei, B content was 4.41 mmol/kg, and at CLAM site, B content was 5.89 mmol/kg. The δ^{11}B value of JADE site is 2.6‰, similar with that in Minami-Ensei (2.4‰), while CLAM site is 1.5‰. Compared to sediment-starved hydrothermal systems in arc and back-arc which are dominated by water-rock reaction, it exhibits higher by 3 - 5 mmol/kg in B contents in Okinawa Trough, while lower by 10 - 30‰ in δ^{11}B values. It seems that basaltic rock even if dacitic rock reacting with seawater can not deplete the δ^{11}B (+39.6‰) of seawater to 1.5 - 2.6‰, and increase the B content (0.41 mmol/kg) of seawater to 4.41 - 5.89 mmol/kg. Therefore, it should be considered that the vent fluids in Okinawa Trough undergo another process such as water-sediment reaction, contribution of subducted material associating with water-rock reaction. In sediment-hosted hydrothermal systems, Okinawa Trough also behaves high B contents and low δ^{11}B relative to those in Guaymas Basin and Escanaba Trough (Table 3). JADE site in Okinawa Trough shows host rock from andesite to rhyolite (Chiba et al., 1997) similar with that in Minami-Ensei, while CLAM site shows basaltic host rock (Chiba et al., 1993). CLAM site is reported having thick sedimentary layer relative to JADE site and Minami-Ensei (Shitashima, 1994). For the various geological settings, vent fluids in Okinawa Trough showing high B contents and low δ^{11}B values should be considered that the vent fluid undergo a complex process including water-sediment reaction, contribution of subducted material associating with water-rock reaction.

Boron combined with caesium can be a useful approach to distinguish whether fluid reacts with sediment since sediment contains large amount of Cs relative to rock (White and Dupre, 1986). The trace mobility was experimented, suggesting that boron and caesium have similar extraction efficiency in fresh basalt (Seyfrield et al., 1984; Seyfrield et al., 1998) and sediments (You et al., 1996; Seyfrield et al., 1998). δ^{11}B vs Cs/B of sediment-hosted hydrothermal systems is plotted compared to those of sediment-starved hydrothermal systems (Figure 12), and the data of δ^{11}B and

Cs/B are concluded in Table 4. In Figure 12, δ^{11}B and Cs/B play a negative linear correlation in sediment-starved hydrothermal systems, relative to positive linear correlation between δ^{11}B and 1/B (Figure 10b). It may be considered that seawater plays an important role in boron exchange during water-rock reaction, while Cs content in seawater is negligible. Given that Cs content in seawater is 0, Cs and B contents in vent fluids are the mixture of those from rock and seawater in simple water-rock reaction pattern, the δ^{11}B value will play a negative linear correlation, according to equation (3). Therefore,

$$Rm = - (\alpha / B_{sw} a) Cs/B + \alpha / B_{sw} + \beta \qquad (6)$$

where, Rm, α, β refer to equation (3). B_{sw} is boron content in seawater. a is for Cs/B ratio from rock, considering as a constant due to the similar extraction efficiency between Cs and B in same host rock.

The plots of δ^{11}B vs Cs/B in sediment-hosted hydrothermal systems are out of the linear correlation, reflecting significantly high Cs contents in vent fluids of sediment-hosted hydrothermal systems. It indicates that the generation of the vent fluid in Okinawa Trough undergoes the water-sediment reaction following the water-rock reaction resulting in significantly high B contents and low δ^{11}B, demonstrating strong sediment contribution (You, et al., 1994). In fact, the sediment

