Fluid-mobile element budgets in serpentinized oceanic lithospheric mantle: Insights from B, As, Li, Pb, PGEs and Os isotopes in the Feather River Ophiolite, California

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Abstract

Serpentinized oceanic lithosphere may be an important source for boron and other fluid-mobile elements that are anomalously enriched in arc volcanic rocks. However, the integrated water/rock ratios associated with different styles of serpentinization may be variable. For example, large water/rock ratios are involved in the serpentinization of abyssal peridotites exhumed to the seafloor, whereas much lower water/rock ratios are likely to dictate serpentinization along deep faults and fractures. To address how fluid-mobile element enrichments vary with serpentinization at different settings, we investigated serpentinized harzburgites from the Feather River Ophiolite (**FRO**) in northern California. Major and trace element systematics indicate that serpentinization of the FRO ultramafics involved seawater. However, FRO serpentinites have unradiogenic Os isotopic compositions and near-chondritic platinum group element relative abundances, contrasting with serpentinized abyssal peridotites, which have radiogenic Os isotopic compositions and disturbed platinum group element systematics. These observations indicate that the integrated water/rock ratio involved in FRO serpentinization was smaller than that involved in abyssal peridotite serpentinization. B concentrations in the FRO (5–15 ppm), while substantially higher than primitive mantle (<0.1 ppm), are still lower than in abyssal peridotites (10–170 ppm). These low values are not due to metamorphic loss as there is no petrographic evidence for prograde metamorphism (the serpentine minerals are low temperature forms like chrysotile and lizardite) and there is no consistency between observed fluid-mobile element (B, As, Pb, and Li) contents and depletions predicted from metamorphic dehydration models. Low B and fluid-mobile element contents in the FRO may thus be an intrinsic feature of low water/rock ratio serpentinization. Such values may be more representative of serpentinized oceanic lithospheric mantle rather than abyssal peridotites, which sample only the top veneer of the lithosphere.
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1. Introduction

Fluid-mobile elements are those elements that are preferentially partitioned into fluids relative to solid phases during melting or metamorphic dehydration or decarbonation reactions. Depending upon the coexisting

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mineral assemblages, many group I and II elements (e.g., Ba, Sr, Na, K, Cs, and Li) as well as elements commonly enriched in ore-forming fluids (e.g., B, As, Pb, and Cd) may be considered to be fluid-mobile. Many of these elements also are selectively enriched in altered oceanic crust and oceanic peridotites during hydrothermal reaction with seawater. For example, recent studies of fluid-mobile element content and behavior in serpentinites (Benton et al., 2001; Hattori et al., 2005, 2003; Pereira et al., 2003; Savov et al., 2005; Scambelluri et al., 2004a,b; Tenthorey and Hermann, 2004) indicate that serpentinized oceanic lithospheric mantle may be a major source for elements such as boron during subduction. If so, many of these fluid-mobile elements could serve as tracers for recycling of seawater-altered material into the mantle.

In the context of subduction zones, critical questions concern (1) the quantity of fluid-mobile elements entering subduction zones via altered oceanic lithosphere, (2) the proportions that are returned to the crust via arc magmatism, and ultimately, (3) what proportion makes it past the arc front to enter the deep interior of the Earth. The third quantity has been addressed using fluid/rock partitioning experiments (Scambelluri et al., 2004b; Tenthorey and Hermann, 2004). The flux of fluid-mobile elements into subduction zones, however, is not so well-constrained. Although there have been numerous studies of fluid-mobile elements in serpentinites, the majority of these studies focus on abyssal peridotites, which represent fragments of oceanic lithospheric mantle that have been exhumed to the surface in fracture zones or low-angle detachments (Schroeder et al., 2002; Snow and Dick, 1995). Growing evidence suggests that even intact oceanic lithospheric mantle, that is, the part that still lies beneath the crust and has not been exhumed, may be serpentinized by the infiltration of water via cracks and faults (Ranero et al., 2003). Deep, crack-controlled serpentinization of the lithosphere probably differs from serpentinization of exhumed mantle, such as abyssal peridotites. Serpentinization of abyssal peridotites probably involves very high integrated water/rock ratios whereas deep, crack-controlled serpentinization of the lithospheric mantle probably involves much lower water/rock ratios (Komor et al., 1985; Snow and Dick, 1995). This begs the question: since abyssal peridotites only sample the top veneer of the lithosphere, is the chemical alteration signal recorded in abyssal peridotites representative of serpentinized oceanic lithospheric mantle? In other words, for a given thickness of serpentinized lithospheric mantle, do abyssal peridotite case studies give over-estimated fluxes of fluid-mobile elements into subduction zones?

Here, we investigate the fluid-mobile element budgets of variably serpentinized harzburgites in the Feather River Ophiolite (FRO) in northern California. The FRO represents fragments of oceanic and sub-arc lithospheric mantle accreted to the western edge of North America during the early Mesozoic. Sm–Nd isotopic studies of peridotites from the Josephine ophiolite, which is nearby, indicate that closure of the Sm–Nd isotopic system occurred shortly before this time (Jacobsen et al., 1984). Li and Lee (2006) suggested on the basis of major and trace element systematics that the harzburgite protoliths were serpentinized by seawater under low water/rock ratios, and argued that the serpentinites represent deeply serpentinized oceanic lithospheric mantle rather than abyssal peridotites. To further test these suggestions, we report here the osmium isotopic and PGE systematics of these serpentinites, both of which appear to be highly disturbed in large water/rock ratio serpentinization processes as exemplified by abyssal peridotites. We then show that B and other fluid-mobile element contents of these serpentinized harzburgites are lower than those of abyssal peridotites, albeit still substantially enriched over typical mantle. We discuss our results in the context of the global boron cycle.

