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The boron systematics of intraplate lavas: Implications for crust and mantle evolution

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Abstract—Ocean island basalts (OIBs) possess uniformly low B contents, and lower B/Nb and B/K_2O ratios than mid-ocean ridge basalts (MORBs). As with Pb, B enrichments in both MORBs and OIBs are substantially lower than those of arc volcanics or continental rocks. The devolatilization of subducting plates and associated arc magmatism efficiently segregate B into crustal reservoirs and return large volumes of B-depleted material to the deep mantle. Subduction processes (and presumably arc volcanism) have thus played a major role in continental crust formation.

While B is depleted in OIBs relative to either MORBs or arc lavas, OIB samples representing EM and HIMU isotopic reservoirs, often ascribed to the effects of ancient subducted materials, cannot be distinguished from other OIBs in terms of B abundances or B ratios. Our results suggest either (1) the differential depletion in B of two distinct mantle reservoirs, one of which now produces MORBs, and the other OIBs or (2) the episodic or continuous mixing of OIB mantle sources with B-depleted subducted materials. The geochemical processes responsible for the isotopic heterogeneity of intraplate lavas may all serve to segregate B from the mantle into crustal rocks and other surface reservoirs.

1. INTRODUCTION

Current models for mantle structure and evolution suggest that ancient subducted materials persist as discrete entities in the deep mantle, based on isotopic heterogeneities in ocean island volcanic rocks (OIBs). Hofmann and White (1982) attributed high $^{206}Pb/^{204}Pb$ signatures, typical of lavas from St. Helena, to the geochemical effects of subducted ocean crust which had undergone hydrothermal enrichment of U over Pb. Zindler and Hart (1986) and Hart (1984, 1988) advocate a subducted sediment origin for high $^{87}Sr/^{86}Sr$ ratios in many intraplate lavas from the southern Pacific and Indian oceans. Hofmann et al. (1986) and Hofmann (1988) use Nb/U and Ce/Pb ratios in ocean ridge basalts (MORBs), OIBs, and continental rocks to suggest that continental crust extraction has imparted a distinctive chemical signature on all of the mantle, and that all isotopic heterogeneities observed in OIBs today result from subduction-related chemical fractionations.

The contention that any material in the mantle has been subducted presumes that a distinctive geochemical signature in marine sediments and/or oceanic crust can be transported into the deep mantle in a recognizable form. However, data from subduction-related metamorphic associations suggest that extensive chemical fractionations occur on downgoing slabs (Leeman et al., 1992; Moran et al., 1992; Bebout et al., 1993, 1995), that are reflected in arc lavas as an attenuating "slab signature" (Edwards et al., 1993; Ryan et al., 1995; Walker et al., 1995; Hochstaedter et al., 1995). Thus, it is likely that materials subducted to great depth will only poorly resemble the input to trenches. Assessing the effects of subduction-related metamorphism on the different constituents of the slab is essential if we are to truly identify "subduction signatures" in the deep mantle.

Boron is one of the most powerful indicators of slab composition and evolution used in studies of arc petrogenesis. Boron concentrations are high in both the sediments and altered oceanic basalts that reach trenches, and B concentrations are substantially greater in arc volcanic rocks than in mid-ocean ridge basalts (Ryan and Langmuir, 1993). B/Be ratios correlate positively with $^{10}Be/^{9}Be$ ratios in young lavas from several arcs (Morris et al., 1990), indicating that most of the B in arc lavas is slab-derived. Data from subduction-related metamorphic and igneous rocks show that B is efficiently stripped from the slab by progressive metamorphic reactions (Leeman et al., 1992; Moran et al., 1992; Bebout et al., 1993; Ryan et al., 1995). Thus, subducted materials in the deep mantle may preserve a distinctively depleted B signature. To assess B as an indicator of subducted materials in the mantle, we have studied the B systematics of young volcanic rocks from intraplate settings at ocean islands (ocean island basalts: OIBs). This work combines preliminary results from Ryan and Langmuir (1993) with new data for a large number of ocean island centers.

2. SAMPLING AND ANALYSIS

The lavas examined include samples from Iceland, the Azores, the Canaries, Ascension, Tristan da Cunha, St. Helena, and Fernando de Noronha in the Atlantic; Hawaii, the Society Islands, and Samoa in the Pacific; Reunion, Kerguelen, and Gough in the Indian Ocean; and the Pribilof Islands in the Bering Sea. Subaerially erupted, fresh and young whole rocks were selected for B analysis whenever possible. More evolved alkaline lavas from Haleakala and St. Helena were also measured to examine B enrichment changes during differentiation. Older basalts from Haleakala and other sites in Hawaii often show

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depletions of K and other alkalies, which is believed to be due to weathering-induced leaching at the surface (West and Leeman, 1987; Leeman et al., 1994b). A similar effect may be in play for B contents in older lavas from the Canaries and Haleakala, though none of the older samples examined contained <1 ppm B, or showed unusual divergences from data arrays.

