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Influence of subduction zone settings on the origin of forearc fluids: Halogen concentrations and ^{129}I/I ratios in waters from Kyushu, Japan

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Abstract

Fluid migration in subduction zones is one of the key phenomena to understand the global mass transfer system. While active volcanoes provide the most recognizable conduits for fluid flow in active margins, the existence of a large number of active fluid seepages demonstrates that other forms of fluid release are also important in subduction zone settings. The authors collected fluid samples from springs and wells across the forearc area in Kyushu, a southwestern island of Japan, covering hot spring activities associated with active volcanism and the Median Tectonic Line (MTL), a major fault system present in the southwestern part of Japan. In order to determine sources of these fluids, halogen concentrations as well as ^{129}I/I and ^{36}Cl/Cl ratios were measured in samples from several locations. While Cl concentrations of the forearc fluids in Kyushu range between seawater and meteoric water value, I concentrations are considerably higher than seawater value. Fluids in the Miyazaki area are much higher in I, and somewhat higher in Br, than waters in the Oita area, which is closely associated with the MTL. The differences between those two areas are also pronounced in ^{129}I/I ratios, which range between 800 and 900×10^{-15} in the Oita area and between 100 and 360×10^{-15} in the Miyazaki area. The ^{129}I/I ratios obtained from the Oita area are compatible with an I derivation from subducting marine sediments, similar to findings from an earlier investigation of fluids collected from Satsuma-Iwojima, an active volcano south of Kyushu Island. In the Miyazaki area, on the other hand, I ages are too old to be derived from currently subducting marine sediments and point to a derivation from old organic-rich materials in the upper plate of the forearc region. The results demonstrate the presence of very different fluid systems in the forearc area of Kyushu: old CH_4-rich fluids dominate in the seaward side of the forearc, while fluids close to the MTL and the Quaternary Volcanic Front demonstrate derivations from subducting marine sediments. The latter fluids in the MTL area probably are transported through the fractures associated with the fault activities, suggesting that this fault system reaches the transition zone between upper and lower plates in this region.

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1. Introduction

Fluids derived from deep sequences in the continental margins are commonly enriched in I and, to a lesser degree, in Br (Fehn et al., 1992; Moran

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et al., 1995; Snyder and Fehn, 2002; Snyder et al., 2002; Fehn and Snyder, 2003). Because of the biophilic nature, in particular of I, these enrichments are explained by derivations from organic-rich formations. In active continental margins, candidates for such source formations include subducting marine sediments (e.g., Snyder and Fehn, 2002) as well as organic-rich formations in the overlying plate (e.g., Fehn and Snyder, 2003) or possibly serpentinized sub-arc mantle wedge (Snyder et al., 2005; Hurwitz et al., 2005). Both high (<940 °C) and low (<200 °C) temperature volcanic condensates in the continental margins are also relatively enriched in I and Br (Taran et al., 1995; Snyder and Fehn, 2002; Snyder et al., 2002) compared to seawater and volcanic rocks (Yoshida et al., 1971; Muramatsu and Wedepohl, 1998), demonstrating a large contribution of organic-rich marine materials to the volcanic system. Therefore, halogens preserve the history of fluid migration and have been used as a proxy for mass transfer in subduction zones because they are petrologically incompatible during diagenesis. In addition, the presence of long-lived radioisotopes of I (^{129}I) and Cl (^{36}Cl) provides age signals for the halogen-rich fluids in the forearc area. The variable fluid ages in several subduction settings well describe the direct I (halogens) delivery from subducting marine sediments (Snyder and Fehn, 2002; Fehn et al., in press-b) and the long-scale I (halogens) remobilization from older formations (Muramatsu et al., 2001; Fehn and Snyder, 2003), which may reflect regional differences of subduction-related fluid systems.

The purpose of this study is the determination of potential source formations across the forearc area in Kyushu, and the influence of the Median Tectonic Line (MTL), a major fault system in the southwestern geological part of Japan, to assess the influence of a subduction system on the origin and fluid migration of forearc fluids. The halogen distribution and radioisotopes of I and Cl were investigated in the fluids which are enriched in halogens, particularly in I, from a variety of settings in southwestern Japan, which are associated with volcanic activities, a large-scale thrust-fault system, and a slab subduction. These geological processes are characterized by the active plate motions which have created the Japanese Island Arc and play an important role in the fluid flux throughout the forearc systems.

2. Halogen systematics

The ^{129}I system has been developed and applied for geochemical studies associated with marine systems. Because photoplanktonic H_2O_2 production with unsaturated C networks proceeds to the formation of nitrogeneous organic I compounds (Luther et al., 1995; Carpenter et al., 1999), the concentration of I in marine sediments is enhanced and ranges from 10 to 100 ppm (Wong, 1991), at least two orders of magnitude greater than that of seawater (0.05 ppm; GERM, 2006). The total amount of I in marine sediments reaches up to 5.90×10^{12} t, equivalent to 68.2% of the total I in the earth's crust (Muramatsu and Wedepohl, 1998). Iodine has one stable isotope (^{127}I) and a long-lived radioisotope (^{129}I; half-life of 15.7 Myr) which is produced by cosmic-ray induced spallation of Xe isotopes in the atmosphere and by spontaneous fission of ^{238}U in the crust. Both of these processes contribute ^{129}I at similar rates to the ocean, the main reservoir of this isotope on the earth's surface (Fabryka-Martin et al., 1985). Since the residence time of I in the oceans (~300 kyr; Broecker and Peng, 1982) is much longer than the turnover time, the isotope ratio is homogeneous in the oceans and in reservoirs such as the atmosphere and biosphere which exchange rapidly with the marine system. This marine ^{129}I/I ratio has been determined to be $(1500 \pm 150) \times 10^{-15}$ (Moran et al., 1998; Fehn et al., in press-a) and is used as the input ratio for calculations on the age of separation from surface reservoirs. The ^{129}I/I ratios are potentially useful for the age determinations of fluids related to I host materials because the range of age information from ^{129}I is appropriate for the fluid-sediment system in the subduction zones. A potential problem in the application of this system is the recent release of anthropogenic ^{129}I from nuclear weapon tests and reprocessing, which has increased the ^{129}I/I ratios in many surface reservoirs by several orders of magnitude (Moran et al., 1999; Snyder and Fehn, 2004).

Chlorine is much less biophilic but more abundant in seawater and marine sediments compared to I. It has two stable isotopes (^{35}Cl and ^{37}Cl) and one radioisotope (^{36}Cl) with a relatively short half-life (0.301 Myr; Bentley et al., 1986). It is produced by cosmic-ray induced spallation of Ar isotopes in the atmosphere and interaction of ^{35}Cl with neutrons in the ocean and earth crust. Recent anthropogenic ^{36}Cl from nuclear weapon tests has also increased the ^{36}Cl/Cl ratio in the atmosphere, but it has returned to the pre-anthropogenic ratio level due to the short residence time of ^{36}Cl in the atmosphere (Elmore et al., 1982; Suter et al., 1987). Because the oceanic ^{36}Cl/Cl ratio is below the detection limit of accelerator mass spectrometry (AMS) (1×10^{-15}) and the half-life of ^{36}Cl is relatively short compared to processes in the subduction system, the ^{36}Cl system is less useful than ^{129}I and used for the detection of anthropogenic input of surface water to the samples (Snyder et al., 2003).