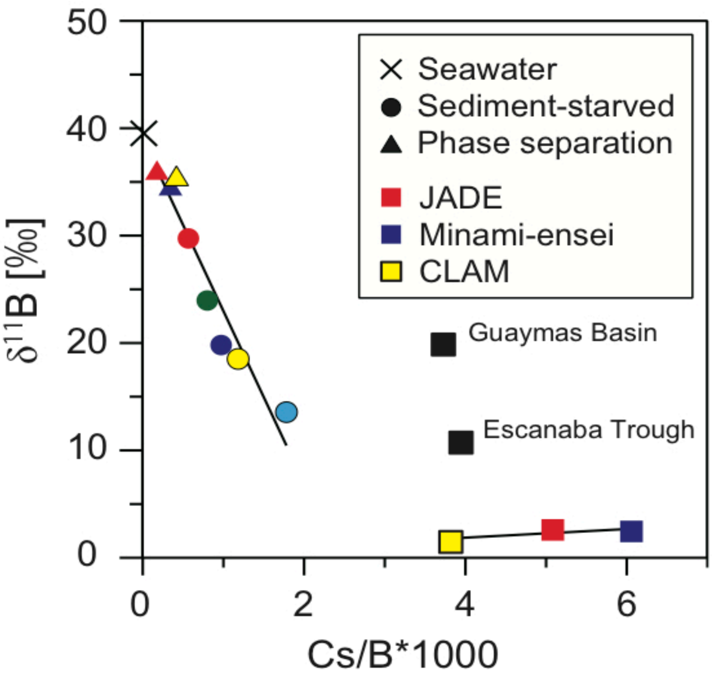

Figure 12. δ^{11}B vs Cs/B in sediment-hosted hydrothermal systems: in sediment-starved sites, δ^{11}B and Cs/B show a negative linear correlation, while in sediment-hosted sites, the plots are out of the range of the correlation line, indicating the significant increase of Cs extracting from sediment. The values of δ^{11}B are low and Cs/B are various in Okinawa Trough, relative to those in Guaymas Basin and Escanaba Trough, reflecting complex geological settings in Okinawa Trough.

Table 4. $\delta^{11}B$ and Cs, B contents, Cs/B of vent fluids in sediment-hosted sites

	Sites	B (mmol/kg)	Cs (mmol/kg)	Cs/B*1000	$\delta^{11}B$ (‰)
Okinawa Trough	JADE	4.74	0.0241	5.1	2.6
	Minami-Ensei	4.41	0.0267	6.1	2.4
	CLAM	5.89	0.0225	3.8	1.5
	Guaymas Basin[1]	1.6-1.7	0.0058-0.0065	3.7	16.5-23.2
	Escanaba Trough[2]	1.7-2.2	0.0077	3.9	10.1-11.5

1. Spivack et al., 1987; Gamo, 1995 2. Palmer, 1991; Gamo, 1995

of Okinawa Trough is mainly originated from the Eurasian continent. Boron is almost contained in neritic clay consists of detrital illite, chlorite, quartz and feldspars, and the B content is reported as 4 - 8 mmol/kg, which is higher than seawater, the $\delta^{11}B$ value is reported as -2.2 - -5.4‰ (Ishikawa and Nakamura, 1993). With the mass balance equation (4), water-sediment ratio can be estimated. Supposing the reaction in a closed system, and use the average values of vent fluid contents obtained in sediment-starved systems, and sediment Cs content of 0.045 mmol/kg (Taylor and McLennan, 1985). Water-sediment ratio can be calculated in the range of 1.4 - 2.3. Although some parameters are presumed, and might deviate from the precise data, the similar water-sediment ratio relative to water-rock ratio in EPR reported by Spivack and Edmond (1987) can respond to the result in Figure 12 that the plots of Cs/B vs $\delta^{11}B$ in sediment-hosted hydrothermal systems are out of the linear correlation of sediment-starved hydrothermal systems. The result suggests that sediment contributes strong influence to vent fluid due to water-sediment reaction following the water-rock reaction.