Boron measurements were made using several techniques: prompt-gamma neutron activation analysis (PGNA), using the reactor at MacMaster University; direct current plasma emission spectrometry (DCP) at Lamont-Doherty Geological Observatory, and inductively coupled plasma emission spectrometry (ICP) at the Department of Terrestrial Magnetism. A description of the PGNA method may be found in Leeman et al. (1992) and Moran et al. (1992), and details of the plasma techniques may be found in Ryan and Langmuir (1993). Both methods are precise to within 10–20% over the B concentration ranges found in ocean island lavas. Table 1 lists standards data collected by both methods. Agreement among the techniques is typically within ±20% at values of 1 ppm B and above.

Table 1: Comparison of Plasma and PGNAA data for Selected USGS Reference Materials

Sample	ICP & DCP B, ppm	PGNAA B, ppm
NBS 688	1.2	1.3
BHVO-1	2.7	2.5
AGV-1	6.5	7.2
RGM-1	29.1	27.8

3. RESULTS AND DISCUSSION

Boron contents range from <1 ppm in ocean island tholeiites up to 20 ppm in trachytes and some basanites (Table 2). The majority of ocean island alkali basalts lie in the 3–6 ppm B range. Figure 1 examines the geochemical behavior of B by comparing B variations in OIB sample suites from the Mauna Ulu eruption of Kilauea (related through different degrees of partial melting: see Hofmann et al., 1984), and from Haleakala (related by crystallization processes; West and Leeman, 1987) to those of other strongly incompatible trace elements. Boron shows greater relative variation than does Be, Ce, or K in both suites, indicating that it behaves more incompatibly than these elements during melting and crystallization. In Fig. 1d, B vs. Nb, a regression line through the Haleakala data intersects very near the origin, suggesting $D_B \approx D_{Nb}$ during OIB crystallization processes; the lack of Nb data for the Mauna Ulu suite precludes direct comparison of the elements during melting. The diagrams in Fig. 1 also include data for the other OIB suites listed in Table 2. The combined OIB data show considerable scatter in Fig. 1a–c. However, in Fig. 1d, B vs. Nb, the three other OIB suites for which Nb data is available converge on a linear array similar to that for the Haleakala lavas. That several unrelated OIB suites plot as a single trend in Fig. 1d suggests that $D_B \approx D_{Nb}$ during both melting and crystallization processes in intraplate volcanic centers. Also, B/Nb ratios of intraplate lavas appear to be relatively uniform, at 0.06 ± 0.02.

The trace element behavioral relationships outlined above differ slightly from those found in mid-ocean ridge basalts (MORBs), where Ryan and Langmuir (1993) found $D_B \approx D_K < D_{Be}$ or D_{Ce}. Few Nb data are available for the MORB suites examined by Ryan and Langmuir (1993) or Chaussidon and Jambon (1994); those which exist suggests B/Nb ratios of 0.2–0.5. However, B/Nb shows uniformity within oceans (B/Nb for Atlantic MORBs: 0.2 ± 0.05) and within well characterized melting suites (primitive Tamayo Fracture Zone MORBs: B/Nb = 0.33–0.52, numbers identical within the error of the B and Nb analyses; see Ryan and Langmuir, 1993; Bender et al., 1984). Thus, if D_B and D_{Nb} are not identical during the formation and crystallization of MORB magmas, they are probably very similar. Such variations as exist in MORB B/Nb appear to be related to variations in source ratios.

The trends in Fig. 1 also highlight an important distinction: B/Nb ratios in OIBs are, on average, nearly a factor of five lower than those in any analyzed MORB. While scattered, B/K and B/Ce ratios of OIBs are also lower than in MORBs, while B/Be ratios of OIBs and MORBs are more similar (Fig. 1).

3.1. The Evolution of Crust and Mantle B Reservoirs

Though OIBs and MORBs differ in ratios such as B/Nb and B/Ce, volcanic arc lavas and continental rocks are more profoundly distinct. Figure 2 compares B/Ce ratios of OIBs and MORBs with those of volcanic rocks from subduction zones. OIB and MORB B ratios contrast strongly with those of typical volcanic arc rocks, which, while variable, are substantially higher. The highest B/Ce ratios observed in the OIB centers studied occur in the Pribilof Islands, which are located behind the Aleutian island arc. Even in these lavas, B/Ce (<0.2) is distinctly lower than in typical arc lavas.

