

# Distribution of boron, lithium and beryllium in ocean island basalts from French Polynesia: implications for the B/Be and Li/Be ratios as tracers of subducted components

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## Abstract

The study focuses on the distribution of B, Be, Li, rare earth elements (*REE*), high-field-strength elements (*HFSE*), Th, U and Pb in fresh and hydrothermally altered ocean island basalts (OIB) from French Polynesia, and evaluates B/Be and Li/Be ratios as potential tracers of subducted components in the mantle. Hydrothermal solutions affecting the rocks during cooling were derived from meteoric water, sea water and magmatic fluids. The concentrations of *REE*, *HFSE*, Th and Be in the OIB were not affected by secondary processes except during advanced stages of subaerial hydrothermal alteration where saponite was a dominant secondary phase. This alteration modified the contents of these elements, changed *REE* patterns and produced a positive Ce anomaly. The subaerial and submarine hydrothermal alteration ( $T \sim 70\text{--}100^\circ\text{C}$ ) may change U concentrations in OIB, whereas Pb was only marginally redistributed during alteration.

Boron was enriched during submarine and subaerial hydrothermal alteration but was not noticeably affected in basalts altered by magmatic fluids at  $T > 200^\circ\text{C}$ . Like B, the mobility of Li during the alteration varies with fluid temperature. Lithium became enriched in the basalts during advanced stages of lower  $T$  hydrothermal alteration ( $<100^\circ\text{C}$ ). However, this element was partly removed from the rocks during higher  $T$  alteration ( $>200^\circ\text{C}$ ) by magmatic fluids. Boron, Be and Li behave as incompatible trace elements in basaltic magmas. Beryllium content in primitive mantle is estimated to be 0.07 ppm. Fresh Polynesian OIB have low abundances of B and Li and low B/Be (2–5) and Li/Be (2.5–5) ratios compared with volcanic arc rocks, marine sediments and altered oceanic crust. Various OIB including even those which have HIMU- and EM-affinities have similar overlapping B/Be and Li/Be ratios. Both B and Li are probably stripped from a lithospheric slab during subduction-related metamorphism and are, thus, not involved in deep mantle recycling. The mantle-normalized trace element abundances of MORB and OIB usually display patterns characterized by negative B, Pb and Li anomalies. The patterns of continental crust and crustal rocks have distinct positive anomalies for these elements whereas continental basaltic rocks have variable relative abundances of B, Pb and Li. The anomalies of these elements in basalts can be useful in discriminating their tectonic setting and constraining the mantle source regions of basalts.

**KEYWORDS:** boron, lithium, beryllium, Ocean Island Basalts, subducted components, French Polynesia.

## Introduction

THE isotopic heterogeneity of some ocean island basalts (specifically the Dupal-type; c.f. Sun and McDonough, 1989) has been frequently attributed to the presence of recycled oceanic crust or sediments in their upper mantle source (Hofmann and White, 1982; Weaver, 1991). However, the crustal component in the mantle source has not yet been convincingly identified by major and/or trace element data. Recent studies of island arc volcanic rocks suggest that B/Be ratios monitor subducted oceanic crust or sediment components in their mantle source (e.g. Morris *et al.*, 1990). This ratio may also be useful for refining and constraining the composition of the upper mantle sources of ocean island basalts (OIB). However, there is limited information on B/Be ratios in OIB. Furthermore, boron, like several incompatible trace elements, is potentially mobile during secondary processes that affect oceanic volcanic rocks (Bergeron, 1989). Thus, before B/Be ratios can be used as an indicator of mantle composition and processes, it is important to evaluate the behaviour of these elements during various alteration processes that affect oceanic volcanic rocks. Similar uncertainties are also associated with Li/Be ratios, another potential indicator of subducted components in the mantle (Ryan *et al.*, 1989). The purpose of this paper is to evaluate the mobility of B, Be, Li, Th, U and Pb during the alteration of ocean island basalts and to discuss the significance of the B/Be and Li/Be ratios as potential tracers of subducted components in the mantle. OIB from French Polynesia were chosen for this investigation since they display considerable isotopic heterogeneity, some of which has been attributed to the presence of recycled crustal components (e.g. Vidal *et al.*, 1984; Chauvel *et al.*, 1992). Some of these rocks were also affected during cooling by various hydrothermal processes involving magmatic fluids and sea and meteoric waters (as indicated by stable isotope measurements; Dudoignon *et al.*, 1992).

Fourteen OIB samples were selected from two drill holes in Mururoa and Fangataufa atolls in French Polynesia to evaluate the behaviour of B, Be and Li during the alteration of OIB. Petrographic investigation by Dudoignon *et al.* (1989) revealed that the drill core material is variably altered. The samples were analyzed for a range of incompatible trace elements including B, Be, Li, U, Th, Pb, rare earth elements (REE), Nb, Ta, Zr, Hf, Ba, Sr, Rb and Cs (Table 1). In addition, B, Be and Li were determined in 31 fresh basaltic samples from French Polynesia (Table 2) which were previously studied by Dupuy *et al.* (1987, 1988, 1989, 1993), Dostal *et al.* (1983) and Liotard *et al.* (1986). On radiogenic isotope plots, some of these

basalts have distinct isotopic signatures (Vidal *et al.*, 1987; Dupuy *et al.*, 1987, 1993) characteristic of mantle end-member components including EM-I and HIMU of Zindler and Hart (1986). Therefore, trace element concentrations in these basalts can geochemically characterize those mantle components and may reflect the effects of different mantle processes responsible for their generation.

## Geological notes

Mururoa (21° 50'S, 138° 53'W) and Fangataufa (22° 19'S, 138° 46'W) atolls are part of the Pitcairn-Gambier-Duke of Gloucester linear island chain in the South Central Pacific Ocean. The volcanism at both atolls was related to a hot spot presently located about 90–100 km southeast of Pitcairn Island (Stoffers *et al.*, 1990; Binard *et al.*, 1992). In Mururoa, the volcanism lasted < 2 Ma (11.9–10.7 Ma; Gillot *et al.*, 1992) prior to subsidence of the volcano below sea-level. The atoll is covered by 180–400 m thick coral reef strata. Fangataufa shows a similar evolution although the volcanic activity lasted longer (12.9–9.6 Ma; Guillou *et al.*, 1990).

The stratigraphy of both atolls has been documented in several drill holes up to about 1 km deep (Bardintzeff *et al.*, 1986; Buigues *et al.*, 1992; Guillou *et al.*, 1990; Maury *et al.*, 1992). In both atolls, carbonate units, outcropping on the surface, are underlain by a transitional zone containing reworked volcanic clasts embedded in a sedimentary matrix, which in turn overlies subaerial lava flows (100–500 m thick). The lowermost part of the sequence in the drill holes is represented by submarine lava flows. These flows are crosscut by dykes and subvolcanic intrusions. The volcanic sequences in both atolls are composed of basalts and hawaiites with typical OIB geochemical characteristics (Dupuy *et al.*, 1993). The samples for this study come from two drill holes each a kilometre deep; one (Fuchsia) located at the southern edge of Mururoa (Destrigneville *et al.*, 1991) and the other (Mitre) at the centre of the Fangataufa atoll.

## Petrography and alteration

The basaltic flows are non-vesicular to vesicular and include both pillow lavas and monolithologic mafic breccias. Some of the basalts are plagioclase-phyric. Subvolcanic mafic intrusions are compositionally similar to the lavas.

Three types of hydrothermal alteration, based in part on stable isotope systematics, have been recognized in the altered basalts from the Mururoa and Fangataufa atolls (Dudoignon *et al.*, 1989, 1992; Destrigneville *et al.*, 1991): submarine (sea water/basalt interaction; exemplified in the present study by

Mururoa submarine lava flows), subaerial (meteoric water/basalt interaction; Mururoa subaerial lava flows) and hydrothermal (magmatic fluid/basalt interaction; exemplified by Fangataufa intrusives). The subaerial and submarine alterations differ from processes related to low temperature weathering or sea water alteration. They took place during the cooling of lavas in subaerial and submarine environments at elevated temperatures (70–100°C; Dudoignon *et al.*, 1992). The altered flows have distinct mineralogy and abundant secondary phases. The alteration assemblage is controlled by the rock/fluid interaction (Dudoignon *et al.*, 1989). The submarine flows were modified by interaction with sea water which led to crystallization of saponites at about 80°C (O and H isotope data; Dudoignon *et al.*, 1989, 1992). Slightly altered inner parts of flows contain 'protoceladonite' and Fe-saponite assemblages which fill vesicles and replace glass and olivine. Strongly altered outer parts of the flows (breccia and pillow lavas) contain Fe-saponite that replaces primary phases (olivine and glass), and Mg-saponite that occurs with Fe-saponite in the inner part of largely replaced olivine crystals and in voids (vesicles, veinlets and cement of breccias). Other saponite-free voids are filled by zeolites, mainly phillipsite.

