Boron systematics of Hisatsu and Kirishima basaltic rocks from southern Kyushu, Japan

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To evaluate the effect of slab-derived fluids from subducted Philippine Sea plate on mantle composition beneath southern Kyushu, we determined the boron (B) contents in basaltic rocks from Hisatsu volcanic province and Kirishima volcano, which erupted since 7.6 Ma. Since B is distinctively concentrated into slab-derived fluids, we have attempted to estimate the influence of subduction-related inputs on the composition of the sub-arc mantle based on the B systematics of the basaltic rocks.

Old (7.6–0.4 Ma) basalts from Hisatsu volcanic province possess relatively low B/Sm (0.8–4.2), B/Zr (0.03–0.12) and B/Nb (0.6–2.5) ratios. In contrast, volcanic products from the comparatively young (<0.3 Ma) Kirishima volcano, located at the volcanic front, show significantly higher B/Sm (4–8), B/Zr (0.2–0.3) and B/Nb (3–5) ratios. In addition, basalts from these two regions show distinct trends on plots of Ba/Zr vs. B/Zr and Ba/Nb vs. B/Nb: the Hisatsu basalts have lower B/Zr, B/Nb and higher Ba/Zr, Ba/Nb ratios than those of the Kirishima basalts.

These observations indicate that B-rich fluids from Philippine Sea plate were added to the mantle beneath Kirishima volcano between 0.4 and 0.3 Ma. Therefore the modern fluid input from the subducted slab to the subarc mantle may be limited beneath the volcanic front in this area.

Keywords: boron, Philippine Sea plate, southern Kyushu, subduction zone, basalt

INTRODUCTION

Boron (B) has great potential as a tracer of subducted slab influence on sub-arc mantle compositions in subduction zones because it is enriched in altered oceanic crust and sea floor sediments (e.g., Ishikawa and Nakamura, 1993; Smith *et al.*, 1995), and is selectively partitioned into the fluid phases that trigger fluid-flux melting at the mantle wedge (e.g., Moran *et al.*, 1992; Bebout *et al.*, 1999). B concentrations observed in arc basalts provides evidence for the recycling of the oceanic slab materials to the arc crust. In contrast, oceanic-island basalt (OIB) and mid-ocean ridge basalt (MORB) have low B contents (Ryan and Langmuir, 1993; Ryan *et al.*, 1996; Leeman and Sisson, 1996; Chaussidon and Jambon, 1994;

Chaussidon and Marty, 1995; Sun and McDonough, 1989) as they have had no interaction with subducted slabderived fluid and/or melt.

In order to identify the involvement of the subducted slab-derived hydrous fluid in the mantle wedge, we employ fluid-mobile/immobile element ratios (B/Sm, B/Zr, B/Nb and Ba/Zr). Previous works (Leeman and Sisson, 1996; Ishikawa and Nakamura, 1994; Ishikawa and Tera, 1997; Ishikawa et al., 2001; Tonarini et al., 2004; Sano et al., 2001) indicate that B/Sm, B/Zr and B/Nb ratios are sensitive indicators of the involvement of the subducted slab-derived fluid because of the following: (1) Since B and Nb have similar solid/melt distribution coefficients under upper mantle and crustal conditions, B/Nb ratios are not significantly controlled by partial melting and fractional crystallization processes; (2) B and the preceding three elements have entirely different chemical behaviors in fluid-related processes. The mobility of B in fluid is distinctly higher than those of Sm, Zr and Nb; (3) The enrichment of B/Nb does not reflect the crustal assimilation process because the B/Nb ratio in the crustal rocks is negligibly low (continental crust: 0.4-0.7; Wedepohl, 1995).

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Fig. 1. (a) Map showing the tectonic setting around southwestern Japan. Data for age of the Philippine Sea plate: Okino et al. (1994), Shibata et al. (1977), Hilde and Lee (1984) and Hickey-Vergas (2006). PSP = Philippine Sea plate. (b) Distribution of volcanic rocks erupted between late Miocene and middle Pleistocene in southern Kyushu (Nagao et al., 1999).