Bromine has a biophilic nature somewhere between I and Cl, but the behavior of Br in fluids of subduction zones has not been studied in detail. Similarly to I, Br concentrations correlate well with those of organic C in sediments (Price et al., 1970; Price and Calvert, 1977), which demonstrates that Br is released from organic materials into the aqueous phase together with I during diagenesis.

3. Geological setting

The Japanese Island Arc is at the junction between the Eurasian (Amur) Plate, the North American (Okhotsk) Plate, the Philippine Sea Plate, and the Pacific Plate (e.g., Taira, 2001); the latter two oceanic plates subduct obliquely beneath the continental plates (Fig. 1a). The Itoigawa-Shizuoka Tectonic Line (ISTL) divides geologically the main island of Japan into northeastern and southwestern parts (Fig. 1a). The Median Tectonic Line (MTL), an arc-parallel large fault system related to the subduction of the Philippine Sea Plate, subdivides the southwestern part of Japan into the older Inner Zone (metamorphic terrane) on the continental side and the younger Outer Zone (sedimentary terrane) on the Pacific Ocean side.

Kyushu is one of four major islands of Japan on the Eurasian Plate (Fig. 1a). The MTL extends from NE to SW in the Oita area (sampling locations O1 to O9 in Fig. 1b), the western termination of the Sambagawa (high-P) and Ryoke (low-P) metamorphic belts lie below this area in the Inner Zone of southwestern Japan. The Sambagawa metamorphic belt appears only in the eastern end of the area along the MTL and was formed by the underplating at depths between 15 and 30 km in an Early Cretaceous accretionary complex (Isozaki and Itaya, 1990). The Ryoke metamorphic belt, which is juxtaposed NW (inner side of the MTL) of the Sambagawa belt and underlies most of the Oita area, consists of abundant granitoids and associated low-P metamorphic complexes of Carboniferous to Late Jurassic ages (Banno and Nakajima, 1992; Nakajima, 1994; Suzuki and Adachi, 1998). It is commonly overlain by Neogene andesitic pyroclastic rocks in this area. Beppu (O10 and O11 in Fig. 1b), a geothermal field ~10 km NW of central Oita, is located in the eastern end of the graben in northwestern Kyushu, which is formed by tectonic rifting due to the subduction of the Philippine Sea Plate beneath the Eurasian Plate (Kamata and Kodama, 1994). Hydrothermal activity in Beppu is maintained by up-flow from a geothermal source region, located ~10 km W, beneath the active Quaternary volcanoes with temperatures between 250 and 300 °C (Allis and Yusa, 1989; Sturchio et al., 1996).

Mt. Aso (A1 and A2 in Fig. 1a) is located in central Kyushu, ~40 km SW of Oita, and consists of basalt to rhyolite (Ono and Watanabe, 1985). Yudamari is the crater lake of Nakadake, one of the youngest cones of Mt. Aso, with temperatures between 50 and 70 °C. It appears only in a calm period of the volcanic activity of Mt. Aso (Ohsawa et al., 2003; Hase et al., 2005).

Surface layers in the Miyazaki Plain (M1 to M16 in Fig. 1c) are mostly shallow marine sediments of Late Miocene to Pliocene age, consisting of sand and silt with abundant tuff layers of 6.5–2 Ma (Torii et al., 2000), which unconformably overlie a highly deformed, subduction-related accretionary complex of pre-Miocene age (Shuto, 1961). Natural gas production wells have been operated there since the 1970s, and sampled fluids are commonly enriched in gases, mostly CH_4.

The MTL runs toward the ISTL through Shikoku Island and the Kii Peninsula. One sample was measured from this section of the MTL, Wakayama (W1 in Fig. 1a) on the inner side of the MTL zone in the northwestern Kii Peninsula, where metamorphic rocks derived from Paleozoic deposits are overlain by Late Cretaceous marine sediments (Isomi, 1968).

While sampling locations can be characterized by their relation to the MTL; the Miyazaki area is in the younger Outer Zone and the Oita area including Beppu and Mt. Aso and Wakayama are in the older Inner Zone, all the areas are located in the forearc setting associated with the subduction of the Philippine Sea Plate beneath the Eurasian Plate along the Japanese Island Arc which was initiated at about 20 Ma (Jarrard, 1986; Jolivet et al., 1989).