The subaerial basaltic lavas were altered by meteoric water inducing saponite crystallization at about 70°C (Dudoignon *et al.*, 1992). Secondary phases of the inner (less altered) parts of the flows include celadonite, chlorite and randomly interstratified chlorite/saponite mixed layer clays. The latter clays occur in the intermediate parts of the lava flows. Saponite is present in the outer, brecciated zones. Using O and H stable isotope data, Dudoignon *et al.* (1992) concluded that water/rock ratios ranged from 5:1 in brecciated parts of flows, to 1:4 and 1:8 in the massive core of the submarine and subaerial lavas, respectively. Temperatures were typically around 70°C during subaerial hydrothermal alteration and around 80–100°C during submarine alteration.

The hydrothermally altered rocks of the Mitre drill hole are from a zone of feeder dikes of the Fangataufa volcano termed 'rift zone' by Dudoignon *et al.* (1992). The hydrothermal processes are probably associated with a perturbed geothermal gradient developed around the rift zones and are related to cooling of the intruded basalts. The mineral assemblage displays a vertical zonation controlled by the thermal gradient from the top to the bottom of the pile: (1) dioctahedral smectite (the lowest temperature of crystallization); (2) saponite; (3) random chlorite/saponite mixed layer; and (4) chlorite (the highest temperature). Secondary mineral paragenesis and C, O and H isotopic data indicate that the alteration involved magmatic water with limited sea

water mixing at the top part of the alteration zone; crystallization temperatures (for calcite and clay minerals) ranged from 300° to < 100°C and the magmatic water/rock ratio varied from 1:10 to 1:4 (Dudoignon *et al.*, 1992).

### Analytical methods

Major elements were determined by the X-ray fluorescence technique at the Geochemical Centre at Saint Mary's University. The trace elements Li, Be, Rb, Cs, Sr, Pb, Th, U, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Hf, Zr, Nb and Ta were analyzed by inductively coupled plasma mass spectrometry (ICP-MS) at Centre Geologique et Geophysique, Universite Montpellier II using the procedure of Ionov *et al.* (1992). Boron was determined by prompt gamma neutron activation using the McMaster Nuclear Reactor. This method has been described by Higgins *et al.* (1984); precision and accuracy have been reported by Shaw and Sturchio (1992). The quality of the trace element data can be judged from replicate analyses of the standard rocks (Appendix 1). The precision of the ICP-MS data is 2–3%. For boron, the precision is generally better than 5% of the concentration where B abundances exceed 5 ppm. The quality of the data is poorer at lower concentrations (10–15%). The distribution of boron in the rocks was investigated by the alpha-track images produced at the McMaster Nuclear Reactor (Truscott *et al.*, 1986). Since Li also generates alpha-emissions during irradiation, the Li and B tracks cannot be readily distinguished. To minimize the possible contribution of Li to the higher-density track spots, particular attention was paid to samples which display a rather small range of Li but significant variations in B. In these samples, the track abundances correlate with the evidence of progressive alteration and with the whole-rock B concentrations. The alpha track images were also used to evaluate the distribution of Li in the altered rocks.

### Geochemistry

Fresh basalts from Mururoa (Dupuy *et al.*, 1993) are usually silica-undersaturated (< 5% normative nepheline) and have REE abundances typical of OIB; La/Yb ratios range from 16 to 29 (Fig. 1). The lower submarine sequence at Fangataufa is composed of olivine- or quartz-normative tholeiites whereas the upper subaerial volcanic sequence consists of silica-undersaturated basalts. The subvolcanic tholeiitic intrusions sampled in the borehole at Fangataufa are related to the lower submarine sequence. The Fangataufa tholeiites have lower abundances of strongly incompatible trace elements (e.g. Th, Rb,

TABLE 1. Major and Trace Element Composition of Basaltic Rocks from Mururoa and Fangataufa Islands

	Altered												Fresh			
	Mururoa						Fangataufa						MUR	FANG		
	Submarine			Subaerial			Hydrothermal			516	589	721			815	
7	11	14	15	16	32	37	40	43	43				SAP	516		589
SiO <sub>2</sub> (%)	41.07	41.95	41.87	40.45	41.35	46.14	44.65	42.69	42.94		44.81	42.91	41.98	43.37	46.01	49.40
TiO <sub>2</sub>	3.78	4.74	4.39	4.05	3.24	3.23	4.06	4.05	4.73		3.07	3.27	3.30	3.20	3.68	2.62
Al <sub>2</sub> O <sub>3</sub>	12.94	14.50	14.15	13.44	10.69	16.95	17.26	16.75	15.07		14.29	14.68	14.26	13.97	15.09	14.41
Fe <sub>2</sub> O <sub>3</sub>	12.40	11.57	13.17	13.38	16.92	10.29	12.12	12.23	14.46		11.79	10.47	11.92	11.23	13.06	11.50
MnO	0.15	0.16	0.22	0.11	0.08	0.15	0.15	0.14	0.15		0.16	0.13	0.13	0.16	0.17	0.15
MgO	6.47	4.58	4.49	6.17	4.52	4.48	4.69	4.58	4.64		3.10	3.26	5.98	3.96	6.73	6.97
CaO	7.51	9.97	11.31	3.28	3.60	8.16	9.88	8.55	9.37		9.40	8.89	8.19	10.59	9.75	11.57
Na <sub>2</sub> O	2.47	2.92	2.10	2.14	1.74	3.07	2.58	2.99	2.72		2.52	2.04	1.90	2.22	3.22	2.49
K <sub>2</sub> O	1.32	1.53	1.28	1.76	2.37	2.08	1.26	1.57	2.02		0.65	0.85	1.01	0.71	1.44	0.53
P <sub>2</sub> O <sub>5</sub>	0.43	0.77	0.54	0.31	0.32	0.90	0.55	0.53	0.60		0.33	0.43	0.42	0.42	0.85	0.36
L.O.I.	11.30	6.00	5.20	15.70	15.90	3.20	1.60	4.10	2.30		9.70	13.50	10.50	10.30		
Σ	99.84	98.69	98.72	100.79	100.73	98.65	98.80	98.18	99.00		99.82	100.43	99.59	100.13	100.00	100.00
Norms																
Ne		3.7	1.0					2.5	3.7							
Ol	13.5	7.6	8.0			9.6	8.8	12.5	11.1							
Qtz				1.2	1.6						3.5	4.7		1.2		
Li(ppm)	7.9	6.5	6.9	9.2	9.0	16.6	6.1	14.8	7.7	45.4	2.4	2.6	4.3	2.9	7.58	4.70
Be	1.56	1.55	1.78	1.74	1.74	2.79	2.12	2.16	1.98	3.11	1.27	1.31	1.34	1.33	2.32	1.11
B	20.3	15.3	21.8	45.9	58.0	24.4	9.6	28.0	14.9	109.8	3.4	3.6	3.8	2.3	5.84	2.67
Rb	22.1	21.7	26.8	32.2	61.0	39.3	26.8	27.5	20.9	7.7	15.4	13.7	18.2	11.3	28.4	10
Sr	507	1052	711	280	208	838	850	729	677	60	578	593	590	560	927	528
Zr	213	284	265	251	212	431	301	300	337	108	166	178	194	174	330	152
Hf	5.6	7.2	6.4	5.9	4.7	9.30	6.6	6.6	8.5	2.7	3.9	4.2	4.3	4.2	7.88	3.63
Nb	40.7	47.9	50	42.6	39.1	86.4	61.9	61.3	67.3	15.6	30.7	34.3	36.7	33.3	74.0	30.0
Ta	2.71	3.03	3.02	2.56	2.24	4.95	3.69	3.56	4.07	0.92	1.78	1.91	2.07	2.01	4.72	1.76
Cs	0.26	0.34	0.32	0.39	0.82	0.23	0.14	0.12	0.06	0.26	0.23	0.24	0.29	0.21	0.38	0.25
Ba	183	238	280	120	29	438	280	282	313	20	181	159	195	171	366	145

TABLE 1. (contd.)