Across-arc variations of B/Nb ratios in basalts from cool subduction zones where old oceanic slab subducted are described by continuous depletion reflecting the gradual depletion of volatiles and fluid-mobile elements during dehydration of the subducting slab (Ishikawa and Tera, 1997; Peacock and Herving, 1999; Wunder et al., 2005). On the other hand, these smooth depletion trends of B/Nb ratios are not observed in warm subduction zones where young oceanic slab subducted (Leeman et al., 2004; Miyoshi et al., 2008a). This indicates that the slabderived fluid is not transported to the backarc region by the hot oceanic slab because large amounts of volatiles and fluid-mobile elements are expelled from the slab at shallow depths in the forearc due to the extremely high geotherm (Hochstaedter et al., 1996; Peacock and Wang, 1999; Leeman et al., 2004; Iwamori, 2007).

Southwest (SW) Japan arc is characterized by the subduction of Philippine Sea plate (Fig. 1). The Philippine Sea plate is divided into two different segments by the NW-SE trending Kyushu–Palau ridge. The northern segment (Shikoku basin) is relatively young and hot (15–26 Ma; Okino *et al.*, 1994), whereas the southern segment is old and cold (37–115 Ma; Shibata *et al.*, 1977; Hilde and Lee, 1984; Hickey-Vargas, 2006) (Fig. 1). Southern Kyushu is characterized by the subduction of the southern (old) segment of the Philippine Sea plate (Kimura *et al.*, 2005; Zhao *et al.*, 2000; Iwamori, 2007).

Between the late Miocene and Pleistocene, volcanism in southern Kyushu was characterized by effusive erup-

tions of lava with diverse chemical compositions (SiO₂ = 51-65 wt. %). These lava flows formed lava plateaus and covered a wide area of southern Kyushu distributed in Hisatsu, Hokusatsu and Nansatsu volcanic provinces (Fig. 2; Nagao *et al.*, 1995, 1999).

The Hisatsu volcanic province was dominated by effusive eruptions between 7.6 and 0.4 Ma (Nagao et al., 1999). Previous works have reported that the Hisatsu volcanic rocks have island-arc-type chemical compositions (Watanabe et al., 1992; Nagao et al., 1999). However, Nagao et al. (1999) noted that the volcanism in Hisatsu volcanic province was not the typical island-arctype on the basis of the following observations: (1) the plateau-forming eruptions typical of the Hisatsu volcanic province are not like those common in island-arc volcanism, which are characterized by the formation of composite volcanoes, (2) the lavas from Hisatsu do not show distinct across-arc variations in chemical compositions, and (3) both island-arc-type andesite and OIB-like basalt were erupted in the backarc region between 10-7 Ma.

The relationship between the origin of the Hisatsu volcanic rocks and the influence of subduction of the Philippine Sea plate is presently under debate. We present a new boron data for the basalts and basaltic andesites from Hisatsu volcanic province and for Kirishima volcano to investigate the influence of subduction of the Philippine Sea plate on the island-arc-type magma genesis in southern Kyushu, Japan.



Fig. 2. Total alkali versus silica plots for basaltic rocks from Hisatsu volcanic province and Kirishima volcano. Thick line indicates boundary between alkali and sub-alkali rocks suites (LeMaitre et al., 1989).

GEOLOGIC SETTING

Tectonic setting

Southern Kyushu is characterized by the subduction of the southern segment of the Philippine Sea plate (Fig. 1). The Wadati–Benioff zone (WBZ) is detected at a depth of 200 km beneath the volcanic front; however it is not detected beneath the backarc region (Shinjo *et al.*, 2000). The lack of the WBZ beneath the backarc region is typical in the Kyushu subduction zone.

Two pronounced low-velocity zones exist in the mantle wedge beneath Kyushu. One zone exists beneath the active volcanoes in northern Kyushu, and the other exists beneath those in southern Kyushu. The low-velocity zone in the mantle wedge extends to the forearc side of the volcanic front in northern Kyushu; however, this is not observed in southern Kyushu (Zhao *et al.*, 2000). Iwamori (2007) interpreted this tomographic feature as the result of the geotherm in the forearc beneath northern Kyushu; the geotherm is hotter than that in southern Kyushu due to the subduction of young, hot Shikoku basin lithosphere (15–26 Ma).

A tomographic low-velocity zone is also observed beneath the backarc of Kyushu. This low-velocity zone is consistent with mantle upwelling around the northeastern edge of the currently rifting Okinawa Trough (Sadeghi *et al.*, 2000; Sibuet *et al.*, 1995) and is believed to have activated volcanism in the Kyushu backarc and Ryukyu arc (Kimura *et al.*, 2005).

