doi: 10.1111/j.1365-3121.2011.00995.x

Serpentinites act as sponges for fluid-mobile elements in abyssal and subduction zone environments

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ABSTRACT

Serpentinization of the oceanic lithosphere contributes significantly to the geochemical cycle from spreading ridges to subduction zones. In situ trace element analysis of oceanic serpentinites from the Mid-Atlantic Ridge and the Greater Antilles (Cuba, Dominican Republic) shows that all serpentine minerals are enriched in fluid-mobile elements (FME: As, Sb, B, Li, Cs, Pb, U, Ba, Sr). We observe no loss of these elements from abyssal to subduction environments during prograde metamorphism. Moreover, the transition from lizardite/chrysotile to antigorite during subduction is marked by a strong over-enrichment in As and Sb in antigorite, indicating late

contamination by a sedimentary source. This suggests that a second stage of serpentinization occurs in the earlier stages of subduction, when newly formed or reactivated normal faults ease fluid penetration, and/or in the subduction channel. Our study shows that, from spreading ridges to forearc environments, serpentines act as sponges for FME. We posit that, until ultimate antigorite breakdown, serpentinites efficiently transport significant amounts of FME down to great depths in the mantle.

Terra Nova, 23, 171-178, 2011

Introduction

Serpentinite is a major component of the oceanic lithosphere formed at slow-spreading ridges and represents between 5% and 15% by volume of the Atlantic seafloor (Cannat et al., 1995; Carlson, 2001; Mével, 2003). Recent studies have highlighted the importance of serpentinites in subduction zone geodynamics (Scambelluri et al., 2001a, 2004b; Hattori and Guillot, 2003, 2007). Serpentinites can hold on average 13 wt% H2O and may be stable down to depths of 170 km (Ulmer and Trommsdorff, 1995; Wunder and Schreyer, 1997); this makes serpentinite a potentially important host of water in subducting lithosphere at mantle Although sediments and hydrated magmatic lithologies of subducting slabs continuously release water during subduction (Schmidt and Poli, 1998; Rüpke et al., 2002), dehydration of serpentinites occurs later, between 120 and 200 km depth (Rüpke et al., 2002). This dehydration may be responsible for deep seismic activity

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(Dobson et al., 2002; Perrillat et al., 2005) and partial melting of the mantle for arc magmatism (Scambelluri et al., 2001a; Hattori and Guillot, 2003; Rüpke et al., 2004). Like arc magmas (Rvan et al., 1995; Leeman, 1996; Noll et al., 1996), serpentinites contain high concentrations of fluidmobile elements (FME: As, Sb, B, Li, Cs, Pb, U, Ba; e.g. Bonatti et al., 1984; Scambelluri et al., 2001a,b, 2004a,b; Hattori and Guillot, 2003, 2007; Sharp and Barnes, 2004; Tenthorey and Hermann, 2004). Therefore, serpentinites are considered to be important in the FME budget in subduction zones (Hattori and Guillot, 2003, 2007). Previous work using in situ analysis of serpentine minerals has shown that these elements are mostly hosted by serpentine phases (Deschamps et al., 2010) but the behaviour of FME in serpentine minerals during subduction processes is still not well established.

This article presents new data on the FME compositions of serpentine minerals acquired from a series of serpentinites sampled at the Mid-Atlantic Ridge near Kane transform fault (23°N, MARK, ODP Site 920) and within the accretionary wedge of the Greater Antilles (Cuba and Dominican Republic), which preserves relics of the subducted proto-Caribbean (i.e. Caribbean Atlantic) oceanic lithosphere. We discuss

the role of serpentinization on the mobility of FME from spreading ridges to subduction zones.