2. Methods

2.1. Boron concentrations

Boron concentrations were obtained using the Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES) Varian Vista Pro at Rice University. Samples were crushed and powdered using an agate mortar. Approximately 0.2 g of the resulting powders were dissolved overnight at 60 °C in Savillex Teflon beakers containing 2 mL of concentrated Seastar HF and 1 mL of a 10 wt.% mannitol solution. After gentle evaporation (60 °C) the residues were re-dissolved in 2 mL of 2 N distilled HCl. After 12 hours at 60 °C, solutions were diluted up to ∼ 15 mL with solutions containing 0.02 wt.% of tetramethyl ammonium hydroxide (which reduces the memory of boron on tubing and glass parts of the ICP-AES) and centrifuged. To ensure a higher precision and to correct for matrix effects and any possible drift of the machine, the standard addition technique was used. Samples were divided into three aliquots of 4 grams each. 2 μg of boron were added to one of them, 4 μg to the next and the last aliquot remained untouched. Analyses were performed measuring boron concentrations on wavelengths 182.527, 182.577, 208.889, 208.956, 249.678

Table 1
Fluid-mobile element concentrations in FRO serpentinized peridotites

Samples	B (ppm)	±	Duplicate (ppm)	±	As (ppm)	Cd (ppb)	Li (ppm)[a]	Pb (ppm)[a]	Ba (ppm)[a]	Th (ppb)[a]
CT1	6.4	1.2	6.5	0.6	0.114	4	1.23		2.9	4.5
CT1-2	8.9	1.3	10.5	0.6	–	–	1.11	0.0147	3.5	3.3
NB24	6.8	0.8	7.8	0.7	0.43	7	0.30	0.284	5.6	4.3
CT3	9.6	1.4			0.04	5	1.86	0.086	1.5	2.9
CT7	10.3	1.3			0.06	10	3.09	0.714	7.2	3.8
CT10	15.6	1.6			0.11	12	0.77	0.473	3.8	3.0
CT11	10.3	0.6			0.07	15	0.76	1.16	7.5	6.6
CT19	10.6	1.2			–	–	0.33	0.115	1.8	2.1
CT23	12.8	0.8			0.15	43	0.41	5.26	6.4	12.3
CT29	15.3	0.6			0.11	15	0.45	0.133	1.3	2.6
Nb2a	10.6	1.0			0.20	6	1.06	0.126	1.7	5.6
NB10	10.8	1.8			0.09	12	0.08	0.102	3.7	1.4
NB22	8.2	1.3			0.06	33	1.61	1.66	5.2	13
NB25	7.6	0.5			0.82	8	0.50	0.367	3.4	2.7
NB28	10.2	1.3			–	–	0.59	1.01		47
NB15	9.5	0.7			0.30	30	0.38	0.779		56.2
NB8	9.3	0.7			0.06	91	1.33	0.164		1.7
CT34	10.1	1.3			0.13	56	1.43	0.348		172

[a] From Li and Lee (2006).

and 249.772 nm. In order to correct for possible interferences, Fe was monitored on wavelengths 249.699, 249.782 and 209.038 nm. Two procedural blanks were analyzed during every session. Measurements were externally calibrated against the JB-2, JR-1, B-5, JA-2, JB-3, JA-3 and B6 international rock standards and several duplicates were analyzed to ensure precision and accuracy (Table 1).

2.2. PGEs, Re and Os isotopes

Chemical procedures follow that proposed by Shirey and Walker (1995). PGE, Re and Os isotopes were obtained by isotope dilution using the single-collector, magnetic sector inductively coupled plasma mass spectrometer (ICP-MS) ThermoFinnigan Element II at Rice University. Samples were dissolved in reverse aqua regia (1 HCl: 3 HNO₃) in sealed Carius tubes. Osmium was extracted by solvent extraction using CHCl₃ and purified by microdistillation. PGE and Re were purified from the matrix by anion exchange column chromatography.

2.2.1. Os isotopes

Os isotopic composition was determined using a method adapted from Shirey and Walker (1995). Approximately 1 g of powder was placed into dry-ice "frozen" quartz Carius tubes. 1 mL of concentrated HCl, 3 mL of concentrated HNO₃ and ~1 g of an accurately weighed tracer solution "PGE-Sp-DIL-1-00-A" (Ru=0.205 ppb, Pt=0.1486 ppb, Pd=0.3084 ppb,

Re=0.1904 ppb, Ir=0.5943 ppb and Os=0.9773 ppb) were successively added. Sealed Carius tubes were placed in an oven for over 48 hours at 220 °C. After this dissolution step, Carius tubes were chilled in dry ice and opened. Os was separated from the rest of the matrix by three sequential solvent extractions involving 3 mL CHCl₃ each. The dense part of the solution containing Os was pipetted out and poured into beakers containing 2 mL concentrated HBr.

After evaporation of the CHCl₃ overnight at room temperature, volumes of the remaining HBr solution were reduced to a 20–50 µL droplet on a hotplate at about 90 °C. Droplets were transferred to small microdistillation vessel caps and then dried down completely. 20 µL of concentrated HBr were placed into the basal cone of the microdistillation vessel, and 25 µL of CrO₃ in concentrated H₂SO₄ were placed in the cap close to the dry sample. Microdistillation vessels were hermetically sealed using Teflon tape on threads. Samples and CrO₃ droplets were then driven into contact in order to oxidize Os. Vessels were wrapped with aluminum foil and placed upside down on a hotplate (temperature of 70 °C) for 5 hours. Caps were removed and the 20 µL droplet of HBr now containing purified Os was gently dried down (90 °C) and dissolved in 0.8 mL 0.1N HCl and run on the ICP-MS. Measurements were operated in low resolution mode (m/Δm=300) for 250 cycles. Presence of Re and Pt were monitored on masses 185 and 194 respectively but remained undetectable. Procedural blanks and the in house standard "NOSY" (Lee et al., 2001) were

Table 2
Platinum group elements and Re concentrations and Os isotope ratios of FRO serpentinized peridotites