Compared to Guaymas Basin and Escanaba Trough (Table 4), which are sediment-hosted in MOR, Okinawa Trough shows entirely high B contents and low $\delta^{11}B$, indicating different geological conditions between back-arc basin and MOR. Since 1/B and $\delta^{11}B$ value has a linear correlation, it is difficult to distinguish the difference between sediment-hosted hydrothermal systems in MOR and sediment-starved hydrothermal systems in arc and back-arc. In Figure 12, supposing that the Cs/B and $\delta^{11}B$ values of vent fluids in Okinawa Trough before reaction between water and sediment plot in the area similar to those in sediment-starved Alice Springs in Mariana Trough back-arc basin, while those of Guaymas Basin and Escanaba Trough have similar compositions with EPR 21ºN, two lines with similar gradient can be drawn from sediment-starved plot area to sediment-hosted area. It suggests that Okinawa Trough should be considered as having high B contents and low $\delta^{11}B$ after water-rock reaction, relative to those in Guaymas Basin and Escanaba Trough, demonstrating that contribution of slab subducting and host rock should not be excluded. Therefore, given that the vent fluid of Okinawa Trough before water-sediment reaction has B content of 0.7 mmol/kg, $\delta^{11}B$ of 20‰, which are similar with those in Alice Springs in Mariana Trough, and the sediment of Okinawa Trough has B content of 8 mmol/kg in the range of 4 - 8 mmol/kg, and $\delta^{11}B$ of -2.2‰ in the range of -2.2 - -5.4‰ (Ishikawa and Nakamura, 1993), when the W/R is 2, Kd is 0.1, α is 0.986, which are supposed in sediment-starved section, the presumed vent fluid after water-sediment reaction shows B content of 4.5 mmol/kg, $\delta^{11}B$ of 1.8. The estimated data are consistent with the boron contents and isotopic compositions experimental data in this study, confirming the suggestion that vent fluid in sediment-hosted Okinawa Trough hydrothermal systems undergoes water-sediment reaction following water-rock reaction with the addition of influence of complex geological conditions in back-arc basin. Therefore, it responds to that boron isotopic composition and boron content combined with caesium are effective to be a tracer in investigating water-sediment reaction in seafloor hydrothermal systems.

6. Conclusions

In this study, boron contents and isotopic compositions of vent fluids from submarine hydrothermal systems in arc and back-arc in the western Pacific were studied systematically. It can complete the water-rock reaction system in submarine hydrothermal systems in the earth, using boron as a tracer. The boron contents and isotopic compositions in arc and back-arc hydrothermal systems are concluded as follows:

1. Compared to well-studied hydrothermal systems in MOR, arc and back-arc hydrothermal systems showed various B contents and δ^{11}B, although the vent fluids end members obtained by extrapolating Mg to 0 showed high B contents and low δ^{11}B relative to seawater. In sediment-starved hydrothermal systems in arc and back-arc, Vienna Woods in Manus Basin showed similar B content and δ^{11}B of vent fluid relative to those in EPR 21ºN of the typical hydrothermal system in MOR, reflecting MORB-like feature of host rock in Vienna Woods in Manus Basin.

2. In sediment-starved hydrothermal systems, PACMANUS in Manus Basin and Suiyo Seamount in Izu-Bonin Arc have dacitic host rock, resulting in high B contents and low δ^{11}B of vent fluids relative to the basalt-hosted hydrothermal systems in arc and back-arc. It is considered that relatively high B contents leached from the dacitic host rocks result in the high B contents and low δ^{11}B of vent fluids due to that the dacitic host rocks commonly contain high B contents. Compared to EPR 21ºN in MOR, Alice Springs and Forecast Vent of Mariana Trough, which are hosted by basalt, showed relatively high B contents and low δ^{11}B of vent fluids. It considered as the contribution of slab subducting since boron is easily extracted into melt and increase the rock boron content. Forecast Vent showed slightly higher δ^{11}B than that in Alice Springs in Mariana Trough. There is a possibility that the relatively low temperature of vent fluid in Forecast Vent can result in slightly high δ^{11}B value due to the boron isotope partition calculation.

3. In North Fiji Basin, where caused a phase separation due to the depleted Cl, B contents and δ^{11}B did not show significant separation. It was considered that B contents and δ^{11}B were hardly influenced by phase separation in North Fiji Basin. Low B contents and high δ^{11}B in White Lady, Kaiyo and LHOS in North Fiji Basin indicated that the boron compositions of the vent fluids resulted from water-rock reaction significantly, compared to those in EPR21ºN. By the result, it can reasonably determine the North Fiji Basin as a MORB-like hydrothermal system.