	7	11	14	15	16	32	37	40	43	43	SAP	516	589	721	815	MUR	FANG
La	24.6	33.5	31.5	25.7	25.6	54.9	37.2	37.1	38.0	15.7	19.0	21.1	21.1	22.4	21.1	45.9	18.5
Ce	58.4	79.6	74.9	63.9	58.6	130.3	87.6	88.1	91.9	60.4	44.6	50.1	53.2	53.2	49.1	103	41.6
Pr	7.3	10.1	9.6	8.2	7.5	16.4	10.9	11.0	11.9	3.9	6.0	6.7	7.2	7.2	6.3		
Nd	32.2	44.1	41.5	35.6	32.9	69.1	47.1	47.1	50.8	14.6	25.6	28.9	31.4	31.4	28.1	49.6	22.4
Sm	6.48	8.93	8.47	7.32	6.67	13.15	9.32	9.22	10.39	2.39	5.67	6.13	6.77	6.77	6.11	11.58	5.57
Eu	2.26	3.11	2.93	2.50	2.25	4.29	3.14	3.13	3.66	0.83	2.16	2.31	2.40	2.40	2.13	3.55	1.86
Gd	5.96	8.19	7.55	6.47	5.85	10.58	7.74	7.79	9.82	1.57	5.67	5.83	6.07	6.07	5.61		
Tb	0.87	1.2	1.09	0.97	0.87	1.56	1.14	1.14	1.45	0.27	0.84	0.87	0.90	0.90	0.83	1.36	0.88
Dy	4.22	5.86	5.31	4.68	4.17	7.29	5.46	5.38	6.96	1.24	4.37	4.22	4.38	4.38	4.28		
Ho	0.73	1.02	0.90	0.81	0.17	1.19	0.90	0.88	1.20	0.21	0.77	0.75	0.75	0.75	0.75		
Er	1.79	2.48	2.20	1.97	1.70	2.82	2.15	2.12	2.81	0.55	1.90	1.79	1.76	1.76	1.86		
Tm	0.23	0.32	0.28	0.24	0.22	0.35	0.25	0.26	0.34	0.07	0.24	0.23	0.23	0.23	0.24		
Yb	1.36	1.89	1.65	1.44	1.23	2.02	1.53	1.53	2.09	0.53	1.51	1.36	1.35	1.35	1.49	2.13	1.50
Lu	0.20	0.28	0.24	0.21	0.18	0.28	0.22	0.22	0.29	0.08	0.22	0.20	0.19	0.19	0.21	0.28	0.22
Pb	1.9	2.3	2.2	2.2	1.7	3.7	2.4	2.3	4.0	1.0	1.8	1.7	1.8	1.8	2.0	3.34	1.78
Th	2.4	3.4	2.9	2.6	2.2	5.4	3.6	3.6	4.1	1.5	1.8	2.0	2.0	2.0	2.0	4.38	1.78
U	0.82	2.21	1.19	1.03	0.55	1.14	1.10	1.05	0.70	0.62	0.58	0.77	0.78	0.78	0.70	1.35	0.56

$Fe_2O_3^T$  — total Fe as  $Fe_2O_3$ ; Norms:  $FeO/(FeO + Fe_2O_3) = 0.85$ ; submarine-altered basalt samples (7, 11, 14, 15 and 16) of the Fuchsia hole (Mururoa) are from depths ranging from between 677.6 and 720.0 m; subaerially-altered basalt samples (32, 37, 40 and 43) of the Fuchsia drill hole are from a depth between 579.4 and 616.2 m below the present surface; hydrothermally-altered samples (516, 589, 721 and 815) of the Mitre drill hole (Fangataufa) are from depths ranging between 516 and 815 m. Alteration temperature:  $\sim 200^\circ C$  (samples 516 and 589) and  $\sim 300^\circ C$  (samples 721 and 815).

MUR — average of five representative fresh samples from Viviane drill hole on Mururoa atoll (V3592, V3970, V4792, V8310, V8502 — Dupuy *et al.*, 1993) supplemented by B, Be, Li, Nb (Table 2), Zr and Pb data, FANG — average of three representative fresh samples from Fangataufa atoll (Fa 608, Fa 682.7, Fa 808 — Dupuy *et al.*, 1993) supplemented by B, Be, Li, Nb (Table 2), Zr and Pb data.

TABLE 2. Boron, beryllium and lithium analysis of Polynesian ocean island basalts

Sample	B(ppm)	Be(ppm)	Li(ppm)	Nb(ppm)	Pb(ppm)	Th(ppm)	U(ppm)	Refs.
<b>Gambier</b>								
MG 10E	2.1	1.42	5.0	48				1
TR 14S	3.0	1.26	4.8	40				1
AG 29D	2.6	1.64	5.1	37				1
AK 34H	1.9	1.18	5.4	33	1.97	2.09	0.53	1
KM 7L	1.9	1.11	5.2	32	1.84	1.91	0.63	1
<b>Mururoa</b>								
V3592	6.4	2.84	8.2	93	3.93	5.23	1.66	1
V3970	3.4	1.66	6.2	47	2.50	3.11	0.86	1
V4792	4.1	1.82	6.3	60	3.19	3.61	1.19	1
V8310	4.3	2.68	9.8	86	3.62	5.06	1.57	1
V8502	3.0	2.62	7.4	84	3.44	4.88	1.48	1
<b>Fangataufa</b>								
FA 608	3.5	1.42	5.6	39	2.31	2.40	0.74	1
FA 682.7	2.1	0.88	4.2	24	1.33	1.46	0.43	1
FA 808	2.4	1.02	4.3	27	1.71	1.49	0.51	1
<b>Ua Pou</b>								
UAP 011	2.9	1.24	5.3					2
UAP 017	2.0	0.92	4.0					2
UAP 024	2.2	1.14	4.1					3,4
UAP 026	5.4	1.94	8.3					2,3
UAP 166	5.2	1.78	6.8					6
UAP 167	2.9	1.05	3.1					6
UAP 171	5.3	2.28	8.8					6
<b>Tubuai</b>								
TBA-09	1.6	1.54	4.4					4
TBA-11	2.6	2.50	6.2					4
TBA-36	2	1.40	5.5					5
<b>Rurutu</b>								
RRT-32	3.8	1.17	6.0					4
RRT-37	5.9	1.49	5.1					5
RRT-60	4.0	2.66	11.0					5
RRT-15	5.9	2.43	9.9					5
<b>Rarotonga</b>								
RTG-32	2.4	1.10	4.6					6
RTG-33	2.8	0.32	5.2					6
RTG-34	2.9	1.21	5.0					6
RTG-35	3.6	1.40	5.3					6

Refs.: 1 — Dupuy *et al.* (1993); 2 — Liotard *et al.* (1986); 3 — Dupuy *et al.* (1987); 4 — Dupuy *et al.* (1989); 5 — Dupuy *et al.* (1988); 6 — Dupuy and Dostal (in prep.)

Nb and La) and lower La/Yb ratios (8–12; Fig. 1) relative to the Mururoa basalts and Fangataufa alkali basalt suite (Dupuy *et al.*, 1993).

#### Effects of alteration

The altered basalts of the Mururoa can be visually subdivided into three categories based on petrography: weakly altered, moderately altered and strongly altered. Petrographically, increasing alteration is seen primarily as an increase of the amount of secondary minerals. In weakly altered samples from the core of the flows, secondary minerals replaced olivine and filled rare veinlets and amygdules. In the strongly altered samples from the outer parts of the flows, most primary phases were replaced by secondary minerals. Moderately altered samples are from the middle part of the flows. Among the submarine-altered basalts, this petrographic series of apparently increasing intensity of alteration correlates to increasing LOI (loss-on-ignition) and leads to silica-oversaturation of the originally silica-under-saturated basalts. The slightly altered basalts of the Mururoa (samples 11 and 14) are, like their unaltered precursors (Dupuy *et al.*, 1993), nepheline-normative, the moderately altered rock (sample 7) is olivine-normative whereas the strongly altered basalts (samples 15 and 16) are quartz-normative (Table 1). The latter basalts are depleted in Ca and Mn relative to the other basalts. The major element composition of the subaerially altered basalts is relatively uniform; they have nepheline and (in some instances) olivine in their norms (Table 1). Sample 43 Sap is a strongly subaerially altered part of a highly brecciated, outer rim of a flow; the sample is composed mainly of saponite.

The basalts of the Fangataufa intrusive bodies are pervasively altered by magmatic fluids (Dudoignon *et al.*, 1992). They mainly differ by the temperature of alteration as determined by stable isotope (C and O) systematics (Dudoignon *et al.*, 1992). Samples 516 and 589 recorded temperatures of 200°C, whereas samples 721 and 815 gave temperatures of 300°C. Their major element composition is relatively uniform (Table 1); they are mostly quartz-normative although some are also olivine-normative. Compared with fresh tholeiitic equivalents from Fangataufa, the major elements of the hydrothermally-altered rocks were not substantially modified.