Sample	Ir (ppb)	Pt (ppb)	Pd (ppb)	Os (ppb)	Re (ppb)	$^{187}Os/^{188}Os$	$\pm_{2\sigma}$
CT1-1	3.9	6.8	–	4.2	0.17	0.1235	0.0011
CT3	3.6	5.9	–	5.6	0.24	0.1237	0.0009
CT7	3.8	7.0	5.8	5.7	0.18	0.1238	0.0013
CT10	–	–	–	5.4	–	0.1175	0.0017
CT19	3.3	7.0	4.5	4.5	0.12	–	–
CT23	3.1	10.1	6.6	3.5	0.03	–	–
CT29	4.0	5.6	3.8	4.7	0.03	0.1217	0.0006
NB2a	4.9	9.2	7.8	5.6	0.08	0.1218	0.0015
NB25	3.6	8.2	6.0	3.1	0.16	0.1256	0.0010
NB15	4.2	6.6	4.9	3.7	0.04	0.1279	0.0024
NOSY std	–	–	–	–	–	0.1074	0.001
Duplicate	–	–	–	–	–	0.1077	0.001
Triplicate	–	–	–	–	–	0.1062	0.001

Os measurements are externally controlled by repetitive analyzes of the NOSY standard of Yin et al. (2001) ($^{187}Os/^{188}Os$=0.10688).

analyzed during each session to check for cleanliness and accuracy of the method. The internal error of samples estimated over the 250 cycles of measurement remained lower than 1.8% for $^{187}Os/^{188}Os$ and blanks were always lower than 40 pg. Accuracy of measurement was externally controlled by analyzing repetitively
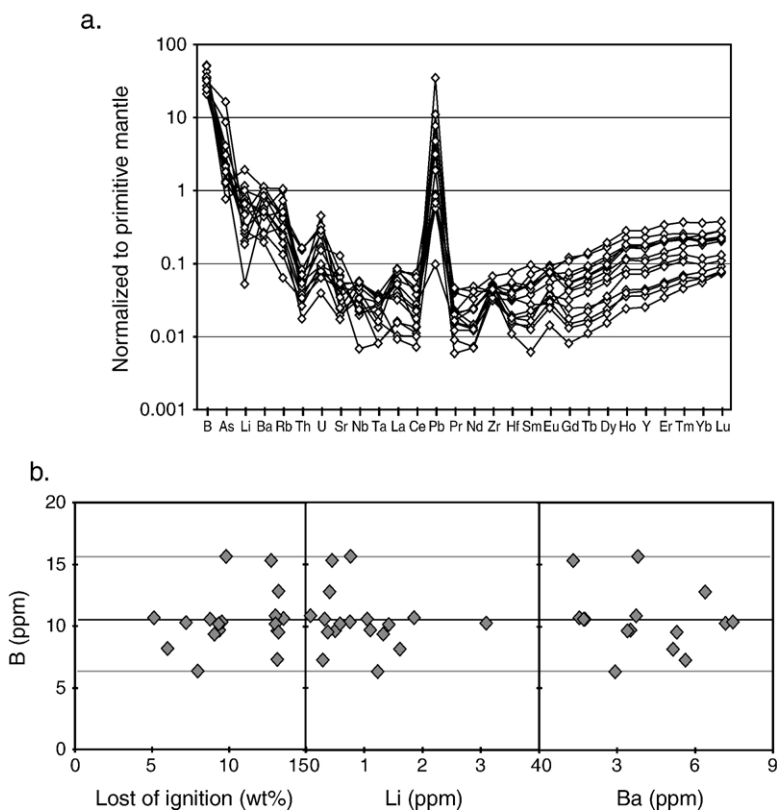

Fig. 1. (a) Primitive mantle-normalized spidergram. Spidergrams are dominated by relative enrichments in fluid-mobile elements, such as B, As, Ba, Rb, U and particularly Pb. The very high Pb content is discussed in Li and Lee (2006). (b) Boron concentrations as a function of water, Li and Ba contents. Boron concentrations are fairly homogeneous ranging from 6 to 15.5 ppm with an average value of 10.5 ppm. These concentrations are lower by a factor of 2 to 10 than those reported for serpentinized oceanic peridotites (see Fig. 2). No correlation between boron, degree of serpentinization (lost of ignition) or other fluid mobile elements are reported. Boron is present in extremely low quantities in mantle peridotites, and boron contained by serpentinites derives therefore from serpentinizing aqueous fluids. The low contents of these samples may reflect either a particularly low fluid/rock interaction during serpentinization, or boron loss by fluid release during post-serpentinization metamorphic processes.

the N.O.S.Y. standard of Yin et al. (2001) as reported in Table 2.

2.2.2. PGE and Re concentrations

Solutions left in Carius tubes after osmium solvent extraction were poured into 10 mL tubes and centrifuged for 4 min at 8000 rpm. Supernatants were taken up, placed into 14 mL Savillex beakers and gently evaporated ($T < 80$ °C). Dry residues were dissolved with 2 mL 0.1N HCl and passed 3 times successively on clean and conditioned 2 mL cation exchange columns (AG50X8 100–200 mesh). The uncolored liquids finally obtained were dried down ($T < 80$ °C) and dissolved with 0.8 mL of 0.1 N HCl. These solutions were analyzed on the ICP-MS in low resolution mode ($m/\Delta m = 300$). The presence of Zr, Mo, Cd, Lu, Hf, W and Hg interferences were monitored on masses 90, 97, 111, 175, 180, 182 and 199 respectively. Significant quantities of ^{90}Zr (presumably coming from Carius tube glass) were detected in all samples and precluded proper Ru and Pd measurements. No other interference could be reported. Cleanliness and accuracy of the method were checked every session by procedural blanks and standard analyses.