4. In sediment-hosted hydrothermal system, JADE site, Minami-Ensei and CLAM site in Okinawa

Trough entirely showed very high B contents and very low $\delta^{11}B$ values. Combined Cs with B contents and plotted with the $\delta^{11}B$ values, it reflected that the fluids underwent the water-sediment reaction following the water-rock reaction. Compared to MORB-type sediment-hosted Guaymas Basin and Escanaba Trough, Okinawa Trough showed relatively high B contents and low $\delta^{11}B$, which is response to the contribution from slab subducting and various host rocks in arc and back-arc hydrothermal systems. The boron data in this study can complete the global hydrothermal system process research, using boron as a tracer.

7. Acknowledgements

It is a privilege to express much appreciation to my supervisor Professor Hodaka Kawahata and Dr. Kyoko Yamaoka of AIST for the overall support. Thank Dr. Kyoko Yamaoka for a lot of advice and suggestions, experiment support, valuable discussion, helpful comments and a lot of supports for my research life. I would like to express my appreciation to Mr. Daisuke Araoka of AORI for many helpful comments and many supports of research life, to Dr. Toshihiro Yoshimura for polishing the graph and many opinions about the research approach.

I would like to express the special appreciation to Professor Toshitaka Gamo of AORI for providing all of the vent fluid samples in this study, and many valuable opinions and discussions. Thank Dr. Atsushi Suzuki of AIST for many supports of research life in AIST, and many opinions for the research. Thank Dr. Tsuyoshi Ishikawa of JAMSTEC in Kochi Core Center for the experiment conducting and valuable discussion, and also the life support in Kochi Core Center. Especially, thank Dr. Jun Matsuoka and Dr. Kazuya Nagaishi for experiment conducting and assistance.

I extend my special thanks to all of the members in OFGS for research life support in AORI, and to my family for all of the support in my master program.

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Boron content and isotope of vent fluids from seafloor hydrothermal systems

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Keywords: boron content, boron isotopic composition, vent fluid, submarine hydrothermal system

1. Introduction

Submarine hydrothermal system is defined by circulatory system where seawater sinks into seafloor through cracks of the crust and is heated by high-temperature magma under seafloor whereupon it rises back to the rock-ocean interface. In this process, seawater reacts with the surrounding rock at high temperature and results in vent fluid whose chemical compositions are very different from the original seawater. So far, a number of hydrothermal systems have been discovered not only along mid-ocean ridge (MOR), but also in arc and back-arc all over the world. In contrast to seafloor hydrothermal systems along MOR, it is known that vent fluids from arc and back-arc hydrothermal systems show various chemical compositions, reflecting complex geological settings.

Boron (B) has been attracting attentions in recent years as a useful tracer during water-rock reaction due to high mobility and occurring large isotopic fractionation in solution. Although a number of studies about chemical compositions of vent fluids from hydrothermal systems have been conducted, it is mainly limited to the hydrothermal systems in mid-ocean ridge (MOR). In this study, boron contents and boron isotopic compositions (δ^{11}B) of vent fluids collected from arc and back-arc hydrothermal systems in the western Pacific were determined. The purposes of this study are to reveal the influence of complex geological settings in arc and back-arc to boron contents and boron isotopic compositions in vent fluids, and deepen the comprehensive understanding of boron behavior during water-rock reaction in submarine hydrothermal systems.

2. Materials and Methods

In this study, vent fluids collected from sediment-starved Manus Basin (Vienna Woods, PACMANUS), Izu-Bonin Arc (Suiyo Seamount), Mariana Trough (Alice Springs, Forecast Vent); phase separated North Fiji Basin (White Lady, Kaiyo, LHOS); sediment-hosted Okinawa Trough (JADE, Minami-Ensei, CLAM) in arc and back-arc in the western Pacific were studied. Among these sites, major elements of samples were analyzed by ICP-AES, and 25 vent fluid samples, whose major elements were consistent with those reference data, were selected for measuring trace elements including B contents by ICP-MS and δ^{11}B values by P-TIMS.