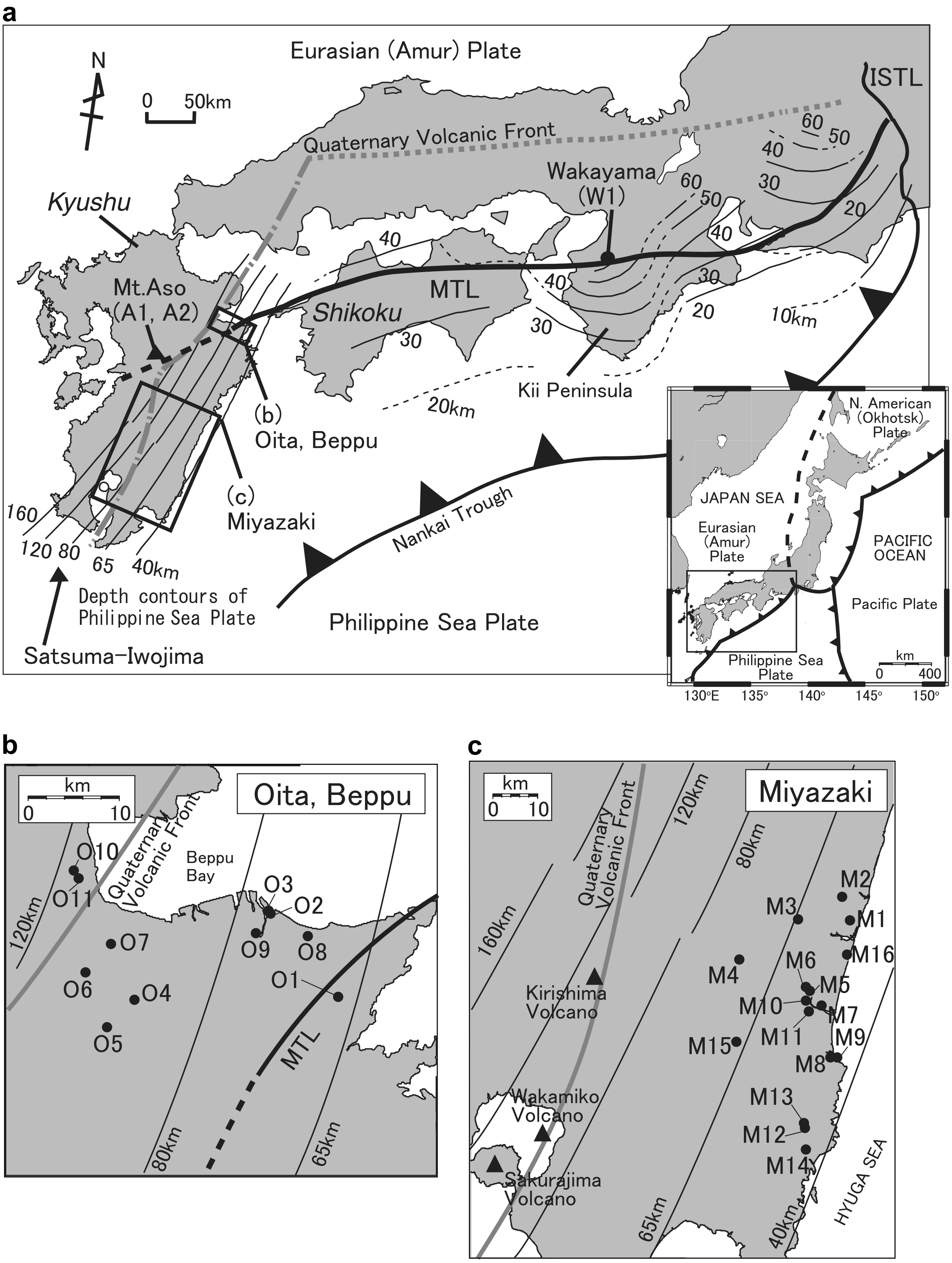

Fig. 1. (a) Geological setting of southwestern Japan and sampling locations in (b) Oita (O1 to O9) and Beppu (O10 and O11) and (c) Miyazaki (M1 to M16). Samples were also collected form Mt. Aso (A1 and A2), central Kyushu Island, and Wakayama (W1) in the Kii Peninsula. The MTL geologically divides the Japanese Island Arc into an older Inner Zone including Oita, Beppu, Mt. Aso, and Wakayama areas and a younger Outer Zone including Miyazaki area. Contour lines represent the depths to the subducting Philippine Sea Plate beneath the Eurasian (Amur) Plate.

4. Materials and methods

Sample fluids were collected from springs and wells in Oita-Beppu (O1 to O11 in Fig. 1b), Miyazaki (M1 to M16 in Fig. 1c), and Wakayama (W1 in Fig. 1a) from 2003 to 2005. In addition, crater lake waters were also collected from Yudamari of Mt. Aso in 2000 (A1) and 2003 (A2) (Fig. 1a) (Ohsawa et al., 2003).

Dissolved Cl concentrations were determined by ion chromatograph, Dionex ICS-1000 with precisions better than 1%, and total Br and I concentrations were measured by inductively coupled plasma mass spectrometer (ICP-MS), Thermo Elemental X7, with precisions better than 3% at the Cosmogenic Isotope Lab, University of Rochester. Dissolved iodine was precipitated as AgI following established methods (Fehn et al., 1992) for the determination of isotopic ratios (^{129}I/I). Iodate in the sample fluid was reduced to I_2 by sodium bisulfite, and pre-concentrated with anion resin. The purified I_2 was extracted into chloroform, back extracted into sodium bisulfite, and then precipitated as AgI with $AgNO_3$. Chlorine is precipitated as AgCl with the method outlined by Snyder et al. (2003) for ^{36}Cl/Cl analyses. The sample fluid was acidified, and AgCl was precipitated with $AgNO_3$. The precipitate was dissolved with NH_4OH solution, and purified with anion resin and then eluted by HNO_3 to obtain pure AgCl for the isotopic analysis. Generally, approximately 1 mg of I or Cl is used for AMS measurements. While this quantity was readily available for the samples from Miyazaki, due to the lower concentrations in the Oita samples, several of these samples had masses below 0.2 mg. Although the ratios obtained for these samples have relatively high uncertainties, the ratios are reliable as shown in a recent investigation of small sample masses, which found that samples with as low as 0.05 mg of I produced reproducible results (Lu et al., in press). The AgI and AgCl targets were analyzed at the AMS of PRIME Lab, Purdue University (Sharma et al., 2000).

5. Results and discussion

5.1. Halogen distribution and fluid characterization

Analytical results of concentrations and isotopic ratios for the samples are listed in Table 1. The Cl concentrations of samples range from 24 to 680 mM in spring and well samples from Oita, Miyazaki, and the one sample from Wakayama, but concentrations in the crater lake from Mt. Aso are considerably higher than those, increasing from 828 mM in 2000 to 1343 mM in 2003. Iodine concentrations in Oita and Wakayama are lower than 8 μM, those in Miyazaki range from 56 to 620 μM and that of Mt. Aso reaches 223 μM.

The Cl concentrations of Oita and Miyazaki samples generally are between meteoric water (0.52 mM; Takaku et al., 1995) and seawater (550 mM; Broecker and Peng, 1982) values, but all I and some Br concentrations are higher than seawater values (Figs. 2 and 3). Because Cl is biophilically and petrologically incompatible (You and Gieskes, 2001), decrease of Cl concentrations from the seawater value observed in deep fluids is explained by freshening due to water of meteoric and/or diagenetic origin, such as biogenic opal recrystallization, clay mineral dehydration (Brown et al., 2001), and clay membrane filtration (Kastner et al., 1991), which also decrease I and Br concentrations. Thus Cl, the most conservative and least biophilic element of these three halogens, preserves best the mixing behavior of the fluids between paleo seawater and fresh waters derived from meteoric sources or during diagenesis. Concentrations of the mixing endmembers for the more biophilic elements I and Br can then be estimated using gradients in diagrams between Cl and the other two halogens (Figs. 2 and 3). Following this approach, dissolved I concentrations of the initial fluids are calculated to be ~16 μM in Oita ($I/Cl = 0.03 \times 10^{-3}$) and ~700 μM in Miyazaki ($I/Cl = 1.3 \times 10^{-3}$), respectively (Fig. 2), suggesting that the initial I concentrations are much higher than that of seawater (0.44 μM; GERM, 2006) but are very different in these two locations.

The samples from the Beppu hydrothermal area (closed triangles) generally show lower Cl and I concentrations than those from other Oita samples, but still fall into the mixing range between meteoric (fresh) water and the initial fluid for Oita samples, indicating similar sources for these two areas. All the samples with Cl concentrations above the seawater value (O8, M16, and W1) were collected from hot spring wells, where compositions can be modified by fluid-rock interaction and/or evaporation. The crater lake samples from Mt. Aso (A1 and A2) show exceedingly high Cl concentrations. The Cl concentration of Mt. Aso has changed widely

Table 1
Analytical results of Cl, Br, and I concentrations and ^{129}I/I and ^{36}Cl/Cl ratios