2.3. As, Cd and other trace elements

As and Cd were extracted from ~ 0.3 g of finely ground sample powders using 2 mL of concentrated HNO_3 in a 10 mL tube. After agitating in an ultrasonicator for 30 min, the tube and its contents were allowed to sit for
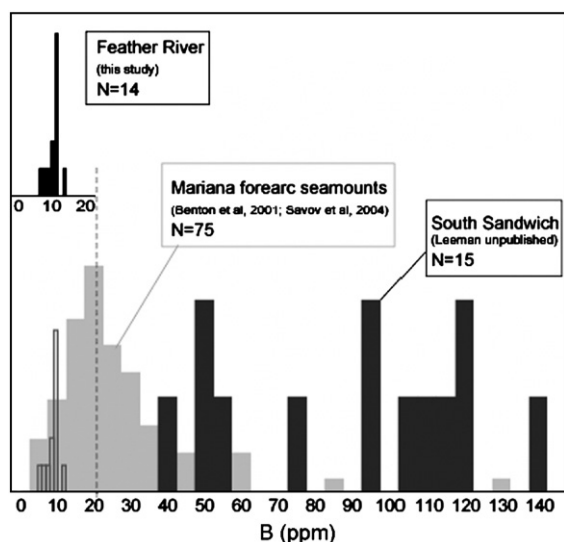

Fig. 2. Histogram of boron concentrations in serpentinites from FRO. Abundances in oceanic serpentinites from various environments (Benton et al., 2001; Savov et al., 2005; Leeman, unpublished) are indicated for comparison.

48 hours. The tube was then centrifuged and the supernatant extracted. The supernatant was then dried down and taken up in 2 wt. % HNO_3 for analysis with the ThermoFinnigan Element 2 ICP-MS in high resolution mode ($m/\Delta m = 10,000$). The Ar dimer was used to correct for magnetic drift over the course of the measurement day. Concentrations of unknowns were determined from calibrations against in house synthetic standards made from dilutions of Alfa-Aesar Specpure ICP standards. Sample concentrations reported have been blank-corrected. Basalt standard BHVO-1 was analyzed as a quality standard. Other trace elements (Li, Cs, Ba, Sr, Rb, Pb and rare-earth elements) were also determined by ICP-MS. For these elements, the methods and data are reported by Li and Lee (2006).

3. Results and interpretations

3.1. Boron and other fluid-mobile elements

Results are reported in Table 1 and illustrated in Fig. 1. As shown in the primitive mantle-normalized spidergram in Fig. 1a, fluid-mobile elements, such as B, As, Li and Pb, are significantly enriched compared to the other elements, such as the rare-earth elements. Concentrations for Pb range from 0.015 ppm to values over 5 ppm, Ba ranges between 1.3 and 6.4 ppm, Li between 0.3 and 3.1 ppm, As between 0.04 and 0.8 ppm and Cd (not shown on Fig. 1) between 4 and 91 ppb.

Overall, B concentrations are very similar and relatively low (5–15 ppm) compared to serpentinized abyssal peridotites as represented by Mariana fore-arc and South Sandwich back-arc serpentinites (5 to 140 ppm) (Fig. 2). No correlation is observed between B concentrations and degree of serpentinization as indicated by water content (estimated as loss on ignition) or contents of any other fluid-mobile elements (Fig. 1b). Although the B contents in our samples are lower than those measured in abyssal peridotites (Benton et al., 2001; Savov et al., 2005; Scambelluri et al., 2004a), the fact that B is present in extremely low quantities in pristine mantle peridotites (0.06 ppm, (Salters and Stracke, 2004) makes the contents in our samples still about 100 to 300 times higher than the depleted mantle. This enrichment may be directly related to the serpentinization processes.

3.2. Osmium isotopes and PGE concentrations

Results are reported in Table 2 and illustrated in Fig. 3. Relatively high Os contents ($\sim 3–6$ ppb) overlap those typically observed for fresh peridotites and extend

for only two of them to values slightly lower than fresh peridotites (cf. Alard et al.; Brandon et al.; Snow and Reisberg, 1995). As shown in Fig. 3, these high values exceed by nearly an order of magnitude the Os contents reported for various serpentinites, including abyssal peridotites (Alard et al., 2005; Brandon et al., 2000; Snow and Reisberg, 1995; Standish et al., 2002). The ^{187}Os/^{188}Os ratios (0.118–0.128) for FRO serpentinites fall well within the field reported for fresh lithospheric mantle peridotites (Snow and Reisberg, 1995). Except for two samples, all are systematically lower than the canonical value of 0.129 for the primitive mantle (Meisel et al., 1996). These unradiogenic values contrast with the more radiogenic and lower Os contents reported so far for serpentinized abyssal peridotites (Standish et al., 2002). Sea water is characterized by very low Os concentrations ($\sim 10^{-2}$ ppt) and very radiogenic ^{187}Os/^{188}Os (~ 1) (Levasseur et al., 1999). Although ancient seawater Os isotopic compositions approached chondritic signatures near the Cretaceous–Tertiary boundary, Paleozoic and early Mesozoic seawater (when the ophiolite formed; Jacobsen et al., 1984), is believed to be radiogenic (Peucker-Ehrenbrink and Ravizza, 2000). Serpentinization involving large seawater/rock ratios thus induces in rocks a dilution effect for Os and a progressive isotopic re-equilibration toward higher values as seen in Fig. 3. Os concentrations and isotopic compositions of serpentinized abyssal peridotites define what appears to be a "mixing" trajectory between the field of fresh peridotites and that of seawater (Fig. 3) (Snow and Reisberg, 1995). The high Os concentrations and unradiogenic Os isotopic compositions in FRO samples are thus inconsistent with extensive interaction with seawater despite their highly serpentinized nature.

Concentrations for Ir (3.1–4.9 ppb), Pt (5.6–10.1 ppb), and Pd (3.8–7.8 ppb) in FRO serpentinites fall within the range of fresh peridotites (Lorand et al., 2000). In Fig. 4a, rhenium and the platinum group element (PGE) concentrations of the FRO samples are shown in the form of a spidergram normalized to chondritic values (Jochum, 1996). Fig. 4b and c show Os versus Ir and Pt versus Ir, wherein light gray open rectangles represent data for serpentinized abyssal peridotites (Snow and Reisberg, 1995; (Luguet et al., 2003). Overall, PGE relative abundances are all fairly chondritic, but Re is significantly depleted relative to the PGE. The low Re concentrations are consistent with the harzburgitic nature of the FRO peridotites as Re is generally seen to be depleted (along with Al) during partial melting (Reisberg et al., 1991; Meisel et al., 1996). Like Os, the absolute abundances of the PGEs

are mostly higher than those previously reported for serpentinites (light gray rectangles).