Volcanism

Modern volcanism in SW Japan is closely related to the reinitiation of subduction associated with backarc spreading that commenced at 17 Ma. Eruptive products include lavas with OIB, island-arc-type basalt (IAB), high-magnesian andesite (HMA) and adakite-type affinities (Kimura *et al.*, 2005). These diverse magma types are also observed in the Kyushu subduction zone.

Between the late Miocene and Pleistocene, volcanism in southern Kyushu was characterized by effusive eruptions of plateau-forming lavas (Nagao *et al.*, 1995). Historically active volcanoes, including Kirishima, Sakurajima, and Kaimon, comprise the volcanic front of southern Kyushu (Fig. 2).

On the backarc side of Hisatsu volcanic province, HMA volcanism was present at 14.2 Ma in Shimoshima island (Fig. 2; Nagao et al., 1992). Relatively small amounts of OIB-type enriched basalts were erupted at 10-7 Ma in Shimoshima (Nagao et al., 1992). During this period, Philippine Sea plate subduction was very slow (<1 cm/year; Kimura et al., 2005) or almost ceased (Kamata and Kodama, 1994). The subduction of the Philippine Sea plate accelerated (4 cm/year) at 6-4 Ma (Kamata and Kodama, 1994). This plate motion change coincided with the opening of the Okinawa Trough (4-2 Ma; Sibuet et al., 1995). Eruption of the plateau-forming lavas in the Hisatsu volcanic province (7.6–0.4 Ma; Nagao et al., 1999) partly overlapped with these tectonic events, while eruption of IAB-type basalts occurred between 7.6-2.5 Ma and 2.0-0.4 Ma in this province (Nagao et al., 1999). After the effusive volcanism of plateau-forming lava (0.3 Ma), volcanic activity shifted to Kirishima volcano (Imura, 1994).

SAMPLES AND METHODS

Twenty-six basaltic lava samples from Kirishima volcano and Hisatsu volcanic province were collected (Fig. 2). All analyzed samples appeared fresh, because they do not contain secondary minerals in their groundmasses. Although some olivine phenocrysts are partly altered to iddingsites, the other phenocrysts are not altered. Thus changes of B concentration due to sample alteration and/ or presence of hydrous minerals should be negligibly small.

The major and trace element chemical compositions of the samples were determined by X-ray fluorescence (XRF) on flux-fused disks with a Philips PANalytical