No	Sample ID	Type	Cl (mM)	Br (μM)	I (μM)	^{129}I/I (10^{-15})	^{36}Cl/Cl (10^{-15})
Oita (Kyushu)							
O1	Rokkasako-Shiomo	Spring	46.2	53.1	0.4	N.A.	
O2	Hanazono	Well	61.8	96.1	1.3	2450 ± 570	8.8 ± 2.5
O3	Ozai	Well	41.4	62.8	0.9	1800 ± 900	
O4	Tsukano	Spring	107	120	2.2	900 ± 300	
O5	Myoken	Spring	111	128	3.0	2300 ± 500	
O6	Hazama	Well	512	537	6.8	800 ± 300	
O7	Kihachi-jigoku	Well	138	161	2.3	1580 ± 260	2.8 ± 1.6
O8-1	Fuchino-HS (collected in 2003)	Well	680	691	6.5	2390 ± 290	7 ± 2.2
O8-2	Fuchino-HS (collected in 2005)	Well	526	511	4.6	2260 ± 160	
O9	Hojuen	Well	56.5	117	2.1	900 ± 400	
O10	Beppu Heiwa-en	Spring	24.4	60.9	1.7	820 ± 460	
O11-1	Beppu Ogura 1-2 N	Spring	26.5	62.9	1.8	4200 ± 700	
O11-2	Beppu Ogura 1-2S	Spring	24.3	59.5	1.7	2590 ± 500	
Miyazaki (Kyushu)							
M1	Shintomi	Well	284	817	324	290 ± 50	
M2	Takanabe	Well	133	432	151	130 ± 40	
M3	Takaya	Well	230	1010	229	280 ± 50	
M4	Aya	Well	44.2	103	81.8	160 ± 30	
M5	Mingas-R2	Gas well	59.2	265	158	2300 ± 700	
M6	Mingas-R4	Gas well	109	278	184	100 ± 40	
M7	Mingas-Oyodo1	Gas well	202	290	222	300 ± 60	
M8	Shizen-Kyuyoson	Well	40.2	79.1	56.6	360 ± 50	
M9	Taiyokaku	Well	47.9	90.4	61.3	320 ± 60	
M10	Konan	Well	528	1517	620	160 ± 30	
M11	Nozaki-HS	Well	65.7	119	93.6	230 ± 50	
M12	Kitago-R1	Gas well	103	156	109	250 ± 50	
M13	Kitago-R6	Gas well	45.1	79.6	59.0	300 ± 50	
M14	Nichinan-Kanpo	Well	150	233	150	280 ± 80	
M15	Aoidake	Well	68.7	86.7	64.8	140 ± 50	
M16	Ishizakihama	Well	608	1564	439	270 ± 110	
Mt. Aso (Kyushu)							
A1	Yudamari (collected in 2000)	Crater lake	828	901	65.2	N. A.	
A2	Yudamari (collected in 2003)	Crater lake	1343	4206	223	2730 ± 200	2.6 ± 1.8
Wakayama (Kii Pen.)							
W1	Nohan-no-sato	Well	648	1260	7.7	250 ± 30	
Comparison							
SW	Seawater	Reference	550[a]	840[a]	0.44[a]	1500[b]	
PMW	Meteoric water (pre-anthropogenic)	Reference	0.52[c]	0.25[a]	0.0079[d]	1500[b]	
AMW	Meteoric water (anthropogenic)	Reference	0.52[c]	0.25[a]	0.0079[d]	7,869,250[d]	

Chlorine isotope ratios are determined for high ^{129}I/I samples.
N.A.; not analyzed.

[a] Broecker and Peng (1982).

[b] Moran et al. (1998).

[c] Takaku et al. (1995).

[d] Snyder and Fehn (2004).

from 440 mM in 1993 to 3160 mM in 2003, reflecting the variable input of volcanic components and, to a lesser degree, fluid-rock interaction (Ohsawa et al., 2003). The Cl–Br diagram (Fig. 3) shows behavior similar to that in the Cl–I diagram (Fig. 2), indicating mixing between fresh water and the initial fluid with a Cl concentration close to seawater for most samples from Oita and Miyazaki. The calculated Br concentrations of the initial fluids are ~850 μM in Oita ($Br/Cl = 1.5 \times 10^{-3}$) and ~1320 μM in Miyazaki ($Br/Cl = 2.4 \times 10^{-3}$), respectively. These are higher than the seawater value (840 μM;

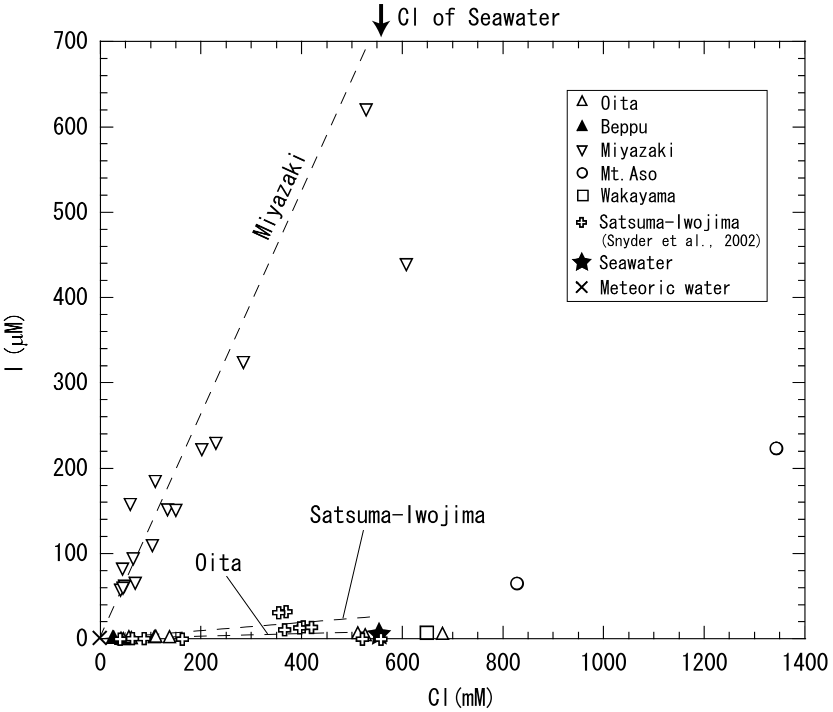

Fig. 2. Cl–I diagram with dashed extrapolation lines for Oita and Miyazaki samples. Data from Satsuma-Iwojima are also shown with an extrapolation line for comparison (Snyder et al., 2002). Assuming that Cl concentrations equal the seawater value, the right ends of these lines indicate initial I concentrations of initial fluids.

GERM, 2006) but the magnitude of condensation compared to seawater is much lower than for I due to the difference in biophilic behavior between these two elements. Halogen concentrations of fluids collected from Satsuma-Iwojima, a small volcanic island 50 km south of Kyushu Island (Fig. 1a), have been reported by Snyder et al. (2002) and are included in Figs. 2 and 3 for comparison. The Cl concentrations of these fluids show also dilution of seawater with meteoric waters as for the two areas investigated here, but the mixing gradients for the Satsuma-Iwojima samples in Figs. 2 and 3 closely follow those for the Oita samples. Although the estimated initial Br concentrations are likely lower (Fig. 3), the I concentrations are again higher than the seawater value (Fig. 2), and these two estimated values are close to those in Oita. The characteristics of halogen concentrations in these fluids are well displayed in I/Cl–I/Br diagram in Fig. 4. Samples in Miyazaki are obviously enriched in I, those in Satsuma-Iwojima range widely, but, overlap mostly with samples in Oita, Beppu, and Mt. Aso. The similarity between the results for Oita and Satsuma-Iwojima is noteworthy in view of the interpretation that I in the latter was derived from subducting marine sediments (Snyder et al., 2002).