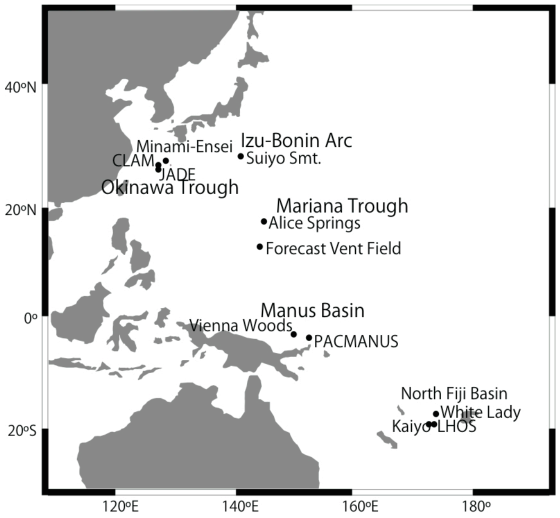

Figure 1. Locations of hydrothermal systems in arc and back-arc

3. Results and Discussions

Although the vent fluid end members obtained by extrapolating Mg to 0, showed high B contents and low δ^{11}B relative to seawater, they showed various B contents and δ^{11}B compared to the EPR 21ºN of the typical hydrothermal systems in MOR (Figure 2). In sediment-starved hydrothermal systems, Vienna Woods in Manus Basin showed similar B content and δ^{11}B in vent fluid relative to those in EPR 21ºN in MOR, reflecting MORB-like feature of host rock in Vienna Woods. While PACMANUS in Manus Basin and Suiyo Seamount in Izu-Bonin Arc exhibited higher B contents and lower δ^{11}B than those in Vienna Woods in Manus Basin and EPR 21ºN in MOR. It is considered as that relatively high B contents leached from the dacitic host rocks result in the high B contents and low δ^{11}B of vent fluids due to that the dacitic host rocks commonly contain high B contents. Alice Springs and Forecast Vent in Mariana Trough showed intermediate values of vent fluids in sediment-starved hydrothermal systems, suggesting that the basaltic host rocks are influenced by the material derived from slab subducting, and result in boron-rich compositions of vent fluid relative to MORB. In phase separated hydrothermal systems, White Lady, Kaiyo and LHOS in North Fiji Basin showed similar B contents and δ^{11}B to those in MOR. According to the result of the laboratory experiment that B contents and δ^{11}B of vent fluids are hardly influenced by phase separation, it is considered that B contents and δ^{11}B of vent fluid from North Fiji Basin resulted from water-rock reaction. The result responds to the suggestion that North Fiji Basin is a MORB-like hydrothermal system. In sediment-hosted hydrothermal system, JADE, Minami-Ensei and CLAM showed very high B contents and low δ^{11}B in vent fluids. According to the correlation of Cs/B and δ^{11}B, it suggested that sediment contributed boron to vent fluid due to the reaction between fluid and boron-rich sediment following the water-rock reaction.

In this study, B contents and δ^{11}B of vent fluids from arc and back-arc were clarified systematically. Due to this study, it reflected that B contents and δ^{11}B were primarily dominated by the boron contents of reacting rock and sediment, and can be an effective index to understand the species of host rock and estimate the existence of sediment.