#### Trace Elements

*REE, HFSE, Th, U and Pb.* Like their fresh equivalents, the altered OIB from Mururoa have higher contents of strongly incompatible trace elements than the altered tholeiites of Fangataufa (Table 1). Chondrite-normalized rare-earth element

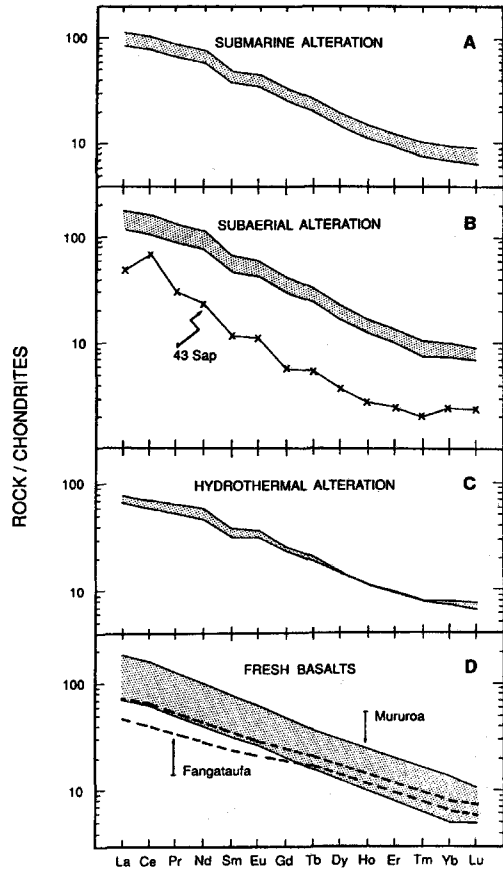


FIG. 1. Chondrite-normalized REE patterns of the altered and fresh basalts from the Mururoa and Fangataufa islands. Normalizing values after Sun (1982).

- A — Range of submarine-altered basalts from Mururoa (sea water alteration)
- B — Range of subaerially-altered basalts from Mururoa (meteoric water alteration)
- C — Range of hydrothermally-altered basalts from Fangataufa (alteration by high- $T$  [ $>200^{\circ}\text{C}$ ] magmatic fluids).
- D — Ranges of fresh Mururoa and Fangataufa basalts (after Dupuy *et al.*, 1993).

(REE) patterns of the altered Mururoa and Fangataufa basalts are typical of OIB, being marked by an enrichment of light REE (LREE), and fractionated heavy REE (HREE) (Fig. 1). They are subparallel (Fig. 1) and fall within the range of fresh basalts from Mururoa and Fangataufa (Dupuy *et al.*, 1993), respectively. The relatively constant LREE distribution was also previously reported by Schiano *et al.* (1993) from variably altered Fangataufa basalts.

The abundances of incompatible elements in the altered basalts normalized to an average for appropriate fresh ones (Table 1) to emphasize chemical differences are shown in Fig. 2. The altered Mururoa basalts are normalized to the average of five fresh basalts from the Viviane drill hole at Mururoa (Table 1) that were considered to be representative of the Mururoa OIB (Dupuy *et al.*, 1993). The normalizing values for the Fangataufa rocks (Table 1) are the average of three fresh basalts reported by Dupuy *et al.* (1993). The patterns suggest that high-field-strength elements (HFSE) and REE were not significantly affected by the alteration. This is further supported by high positive correlation coefficients for element pairs such as Zr-Ta (0.98), Nb-La (0.99), Ta-La (0.97), Zr-Sm (0.99), Nb-Ta (0.99), Hf-Sm (0.97) and Zr-Hf (0.97) in the set containing fresh and altered rocks from Mururoa and Fangataufa. The exception is saponite sample 43 Sap, which is significantly depleted both in REE and in HFSE. The saponite has a higher La/Yb ratio (30; Fig. 1) than the basaltic samples, and a positive Ce anomaly indicating some REE mobility under very advanced subaerial alteration. The positive Ce anomaly in secondary minerals, such as saponite, which are common in oceanic crust, may significantly contribute to the origin of the negative Ce anomaly characteristic of sea water (de Baar *et al.*, 1985).

The patterns of the altered rocks (Fig. 2) indicate that Th is inert during secondary processes. This is also shown by the positive correlation of Th with immobile incompatible trace elements such as Nb and the constancy of the Th/La ratios within and between three alteration types (Fig. 3). The values of these ratios are close to those of the fresh basalts from Mururoa, Fangataufa and Gambier (Fig. 3). Unlike Th, uranium appears to be mobile during subaerial and submarine alteration as previously suggested by Hart and Staudigel (1986). In the subaerially strongly altered basalts, U is slightly depleted (Fig. 2). In the submarine altered basalts, U is enriched in weakly altered samples (Fig. 2), particularly in sample 11 which contains a small amount of zeolites. Uranium is slightly depleted in strongly altered clay mineral-rich sample 16. The distribution of U does not seem to be distinctly affected in the hydrothermally altered basalts (Figs. 2 and 3). This suggests that hydrothermal alteration does not have a significant effect on U concentrations in OIB and is consistent with the studies of Michard *et al.* (1983, 1984) who have shown that high temperature alteration of oceanic crust does not noticeably affect U abundances. The immobility of U in hydrothermal systems may be due to reducing conditions of hydrothermal fluids as opposed to an oxidizing environment during subaerial and submarine low-temperature alteration.

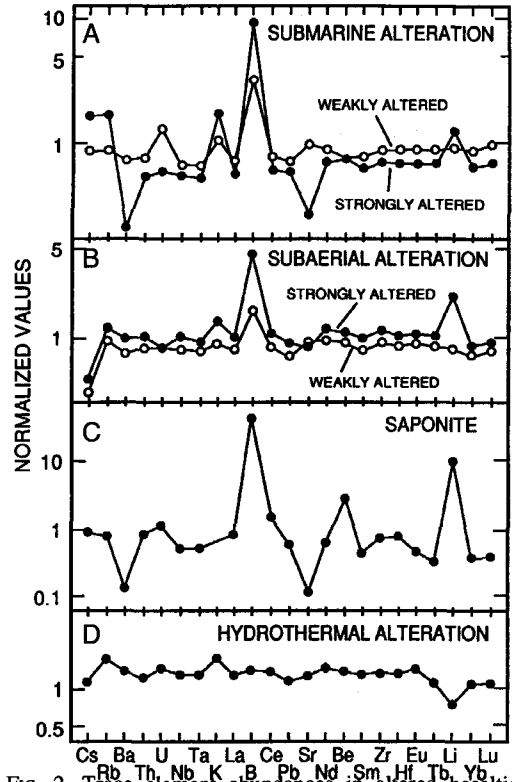


Fig. 2. Trace element abundances in altered basaltic rocks from the Mururoa and Fangataufa islands normalized to fresh basaltic equivalents.

A — Submarine alteration : Weakly altered (average of samples 11 and 14) and strongly altered (average of samples 15 and 16)

B — Subaerial alteration : Weakly altered (sample 37) and strongly altered basalts (average of samples 32 and 40)

C — Saponitic sample (43 Sap) from subaerially altered basalt

D — Hydrothermally-altered basalts (average of samples 516, 589, 721 and 815).

The Mururoa altered samples (A, B and C) were normalized to average of 5 fresh Mururoa basalts, whereas the Fangataufa samples (D) altered by high temperature (> 200°C) magmatic fluids were normalized to average of 3 fresh tholeiitic basalts from Fangataufa (Table 1).

The scatter of Pb data from the drill-hole samples as compared with those from the fresh basalts when plotted against Nb (Fig. 3) indicates a small degree of Pb redistribution during subaerial and submarine alteration. The distribution of Pb in these rocks implies that the ratios of Ce/Pb and Th/Pb in OIB,



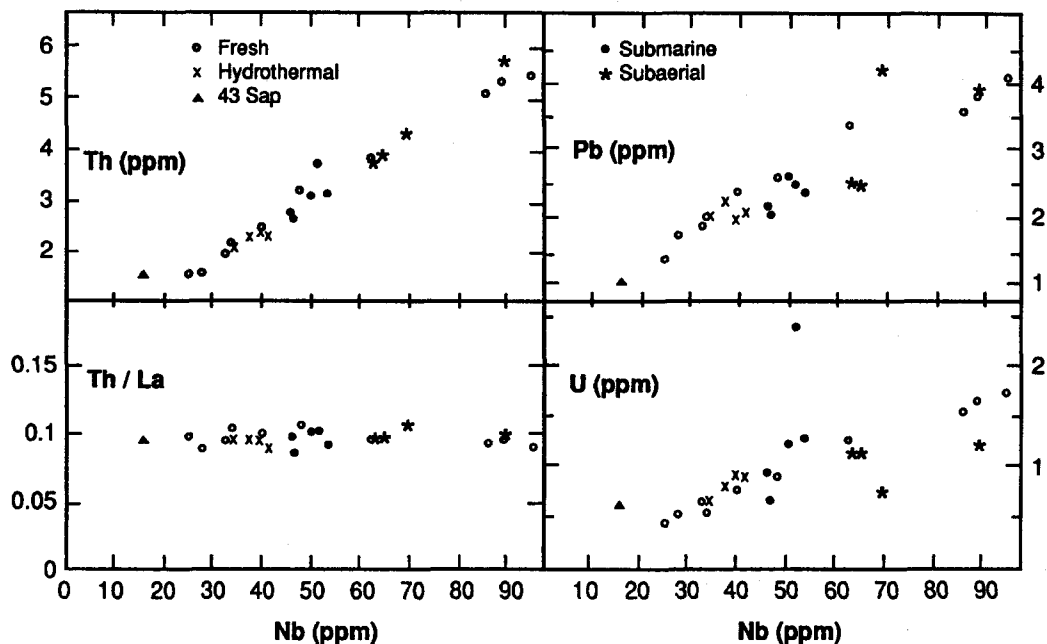


FIG. 3. The variations of Th, Pb and U concentrations (in ppm) and Th/La ratios versus Nb (in ppm) in the altered and fresh basaltic rocks of the Mururoa, Fangataufa and Gambier islands. Full circles: subaerially-altered basalts (meteoric water alteration); asterisks: submarine-altered basalts (sea water alteration); x : hydrothermally-altered basalts (alteration by magmatic fluids); full triangle: saponite-rich sample 43 Sap. Empty circles: fresh basalts from the Mururoa, Fangataufa and Gambier islands (Tables 1 and 2; Dupuy *et al.*, 1993).

which have been used to characterize the mantle sources (Sun and McDonough, 1989; Weaver, 1991), can be confidently used to constrain the petrogenetic processes even in moderately altered rocks.