Because the biophilic behavior of I is the most pronounced among halogens, marine organic materials are enriched in I and their I/Br ratios are generally higher than that of seawater (Price et al., 1970; Pedersen and Price, 1980; Elderfield and Truesdale, 1980). The I/Br ratio of pore water in marine sediment commonly increases because I enrichment is controlled by reduction and oxidation of IO_3 (Price and Calvert, 1973; Kennedy and Elderfield, 1987a,b; Martin et al., 1993). All the I/Br ratios in this study are higher than the seawater ratio (Fig. 4), indicating that all the I and Br sources are marine organic materials. Although Wakayama is located far from Kyushu Island, the I/Br ratio is as low as those of the Oita samples, which reflects similarities in the geological position of these two locations in the older Inner Zone. On the other hand, relatively high I concentrations in Miyazaki samples likely characterize derivation from the terrestrial terrane in the younger Outer Zone.

5.2. Iodine and chlorine isotopes

5.2.1. ^{129}I/I ratios and minimum iodine ages

The results of I isotopic determinations are shown in Fig. 5. It is immediately clear that two

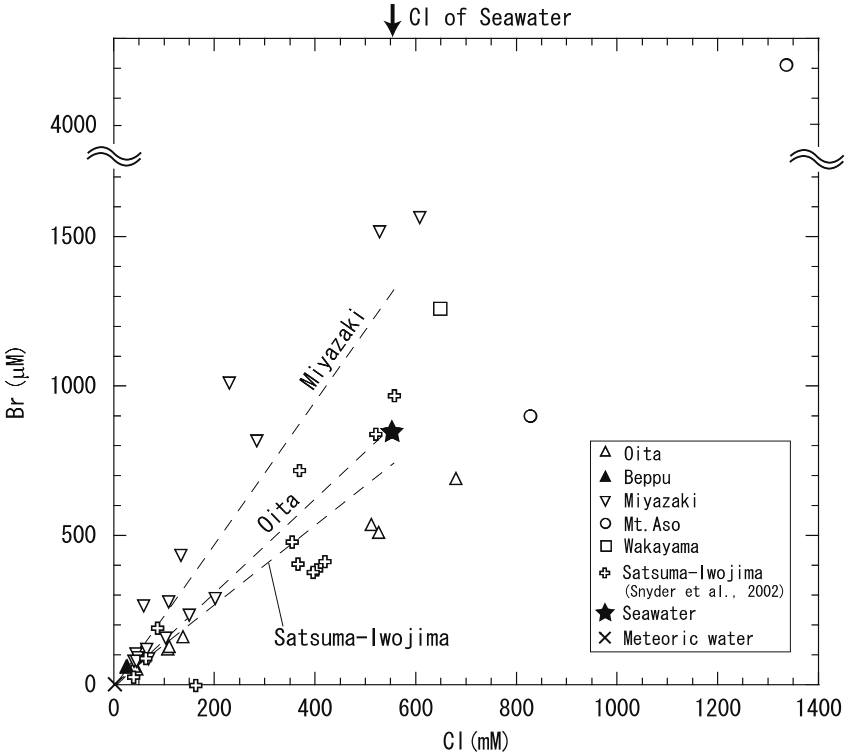

Fig. 3. Cl–Br diagram with dashed extrapolation lines for Oita, Miyazaki and Satsuma-Iwojima samples. One sample from Mt. Aso has extremely high Br concentration (4206 μM). The right ends of these lines indicate Br concentrations of initial fluids.

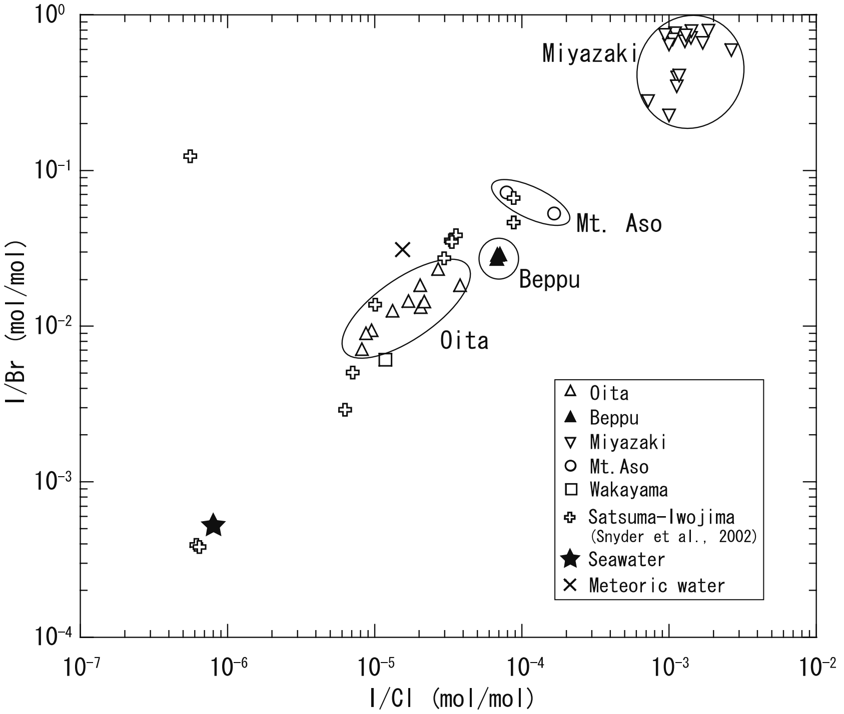

Fig. 4. I/Cl–I/Br diagram. Samples in the Miyazaki area are relatively enriched in I, but all samples have I/Br higher than seawater.

clusters of results exist: the ^{129}I/I ratios of Oita samples plot around the pre-anthropogenic value (1500×10^{-15}), while those of Miyazaki samples are well below that value, reaching values as low as 100×10^{-15}. To examine the effects on ^{129}I/I ratios from other potential ^{129}I sources, mixing lines between the samples with the highest I concentrations in Oita (O6) or Miyazaki (M10) and pre-anthropogenic seawater (SW), pre-anthropogenic meteoric water (PMW), and anthropogenic meteoric water (AMW) of which compositions are listed in Table 1, are displayed. The ^{129}I/I ratios of the Miyazaki samples are likely independent of anthropogenic ^{129}I, but might show some modifications by pre-anthropogenic waters. Due to the lower I concentrations in the Oita samples, they are more likely be shifted by small additions of anthropogenic meteoric water or of pre-anthropogenic water than the Miyazaki samples.

Eight of the 12 samples from Oita have ^{129}I/I ratios exceeding the pre-anthropogenic value and likely have a low degree of contamination of anthropogenic and/or pre-anthropogenic components. The ^{129}I/I ratios of the samples from Mt. Aso (A2) and Miyazaki (M5) are probably also increased by the presence of anthropogenic ^{129}I. The presence of anthropogenic components is also suggested by the results of stable isotope investigations of waters in the Mt. Aso crater lake (Ohsawa et al., 2003). The δD (+8.0 ‰) and δ^{18}O (+11.9 ‰) values in the fluids at Mt. Aso are very high compared to those of cold seep waters from the same area and high temperature volcanic gases in the subduction zone, suggesting that isotopic fractionation takes place predominantly during evaporation in the crater lake which is open to anthropogenic components. As is the case with the halogen compositions, I isotopic compositions of Satsuma-Iwojima samples (Snyder et al., 2002) are close to those of the Oita samples. The sample from Wakayama, however, has an isotopic value close to that from Miyazaki, in spite of having halogen systematics similar to those of the Oita area.