A characteristic of ocean crust and sediments reaching subduction zones today is substantial B enrichment (sediments: 100–150 ppm B; altered crust 10–100$^+$ ppm B; Donnelly et al., 1980; Dean and Parduhn, 1983). In Fig. 2 OIB and MORB data are also compared to marine sediments, continental crustal rocks, and various metamorphic rock associations, based on the ranges in B content observed by Moran et al. (1992) and Bebout et al. (1993). Ocean ridge and intraplate basalts are lower in B/Ce than any of these materials. Volcanic arc B/Ce ratios overlap the crustal and sedimentary fields, consistent with their derivation from mantle source regions contaminated through chemical interaction with the slab (Morris et al., 1990; Ryan and Langmuir, 1993). Also in Fig. 2 is a field for chondrites, based on B data from Curtis and Gladney (1985) and Curtis et al. (1980). B/Ce is higher in chondrites (≈0.5) than in either MORBs or OIBs.

B/Ce variations are similar to Pb/Ce systematics in that lavas from oceanic mantle sources differ from both continental and primitive solar system materials. Hofmann (1988) also suggests that the Pb content of average continental crust is unusually high, and that average oceanic crust is unusually low, based on "spidergrams" in which element abundance averages are ratioed to "primitive mantle" abundances, with the elements plotted in order of increasing $D_{s/l}$ values in MORBs. To assess whether boron shows abundance anoma-

Table 2: Ocean Island Basalt Data*

Sample	B	Be	Ce	Nb	K2O	SiO2	MgO	Ref.
Hawaii								
HHM-1	1.2	1.01		17	0.31	47.8	8.11	1
HHM-6	1.8	0.89		12	0.16	48.2	10.0	1
HHM-9	1.0			12	0.29	48.8	6.77	1
HKU-7	3.5		84	36	1.26	48.0	4.06	1
HKU-10	1.4		74	29	1.00	48.0	4.54	1
HK-11	2.4	1.48	63	29	0.96	47.2	6.56	1
HK 25	4.9				2.57			1
HK-26	4.5	3.40	144	78	2.59	55.3	2.36	1
HK 27	4.0				2.53			1
HK-30	2.4	1.93	87	47	1.36	48.9	4.84	1
HK-57	3.4		60	29	0.81	43.6	7.15	1
HH-3	1.8		83	48	1.35	45.6	7.34	1
HK-28	3.8		134	79	2.50	54.5	3.20	1
HK-29	3.1		87	47	1.35	49.0	4.83	1
HK-31	1.9		80	44	1.28	46.7	4.93	1
HK-32	1.2		80	44	1.28	47.1	4.67	1
HK-33	1.6		78	43	1.23	46.9	4.83	1
HK-34	1.1		68	36	1.08	45.1	6.58	1
HK-35	2.4		68	36	1.02	44.9	6.84	1
HK-36	1.8		68	37	1.01	44.9	6.78	1
HK-37	4.8		141	72	2.21	52.4	2.90	1
HK-50	1.8		64	33	1.00	43.8	6.33	1
HK-46	2.8		87	46	1.33	48.5	4.72	1
HK-48	4.1		124	77	2.34	52.4	3.59	1
HH-18	3.8		123	71	2.04	47.2	4.44	1
HH-20	2.0		71	42	1.04	44.9	6.57	1
HKT	11.5	3.50	216	229	5.09	64.2	0.12	1
DAS69-1-2	2.5	0.99	34		0.46	49.8	9.14	2,3
DAS69-7-1	1.7				0.47	48.6	13.7	2,3
DAS70-1213-35	1.9		31		0.41	49.5	10.0	2,3
DAS70-1213-62	1.5	0.88	29		0.40	49.1	12.0	2,3
DAS70-1213-122	1.6		28		0.37	49.3	11.4	2,3
k1919	2.5	0.99	37		0.54	50.0	7.01	2
DAS70-1213-41	2.3		31		0.41	49.7	9.57	2,3
DAS70-1213-124	1.4				0.38	49.3	11.37	2,3
BHVO-1	2.7	1.01	37		0.54	49.6	7.26	2,3
KL-2	2.5							*
ML-3B	1.9							*
Society Islands								
73-186	1.2	1.69	90	41	1.85	47.1	10.8	*
73-204	2.3	1.38	77	33	1.72	47.0	12.8	*
73-234	2.4	1.33	76	34	1.45	47.6	9.59	*
73-416	1.3	1.35	69	34	0.79	44.4	15.8	*
73-95	1.1		89	43	2.05	48.8	9.80	*
73-332	1.7		65	29	1.52	45.9	13.9	*
T85-36	1.9	1.99			1.89		4.99	4
T85-29	1.0	1.35			1.02		15.6	4
Samoa								
UPO-7	3.9	2.46	169		1.78	41.0	11.8	5
84-MT-15	2.9	1.63	68		0.88			5
St. Helena								
STH 2935	5.7	2.98			4.47	63.9	0.15	*
STH 2933	10.3	9.39			5.06	66.3	0.05	*
STH 2894	7.6	3.74			1.17	46.07	4.91	*
STH 2878	3.7	1.88			2.39	55.7	2.14	*