4. Discussion

4.1. Conditions of serpentinization and boron contents

The high PGE contents and unradiogenic ^{187}Os/^{188}Os of the FRO serpentinites are indistinguishable from those estimated for "depleted mid-ocean ridge basalt mantle" and do not match those of serpentinized abyssal peridotites. Because seawater has very low Os concentrations, the anomalously radiogenic signatures of abyssal peridotites require enormous integrated water/rock ratios if one assumes that the disturbed Os isotopes are due to mixing with seawater (cf. Alard et al., 2005). Since our values are identical to depleted mantle, the integrated water/rock ratio is nearly negligible to within error. Thus, the FRO serpentinites appear to have been serpentinized under very low water/rock (W/R) ratios compared to abyssal peridotites. Instead, we suggest that instead of experiencing continuous open-system fluxing
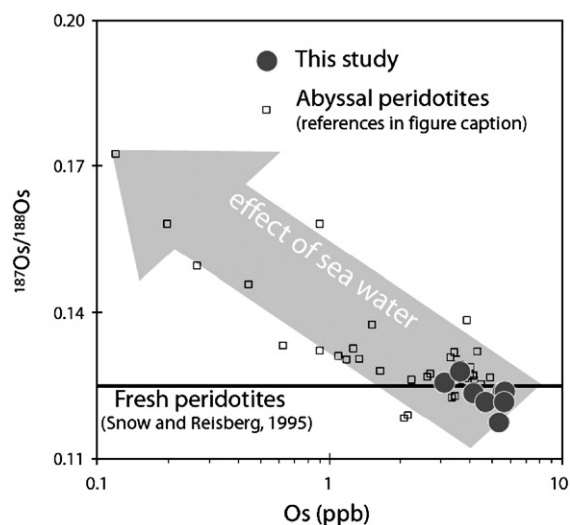

Fig. 3. Variation of ^{187}Os/^{188}Os versus Os concentration. All samples from this study lie within error bars in the field attributed to fresh peridotite by Snow and Reisberg (1995). Values reported for serpentinized abyssal peridotites by Snow and Reisberg (1995), Brandon et al. (2000), Standish et al. (2002) and Alard et al. (2005) describe a much larger trend spreading from values similar to those of this study to very low Os contents and higher ^{187}Os/^{188}Os ratios reflecting the increasing modification of serpentinites by sea water. It is very unlikely that fluid release during metamorphic processes subsequent to serpentinization would modify Os isotopes. This therefore suggest that serpentinites from the FRO had very little, interaction with sea water during serpentinization.
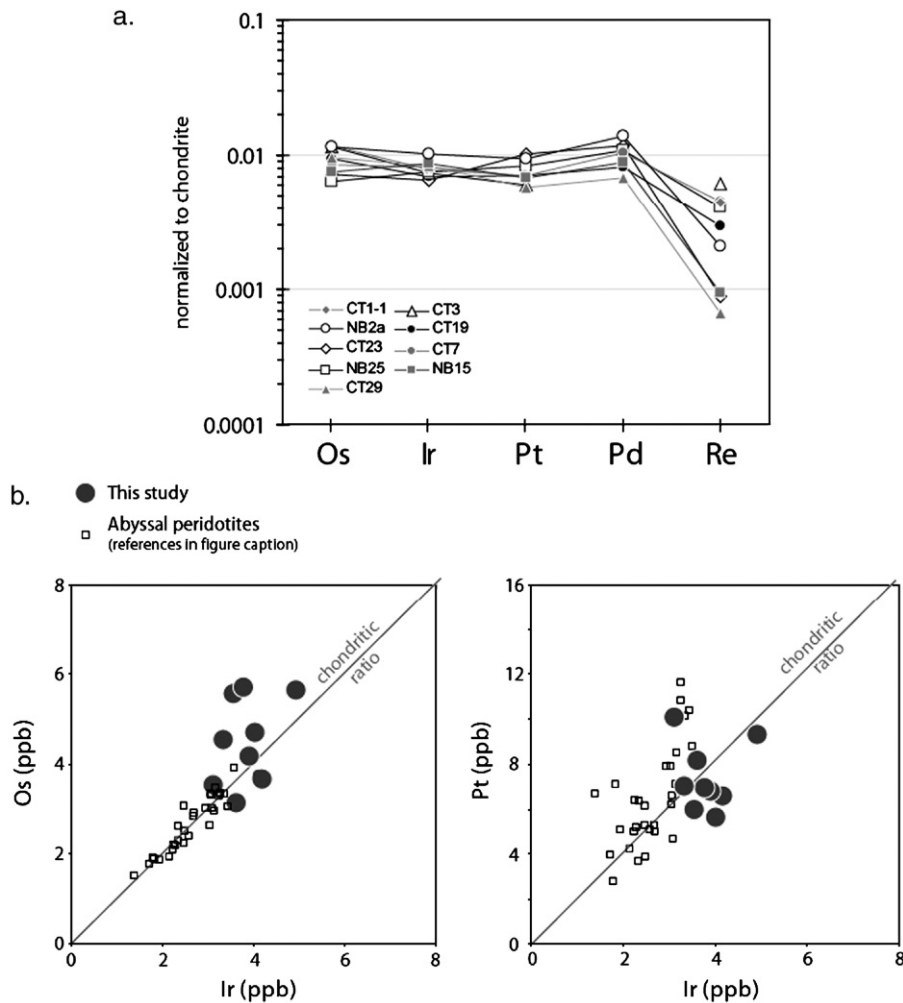
Fig. 4. PGE and Re compositions of FRO serpentinites. (a) Chondrite-normalized spidergram (Jochum, 1996), Serpentinization processes did not affect the chondritic pattern of PGE in FRO peridotites. Low Re contents are consistent with the harzburgitic nature of the FRO peridotites as Re is depleted during partial melting. (b) Os and Pt as functions of Ir content in FRO peridotites. The PGE contents in FRO serpentinites appear to reflect a much "fresher" nature (higher PGE contents) than oceanic serpentinites from the literature (gray open rectangles, these samples are not the same as open rectangles of Fig. 3; Snow and Reisberg, 1995; Luguet et al., 2003).

of water, the FRO serpentinites formed in a closed system mixture of infiltrated seawater and peridotite with little to no fluxing. Since serpentine minerals contain ~10% water, this means that the water/rock mass ratio involved in FRO serpentinization may have been less than one. This conclusion is consistent with the hypothesis of Li and Lee (2006) that the FRO serpentinites are not the products of serpentinization of mantle fragments exhumed to the crust–seawater interface. Instead, they were serpentinized by deep infiltration of water into intact lithosphere. They based their conclusion on the absence of significant Mg depletion, which typically is seen in abyssal peridotites.