Samples' key features

The studied serpentinites were selected in order to characterize the composition of serpentinized slow-spreading oceanic lithosphere from accretion (abyssal serpentinites) to subduction. Abyssal serpentinites were sampled at ODP Site 920 (23°N Mid-Atlantic Ridge, near its intersection with the Kane transform fault; MARK). The studied samples are 60-100% altered and display pseudomorphic textures and several generations of serpentine veins (Andreani et al., 2007). The Cuban and Dominican Republic subducted serpentinites are parts of the Greater Antilles forearc serpentinite belt on the northern margin of the Caribbean plate. They comprise relics of the partially altered subducting oceanic lithosphere (subducted abyssal serpentinites), as well as forearc serpentinites, which represent the hydrated mantle wedge (Deschamps, 2010; Saumur et al., 2010; Deschamps et al., in preparation). For this study, we focus our sampling on the Cuba and Dominican Republic subducted abyssal serpentinites. These serpentinites were distinguished from forearc serpentinites on the basis of geochemical data (Deschamps et al., in prepa-

ration) using the criteria defined by Hattori and Guillot (2007) and Deschamps (2010) and the assumption that peridotites in oceanic lithosphere are generally low to moderately depleted, while all hanging-plate peridotites are exclusively highly refractory. Subducted abyssal serpentinites are characterized by a moderately depleted protolith (moderate Al/Si weight ratios > 0.03), rare earth element (REE) compositions similar to abyssal peridotites (Niu, 2004; Paulick et al., 2006) and low-to-moderate Cr# in chromium spinel (ranging from 0.2 to 0.6). In contrast, forearc serpentinites are highly refractory with low Al/Si < 0.03, have U-shaped REE patterns similar to those described for Tso Morari forearc serpentinites by Deschamps et al. (2010) and high Cr# in chromium spinel > 0.5 (refer to Deschamps et al., in preparation). We selected three samples from Cuba (CU 54, CU 56 and CU 65) and four from the Dominican Republic (RD 8E, RD 57, RD 94 and RD06 52A). These samples are associated with metabasic rocks, and we assume that the two rock types shared a common metamorphic history and that the metamorphic conditions experienced by the serpentinite samples can be partially constrained from the metabasites. The Cuban serpentinites come from the 'Northern Ophiolite' representing non-metamorphosed and metamorphosed obducted oceanic and/or forearc lithosphere associated with exotic blocks of high-pressure metamorphic rocks, and from the Escambray massif, which is a relic of a high-pressure platform terrane subducted during the late Cretaceous (Somin and Millán, 1981; Millán, 1997: Iturralde-Vinent, 1998: García-Casco et al., 2008). The Northern Ophiolite serpentinites have undergone contrasting P-T conditions: lizardite-serpentinite CU 56 is associated with metabasic rocks characterized by a low-pressure (LP/HT) amphibolitic assemblage (< 0.6 GPa, 400-500 °C; Spear, 1993; Auzende et al., 2002) and antigorite-serpentinite CU 54 is associated with HP/MT epidote amphibolite/eclogite metamorphic facies conditions (>0.3 GPa, >500 °C; Spear, 1993; Auzende et al., 2002; up to 2.0 GPa, 550-600 °C; García-Casco et al., 2002). The Escambray serpentinite

CU 65 comes from the zoisite-eclogite facies nappe of the Escambray massif and is associated with high-pressure rocks that have experienced metamorphic conditions of approximately 1.5-1.6 GPa at 600-650 °C (Schneider et al., 2004; García-Casco et al., 2006; Stanek et al., 2006). Three of the Dominican Republic serpentinites (RD 8E, RD 94, RD06 52A) are Gaspar Hernandez serpentinites from the northern part of the Rio San Juan Complex (RSJC; Deschamps, 2010; Saumur et al., 2010; Deschamps et al., in preparation). They are associated with metre-scale blocks of omphacite blueschist (1.6–1.8 GPa/340–380 °C; RD 94) and eclogite (2.3 GPa/750 °C; Krebs et al., 2008; RD 8E and RD06 52A). Sample RD 57 comes from Rio Cuevas in the southern part of the RSJC and has undergone low-grade metamorphism based on the lizardite/chrysotile paragenesis; however, precise determination of its P-T conditions are difficult because no metamorphic rocks are clearly associated with this sample.