Sample	B	Be	Ce	Nb	K2O	SiO2	MgO	Ref.
SH 65	3.1	2.14	103	72	1.48	46.6	4	6
SH 105	6.5	2.11	104	74	1.52	48.1	4	6
SH 120	3.4	1.85	92	64	1.52	46.4	5.01	6
SH 216	6.2	2.93		82				6
Fernando de Noronha								
FDN-25	3.4		86	37	1.29	45.2	11.0	*
FDN-31	4.2		137	98	1.25	40.3	12.3	*
FDN-54	10.0		208	167	5.30	54.0	1.82	*
FDN-76	3.8		190	81	12.7	41.8	12.3	*
FDN-72	3.0		138	83	2.82	49.7	6.56	*
Tristan de Cunha								
TR-1	5.4		209		4.82	56.4	1.38	5
TR-4	4.1		122		2.47	44.4	6.67	5
Gough Is.								
G22	5.0	1.54	96	48	2.45	48.6	4.15	6
G79	12.5	6.92	254	178	6.48	60.1	0.52	6
G142	2.6	1.14	83	47	2.11	46.3	12.9	6
1927-1253	3.6	1.67	161	79	4.69	55.0	2.22	6
Pribilof Is.								
STP-4	8.4	2.60	86		2.54	45.6	5.35	7
STP-7M	7.4	1.26	47		1.11	44.3	8.90	7
STP-25	5.1	1.54	50		1.25	43.9	10.8	7
STP-5	2.9	2.11						*
STP-14	2.4	2.40						*
Azores								
GU 22	2.7	1.49			1.37			*
TERC. 200	1.9	1.03			1.35			*
E-20	2.2				0.37	47.2	9.89	5
SM-6	1.6		135		2.08	47.0	7.91	5
F-33	3.1		75		1.72	48.2	7.54	5
Canaries								
LP 15	8.2	6.85						*
TF 96	1.7	4.84						*
LZ 105	5.4	1.95						*
GC 1433	2.6	1.49						*
LG 58	2.0	2.30						*
LZU 8	2.0	1.07						*
Ascension								
ASC 2740	2.4	1.29			1.49	48.8	4.65	*
ASC 2716	5.2	3.85			4.88	67.2	0.16	*
ASC 2775	17.2	8.03			4.60	74.0	0.00	*
ASC 2765	4.3	1.80			1.26	48.0	4.67	*
Iceland								
Hekla 1971	1.3	2.25			1.20	55.7	3.08	*
075 Hekla	1.8	0.87			0.67	47.3	5.17	*
AU 389	0.6	0.17			0.14	48.6	6.70	*
Reunion								
OI 1977	2.0	0.61			0.81	49.1	6.78	8
BO 1979	2.2	1.04			0.47	43.3	23.4	8

* Trace elements in ppm; oxides in % wt. Boldface values represent new data collected for this study. Remaining B and Be data appeared previously in RYAN and LANGMUIR (1988;1993).

1. WEST and LEEMAN 1987
2. HOFMANN et al. 1984
3. WRIGHT et al. 1975
4. NATLAND and TURNER 1985
5. W. WHITE, unpub. data
6. WEAVER 1987
7. KAY 1980
8. ALBAREDE and TAMAGNAN 1988