76 utsu 8 OpPI	.75 .15 .25 .15	21 29 22 83 83		. 3 . 3 . 78 . 94 . 19
SK Hisa 22 OICpt	53. 20. 8.	6 6 9 9 9 100 0	11 0 463 2 2 2 2 32 0 11 1 11 202 202 4	⊢ ○ ∞ ○ 4 ○
SK65 Hisatsu 249 CpOpHbPl	56.65 0.92 17.10 8.32 0.13	4.49 7.82 3.38 1.16 0.15 100.11	25 0 1 25 25 0 1 0 235 5 235 5 5 5 5 5 5	6.6 0.3 4.12 0.16 4.52 0.25
SK64 Hisatsu 212 CpOpPl	55.75 0.93 16.82 9.60 0.16	4.64 7.86 3.04 1.12 0.17 100.08	$23 \\ 0 \\ 487 \\ 27 \\ 27 \\ 0 \\ 0 \\ 5 \\ 5 \\ 5 \\ 5 \\ 5 \\ 5 \\ 5 \\ 5$	5.9 0.3 4.4 0.2 3.7 0.33
SK63 Hisatsu 212 CpOpPl	55.06 0.92 16.60 9.43 0.17	5.07 8.43 2.94 1.06 0.18 99.85	$\begin{array}{c} 19\\ 555\\ 26\\ 26\\ 0\\ 1\\ 233\\ 5\\ 5\\ 3\\ 3\\ 3\end{array}$	6.8 0.4 0.2 0.2 0.35
SK62 Hisatsu 212 CpOpPl	55.99 0.92 16.89 9.41 0.17	$\begin{array}{c} 4.90\\ 8.23\\ 3.01\\ 0.88\\ 0.18\\ 0.18\\ 100.58\end{array}$	$\begin{array}{c}17\\545\\545\\34\\0\\0\\6\\0\\206\\4\end{array}$	6.6 0.3 5.68 0.22 5.01 0.32
SK60 Hisatsu 212 CpOpPl	54.94 0.94 17.13 9.50 0.17	5.03 8.40 2.95 0.95 0.18 100.19	15 567 22 94 1 1 206 0 206	6.2 0.4 0.3 4.3 0.37
SK58 Hisatsu 212 CpOpPl	55.51 0.94 17.10 8.97 0.17	5.04 8.38 2.87 1.15 0.15 100.29	25 1 385 385 0 95 0 214 2 14	9.2 0.5 0.3 3.8 0.36
SK57 Hisatsu 212 CpOpPl	56.01 0.92 16.89 8.96 0.17	5.02 8.32 2.80 1.12 0.15 100.35	31 1 1 27 27 0 95 1 1 217 2 5 5 5 5	9.9 0.4 1.61 0.20 2.35 0.22
SK55 Hisatsu 279 CpOpPl	57.08 1.12 19.39 7.08 0.12	2.32 7.51 3.71 1.53 0.23 100.09	36 467 29 29 29 29 29 136 10 314 314	10.1 0.5 5.1 0.3 4.6 0.4
SK27 Hisatsu 237 CpOpPl	55.99 0.87 16.59 8.18 0.14	4.88 8.19 3.47 0.68 0.14 99.13	7 0 356 33 1 1 8 6 198 0 0 198	6.2 0.3 6.40 5.04 0.23 0.29
SK24 Hisatsu 239 CpOpPI	56.38 0.81 17.06 8.36 0.14	4.46 8.16 3.31 0.75 0.15 99.56	$\begin{array}{c}11\\43\\-27\\0\\-27\\-27\\-27\\-27\\-27\\-27\\-27\\-27\\-27\\-27$	6.1 0.3 4.82 0.19 4.09 0.27
SK23 Hisatsu 230 OICpPI	50.63 0.98 17.00 10.20 0.18	$\begin{array}{c} 6.87\\ 9.53\\ 2.89\\ 0.70\\ 0.18\\ 0.18\\ 99.15\end{array}$	$\begin{array}{c} 10\\ 470\\ 2\\ 2\\ 2\\ 3\\ 1\\ 1\\ 2\\ 2\\ 5\\ 5\\ 5\\ 5\\ 5\end{array}$	$5.1 \\ 0.3 \\ 4.37 \\ 0.17 \\ 3.92 \\ 0.25 \\ 0.$
SK20 Hisatsu 225 OICpPI	51.65 0.79 14.55 9.67 0.16	9.83 9.94 2.24 0.60 0.14 99.57	21 0 449 20 0 83 83 190 190	4.5 0.3 3.67 0.16 3.77 5.36
SK21 Hisatsu 225 OICpOPPI	52.65 1.03 19.13 9.62 0.15	3.83 8.67 3.43 0.78 0.20 99.47	12 557 2 2 2 2 2 2 1 1 2 6 6 0 2 67 6	5.1 0.2 5.05 0.20 5.58 0.15
SK19 Hisatsu 228 OIPI	53.51 0.98 19.63 8.92 0.14	3.09 8.15 3.60 1.24 0.21 99.47	30 551 2 38 38 1 104 1 104 347 7 7 7	12.5 0.5 4.85 0.30 5.44 0.21
SK18 Hisatsu 228 OIPI	53.95 0.98 19.63 8.69 0.14	3.05 8.09 3.64 1.26 0.21 99.64	31 549 52 32 32 32 0 106 1 1 1 347 7 7	11.1 0.4 4.81 0.29 5.51 0.21
Sample No. Area D (km) ^a Phenocrysts	SiO ₂ (wt. %) TiO ₂ Al ₂ O ₃ Fe ₂ O ₃ MnO	MgO CaO K ₂ O P ₂ O ₅ Total	Rb (ppm) Error Sr Error Y Error Sr Error Ba Error	B (ppm) ^b Error Gd ^b Error Sm ^b Error

Table 1. Major and trace element contents of basaltic rocks from Hisatsu volcanic province and Kirishima volcano