MARK serpentinites comprise lizardite and minor chrysotile (Andreani et al., 2007). The subducted serpentinites sampled in the Greater Antilles comprise serpentinites composed of lizardite/chrysotile assemblages with few and small relics of primary minerals such as forsterite, diopside and enstatite (CU 56, RD 57 and RD 94), having undergone lowgrade metamorphism, and a group of high-grade serpentinites with only antigorite without pseudomorphic texture (CU 54, CU 65, RD 8E and RD06 52A; Hattori and Guillot, 2007; Saumur et al., 2010). Rare chlorite, talc and amphiboles (edenite. Mg-hornblende) are associated with serpentine in most Caribbean antigorite-serpentinite samples, which indicates that these samples have undergone medium-grade metamorphism (blueschist to amphibolite facies; Evans, 1977) during their subduction. In contrast to serpentinites from the Tso Morari complex (Guillot et al., 2001), Erro-Tobbio massif (Scambelluri et al., 1995, 1997, 2001b), Cerro del Almirez massif (Scambelluri et al., 2001a; Garrido et al., 2005) and Zermatt-Saas ophiolite complex (Li et al., 2004), metamorphic olivine is not observed in the high-grade samples, indicating that

the selected Cuban and Dominican serpentinites did not experience dehydration due to the antigorite breakdown. In addition, there is no evidence that the serpentine phases might be retrograde products. Previous studies in Cuban serpentinites (Auzende et al., 2002; Hattori and Guillot, 2007: Schwartz et al., submitted) have shown that lizardite formed first, probably in an oceanic environment, then antigorite appeared at higher temperature/higher pressure, probably during burial in the subduction zone. Identical conclusions were reached for Dominican serpentinites by Saumur et al. (2010) who observed primary lizardite overprinted by pervasive blades of antigorite.

Geochemistry of serpentine phases

We determined the compositions of serpentine minerals, including trace elements, using a Laser ablation system coupled to a ThermoFinnigan Element 2 HR-ICPMS (Table 1). The analytical procedure is reported in Appendix S1, and a detailed description of the analytical procedure is reported in Deschamps *et al.* (2010).

Abyssal serpentinites sampled at MARK (Andreani et al., 2008) and in the Greater Antilles (Deschamps et al., in preparation) are characterized by low bulk-rock concentrations of incompatible elements [e.g. Y, Zr, REE $< 1 \times \text{primitive mantle (PM)};$ McDonough and Sun, 1995] and have similar compositions to oceanic peridotites: for example, REE concentrations overlap those of abyssal peridotites (Niu, 2004; Paulick et al., 2006). The serpentine phases also preserve the geochemical characteristics of the primary mineral phases (olivine, orthopyroxene and clinopyroxene; Deschamps et al., 2010) for these elements. This observation is consistent with the results of previous serpentinite studies suggesting moderate (e.g. REE) or no mobility of many incompatible elements (e.g. Sc, Ti, Y) at the scale of the sample in spite of extensive hydration (Deschamps et al., 2010). Yet, all abyssal serpentinite samples studied here are characterized by significant bulk-rock enrichments in FME, a feature that we attribute to interaction with seawater during serpentinization (Deschamps, 2010; Deschamps et al.,

Table 1 Average and standard deviations of FME (B,	Li, As, Sb, Pb, U, Ba, Sr and Cs) concentrations measured from in situ
analyses of abyssal and subducted serpentine phases.	

Rocks Mineralogy Location Elements (μg g ⁻¹)	Abyssal serpentinite		Subducted serpentinite	•	Subducted serpentinite	2
	Chrysotile and lizardite MARK		Chrysotile and lizardite Greater Antilles		Antigorite Greater Antilles	
	В	47.77	26.97	41.25	32.27	14.27
Li	2.66	5.43	1.46	1.38	1.04	0.80
As	0.31	0.44	0.27	0.16	1.03	0.53
Sb	0.18	0.30	0.04	0.05	0.13	0.11
Pb	0.66	0.79	0.27	0.34	0.21	0.24
U	0.43	1.33	0.01	0.01	0.10	0.16
Ba	1.43	3.25	4.03	11.15	0.65	0.72
Sr	1.75	1.49	5.33	11.66	3.43	9.34
Cs	0.11	0.13	0.06	0.10	0.06	0.06

FME, fluid-mobile element.

Analytical methods are reported in Deschamps et al. (2010).