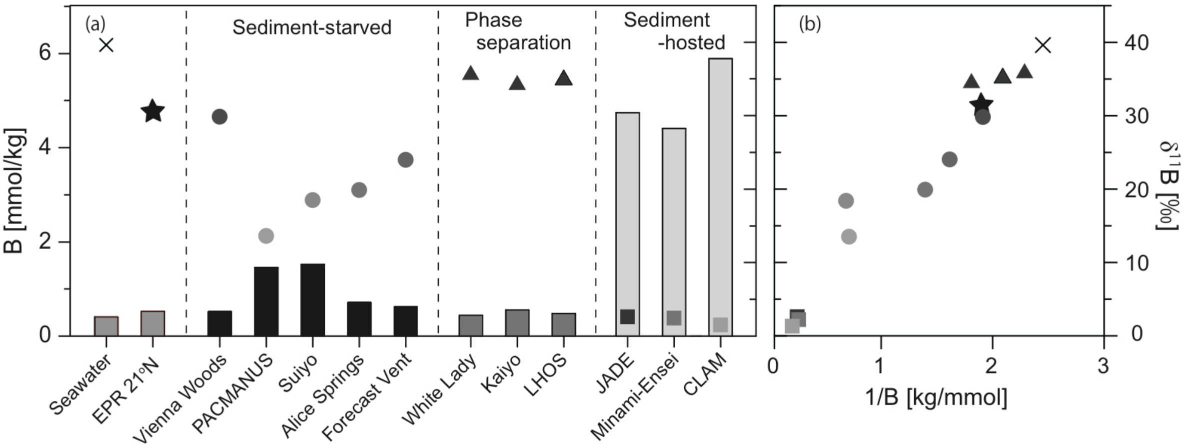

Figure 2. Boron contents and isotopic compositions in arc and back-arc hydrothermal systems: (a) bar graphs are boron contents; symbols are boron isotopic composition. (b) 1/B vs boron isotopic compositions. The positive correlation means higher boron contents derived from host rock or sediment can result in higher boron contents and lower boron isotopic compositions of vent fluids during water-rock or water-sediment reaction.

海底熱水活動域から採取された熱水のホウ素濃度と同位体組成

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キーワード：　ホウ素濃度，ホウ素同位体組成，噴出熱水，海底熱水活動

1. はじめに

海底熱水活動は、海水が海底の割れ目から浸透し、地下の高温のマグマによって加熱され、海底面に噴出するという熱水循環系である。海水が周囲の岩石と高温で反応する結果、噴出熱水の化学組成はもとの海水とは大きく異なるものとなる。現在までに、中央海嶺だけでなく島弧・背弧海盆においても多くの熱水活動域が発見されてきた。中央海嶺の熱水と比べ、島弧火山や背弧海盆の熱水は多様な化学組成を示し、複雑な地質条件を反映していることが知られている。しかし、中央海嶺の熱水系に対し、噴出熱水の地球化学的な研究は限られている。

ホウ素は流体とともに動きやすく、同位体分別が大きいことから、水–岩石反応における有用なトレーサーとして近年注目されている。これまで噴出熱水の化学組成については多くの研究が行われてきたが、ホウ素をトレーサーとした研究は、主に中央海嶺の熱水系に限られている。本研究では、西太平洋の島弧および背弧海盆の熱水活動域に着目し、噴出熱水のホウ素濃度およびホウ素同位体組成の分析を行った。本研究の目的は、島弧および背弧海盆の複雑な地質条件が、噴出熱水中のホウ素濃度とホウ素同位体組成にどのような影響を及ぼすかを明らかにし、海底熱水系の水–岩石反応におけるホウ素の挙動について統合的な理解を深めることである。

2. 試料と方法

本研究では、(1) 堆積物のない熱水系であるマヌス海盆（Vienna Woods, PACMANUS）、伊豆小笠原弧（Suiyo Seamount）、マリアナトラフ（Alice Springs, Forecast Vent）、(2) 二相分離が起こっている熱水系である北フィジー海盆（White Lady, Kaiyo, LHOS）、(3) 堆積物に被覆された熱水系である沖縄トラフ（JADE, Minami-Ensei, CLAM）において採取された噴出熱水試料を用いた（図 1）。試料はあらかじめ ICP-AES により主要元素分析を行い、先行研究で報告されている濃度と調和的な値を示した試料を 25 個選び、高知コアセンターにおいて、ICP-MS でホウ素濃度を、P-TIMS でホウ素同位体組成を測定した。