These results support previous studies on trace element behaviour during rock alteration (e.g. Staudigel and Hart, 1983; Bienvenu *et al.*, 1990; Gillis *et al.*, 1992) which showed that the least mobile incompatible trace elements are HFSE, REE and Th. The relative mobility of B, Be and Li during the OIB alteration is therefore evaluated with respect to these elements.

**Beryllium.** The Be contents in the altered rocks vary within a narrow range (Table 1) and are comparable to those of the fresh OIB (Figs. 2 and 4). This similarity and the constancy of the Be/Nd ( $0.045 \pm 0.005$ ; Fig. 4) as well as Be/Hf ( $0.30 \pm 0.04$ ; Fig. 4) and Zr/Be ( $145 \pm 16$ ) ratios suggest that alteration did not affect Be distribution. Beryllium correlates with other incompatible elements (Fig. 4). The decrease of the Be/La and Be/Ce ratios and the constancy of the Be/Nd ratios with the increase of the abundances of strongly incompatible trace elements such as Ta or Nb (Fig. 4) indicate that Be is less

incompatible than La and Ce (Ryan and Langmuir, 1988) and has bulk solid-liquid partition coefficients for basaltic melts close to those for Nd and Sm. The high Be/Nd ratio in the saponite 43 Sap (Be/Nd = 0.21) is related in part to the decrease of the Nd content (Fig. 1; Table 1) and probably in part to a Be enrichment in this sample (Fig. 4).

Beryllium contents of fresh Polynesia OIB vary from < 1 ppm to 3 ppm (Table 2; Fig. 5), within a range of young OIB given by Ryan and Langmuir (1988). These values are generally higher than those of mid-ocean ridge basalts (MORB) and arc basalts which are low and undistinguishable (Fig. 5; Ryan and Langmuir, 1988). All these rocks have a similar Be/Nd ratio ( $\sim 0.05$ ) that is also similar to chondritic values ( $\sim 0.05$ ) but significantly lower than that of continental crust ( $\sim 0.09$ ; Taylor and McLennan, 1985; Ryan and Langmuir, 1988). The high Be/Nd ratio in the continental crust relative to the mantle probably reflects fractionation of these elements during the formation of continental crust. Assuming analogous bulk distribution coefficients during mantle melting for Nd and Be and a primitive mantle content of 1.354 ppm Nd (Sun and

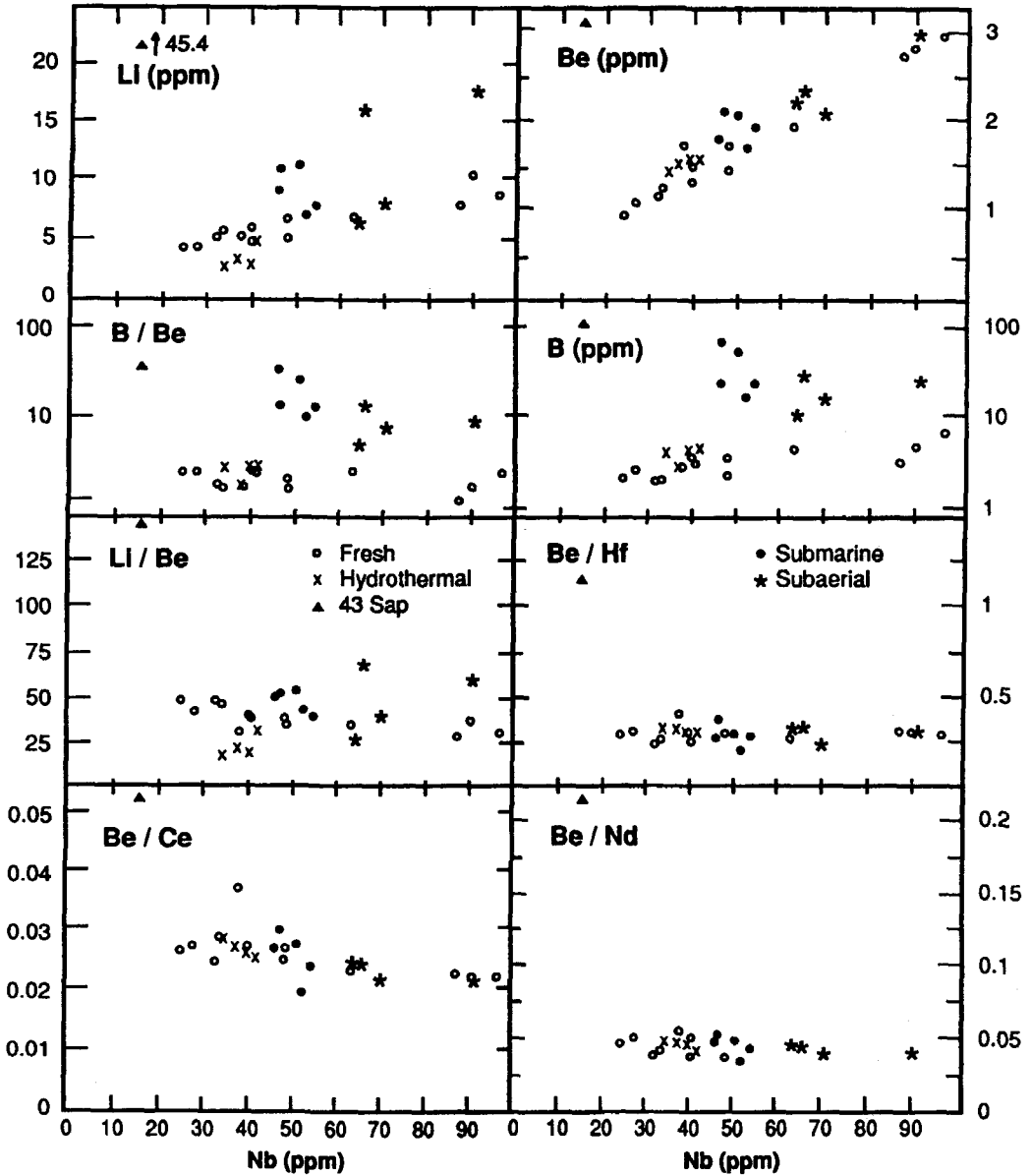


FIG. 4. The variations of B, Li and Be concentrations (in ppm) and B/Be, Li/Be, Be/Hf, Be/Ce and Be/Nd ratios versus Nb (in ppm) in the altered and fresh basaltic rocks of the Mururoa, Fangataufa and Gambier islands. Full circles: subaerially-altered basalts (meteoric water alteration); asterisks: submarine-altered basalts (sea water alteration); x: hydrothermally-altered basalts (alteration by magmatic fluids); full triangle: saponite-rich sample 43 Sap. Empty circles: fresh basalts from the Mururoa, Fangataufa and Gambier islands (Tables 1 and 2; Dupuy *et al.*, 1993).