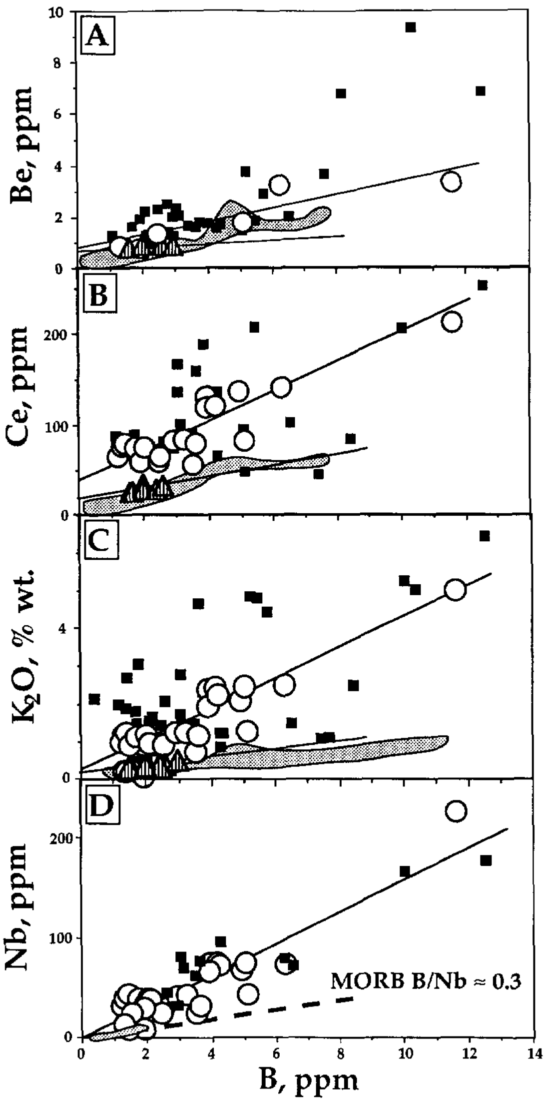

FIG. 1. Covariation diagrams. (a) B vs. Be. (b) B vs. Ce. (c) B vs. K_2O. (d) B vs. Nb. Open circles represent the Haleakala suite, and shaded triangles the Mauna Ulu suite from Kilauea; all other OIB data denoted by smaller black squares. Shaded fields represent variation ranges of mid-ocean ridge basalts, based on data from Ryan and Langmuir (1993), Chaussidon and Jambon (1994), and sources therein. Data sources for OIB suites as in Table 2. Lines through Haleakala and Mauna Ulu data are regression lines used to determine relative distribution behavior of the plotted elements; inferred order of incompatibility is $D_B \approx D_{Nb} < D_K < D_{Ce} < D_{Be}$. Dotted line in Fig. 1d denotes slope and B/Nb ratio of MORBs.

lies in the crust, we have added B to the Hofmann (1988) spidergram (Fig. 3), placing it between Nb and K, based on our D_B inferences from Fig. 1 and results for MORB suites (Ryan and Langmuir, 1993).

Primitive mantle abundance estimates for B range from ~0.5 ppm (Higgins and Shaw, 1984) to <0.1 ppm (Leeman et al., 1992). Chaussidon and Jambon (1994) suggest 0.25 ppm B in the mantle based partly on similar B/Rb ratios in MORBs and continental rocks. B/Rb ratios for our OIB suites are markedly lower than for MORBs (.03–.2 vs. ~0.4); also, B/Rb declines with increasing extents of crystallization in OIB suites, suggesting $D_B > D_{Rb}$. Inverse modeling results for FAMOUS area MORBs suggest $D_B \leq .01$ and source abundances of 0.08–0.17 ppm B (Ryan and Langmuir, 1993), while partial melting calculations on Mauna Ulu suite lavas, assuming 6–7% melting (see Hofmann et al., 1984) suggest ~0.12 ppm B in the Kilauea source region. We thus believe the B abundance of primitive mantle lies between 0.1 and 0.25 ppm.

Results for primitive MORB glasses (Ryan and Langmuir, 1993) suggest a B content of 0.3–0.6 ppm for oceanic crust. Taylor and Mclennan (1985) suggest a continental crust B content of 10 ppm, but recent results indicate very low B in the lower crust (≤2 ppm; (Truscott et al., 1986; Leeman et al., 1992), and higher, but variable B contents in upper crustal rocks depending on metamorphic grade (Moran et al., 1992; Bebout et al., 1993). In addition, a significant B reservoir exists in marine sediments and altered ocean crust (marine muds: ~80–120 ppm B; carbonates 10–70 ppm B; altered crust 5–40 ppm B; Dean and Parduhn, 1983; Hemming and Hanson, 1992; Vengosh et al., 1991; Donnelly et al., 1980). This "marine" B is continentally derived, and does not recycle into the deep mantle (see Ryan and Langmuir, 1993 and discussion below); as such, it must be considered "continental" B. We thus suggest a higher continental B abundance than Taylor and Maclennan (1985) of 15–20 ppm.