図 1. 西太平洋の島弧火山および背弧海盆の熱水試料採取地点

3. 結果と考察

Mg 濃度を 0 に外挿することにより得られた島弧および背弧海盆の熱水端成分の組成は、海水より高いホウ素濃度と低いホウ素同位体比を持つが、代表的な中央海嶺熱水系である EPR 21ºN の熱水と比べ、多様なホウ素濃度と同位体組成を示した（図 2)。堆積物で被覆されない熱水系の代表であるマヌス海盆 Vienna Woods の噴出熱水では、ホウ素濃度と同位体組成が中央海嶺 EPR 21ºN の熱水と類似しており、これは母岩が中央海嶺玄武岩(MORB)に似た組成を持つためと考えられる。一方、マヌス海盆 PACMANUS と伊豆小笠原弧 Suiyo Seamount は、中央海嶺 EPR 21ºN やマヌス海盆 Vienna Woods に比べ、高いホウ素濃度と低い同位体比を示した。これは、一般的に高いホウ素濃度を持つデイサイトが母岩であるため、より多くのホウ素が岩石から溶出され、高いホウ素濃度と低いホウ素同位体比を持つ熱水が形成されたと考えられる。マリアナトラフの Alice Springs と Forecast Vent の熱水はこれらの中間的な値を示し、母岩である玄武岩が沈み込むスラブに由来する流体の影響を受け、MORB に比べてホウ素に富んだ組成を持っていることを反映している。地下での二相分離によって気相に富んだ熱水が噴出している北フィジー海盆 (White Lady, Kaiyo, LHOS) では、低いホウ素濃度と高いホウ素同位体比という中央海嶺熱水系と似た特徴を示した。熱水のホウ素濃度および同位体比は二相分離にほとんど影響を受けないという室内実験の結果を踏まえると、この特徴は主に水–岩石反応により獲得されたと考えられる。この結果は、北フィジー海盆の母岩が MORB 的であるという先行研究と調和的である。堆積物に覆われた熱水系である沖縄トラフ (JADE, Minami-Ensei, CLAM) の熱水は、非常に高いホウ素濃度と低いホウ素同位体比を示し、Cs/B 比と δ^{11}B の関係から、熱水が岩石だけでなく、非常にホウ素に富んだ堆積物とも反応することより、堆積物から熱水にホウ素が供給されたことが示唆された。

本研究は、島弧および背弧海盆における熱水のホウ素濃度と同位体組成を体系的に明らかにした。本研究により、噴出熱水のホウ素濃度および同位体比は、基本的に反応した岩石または堆積物のホウ素濃度に支配されるため、母岩の種類または堆積物の有無の推定に有効な指標となることが示された。

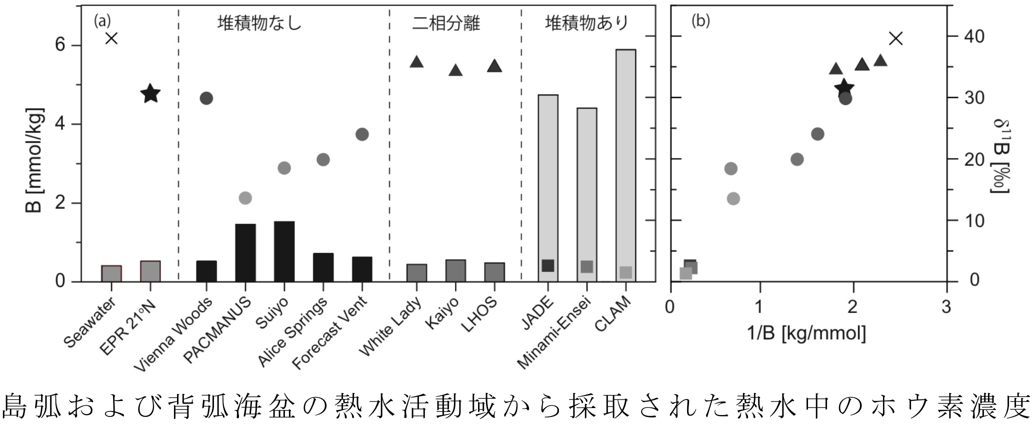

図 2. 島弧および背弧海盆の熱水活動域から採取された熱水中のホウ素濃度および同位体組成：(a)棒グラフはホウ素濃度、プロットはホウ素同位体組成を示す; (b) ホウ素濃度分の一(1/B)とホウ素同位体組成. 正の相関性を示すのは、より多くのホウ素が岩石あるいは堆積物から熱水に溶出したため、水–岩石反応あるいは水–堆積物反応により、高いホウ素濃度と低い同位体比をもつ熱水が形成されたと考えられる。