R.V.		30.2	3.28	2.31
PGA		31.7 0.8^{e}	3.10	0.12 2.45 0.25 ^e
R.V.		9.35	4.90	5.13
PGA		8.9 0.28°	4.63 0.12e	5.33 0.14 $^{\circ}$
Kirishima 188 OlCpOpPl	53.62 0.75 0.75 8.67 0.16 9.82 9.82 9.82 0.88 0.88 0.88 0.12 1 1 0.12 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1	15.2 0.5	2.83	2.53 0.22 0.22
Kirishima 188 OlCpOpPI	$\begin{array}{c} 54.69\\ 0.76\\ 0.76\\ 18.30\\ 8.76\\ 0.16\\ 0.16\\ 1.00\\ 1.00\\ 1.00\\ 1.00\\ 1.00\\ 1.00\\ 2.90\\ 1\\ 1\\ 1\\ 1\\ 1\\ 2.0\\ 0\\ 1\\ 1\\ 1\\ 2.0\\ 0\\ 0\\ 2.0\\ 0\\ 0\\ 1\\ 1\\ 1\\ 1\\ 1\\ 2.0\\ 0\\ 0\\ 0\\ 1\\ 1\\ 1\\ 1\\ 1\\ 1\\ 1\\ 1\\ 1\\ 1\\ 1\\ 1\\ 1\\$	19.5 0.6	3.17	0.1.0 3.37 0.26
Kirishima 188 OlCpOpPI	57.09 0.77 18.18 8.63 8.63 8.63 4.71 6.59 0.12 1.52 1.55 1.1 2.67 1.55 1.255 1 1 2.67 1.267 1.255 1 1 2.67 1.18 1.18 1.18 1.18 0.12 0.12 0.12 0.12 0.12 0.12 0.12 0.12	26.9 0.8	3.58	0.15 3.28 0.22
Kirishima 188 OlCpOpPI	$\begin{array}{c} 51.51\\ 0.82\\ 0.82\\ 0.30\\ 0.19\\ 0.19\\ 0.10\\ 0.10\\ 0.10\\ 0.10\\ 0.10\\ 0.10\\ 0.10\\ 0.10\\ 0.10\\ 0.10\\ 0.10\\ 0.10\\ 0.10\\ 0\\ 0\\ 0\\ 0\\ 0\\ 0\\ 0\\ 0\\ 1\\ 1\\ 1\\ 1\\ 1\\ 1\\ 1\\ 1\\ 1\\ 1\\ 1\\ 1\\ 1\\$	10.8 0.4	3.36	2.71 2.71 0.20
Kirishima 188 CpOpPI	56.31 0.81 18.57 8.32 8.32 8.22 8.22 1.11 1.11 1.11 1.11 1.11 1.1	18.2 0.6	3.89	0.10 3.94 0.23
Kirishima 188 CpOpPI	54.83 0.80 19.30 8.86 0.16 3.83 8.86 2.93 1.02 1.02 1.02 1.02 1.02 1.02 1.02 1.02	20.5 0.7	3.76	3.70 0.16
Kirishima 188 OlCpOpPI	48.64 0.69 9.86 0.16 9.86 0.16 5.62 5.62 0.10 96.75 1 1 1 1 1 1 1 1 1 1 1 1 1 1 3 3 7 3 3 7 1 1 1 1	8.6 0.3	2.58	2.17 2.17 0.18
Hisatsu 209 OICpOpPI	56.26 0.82 0.82 8.51 0.15 5.38 8.54 3.16 1.41 1.41 1.41 0.17 1.41 0.17 1.41 1.41 1.41 1.41 1.41 1.41 1.41 1	12.0 0.4	4.83	5.05 5.05 0.28
Hisatsu 219 CpOpPl	$\begin{array}{c} 54.87\\ 1.01\\ 1.01\\ 8.78\\ 8.78\\ 0.16\\ 3.80\\ 3.52\\ 0.96\\ 0.96\\ 0.24\\ 100.67\\ 100.67\\ 100.67\\ 10\\ 22\\ 22\\ 29\\ 0\\ 11\\ 1\\ 1\\ 1\\ 1\\ 2\\ 2\\ 2\\ 2\\ 2\\ 2\\ 2\\ 2\\ 2\\ 2\\ 2\\ 2\\ 2\\$	7.5 0.3	4.58	0.20 4.99 0.19
Hisatsu 226 OICpOpPI	$\begin{array}{c} 52.35\\ 1.20\\ 20.94\\ 8.81\\ 0.16\\ 3.48\\ 9.00\\ 3.54\\ 0.54\\ 0.54\\ 0.54\\ 0.22\\ 100.23\\ 3.3\\ 3.3\\ 3.3\\ 3.3\\ 3.3\\ 3.3\\ 11\\ 1\\ 1\\ 1\\ 1\\ 1\\ 1\\ 1\\ 1\\ 1\\ 1\\ 1\\ 1$	4.0 0.2	4.23	5.20 5.20 0.17
Area D (km) ^a Phenocrysts	$\begin{array}{c} \text{SiO}_2 \ (wt. \ \%) \\ \text{TiO}_2 \\ \text{Al}_2 O_3 \\ \text{Fe}_2 O_3 \\ \text{MnO} \\ \text{Perror} \\ \text{Error} \\ \text{Nb} \\ \text{Error} \\ \text{Ba} \\ \text{Error} \\ \text{Ba} \end{array}$	B (ppm) ^b Error	Gd ^b	Error