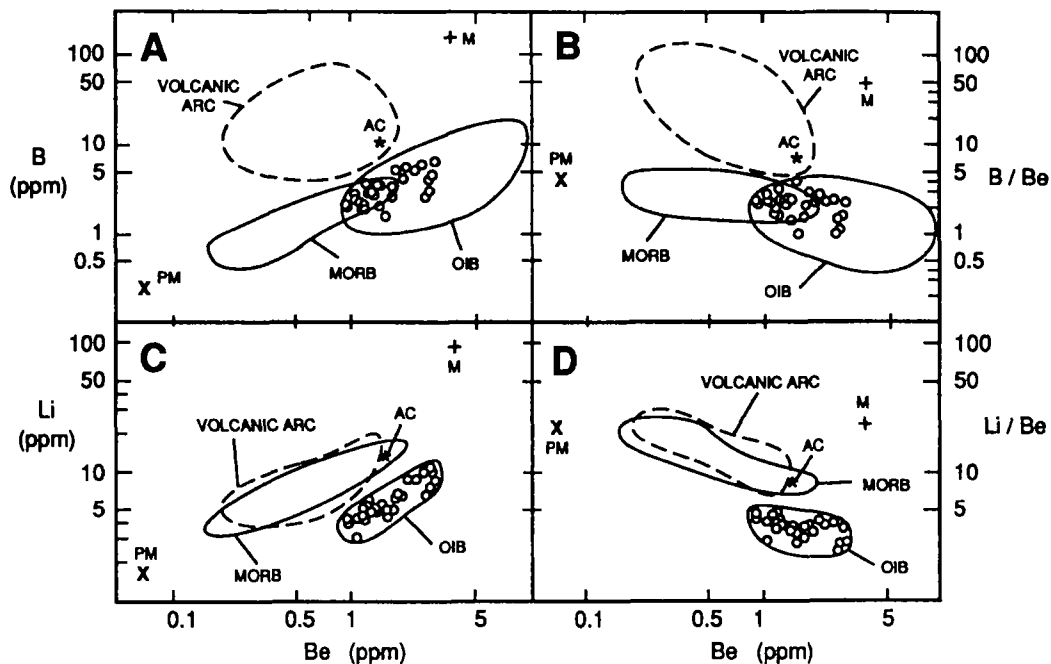


FIG. 5. The variations of B and Li concentrations (in ppm) and B/Be and Li/Be ratio versus B (in ppm) in presumed fresh basalts from various Polynesian Islands (Fangataufa, Mururoa, Gambier, Ua Pou, Tubuai, Rarotonga and Rurutu, Table 2). The fields for MORB, OIB and volcanic arc basaltic rocks are from various published sources, particularly Ryan and Langmuir (1987, 1993), Morris *et al.* (1990) and Edwards *et al.* (1993). PM — primitive mantle (B — Chaussidon and Jambon, 1994; Be — this study; Li — Sun and McDonough, 1989); AC — bulk continental crust (Taylor and McLennan, 1985); M — USGS standard marine mud MAG-1 (Govindaraju, 1994).

McDonough, 1989), the Be content of primitive mantle should be about 0.07 ppm. This value is close to the Be data for chondritic meteorites which range between 0.025 and 0.05 ppm (Quandt and Herr, 1974; Anders and Ebihara, 1982). The mantle-normalized values for Be in OIB from French Polynesia are comparable to those of Sm, Nd, Zr and Hf (Fig. 6).

#### Relatively mobile trace elements

Unlike the HFSE, REE and Be, several other incompatible trace elements including Sr, Ba, Rb, Li and B in the altered basalts have been affected by secondary processes. The patterns of the trace element abundances normalized to the fresh basalts (Fig. 2) show that the rocks affected by strong submarine alteration (samples 15 and 16) and also the saponite-rich sample (43 Sap) are depleted in Ba and Sr (and also CaO) relative to the other incompatible elements. The depletion is probably related to the breakdown of glass because fresh plagioclase is still

present. These rocks are enriched in K, Rb and Cs (Fig. 2), possibly due to the abundance of secondary phyllosilicates (Staudigel and Hart, 1983). The subaerially-altered rocks are depleted in Cs whereas the basalts altered by magmatic fluids are slightly enriched in K and Rb (Fig. 2). In the various types of altered rocks, Rb and Cs have high correlation coefficients ( $R = 0.99$ ).

**Lithium.** The tholeiitic basalts altered by relatively high  $T$  ( $> 200^{\circ}\text{C}$ ) magmatic fluids are slightly impoverished in Li ( $< 5$  ppm) compared with the fresh Fangataufa basalts (Figs. 2 and 4). The decrease in Li concentrations leads to fractionation of the K/Li ratio which significantly increased (to  $> 2,000$ ) from the values of 600–1000 in the fresh Fangataufa tholeiites. Lithium does not appear to be affected in basalts modified weakly by the submarine and subaerial alteration. However, Li abundances slightly increased during advanced subaerial and submarine alteration (Fig. 2) and are enhanced relative to REE in the strongly altered samples. The saponite sample is distinctly enriched in Li (Fig. 2). The Li

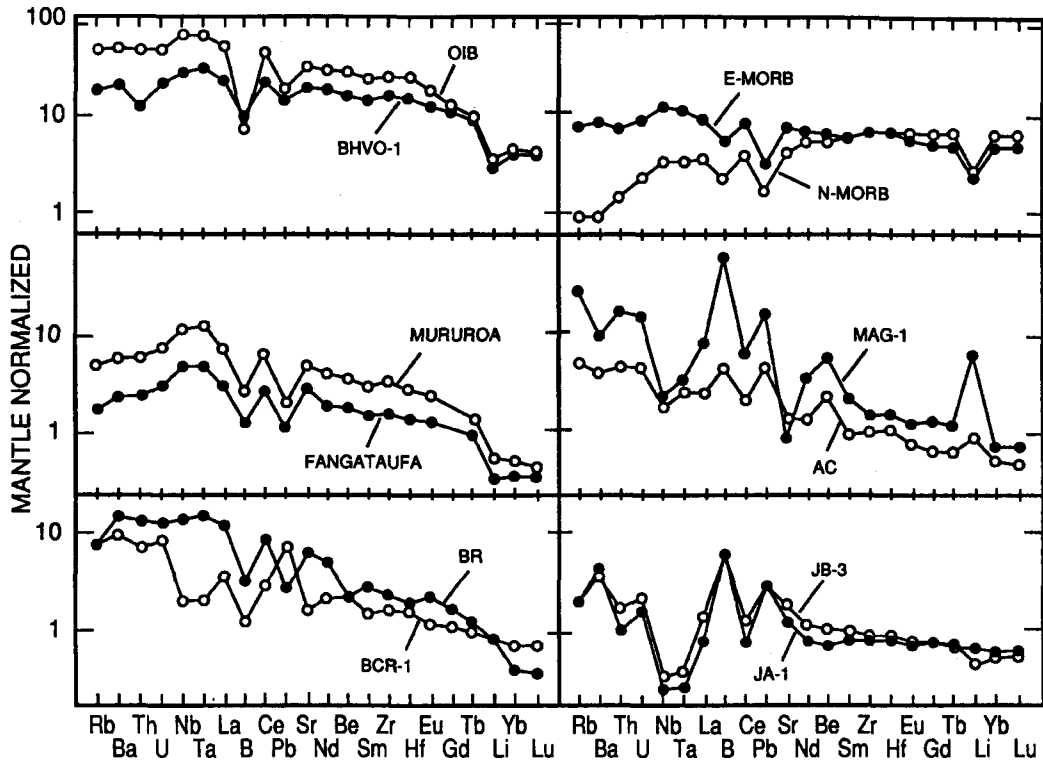


FIG. 6. Primitive mantle-normalized trace element abundances. A: OIB — average ocean island basalt of Sun and McDonough (1989) with B value of Chaussidon and Jambon (1994) and Be calculated from  $Be/Nd = 0.05$ , BHVO-1 — USGS standard basaltic lavas from Kilauea, Hawaii (Govindaraju, 1994); B: N-MORB and E-MORB — average composition of N-type and E-type MORB of Sun and McDonough (1989) with B value of Chaussidon and Jambon (1994) and Be calculated from  $Be/Nd = 0.05$ ; C: Mururoa and Fangataufa — average compositions of fresh Mururoa alkali basalts and Fangataufa tholeiitic basalts, respectively (Table 1); D: AC — average composition of continental crust (Taylor and McLennan, 1985), MAG-1 — USGS standard marine mud MAG-1 (bottom sediment, Gulf of Maine; Govindaraju, 1994); E: BCR-1 — USGS standard Columbia River Group basalt, BR — CRPG standard continental alkali basalt from Essey-la-Cote, Nancy, France (Govindaraju, 1994); F: JA-1 — GSJ standard Quaternary augite-hypersthene andesite, Hakone, Japan; JB-3 — GSJ standard high-alumina basalt, Fuji, Japan (Govindaraju, 1994). Normalizing values of primitive mantle after Sun and McDonough (1989) with B values of 0.25 ppm after Chaussidon and Jambon (1994) and Be of 0.07 ppm (this study).

concentrations in the basalts altered by sea water and meteoric water correlate with LOI showing high correlation coefficients ( $R = 0.98$  and  $0.87$ , respectively). The relative decrease of Li in basalts during higher temperature alteration but its increase during lower temperature processes is consistent with the experimental study of Seyfried *et al.* (1984) which showed that Li is highly soluble at  $375^{\circ}\text{C}$  and can be leached from basalt. Seyfried *et al.* (1984) also found that, at lower temperature ( $150^{\circ}\text{C}$ ), Li can be removed from seawater and incorporated into altered basalt. Shaw and Sturchio (1992) attributed the increase of Li in rhyolites during low- $T$  aqueous

alteration to its absorption on clay minerals, and Li depletion in hydrothermally-altered rocks to leaching. A similar explanation can probably be invoked for the basalts analysed in this study. The alpha tracks show that in the submarine- and subaerially strongly altered rocks, Li is mainly present in secondary phases and primary minerals have low abundances. Primary and secondary minerals have uniformly low Li concentrations in samples subjected to higher  $T$  hydrothermal alteration.