The mixing lines in Fig. 5 demonstrate that the two populations are derived from different sources, in Miyazaki from a source with high concentrations of I and ^{129}I/I ratios close to 150×10^{-15} and in Oita from a source with relatively low I concentrations

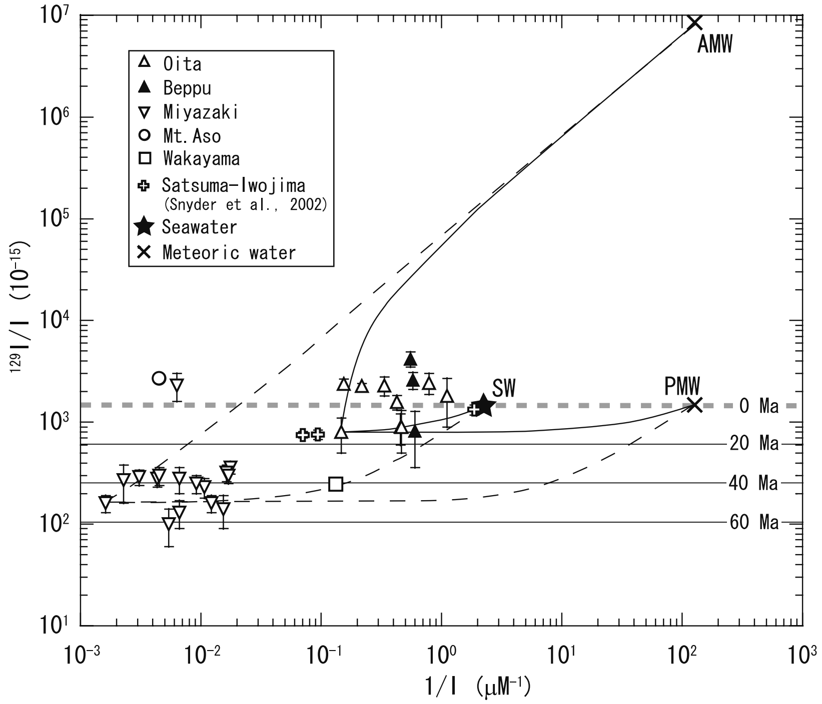

Fig. 5. Mixing diagram in the 1/I–^{129}I/I space. Lines indicate mixing between pre-anthropogenic meteoric water (PMW), seawater (SW) and anthropogenic meteoric water (AMW) with the highest I samples in Oita (solid lines) and Miyazaki (dashed lines). The ^{129}I/I ratios of some Oita samples are likely increased by the input of anthropogenic ^{129}I. Age contours reflect minimum ages derived from the ^{129}I/I ratios using Eq. (1).

and ^{129}I/I ratios close to 800×10^{-15}. A close-up of the samples with ^{129}I/I ratios below the pre-anthropogenic value demonstrates the different origin and mixing behavior for these two regions (Fig. 6).

The ^{129}I/I ratios provide apparent ages of the I(t) in fluids using the decay equation:

$$R_{\mathrm{obs}} = R_{\mathrm{i}} \mathrm{e}^{-\lambda t} \tag{1}$$

with the initial pre-anthropogenic ^{129}I/I ratio of $R_{\mathrm{i}} = 1500 \times 10^{-15}$ (Moran et al., 1998; Fehn et al., in press-a) and decay constant for ^{129}I of $\lambda = 4.41 \times 10^{-8}\ \mathrm{yr}^{-1}$. Because the anthropogenic and fissiogenic inputs of ^{129}I to the fluids may increase ^{129}I/I ratios, these ages are minimum values. The samples with a ^{129}I/I ratio lower than R_{i} yield ages of 11–14 Ma in Oita (O4, O6, O9, and O10), 32–61 Ma in Miyazaki (M1 to M16 except M5), and 40 Ma in Wakayama (W1) as shown in Fig. 6. If the anthropogenic contribution is very small, as is likely for the Miyazaki samples, the ^{129}I/I ratio of fluid is modified only by the addition of ^{129}I in the subsurface. The amount of ^{129}I in the crust produced from spontaneous fission of ^{238}U is calculated using the following equation (Fabryka-Martin et al., 1989):

$$N_{129} = N_{238} \lambda_{\mathrm{sf}} Y_{129} \rho (E/P)(1 - \mathrm{e}^{-\lambda 129 t})/\lambda_{129} \tag{2}$$

where N_{129} and N_{238} are the number of ^{129}I and ^{238}U atoms, λ_{sf} and λ_{129} are the decay constants for spontaneous fission of ^{238}U ($8.5 \times 10^{-17}\ \mathrm{yr}^{-1}$) and ^{129}I ($4.4 \times 10^{-8}\ \mathrm{yr}^{-1}$), Y_{129} is the spontaneous fission yield at mass 129 (3×10^{-4}; Hebeda et al., 1987), ρ is the rock density, E is the proportion of fissiogenic ^{129}I released from the rock, and P is the effective porosity. Although the E value itself is not well known, it is somewhat correlated with the P value, and E/P ratios generally fall into a range between 1 and 3 (Fabryka-Martin et al., 1989; Fehn et al., 1992; Moran et al., 1995) Assuming an U concentration in the rock of 1 ppm, a rock density of 2.7 g/cm^3, and an E/P ratio of 2 (Snyder et al., 2003), the corrected ages for Miyazaki samples are <4 Ma older than the ages calculated with Eq. (1), i.e., within the error margins of the AMS measurements. The young age of the Oita samples, combined with the relatively large error margins, make a correction for fissiogenic contribution unnecessary there.

5.2.2. Presence of ^{36}Cl

The ^{36}Cl/Cl ratios can be used to test for the presence of a meteoric component in ground waters. The ^{36}Cl/Cl ratios were determined in 3 samples from Oita (O2, O7, and O8-1) and one from Mt. Aso (A2), all of which have ^{129}I/I ratios higher than the pre-anthropogenic value, 1500×10^{-15}. The ^{36}Cl/Cl ratios for these samples are between 2.6

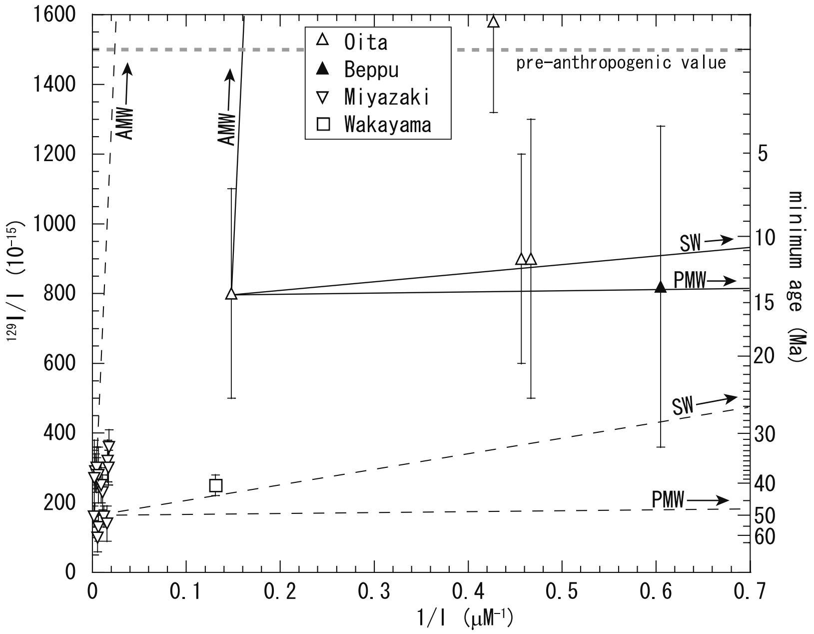

Fig. 6. Close-up of Fig. 5 for the area with ^{129}I/I ratios below the pre-anthropogenic ratio. Solid and dashed lines represent the mixing between samples and other fluids as in Fig. 5. Ages on the right axis indicate minimum values corresponding to the measured ^{129}I/I ratios at the left.