^a D: distance from the trench. ^b B, Sm and Gd contents are determined by the PGA. Error shows the standard deviation (one sigma) due to counting statistics only. ^c Average values obtained for
standard JB-1 and JB-2 (standard rocks from the Geological Survey of Japan). Numbers in parentheses are number of measurements. ^d Recommended values for the standard JB-1 and JB-2
(Imai et al., 1995). "Standard deviations (one sigma) of all measurements for standard JB-1 and JB-2. The contents of the other elements are determined by XRF. Errors represent the standard
deviation (one sigma) of the measurement of multiple glass beads which were prepared from the same sample. Data of *SK105, *SK109 and *SK114U are from Miyoshi et al. (2008b). PGA =
prompt gamma-ray analysis.



Fig. 3. N-MORB normalized incompatible trace element patterns for the basaltic rocks from (a) Hisatsu volcanic province, (b) Kirishima volcano, (c) Shimoshima (Miyoshi et al., 2008a) and (d) crustal rocks. Data for the upper and lower crusts are from Wedepohl (1995), and the data for crustal rocks beneath Japan (JG-1, JG-2, JG-3 and JGb-1) are from Imai et al. (1995). Data for crustal xenoliths (CXL) are obtained from Miyoshi et al. (2008a). Data for OIB are obtained from Abbey (1983), Flanagan (1976), Govindaraju (1994), and the data for IAB are obtained from Moriguti et al. (2004). Abundances are normalized by the following values: Rb (0.56), Ba (6.3), K (600), B (0.5), Nb (2.33), Sr (90), Sm (2.63), Zr (74), Gd (3.68), Y (28) (ppm, Sun and McDonough, 1989).

MagiX PRO spectrometer at Kitakyushu Museum of Natural History and Human History. The details of the analytical procedures are described by Mori and Mashima (2005). Nine Japanese standards (JB-1a, JB-2, JB-3, JA-2, JA-3, JR-1, JG-1a, JG-2 and JGb-1) and seven international standards (GS-N, DR-N, BCR-2, DNC-1, DTS-2b, BHVO-2 and AGV-2) were used for calibration.

Boron, Sm and Gd were determined by neutroninduced prompt gamma-ray analysis (PGA) at the thermal neutron beam guide of the JRR-3M reactor, Japan Atomic Energy Research Institute, using the method of Yonezawa (1993). Powdered samples (0.8 g) were dried for more than 24 h at 110°C in an oven and cold pressed into disks (12 mm in diameter and 2–3 mm in thickness). Disks were heat-sealed in 25- μ m thick fluorinated ethylenepropylene resin films with sizes smaller than 14 × 14 mm². A Compton suppression PGA spectrum was accumulated for 1000–7200 s. Geological Survey of Japan standards JB-1 and JB-2 were used for calibration of B, Sm and Gd. Variations in count rate of B, Sm and Gd caused by neutron flux fluctuation and sample geometry were corrected by the Si factor (i.e., Si count rate divided by the Si content of the same sample). The details of the analytical procedures have been described by Sano *et al.* (1999, 2006).

RESULTS

Major and trace element contents obtained in this study are listed in Table 1. The basaltic rocks from Kirishima and Hisatsu volcanic province are all sub-alkaline on the basis of their SiO₂ and total alkali compositions (Fig. 2).

When trace element contents were normalized to N-MORB (Sun and McDonough, 1989), the Hisatsu and Kirishima basalts exhibited the IAB-like patterns (Figs. 3a and b). The Kirishima basalts are clearly enriched in B and depleted in Nb compared with the Hisatsu basalts. In contrast Shimoshima basalts show OIB-like patterns (Fig. 3c). The trace element patterns of crustal xenoliths from Kyushu (Miyoshi *et al.*, 2008a) are similar to those of upper and lower crusts (Fig. 3d).