Our "mantle normalized" estimates for B in oceanic and continental crust are plotted in Fig. 3, and like Pb, B shows an enrichment in the continents and a depletion in ocean crust relative to elements of similar distribution coefficients. High continental Pb, and the uniformity of Ce/Pb ratios in MORBs and OIBs, led Hofmann (1988) to suggest that the processes of continental crust extraction differed from those of ocean crust extraction, and that the continent extraction event resulted in the homogenization of the residual mantle. Like Pb, B systematics suggest differences between the processes which have formed continental and oceanic crust through Earth's history.

Boron and Pb also show similar systematics in subduction zone settings. Moran et al. (1992) found that B contents decline progressively with increasing thermal grade in metamorphic rocks due to the progressive devolatilization reactions characteristic of prograde metamorphism. Bebout et al. (1993, 1995) focused specifically on metasediments in the Catalina Schist "subduction complex" massif, and found correlated declines in B, Cs, N, and H_2O contents as metamorphic grade increased from lawsonite/albite to amphibolite. Morris et al. (1990), Ryan and Langmuir (1993), Edwards et al. (1993), Ishikawa and Nakamura (1994), and Ryan et al. (1995) have observed patterns of B abundance decline across volcanic arcs: volcanic front lavas have high B contents and high B/Be or B/Nb ratios, while lavas from volcanoes behind the front show consistently lower values. Ryan et al. (1995) found that B/Be ratios decline systematically with increasing slab depth in the Kurile arc, approaching MORB-OIB values in lavas from centers above the deepest slab segments.

While the behavior of Pb during metamorphism is less well documented than that of B, Noll et al. (1995) observed declines in both Pb abundances and Pb/Ce ratios across the

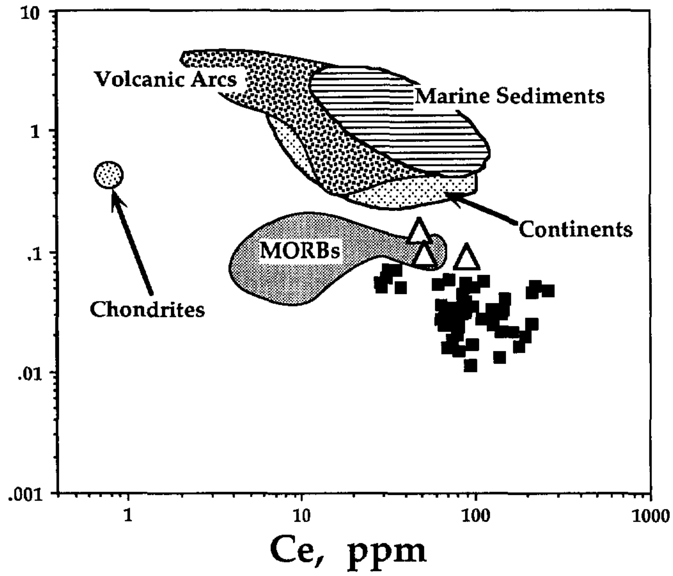

FIG. 2. B/Ce vs. Ce. Fields as labeled. Open triangles: Pribilof islands; all other OIB samples represented by smaller black squares. OIB and MORB data sources as in Table 2; arc field based on data from Ryan and Langmuir (1993), Leeman et al. (1994a) and Morris et al. (1990). Ce data for continental crust from Taylor and Maclennan (1985) and Hofmann et al. (1986). Marine sediment field based on data of Dean and Parduhn (1983), Plank (1992) and Zheng and Morris (unpubl. data). Chondrite data is from Curtis et al. (1980), Curtis and Gladney (1985) and Anders and Ebihara (1982).

Kuriles and several other arcs which parallel B variations. Lead also shows similarities to B in the marine setting, as both are enriched in seafloor hydrothermal fluids (Spivack et al., 1987; Von Damm et al., 1985), and both show elevated concentrations in marine sediments. Integrating Pb/Ce and lead isotope data for two closely associated volcanoes in the Aleutian arc, Miller et al. (1994) demonstrated that Pb is extracted from subducting slabs via fluid phases, and that up to 60% of slab-derived Pb comes from subducted ocean crust. Correlations between B/Be and ^{10}Be/^{9}Be in arc lavas demonstrate the slab origins of B, and its close affinities to volatiles during metamorphism strongly suggest hydrous fluids as its medium of transport. ^{10}Be enrichments in arc lavas require inputs from subducted sediments, but the high B/^{10}Be ratios observed in most arcs permit inputs of B from altered ocean crust, in which ^{10}Be ≈ 0 (Morris et al., 1990). Based on boron isotope systematics, Ishikawa and Nakamura (1994) suggest that ~90% of the B in Izu–Bonin arc lavas is derived from altered crust, and the occurrence of high B contents in lavas from sediment-starved arcs such as the Marianas also suggests a role for subducted crust as a boron source (Leeman, 1994 and unpubl. data).