and 8.8×10^{-15}, i.e., just above the detection limit for AMS (1×10^{-15}). The natural ^{36}Cl/Cl ratio of meteoric water starts at values of about $<20 \times 10^{-15}$ near the shore and increases with increasing distance from the oceans to values up to $>640 \times 10^{-15}$ (Bentley et al., 1986), but anthropogenic values reached levels above 2000×10^{-15} associated with the period of atmospheric weapon tests (Fehn et al., 1992; Davis et al., 2000; Snyder et al., 2003). In contrast to the ^{129}I/I ratios which remain high due to continued releases from nuclear reprocessing, ^{36}Cl/Cl ratios in surface reservoirs have largely returned to the pre-anthropogenic value (e.g., Suter et al., 1987), the pre-anthropogenic and very recent (<15 yr) waters cannot be distinguished in the ^{36}Cl system. The comparison between ^{36}Cl/Cl and ^{129}I/I is useful to determine the presence of meteoric water in ground waters (Fig. 7). For the 3 samples from Oita, a positive regression line is calculated between ^{36}Cl/Cl and ^{129}I/I, (dashed line; $r^2 = 0.95$), which points to an initial ^{129}I/I ratio of $\sim 1200 \times 10^{-15}$, which, given the uncertainties associated with these determinations, is reasonably close to the values determined for the Oita samples ($\sim 800 \times 10^{-15}$). An estimate of the proportion of anthropogenic (AMW, see Section 5.2.1) and pre-anthropogenic (PMW, Section 5.2.1) components present in the meteoric waters (compositions in Table 1) mixed into the initial fluid (^{129}I/I of 1200×10^{-15} and ^{36}Cl/Cl of 0×10^{-15}; Cl of 512 mM and I of 6.8 μM, from O6), suggests that meteoric water in these Oita samples is mostly of pre-anthropogenic or very recent origin (99.9%) (Fig. 7). The presence of only one sample available for this test prevents a similar determination for Mt. Aso, but the direction also points to input of meteoric waters with a small anthropogenic component (0.3%), in good agreement with the conclusions reached from ^{129}I/I ratios and stable isotope results.

5.3. Implication of iodine age signals

The I ages in Oita (11–14 Ma) are younger than those in Miyazaki (32–61 Ma), although the Oita area is located in a geologically older zone on the continental side of the MTL. The age of the Philippine Sea Plate at the Nankai Trough is ~20 Ma (Jarrard, 1986), the travel time of this oceanic crust

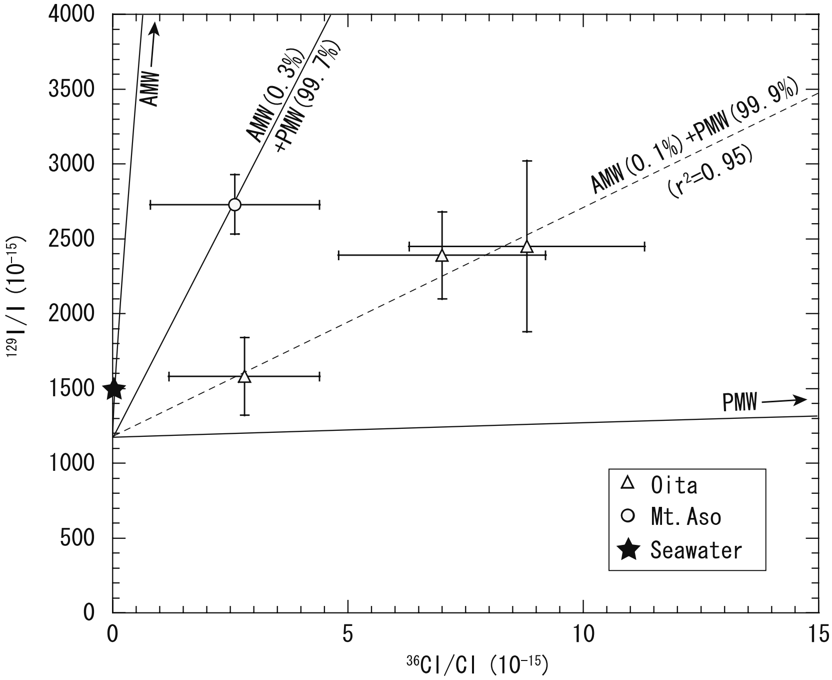

Fig. 7. ^{36}Cl/Cl–^{129}I/I diagram with dashed regression line for Oita samples. Solid lines represent mixing between pre-anthropogenic (PMW) and anthropogenic (AMW) meteoric waters with the initial fluid (^{129}I/I = 1200×10^{-15}, ^{36}Cl/Cl = 0×10^{-15}, I = 6.8 μM, and Cl = 512 mM). The ^{36}Cl/Cl ratios are assumed to be 40×10^{-15} for PMW and 2000×10^{-15} for AMW.

from the trench to below the sites can be calculated using the subduction rate of the Philippine Sea Plate beneath the Eurasian Plate of 3.5 cm/a (van der Hilst and Seno, 1993), depths of the subducted Philippine Sea Plate (Fig. 1) and the distance from the trench axis. The estimated average ages of sediment columns are between 4.7 and 24 Ma in Kyushu, and are similar in Wakayama. The age range found for Oita samples agrees well with that of the subducting marine sediments in this area, indicated in Fig. 8, and with the ages found for the fluids from Satsuma-Iwojima (Snyder et al., 2002). This comparison suggests that fluids in the Oita area receive I from the subducting marine sediments, just as the results for volcanic fluids from other active volcanic areas have indicated (e.g., Central America, Snyder and Fehn, 2002; New Zealand, Fehn and Snyder, 2003). The difference here is that fluids in the Oita area are associated with the fault system of the MTL and not directly related to active volcanism, reflecting the presence of fractures and crustal structures as fluid paths in the MTL zone (Wood, 1995; Goto et al., 1998; Tabei et al., 2002). While the MTL in the Oita area apparently draws fluids with the signature of the subducting marine sediments, this might not be the case in the eastern part of the MTL. The sample from the latter area (Wakayama; 40 Ma) more resembles in age the samples from Miyazaki than from Oita, although it has geochemical characteristics similar to those of the other samples associated with the MTL. The activity of fault systems associated with the MTL near Wakayama, ~10 m/kyr, is one order magnitude higher than that in the Oita area, 1 m/kyr (Okada, 1992) which may result in different subsurface structures between these two areas. A more conclusive statement on this question has to wait until more samples have been analyzed from other areas of the MTL.