Across-arc variations of the southern Kyushu basalts



Fig. 4. Plots of element ratios of the basaltic rocks for across-arc transects in and around the Hisatsu volcanic province. The data sources of Kurile, Izu, NE-Japan and Cascade basalts are Ishikawa and Tera (1997), Ishikawa and Nakamura (1994), Moriguti et al. (2004) and Leeman et al. (2004), respectively. The mantle values (MORB and OIB compositions) are from Ryan et al. (1996).

are shown in Fig. 4. Between 10 and 0.4 Ma, B/Sm, B/Zr, B/Nb and Ba/Zr ratios of the Hisatsu volcanic rocks do not show the clear across-arc variations (Fig. 4). The B/Nb ratios of the backarc Shimoshima basalts are similar to those of the mantle values (0.05–0.5; Ryan *et al.*, 1996).

The Kirishima basalts, which erupted after 0.3 Ma in the volcanic front, have distinctly higher B/Sm (4–8), B/Zr (0.2–0.3) and B/Nb (3–5) ratios than those (0.2–4.2; 0.01–0.12; 0.1–2.5) of the old (10–0.4 Ma) basaltic rocks.



Fig. 5. FeO^*/MgO vs. B/Sm, B/Zr and B/Nb diagrams for Hisatsu and Kirishima basalts. $FeO^* = total$ iron as FeO. The data of crustal xenoliths are from Miyoshi et al. (2008a).

DISCUSSION

Use of B as an indicator of descending slab

One goal to understand the magmatism in subduction zones is to evaluate the contributions of the subducted slab to mantle in arc magma genesis. The descending slab releases hydrous fluids during dehydration at high pressures. These slab-derived fluids may be added to the sources of arc magmas (e.g., Tatsumi and Eggins, 1995) and tracked via elemental or isotopic indicators (e.g., ¹⁰Be; Tera *et al.*, 1986).

Both B and Ba are powerful tracers used to identify contributions from slab-derived fluid to source mantle (e.g., Ryan *et al.*, 1996), because these elements are enriched in the downgoing slab (Ishikawa and Nakamura, 1993; Smith *et al.*, 1995; Plank and Langmuir, 1998). In



Fig. 6. (a) Ba/Zr vs. B/Zr and (b) Ba/Nb vs. B/Nb diagrams for Hisatsu and Kirishima basalts. The data of the northwestern (NW)-Kyushu OIB-type basalts, Aso basalts, northern Kyushu backarc tholeiitic basalts (NKB) and crustal rocks (gneiss, gabbro and granitic rocks) are from Miyoshi et al. (2008a). The data of the western pacific arc (WPA: Kurile, Kamchatka and NE-Japan) basalts are from Ishikawa and Tera (1997), Ishikawa et al. (2001) and Moriguti et al. (2004).

addition, the following observations indicate the advantage of B as the tracer to evaluate the involvement of slabderived fluids over Ba: (1) the mobility of B is higher than that of Ba (Brenan et al., 1995; Kogiso et al., 1997; Aizawa et al., 1999) and (2) although Ba is also enriched in upper and lower crustal plutonic rocks, B is depleted in them (Sano et al., 2001). Figure 5 shows that the B/ Sm, B/Zr and B/Nb ratios of the crustal rocks from Kyushu (Miyoshi et al., 2008a) are quite lower than those of Kirishima basalts. Thus B-enrichment of the Kirishima basalts is not explained by the crustal assimilation. Although the B/Sm, B/Zr and B/Nb ratios of the crustal rocks are partly overlapped with those of Hisatsu basalts, the plots of the Hisatsu basalts show no clear correlation between B/Sm, B/Zr, B/Nb and FeO*/MgO (Fig. 5). Therefore the involvement of the crustal assimilation in Benrichment or B-depletion of the basalts during magma ascent is negligibly small when we use B/Sm, B/Zr and B/Nb ratios.

Kirishima basalts have higher B/Sm, B/Zr and B/Nb ratios than the Hisatsu and Shimoshima basalts (Figs. 4 and 5). This observation suggests that B-rich slab-derived fluids are probably added to the mantle beneath Kirishima volcano. On the other hand, the Ba/Zr ratios of the Kirishima basalts are similar to those of the Hisatsu and Shimoshima basalts (Fig. 4). This implies that the Ba/Zr ratio is not a good indicator to determine the differences in influence of the slab-derived fluid on the source mantle composition. Previous works did not identify the chemical difference between Hisatsu and Kirishima basalts because of the lack of the B data. Therefore, differences in B data from Kirishima, Hisatsu and Shimoshima basalts identify first-order differences in the influence of the subducted slab on the mantle beneath southern Kyushu.