Lithium abundances in fresh OIB, including those from Mururoa and Fangataufa, usually range between 3 and 10 ppm (Fig. 4). These concentrations are

typical of OIB (Fig. 5; Ryan and Langmuir, 1987) and are similar to those of MORB (usually 5–6 ppm; Bailey and Gwozdz, 1978, Bryan *et al.*, 1979) and arc basalts. In the Polynesian OIB, Li correlates positively with other incompatible elements (Figs. 4 and 5).

Compared with fresh volcanic rocks, ocean sediments and altered oceanic crust are significantly enriched in Li (Holland, 1980; Donnelly *et al.*, 1980). In marine sediments, Li ranges between 10 and 150 ppm. Since Li is distinctly enriched in altered oceanic crust and ocean sediments, the element could serve as an indicator of a subducted slab contribution to the mantle source regions of arc and OIB magmas. However, the data show that there is no obvious difference in Li abundances between HIMU (long-term high U/Pb)-type (Rurutu, Ua Pou, Tubuai) and EM (enriched mantle)-type (Rarotonga) OIB (Table 2).

**Boron.** The large range of B concentrations in the drill samples reflects its mobility during alteration processes. The abundances of B in basalts altered by submarine and subaerial processes are significantly higher than in fresh OIB (Fig. 4) and display a distinct positive anomaly on the fresh-rock normalized plots (Fig. 2), even in the weakly altered rocks. In the altered rocks, B correlates with LOI ( $R = 0.89$  — submarine and  $0.99$  — subaerially-altered rocks, respectively). Among the subaerially-altered samples, the highest B abundances are in saponite-rich sample 43 Sap ( $\sim 110$  ppm) whereas clay mineral-rich sample 16 (B  $\sim 60$  ppm) has the highest B content encountered among the submarine-altered samples. In the submarine- and subaerially-altered suites, B correlates with Li concentrations ( $R = 0.89$  and  $0.94$ ). The data indicate that B is mobilized and enriched during earlier stages of the alteration process more readily than Li (Fig. 2), alkalis and alkali earth elements. B contents and B/Nb in the samples altered by magmatic fluids at  $T > 200^\circ\text{C}$  are comparable to the fresh OIB (Fig. 4) and do not appear to be affected by this secondary process.

Alpha-track images were used to evaluate the distribution of B in the altered basalts. In the submarine- and subaerially-altered basalts, the bulk of B is present in secondary phases. Primary minerals have very low B abundances. Saponite and mixed chlorite/celadonite layer clays, which occur in amygdules and veinlets and also replace glassy groundmass, appear to be the main B carriers. Rare, reddish Fe oxides strongly concentrate B. Phillipsite and other zeolites have lower B abundances. All secondary minerals including saponite, carbonates, chlorite/saponite and other clays have uniformly low B concentrations in the magmatic fluid-altered basalts.

During processes which involve a fluid phase, one of the factors which affects the behaviour of B is the

fluid temperature. Boron, like Li, can be extracted from fluids during low- $T$  alteration ( $< 100^\circ\text{C}$ ). It is scavenged by secondary silicate minerals such as saponite (Fig. 2). The increase of boron during low-temperature rock alteration has already been documented by experimental studies of Seyfried *et al.* (1984). They showed that B is extracted from sea water by alteration phases at  $150^\circ\text{C}$  and is more readily mobilized than Li and other alkalis. During higher-temperature hydrothermal alteration by magmatic fluids ( $T > 200^\circ\text{C}$ ), solubility of B in fluids exceeds that in alteration assemblages even if phases such as saponite are present. This is also consistent with the experimental studies of Seyfried *et al.* (1984) which indicate that B has an affinity for the fluid phase at  $375^\circ\text{C}$  when it was leached from basalt. Similarly, Spivack *et al.* (1992) showed that B is strongly partitioned into the fluid phase when a typical oceanic slab material is heated above  $150^\circ\text{C}$ . The temperature dependant behaviour of B is also supported by Bonatti *et al.* (1984) who noted that B contents of serpentinite correlate negatively with serpentinization temperature.

In the fresh Polynesian OIB rocks, B shows a positive correlation with other strongly incompatible elements such as Nb (Fig. 4), LREE, Be (Fig. 5), Li and K. In these rocks (Table 2), the concentration of B varies from 1 to 8 ppm (Fig. 5). A similar range of B abundances in OIB was reported by Morris *et al.* (1990) and Ryan and Langmuir (1993). A comparison with their data indicate that the Dupal-type OIB (cf. Sun and McDonough, 1989) are not enriched in B relative to other OIB. Likewise, there is no obvious difference in B among the basalts containing the contrasting mantle end-member components of Zindler and Hart (1986), in particular between the HIMU- and EM-type (Table 2). Compared with MORB (Ryan and Langmuir, 1993; Chaussidon and Jambon, 1994), B is usually higher in OIB (Fig. 5). However, both these types are significantly lower in B than arc rocks (Fig. 5). The B abundances in these mantle-derived basalts are usually lower than those of the average continental crust ( $\sim 10$  ppm — Taylor and McLennan, 1985) and sedimentary rocks (Fig. 5). Shales and marine sediments contain on average about 100 ppm B (Harder, 1970; Dean and Parduhn, 1983).

#### *Significance of B/Be and Li/Be ratios*

Since in basaltic systems B has a degree of incompatibility similar to Be, the B/Be ratio is not significantly modified by partial melting and fractional crystallization processes (Morris *et al.*, 1990; Edwards *et al.*, 1993). Therefore, the B/Be ratio of fresh volcanic rocks might be an important petrogenetic indicator of the presence of altered

oceanic crust or a sedimentary component in a mantle source provided that B/Be has not been affected by alteration processes. The B/Be ratios in the altered basalts vary widely (Fig. 4) because of boron mobility. Both altered subaerial and submarine basalts have B/Be ratios  $> 5$  with the highest values ( $\sim 33$ – $36$ ) in clay- and saponite-rich ( $\sim 36$ ) samples (16 and 43 Sap, respectively). These values are significantly higher than the B/Be ratios for the fresh basalts (1–4) which resemble MORB and other OIB (Fig. 5; Ryan and Langmuir, 1993). Arc tholeiitic and calc-alkaline volcanics have significantly higher B/Be ratios (Fig. 5; Ryan and Langmuir, 1993; Edwards, *et al.*, 1993). The high B/Be ratio in arc rocks probably results from hydrous fluids stripping the subducted slab (Ryan and Langmuir, 1993; Edwards *et al.*, 1993).

Ocean sediments and altered oceanic crust that are significantly enriched in B, have high B/Be ratios ( $\sim 100$  and  $30$ – $170$ , respectively; Edwards *et al.*, 1993). However, the various OIB representing different isotopic end-member components in the mantle source, including HIMU and EM, have similar B/Be ratios that are also comparable to MORB (Fig. 5; Table 2). The relatively small range for this ratio implies that the mantle source region for OIB and MORB is rather homogeneous in terms of B/Be ratios. However, the low B/Be ratio in the OIB rocks does not necessarily indicate that a subducted component (altered basalt or sediment) is absent in the mantle source region. The data from the subduction-related metamorphic assemblages (Morgan *et al.*, 1992; Bebout *et al.*, 1993) show that boron contents and B/Be ratios decrease steadily during prograde subduction-related metamorphism such that sediments and altered crust, starting with  $\sim 100$  ppm B and a B/Be ratio of  $80$ – $100$ , end up with B/Be  $\sim 10$ – $20$ . Thus, the high B/Be ratios seen in volcanic arcs require an effective process of distilling B out of the slab, leaving the residue even more depleted in B. This is supported by low B/Be ratios ( $< 10$  and often  $< 5$ ) in behind-the-front volcanoes in the Aleutians and the Bismarck Sea (Morris *et al.*, 1990) and in Kuriles (Ryan and Langmuir, 1993). Also, granulites are distinctly depleted in B compared with upper continental crust (Truscott *et al.*, 1986; Leeman *et al.*, 1992). If B is effectively stripped from the slab during subduction processes, a subduction component in the OIB source would not be enriched in B.

Compared with the fresh Polynesian basalts with Li/Be values (2.5–5) close to the average (4) for OIB of Ryan *et al.* (1989), the hydrothermally-altered basalts (Fig. 4) have slightly lower Li/Be ratios (2–3), reflecting the minor loss of Li. The strongly subaerially-altered basalts have higher Li/Be ratios (7 and 15) probably due to the gain of Li. Like B, the

behaviour of Li is also affected by hydrous fluids, although Li is less mobile (Seyfried *et al.*, 1984).