We also note that the high Os concentrations and unradiogenic Os isotopic compositions of FRO perido-tites do not match those reported for peridotite xenoliths believed to represent sub-arc mantle that has been extensively fluxed by subduction-related fluids. Such peridotites are characterized by very low Os concentra-tions and radiogenic signatures (Brandon et al., 1996). This suggests that the FRO peridotites probably represent oceanic lithospheric mantle rather than sub-arc mantle. Although speculative, this interpretation is consistent with the lack of a subduction-related trace element signature (Li and Lee, 2006). For example, the FRO peridotites do not have any significant depletions in Nb relative to La as would be expected if the peridotites had been metasomatized by subduction-related fluids (Gammons et al., 1996; Keppler, 1996; Saunders et al., 1980).
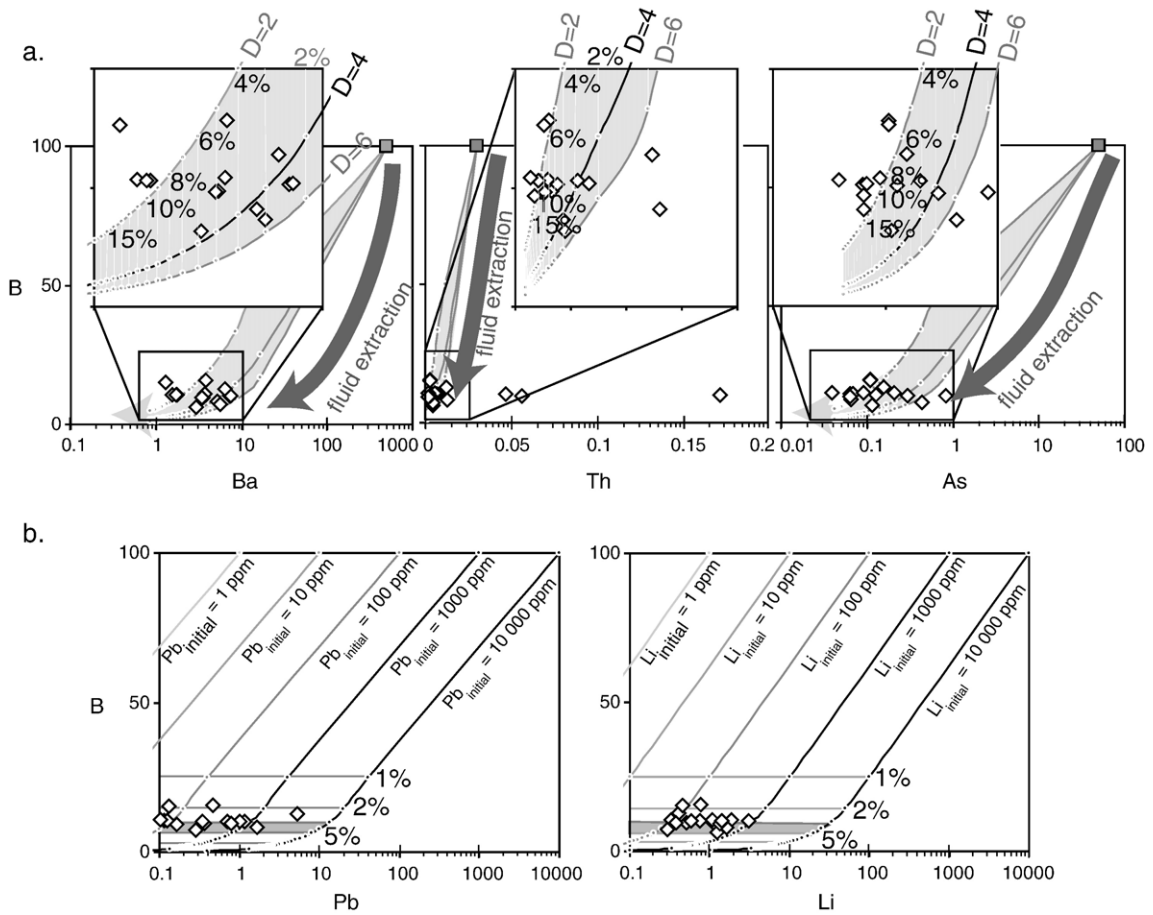
Fig. 5. Fluid extraction calculations. All numbers refer to ppm. Fluid/rock partition coefficient considered for B is 4±2 considering both experimental work (Tenthorey and Hermann, 2004) and natural observations (Scambelluri et al., 2004b). Average initial (before fluid extraction) concentrations were estimated from oceanic serpentinites (Benton et al., 2001; Hattori et al., 2005, 2003; Pereira et al., 2003; Savov et al., 2005; Scambelluri et al., 2004a,b; Tenthorey and Hermann, 2004). Partition coefficients for other elements are adopted from Tenthorey and Hermann, (2004). In (a) concentrations of B, Ba, Th and appear to be consistent with about 3 to 10% fluid extraction from an abyssal peridotite. In (b) however, it is shown that even for a minimal fluid extraction (3%), present day high concentrations of Pb and Li imply unrealistically high initial concentrations (ca. 100–2000 ppm).