Influences of ancient subducted slab and the modern Philippine Sea plate

The across-arc variation of B/Nb of Hisatsu basalts is not similar to that of subduction zone basalts from arcs with cool downgoing plates (Kurile, Izu and NE-Japan). Across-arc variations of the B/Nb ratios in the basalts from such cool subduction zones are described as a gradual depletion trend (Ishikawa and Tera, 1997; Fig. 4). On the other hand, the across-arc variation of Hisatsu basalts is not clear, and is similar to that of Cascade basalts which were generated by effect of hot descended slab (Fig. 4).

The weak subduction signature of Cascade basalts has been explained by the influence of ancient subduction magmatism (Leeman et al., 2004). Leeman et al. (2004, 2005) proposed that the IAB-like basalts erupted in the Cascades were derived from the lithospheric mantle, which was metasomatized by an old subduction component. These IAB-like magmas were generated by the remelting of the lithospheric mantle due to the injection of high-temperature magma derived from the deep asthenospheric mantle (Leeman et al., 2004). The weak subduction signature observed in the Hisatsu basalts probably also indicates the influence of ancient (>20 Ma) slabderived fluid. A candidate source for an ancient slabderived fluids is the old Pacific plate (130 Ma; Pitman et al., 1974), which was subducted beneath the southern Kyushu (Kimura et al., 2005). The Pacific plate was separated into two plates (the Philippine Sea plate and present Pacific plate) by generation of Izu-Bonin arc (Maruyama et al., 1997). This metasomatized lithospheric mantle may therefore be partially melted when hot asthenospheric flows were injected from Okinawa Trough between 10 and 0.4 Ma (Fig. 1).

The subduction signatures in the Hisatsu and Kirishima basalts can be identified by B/Zr-Ba/Zr and

B/Nb–Ba/Nb diagrams (Fig. 6); The Hisatsu basalts have lower B/Zr and B/Nb ratios than the Kirishima basalts. This observation indicates that the composition of involved fluid of the Hisatsu basalts was different from that of the Kirishima basalts.

The compositional trends of Hisatsu basalts are similar to those of the basalts from the most backarc side of western pacific arcs (Kurile: Ishikawa and Tera, 1997; Kamchatka: Ishikawa et al., 2001; NE-Japan: Moriguti et al., 2004; Fig. 6). The source mantle composition of these backarc basalts were weakly metasomatized by fluids derived from cold (and old) deep slab. In addition, the compositional trends of the Hisatsu basalts are similar to those of the IAB-like tholeiitic basalts from backarc region of northern Kyushu (Miyoshi et al., 2008a). Although the descending slab does not reach the backarc region of northern Kyushu, these IAB-like basalts show slight B-enrichments. Miyoshi et al. (2008a) suggested that the source mantle compositions of these IAB-like basalts were not metasomatized by the modern slabderived fluid, but were influenced by the ancient slabderived fluid. These observations are consistent with our hypothesis that the source mantle of the Hisatsu basalts were metasomatized by the ancient slab-derived fluid. Therefore, the compositional trends of the Hisatsu basalts are probably explained by mixing between the unmetasomatized mantle source and the ancient slabderived fluid from cold deep Pacific plate (Figs. 6a and b).

On the other hand, the Kirishima basalts show significantly B-enriched trends (Figs. 6a and b). The compositional trends of the Kirishima basalts are similar to those of the Aso basalts (Miyoshi et al., 2008a), and extend to the compositional range of the basalts from volcanic front in western pacific arcs (Kurile: Ishikawa and Tera, 1997; Kamchatka: Ishikawa et al., 2001; NE-Japan: Moriguti et al., 2004; Fig. 6). Miyoshi et al. (2008a) suggested that the high B/Nb, B/Zr and B/Sm ratios of Aso basalts reflect the modern fluid-addition to their source mantle. Thus the B-rich Kirishima basalts appear to have influenced by the modern fluid input from the Philippine Sea plate to their source mantle. The compositional trends of Kirishima basalts may indicate a mixing between the pre-existed source of Hisatsu basalts and B-rich modern slab-derived fluid. The modern fluid input from the subducted slab to the subarc mantle may be limited beneath the volcanic front in this area, and occurred between the Hisatsu (0.4 Ma) and Kirishima (0.3 Ma) volcanisms.

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