In basaltic systems, Li behaves as incompatibly as B and Be (Ryan *et al.*, 1989) and like B/Be, the Li/Be ratio can be used to constrain the chemical characteristics of the mantle sources and/or processes. Li is strongly enriched in ocean sediments and altered oceanic crust (Li/Be  $\sim 20$ – $30$ ) and is partitioned at higher temperatures into hydrous fluids. Therefore, Li/Be as well as Li/K could potentially be indicative of the presence of recycled crust in the mantle source region. Figure 5 shows that the OIB have lower Li/Be ratios than the MORB and arc basalts. In fact, OIB including those which show isotopic effects of a subducted crust or sediment component, have low and similar Li/Be ratios. However, as in the case of the B/Be ratio, the low Li/Be values do not preclude the recycled oceanic crust or sediments in the OIB mantle source. Sighinolfi and Gorgoni (1978) found that most of Li in rocks is released during granulite facies metamorphism suggesting that Li is stripped from rocks during subduction. Furthermore, Ryan *et al.* (1989) noted that the Li/Be ratio, like B/Be, decreases away from the arc front indicating that in the subduction zone, Li was released into a hydrous fluid phase that invaded the overlying mantle wedge. The low Li/Be and B/Be ratios in OIB indicate that both Li and B were removed from the subducted slab at shallow depths and were not involved in the deep recycling.

#### *Distribution of B and Li in basaltic rocks*

Hofmann (1988) has shown that the mantle-normalized element compositions of continental and oceanic crusts (latter represented by MORB), plotted according to increasing bulk partition coefficient values in MORB, form complementary concentration patterns. In addition to contrasting shapes, the plots differ by the presence of complementary anomalies for Nb-Ta and Pb. The oceanic pattern is characterized by a positive Nb-Ta and a negative Pb anomaly whereas the continental one is marked by the relative depletion of Nb-Ta and enrichment of Pb. The element relationships were interpreted in terms of a two-stage differentiation model of the mantle. Hofmann (1988) argued that after the initial extraction of continental crust, the residual mantle was rehomogenized prior to the second melting events which generated the oceanic crust. The anomalous behaviour of Pb, Nb and Ta was attributed to contrasting bulk partition coefficients of these elements during two distinct geochemical processes which produced continental and oceanic crusts, respectively.

The addition of B, Be and Li to the mantle-normalized concentration plots can provide some further information on the mantle source regions. The

sequence of elements in Fig. 6 corresponds to the increasing order of trace element incompatibility in oceanic basalts according to Sun and McDonough (1989). In addition, since Be and Nd behave very similarly during basalt genesis (Ryan and Langmuir, 1988), Be was placed next to Nd in Fig. 6. Ryan and Langmuir (1993) noted that a degree of incompatibility of B in MORB is comparable to light REE and hence B is plotted between La and Ce (Fig. 6). The behaviour of Li in MORB and OIB is analogous to Yb and Dy (Ryan and Langmuir, 1987) and thus as Sun and McDonough (1989) suggested the element is next to Yb in Fig. 6.

The patterns of the average compositions of N-MORB and E-MORB show relative depletion of Pb and also of B and Li (Fig. 6). Ocean island basalts, represented by the OIB average of Sun and McDonough (1989), USGS standard Hawaiian basalt BHVO-1 and the averages of Mururoa and Fangataufa basalts in Fig. 6, are also depleted in B, Pb and Li. Like the case of Pb (Hofmann, 1988), the negative B and Li anomalies of oceanic basalts suggest that these elements are depleted relative to other incompatible elements in oceanic mantle. On the other hand, the average continental crust (Taylor and McLennan, 1985) and typical crustal rocks including USGS standard marine mud (MAG-1), are distinctly enriched in Pb, B and Li (Fig. 6), and display patterns complementary to oceanic basalts. The depletion of B and Li in oceanic basalts and their enrichment in continental crust is probably due to the same processes as the anomalies of Pb and Nb and can be explained by the two-stage model of Hofmann (1988) for crustal generation.

The continental mantle appears to be heterogeneous in terms of the distribution of these elements. The contrasting patterns of various continental basaltic rocks indicate that there are probably different causes for the B, Li and Pb anomalies in continental rocks. The size of the positive B anomaly in various continental rocks is significantly affected by processes associated with subduction, particularly by a release from the slab of hydrous fluids enriched in B (Edwards *et al.*, 1993; Ryan and Langmuir, 1993). On the one hand, the patterns of arc basalts and andesites like those from Japan (standard rocks JB-3 and JA-1, Fig. 6) display negative anomalies for Nb and Ta but positive ones for Pb and B probably reflect the continental environment and the effect of the subduction zone. On the other hand, the Columbia River plateau basalt BCR-1 with negative Nb, Ta and B anomalies accompanied by a Pb enrichment (Fig. 6) may indicate a continental environment without the subduction-related enrichment of the source. Some continental within-plate basalts, including alkali basalt from Nancy, France (standard rock BR — Fig. 6), show a pattern similar

to those of OIB characterized by negative Pb and B anomalies. These similarities suggest their generation from a source region analogous to the source of oceanic alkali basalts and without significant upper crustal contamination. It appears that these elements can be useful indicators of tectonic setting and the effects of subduction or suprasubduction in mantle source regions.

### Conclusion

Beryllium is an incompatible trace element which is relatively immobile during the hydrothermal alteration of OIB. The beryllium content of the primitive mantle is estimated to be about 0.07 ppm. In basaltic magma systems, B behaves like Be. However, during lower-*T* hydrothermal alteration, B is mobile and typically becomes enriched in altered volcanic rocks. The increase of the B/Be ratio in these rocks is related to the presence of secondary minerals such as saponite and other clay minerals which preferentially contain boron. Higher *T* hydrothermal alteration (>200°C) of OIB does not appear to affect the bulk B content. During low *T* hydrothermal alteration, Li is mobile only at more advanced stages. Unlike B, Li is partially removed from the OIB during higher *T* hydrothermal alteration (> 200°C). Low *T* alteration leads to an increase of B/Be, Li/Be and B/K ratios while higher *T* hydrothermal alteration leads to a decrease of the Li/Be and Li/K ratios. Fluid temperature appears to be an important factor in the behaviour of B and Li.

The fresh OIB from Polynesia including those which have radiogenic isotopic signatures indicative of a component of subducted crust or sediments, have low B/Be and Li/Be ratios compared with volcanic arc rocks, marine sediments and altered oceanic crust (B/Be = 50–200; Li/Be = 20–30). The uniformly low values of these two ratios in the OIB mantle source regions suggest that Li and B were probably removed from the down-going slab during subduction related metamorphism and did not take part in deep-level mantle recycling.

In the case of the altered Polynesian OIB, high B/Be can be attributed to alteration and concentrations of B in secondary minerals. This has implications for the elevated B/Be ratio of orogenic volcanic rocks which, along with high concentrations of <sup>10</sup>Be, provided evidence for presence of sediments in their source (Morris *et al.*, 1990). The subduction of oceanic crust with high B/Be ratios like those of the altered basalts in this study or altered oceanic crust of Ryan *et al.* (1989) may be an alternative explanation for the high B/Be ratios in orogenic volcanic rocks which lack <sup>10</sup>Be enrichment.

The presence of negative and positive B and Li anomalies on the primitive mantle-normalized

incompatible element plots of oceanic and continental rocks, respectively, suggest that these elements can be useful geochemical discriminators in deciphering basalt petrogenesis.

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#### Appendix 1. Trace Element Analysis of Standard Rocks

	W-1		BHVO-1		RGM-1	
	<i>x</i>	<i>s</i>	<i>x</i>	<i>s</i>	<i>x</i>	<i>s</i>
Li (ppm)	13.2	0.21				
Be	0.72	0.01				
B			3.15	0.21	30.0	0.05
Rb	22.9	0.14				
Sr	203	4.95				
Zr	92	1.4				
Hf	2.30	0.00				
Nb	8.05	0.21				
Ta	0.48	0.01				
Cs	1.06	0.01				
Ba	170	1				
La	11.2	0.21				
Ce	25.1	0.57				
Pr	3.20	0.03				
Nd	14.1	0.07				
Sm	3.31	0.06				
Eu	1.20	0.01				
Gd	3.92	0.04				
Tb	0.64	0.01				
Dy	3.78	0.01				
Ho	0.77	0.01				
Er	2.16	0.01				
Tm	0.30	0.01				
Yb	1.94	0.04				
Lu	0.31	0.01				
Pb	7.41	0.15				
Th	2.38	0.03				
U	0.57	0.01				

*x* = mean; *s* = 1 standard deviation

Note: W-1 = average of 12 determinations of international reference standard W-1; BHVO-1 and RGM-1 = averages of four determinations of standards BHVO-1 and RGM-1, respectively.