The ages found for Miyazaki (and Wakayama) are considerably older than those of the subducting slab and sediments in this area and can therefore not be derived from these sources. Likely sources for these fluids are then organic-rich formations in the overlying plate, presumably of an age of 40 Ma or older. All the I ages in Miyazaki fall into the Eocene epoch, corresponding well to the Eocene to Oligocene Hyuga Group underlying the Miyazaki Plain of Late Miocene to Pliocene age (Kimura et al., 1991), which is composed of highly deformed accretionary complexes of trench fill deposits related to the subduction of the Philippine Sea Plate (Nishi, 1988; Sakai, 1989).

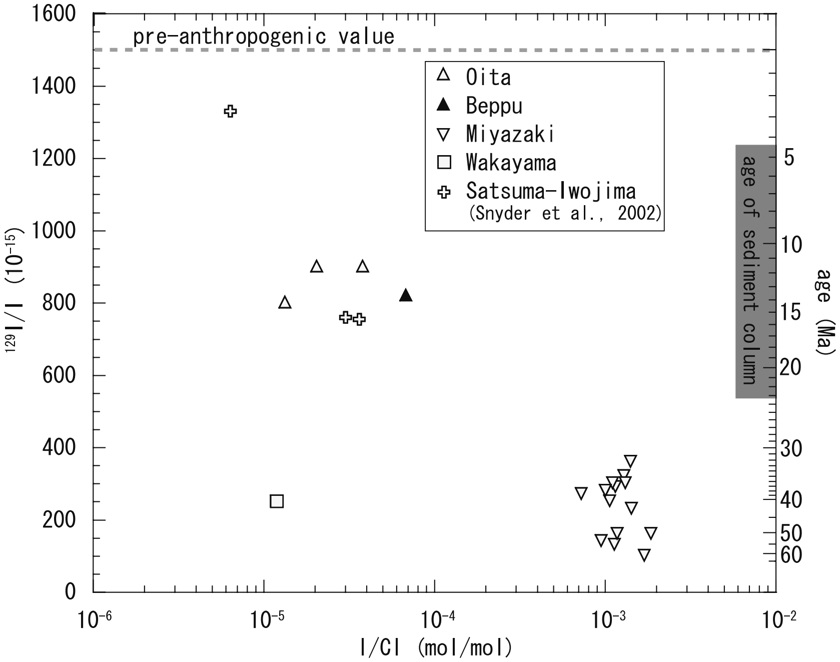

Fig. 8. Comparison of halogen ratios (I/Cl) and ^{129}I/I results. The I/Cl ratios characterize relative I enrichment among the locations. The gray bar on the right represents the age range of subducting sediments under Kyushu and Wakayama.

An alternative scenario for the derivation of the high I concentrations in the Miyazaki samples may be related to the halogen fractionation process during diagenesis identified in the pore waters from the Mariana forearc region (Snyder et al., 2005). Iodine concentrations there reach values of ~800 μM without appreciable Cl changes and the I/Cl ratios of 1.5×10^{-3} observed there are comparable to those in the Miyazaki samples. The ultramafic clasts and the associated serpentinized mud are also enriched in I, reaching ~100 μmol/kg, which reflects that serpentinization is a process which can increase I concentrations (Hurwitz et al., 2005). Thus, the sub-arc serpentinized materials beneath Kyushu Island can be an alternative source for I-rich fluids in Miyazaki. Although significant amounts of serpentinites are not observed in the drilled intervals of wells in Miyazaki, the presence of the serpentinite-rich Sambagawa metamorphic belt in the Kyushu area is evidence for serpentinization taking place in the sub-arc of this area.

Speaking against this model is the strong association of I occurrence with abundant CH_4 in the Miyazaki area, which suggests that I release occurs during CH_4 generation. Because the estimated peak metamorphic temperature of 800 °C in the Sambagawa belt (Banno, 2004; Enami et al., 2004) is considerably higher than the temperature of thermogenic gas generation, ~180 °C (Rooney et al., 1995), serpentinization in this area is probably not accompanied by CH_4 release at depth. Thus, derivation of I from serpentinized materials is less likely than from the overlying Hyuga Group. In addition, the age of the subducting slab (<20 Ma) is too young to support derivation of I with ages in excess of 30 Ma.

The most likely source for the I in the Miyazaki area is thus from organic-rich formations in the overlying plate with minimum ages of 30 Ma. The observation that fluids in the forearc area of Miyazaki are derived from old organic-rich sources matches well results from other forearc areas such as New Zealand (Fehn and Snyder, 2003; Fehn et al., in press-b) or Central America (Snyder and Fehn, 2002; Fehn et al., 2004) and also agrees with the presence of high concentrations of CH_4 in these fluids.

6. Conclusions

Based on the halogen concentration analyses, the fluids in Kyushu, forearc region of Japan, are enriched in I relative to seawater, and sometimes in Br. In particular, I concentrations of the initial fluids in Miyazaki are more than three orders of magnitude higher than those of seawater. Although I/Br ratios in Oita, Miyazaki, and Mt. Aso indicate different source formations, they are all derived from organic-rich marine sources. The ^{129}I/I ratios in Miyazaki fall into the range from 100 to 360×10^{-15}, while the likely range for the Oita area is around 800×10^{-15}. Due to the presence of anthropogenic ^{129}I, some of the samples from Oita as well as those from Mt. Aso exceed the pre-anthropogenic value of 1500×10^{-15}, but a correction using ^{36}Cl/Cl analyses for high ^{129}I/I samples points to an initial I isotopic ratio close to that of the other Oita samples. The results demonstrate the presence of two different types of fluids in the forearc area: in the Miyazaki area, fluids are highly enriched in I, the dominant gas phase is CH_4 and the I ages are considerably older than the marine sediments on the subducting slab in this region. These fluids are likely derived from organic-rich marine formations of Eocene age, located in the upper plate. A potential source for these fluids is the Hyuga Group underlying the Miyazaki plain. The situation is very different in the Oita area, where fluids are still enriched in I, but considerably less than those in Miyazaki, have less association with CH_4 and have ages in good agreement with the age range of the subducting marine sediments. In this case, fluids likely have access to the transition zone between upper and lower plates and travel through the extensive fracture system associated with the MTL in this area. These fluids closely resemble those collected from Satsuma-Iwojima, an active volcano system in this region. The one sample from the eastern part of the MTL, Wakayama, is similar in geochemical characteristics to those from Oita, but has an ^{129}I/I ratio close to that of the Miyazaki samples. Although only one sample was available from Wakayama, the comparison might indicate that fluid regimes along the MTL differ depending on the activity of fault system. The results of this study demonstrate the presence of fluids derived from different source formations in the forearc area and the influence of major fault systems, such as the MTL, on the flow regimes.

The co-existence of I from different sources is common in subduction zones; i.e., Central America (Snyder and Fehn, 2002; Fehn et al., 2004) and New Zealand (Fehn and Snyder, 2003). The remobilization of I expelled from the subducted sediments to the surface is essentially associated with the flow regime in the subduction zones, but a large quantity of I is also derived from old overlying or accreted sediments. The contrast of I sources between Oita (subducted marine sediments) and Miyazaki (overlying older sediments) demonstrates that fluid flow systems are distinctly related to the history of the regional geology.

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