We now consider why the FRO serpentinites show only moderate B-enrichment compared to depleted or primitive mantle, and a factor 2 to 20 lower than those reported for serpentinized abyssal peridotites. We consider two scenarios to explain this discrepancy. First, B could have originally been at higher concentrations similar to abyssal serpentinites, but subsequently depleted during metamorphic processes accompanying tectonic emplacement of the ophiolite (Bebout et al., 1993, 1999). Alternatively, B may never have been strongly enriched in the FRO serpentinites due to lower water/rock ratios and specific fluid compositions associated with deep, crack-controlled serpentinization of the lithosphere.

The first scenario seems unlikely for the following reasons. Petrographic investigation of the FRO peridotites show that prograde metamorphism was minimal as

no detectable facies change occurred in the FRO serpentinites (serpentine is in the form of lizardite and chrysotile). Nevertheless, we can still assess the plausibility of the metamorphic loss scenario by considering a model for fluid-mobile element loss during dehydration of serpentine. For example, B loss can be modeled by a simple batch dehydration model:

$$[i] = \frac{[i]_{\text{initial}}}{(1-F) + F \cdot {}^{\text{fluid/rock}}D_i}$$

where $[i]_{\text{initial}}$ is the element concentration i before dehydration, F is the mass fraction of fluid extracted, and ${}^{\text{fluid/rock}}D_i$ is the fluid/rock partition coefficient. Fluid/rock partition coefficients during serpentine dehydration were taken from experimental determinations by
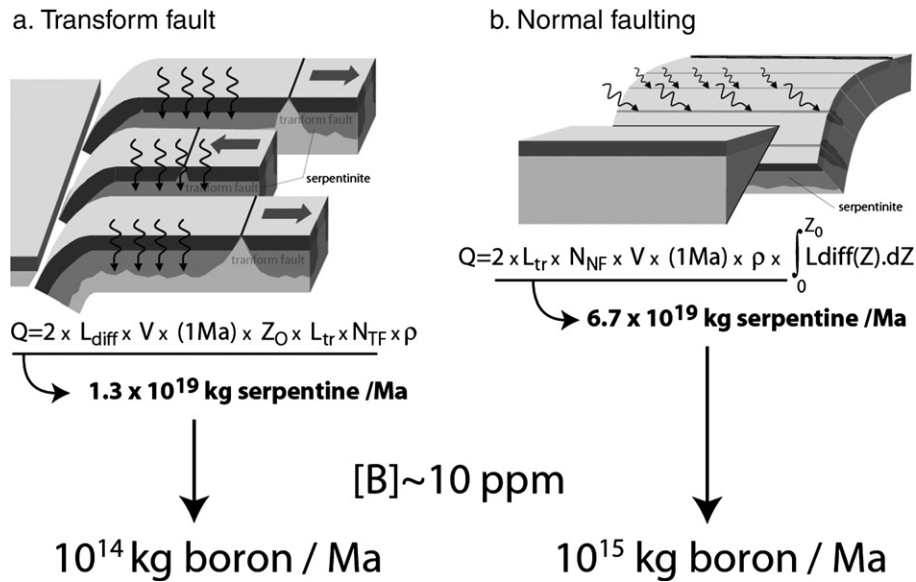
Fig. 6. Adapted from Li and Lee (2006). They propose two reasonable scenarios for deep water infiltration within the lithospheric mantle. (a) Water infiltrates along transform faults. (b) Water infiltrates along normal faults activated by slab bending during subduction. Considering both hypotheses, Li and Lee propose mass balance calculations for the quantity of serpentinites produced by each of these processes and subducted into the mantle though time (see details in the Appendix of Li and Lee, 2006). We use these result to make an estimation of the boron flux in subduction zones. The results of the order of magnitude of 10^{14} to 10^{15} kg/Ma are commensurate with the total content of the upper/depleted mantle estimated from Salters and Stracke (2004). The residence time of boron in the upper mantle would therefore be very short, of the order of a million years. Boron flux at ridges can be estimated as no larger than 10^7 tonnes/Ma. Accordingly, most of the subducted boron is directly released in subduction zones during slab dehydrations. Parameters used in Li and Lee (2006)'s equations: Q = serpentinites flux; L_{diff} = diffusion length; V = subduction rate; Z_o = maximum depth of serpentinization; L_{tr} = trench length; N_{TF} = number of transform faults; ρ = average density of lithospheric mantle. For numbers, see Li and Lee (2006).

Tenthorey and Hermann (2004) for B, Ba, Th, As, Li and Pb. Fig. 5a presents an attempt to model the degree of dehydration needed to reduce B, Ba, Th and As contents of a serpentinized abyssal peridotite down to the levels observed in the FRO. Initial concentrations (B=100, Ba=500, Th=0.03 and As=50 ppm) for an abyssal peridotite protolith were taken as averages from the literature (i.e. Savov et al., 2005; Benton et al., 2001). In Fig. 5a, the three curves bounding the shaded region represent fluid extraction pathways for $^{fluid/rock}D_B=2$, 4 and 6, which largely covers the range of values reported by Tenthorey and Hermann (2004) ($^{fluid/rock}D_B=4\pm1$) and Scambelluri et al. (2004a,b) ($^{fluid/rock}D_B=5$). Partition coefficients for Ba, Th, Pb, and As are those proposed by Tenthorey and Hermann (2004): $^{fluid/rock}D_{Ba}=30$, $^{fluid/rock}D_{Th}=1.5$, $^{fluid/rock}D_{Pb}=250$ and $^{fluid/rock}D_{As}=60$. The calculations show that, with these partition coefficients, the range of concentrations observed in FRO serpentinites can be attained after 3 to 10% fluid extraction. At face value, these numbers look realistic since they are commensurate with typical water contents of serpentinites. We note, however, that ~10% H_2O contained in FRO serpentinites (Li and Lee, 2006) most probably reflects their original water content (~10–15%)

and that these rocks have therefore not undergone significant dehydration. Fig. 5b illustrates an additional shortcoming of the dehydration hypothesis. Assuming that the 3 to 10% fluid extraction estimated above is correct, we can use these numbers to calculate the initial protolith concentration of Pb and Li by reversing our calculation. This results in a protolith having 100 to 2000 ppm Pb and Li. Such high contents for these elements have never been reported for abyssal peridotites and are considered unrealistic. Thus, we discard the metamorphic loss model to explain low boron contents in FRO serpentinites.