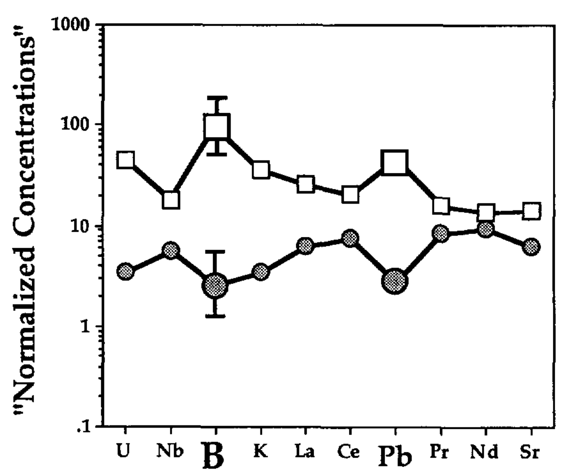

FIG. 3. Portion of a "mantle normalized" spider diagram for average oceanic (lower) and continental (upper) crust from Hofmann (1988; Fig. 7) including new values for B. Element order based on increasing distribution coefficients during ocean ridge basalt generation; the position of B is determined from the relationships in Fig. 1 and in Ryan and Langmuir (1993). Sources and averaging approaches for B data are discussed in the text; error bars reflect the total range of boron values given our uncertainties in mantle and crustal estimates.

Subduction processes efficiently extract both B and Pb from downgoing plates and transfer it into crustal reservoirs. As suggested by Miller et al. (1994) for Pb, it is likely that subduction-related chemical extraction processes have produced the differences in B abundance between continental and oceanic crust over time. The low B abundances of intraplate and ocean ridge lavas thus record the effects of ancient subduction events.

3.2. Distinctions Between MORB and OIB Reservoirs

Let us now address the differences between the MORB and OIB B datasets. Figure 4 recasts the data from Fig. 1 on ratio-element plots to highlight differences between MORBs and OIBs and distinctions among different ocean islands. On such diagrams, cogenetic lavas will form curvilinear arrays with

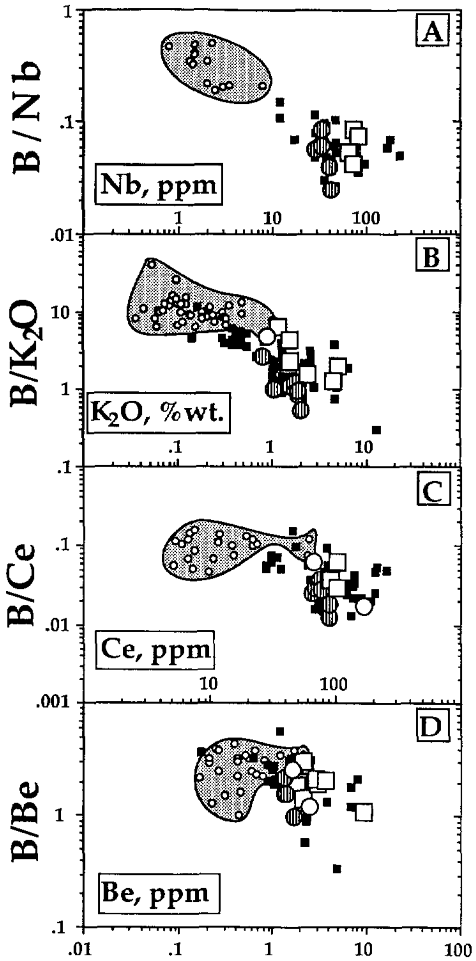

FIG. 4. Diagrams comparing OIB and MORB B enrichments. (a) B/Nb vs. Nb. (b) B/K_2O vs. K_2O. (c) B/Ce vs. Ce. (d) B/Be vs. Be. Symbols as follows: shaded circles—Society islands; open circles—Samoa; open squares—St. Helena. MORB data are shown as open circles with the shaded MORB field. Niobium data for MORBs from Bender et al. (1984), Langmuir et al. (1977), and Bougault and Treuil (1980). Mean values of OIB:MORB datasets for each ratio: B/Nb—0.06:0.3; B/K_2O—2.6:11; B/Ce:—0.04:0.1; B/Be:—2.1:2.8.