By process of elimination, we go with the working hypothesis that the low B contents in the serpentinized FRO peridotites are an intrinsic feature of serpentinized oceanic lithospheric mantle. We speculate that the low B contents are a product of the low integrated W/R ratio serpentinization compared to the much higher W/R ratios associated with mantle exhumed directly to the seafloor.

4.2. Consequences for the Boron cycle

If the above interpretations are correct and if the FRO B contents can be taken as more representative of serpentinized oceanic lithospheric mantle than abyssal

peridotite B contents, then the concentration of B in serpentinized lithosphere entering subduction zones must be revised downward compared to models based on compositions of abyssal peridotites. Feather River Ophiolite concentrations can be used to make a first order estimate of boron subduction fluxes given estimates of the degree of serpentinization for oceanic lithospheric mantle, which is likely to vary spatially and temporally according to tectonic and other factors (age of seafloor, degree of plate bending at subduction zones). Unfortunately, the vertical and lateral extent to which oceanic lithospheric mantle is serpentinized is poorly constrained at present. The presence of dipping seismic reflectors extending well below the oceanic Moho and the presence of double intraslab seismic zones together hint that serpentinization may extend well into the lithospheric mantle, possibly down to depths of ∼50 km below the surface of the slab (Ranero et al., 2003; Peacock and Wang, 1999). Li and Lee (2006) assumed that the FRO peridotites formed in a simple passive upwelling regime, such that their original structural depths within the oceanic lithosphere corresponded to the depth at which they last experienced melting in a polybaric melting column. They made the bold assumption that, if the serpentinization of the FRO predates any telescoping effects associated with tectonic emplacement, the depth extent of serpentinization in a given peridotite was equivalent to its original structural depth in the lithosphere. With these caveats in mind, Li and Lee estimated that the FRO peridotites were serpentinized down to maximum depths of 30 to 40 km below the seafloor.

This vertical extent of serpentinization with all the caveats described above was used by Li and Lee (2006) to estimate the global subduction rate of serpentinized oceanic lithosphere (Fig. 6) (See Appendix of Li and Lee, 2006 for details of calculation.). For the purposes of this paper, we adopt their value for a global serpentine re-injection rate of about 10^{19} kg/Ma (Li and Lee, 2006). Taking the average B concentration in FRO serpentinites (∼10 ppm) as a minimum value for serpentinized oceanic lithospheric mantle, we find a global B recycling rate on the order of 10^{14} to 10^{15} kg/Ma. The total B content in the present day upper mantle (above 670 km) is ∼10^{15} kg (Salters and Stracke, 2004). If our calculations are meaningful, this implies that the residence time of B in the mantle is relatively short, on the order of 1 to 10 million years. If the average B concentrations in fresh MORB range from 0.3 to 3 ppm (Ryan and Langmuir, 1988; Ryan and Langmuir, 1993), we use a linear oceanic crust production rate of 62.3 km/Ma (Bird, 2003) and an average basaltic crust thickness of about 5 km to estimate

the B output from the mantle via ridges to be about 10^9 to 10^{10} kg/Ma. These numbers are over 5 orders of magnitude lower than our estimated subduction recycling rates of B. If the global B cycle is roughly at steady state, this predicts that 99.99% of serpentinite B must be released in subduction zones in the form of arc magmas, hydrothermal fluids, or mud volcanoes as proposed by (Savov et al., 2002, 2005).

This number can be revised downward if the amount of serpentine being subducted is decreased. Indeed, the depth and extent of serpentinization estimated by Li and Lee (2006), in retrospect, is likely to be a maximum bound as it considers serpentinization of old and cold oceanic lithosphere. However, even if we were to decrease the amount of serpentine being subducted by a factor of 100, it would still mean that 99% of subducted B must ultimately be short-circuited in arcs. Alternatively, some amount of B could bypass the arcs and be released into the mantle wedge and over-riding lithospheric mantle. Some of our ongoing studies are showing that relatively high boron olivines (above 10 ppm) can be found in mantle xenoliths from western North America. This, together with fluid rock partition coefficients of (Scambelluri et al., 2004b; Tenthorey and Hermann, 2004), hint that significant quantities of boron could also be retained by olivines during fluid ascent through the mantle wedge. Investigations will continue to assess whether incorporation of B by metasomatized peridotites could explain the apparent imbalance between the high subduction input into the mantle and the low ridge output without involving the complete B release in arcs.

5. Conclusion

High platinum group element concentrations, chondritic platinum group element relative abundances, and unradiogenic Os isotopic compositions of the serpentinized FRO peridotites are typical of fairly fresh peridotites and atypical of serpentinized abyssal peridotites, the latter representing mantle fragments exhumed to the seafloor and serpentinized under high water/rock ratios. These observations indicate that the FRO peridotites were not serpentinized under large integrated water/rock ratios, but were most likely serpentinized in low water/rock ratio environments, as might occur during deep serpentinization of the oceanic lithospheric mantle. FRO peridotites may thus be more representative of serpentinized oceanic lithospheric mantle than abyssal peridotites, which sample only veneers of locally exhumed oceanic mantle.

Boron contents in the FRO peridotites (∼10 ppm) are hundreds of times higher than in depleted upper mantle, but are an order of magnitude lower than serpentinized

abyssal peridotites. We interpret this difference to be the result of lower integrated water/rock ratios experienced by the FRO serpentinites compared to serpentinized abyssal peridotites. Taking the B contents of the FRO peridotites as more representative of serpentinized oceanic lithospheric mantle, we speculate about the global recycling rate of B and find the inferred residence time of B in the upper mantle to be 1–10 million years. Combined with the very low ridge output rates of B, our analysis corroborates the suggestion that even if some of it could be sequestered by olivines in the upper parts of the mantle wedge, much of the boron being recycled in subduction zones is released in the subduction process in the form of arc lavas, hydrothermal fluids or mud volcanoes.

Acknowledgments

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