slopes related to the distribution coefficients of the ratioed elements. Figure 4a,b compares B to Nb and K, respectively. If MORBs and OIBs are generated from mantle sources of broadly similar relative abundances of incompatible elements (as inferred by Hofmann et al., 1986; Hart, 1995), then, as $D_B \approx D_{Nb}$, and $D_B \leq D_K$, the combined MORB and OIB data should form nearly horizontal arrays, with the trend in Fig. 4b showing a slight positive slope, as B/K_2O ratios should be higher at higher K_2O contents. However, B/Nb and B/K_2O are distinctly lower in OIB suites than in MORBs. Figure 4c,d should show positively sloped arrays, as $D_B < D_{Ce} < D_{Be}$, and B/Ce and B/Be ratios should be higher in OIBs. Instead, B/Ce ratios in OIBs are generally lower than in MORBs, with considerable overlap, while OIB and MORB B/Be ratios are nearly indistinguishable.

Given the distribution behaviors of the elements plotted in Fig. 4, it is impossible to generate ocean ridge and intraplate lavas from a mantle source of similar relative trace element abundances. These differences between MORBs and OIBs can only be explained assuming a pervasive depletion of B in intraplate source regions as compared to elements of similar distribution coefficients. B/Nb and B/K_2O are markedly lower in all OIBs; B/Ce and B/Be show progressively less difference between the settings because $D_{Be} > D_{Ce} > D_B$. B/Be and B/Ce will thus be higher at the lower extents of melting presumed for most OIBs, making MORB and intraplate lava ratios similar despite lower B/Be and B/Ce in OIB source regions. The sources of intraplate lavas thus appear to be systematically depleted in B relative both to continental rocks and to the mantle source of MORBs. Samples from St. Helena, Samoa, and the Society islands, centers which respectively reflect the HIMU and EM isotopic endmembers of Zindler and Hart (1986), cannot be distinguished from other OIBs in terms of B concentrations or any of the ratios in Fig. 4. Thus, aside from the lower B/Nb and B/K ratios common to all OIBs, no unusual B depletions or enrichments are evident in those intraplate centers whose isotopic systematics are believed to reflect subducted materials.

The B systematics of intraplate lavas record a global fractionation that has resulted in the generation of two mantle reservoirs, both of which are B-depleted relative to the crust. If continental crust formation was the result of subduction processes operating in ancient times, leaving behind a residual mantle capable of generating ocean crust, then it is possible that the B-depleted nature of modern intraplate lavas results from more recent subduction processing, and reflects the continued removal of B from portions of the mantle. Such a model for OIB sources is consistent with the elevated Nb/Th ratios observed in lavas from Kahoolawe (Leeman et al., 1994b) and with high Nb and Ta contents in OIBs generally, as the metamorphic distillation of slabs during subduction should produce residues with relatively high abundances of insoluble species such as high field strength elements. Recent subduction additions might also explain the elevated $^{87}Sr/^{86}Sr$ of the EM II isotopic endmember, but the origins of the elevated $^{206}Pb/^{204}Pb$ of HIMU and many of the other isotopic characteristics of OIBs (in particular elevations in $^{3}He/^{4}He$ and other rare gas ratios) are less clear. A variety of origins have been suggested for the isotopic diversity of intraplate lavas, leading to many different "flavors" of mantle sources (Zindler and Hart, 1986; Hart, 1988, 1995). The differing levels of B enrichment in MORBs and OIBs constrain that all intraplate source regions, regardless of their isotopic characteristics, must have experienced B depletion following continental crust extraction. If this depletion is related to subduction, then its timing relative to the development of isotopic heterogeneities is uncertain. The uniformity of the B depletion in OIBs may indicate a global event which generated two mantle reservoirs distinct in their B abundances, followed by further chemical segregation, which with time results in divergent isotopic signatures. However, given the extreme mobility of B during metasomatic interactions and the effectiveness of subduction processes at segregating B from downgoing plates into surface reservoirs, it is more likely that distinctions between MORB and OIB source regions developed progressively (or episodically) as more and more B-depleted slab materials were added to the mantle. Boron depletions and isotopic heterogeneities could therefore develop simultaneously.

4. CONCLUSIONS

Boron abundances in intraplate lavas are depleted relative to continental materials, and also show depletions relative to MORBs, recording at least two B fractionation "events": continental crust formation and the development of OIB mantle sources. Subduction-related metamorphic processing efficiently strips B from downgoing slabs and as such, it is possible that both continent formation and the segregation of OIB sources are recording the effects subduction at different stages in Earth's history.

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