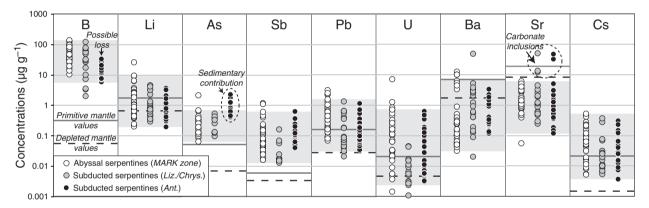


Fig. 1 Plots of concentrations of selected fluid-mobile elements (B, Li, As, Sb, Pb, U, Ba, Sr and Cs) in abyssal serpentines from ODP Site 920 (23°N, MARK Zone; white circles) and in subducted serpentines from Cuba and the Dominican Republic (lizardite/chrysotile assemblage = grey circles; antigorite assemblage = black circles). Values of primitive mantle after McDonough and Sun (1995) and depleted mantle after Salters and Stracke (2004) are also reported (grey lines). Grey boxes represent the typical ranges of each fluid-mobile element observed in serpentine phases analysed during this study.

in preparation). This increase in FME occurs in most serpentine minerals, whatever the mineral they replace (As, Sb, B and to a lesser extent Cs, U and Pb; Fig. 1), but FME concentrations remain very low in magnetite and Crspinel (F. Deschamps, unpublished data; Deschamps *et al.*, 2010).

Origin and timing of fluid-mobile element enrichments

Abyssal peridotites are hydrated during their exposure to seawater on the seafloor or at shallow depths during ridge hydrothermal activity. Andreani *et al.* (2007) have demonstrated that MARK serpentinites were formed

after tectonically controlled penetration of seawater into mantle peridotites to depths of 3-8 km (Andreani et al., 2007) at T < 300-350 °C (Allen and Seyfried, 2003). Abyssal serpentines from MARK are characterized by significant enrichments in B (10.5-136 $\mu g g^{-1}$), Li (0.20–26.1 $\mu g g^{-1}$), As $(0.07-2.16 \ \mu g \ g^{-1}), \quad \text{Sb} \quad (0.02-1.19)$ $\mu g g^{-1}$), U (up to 7 $\mu g g^{-1}$), Pb (up to 3 $\mu g g^{-1}$) and Cs (up to 0.52 $\mu g g^{-1}$) compared with primitive mantle values (McDonough and Sun, 1995) and depleted mantle values (Salters and Stracke, 2004; Fig. 1). Such enrichments in FME are common in serpentinites (Hattori and Guillot, 2007) and are explained by

intense hydrothermal activity under high fluid/rock ratios. A comparison between the chemical compositions of serpentines and fluids from the Logatchev hydrothermal field (Schmidt et al., 2007) reveals that serpentine is enriched in FME by 10-100 times compared with fluids. This implies extreme fluid/rock ratios, between \sim 20 and up to 10⁶, during the hydration of abyssal serpentinites (Delacour et al., 2008). B is enriched in all serpentine phases, while Li is relatively depleted compared with PM values (McDonough and Sun, 1995) and primary phases (Fig. 2), yet both B and Li have high solubilities in aqueous fluids and are commonly

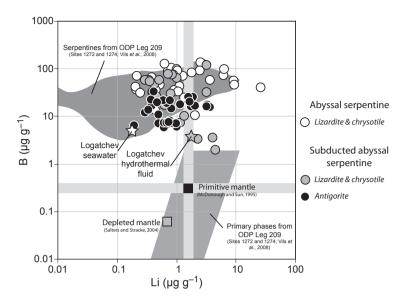


Fig. 2 B vs. Li concentrations (μg g⁻¹; modified from Vils *et al.*, 2008) for serpentine from abyssal serpentinites (MARK Zone; open circles) and Cuban and Dominican subducted serpentinites (grey circles are for lizardite/chrysotile-bearing samples and solid circles are for antigorite-bearing samples). Dark grey field and light grey box represent compositions of serpentines and associated primary (olivine and pyroxene) phases, respectively, from abyssal peridotites of ODP Leg 209 (Vils *et al.*, 2008). Compositions of primitive mantle (solid square; McDonough and Sun, 1995) and depleted mantle (grey square; Salters and Stracke, 2004) are also shown for comparison. Logatchev seawater (white star) and hydrothermal fluid (grey star) compositions are from Schmidt *et al.* (2007).

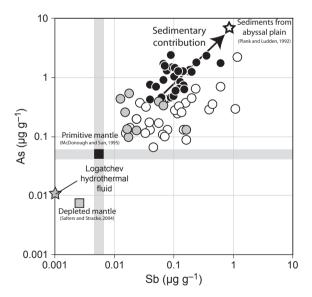


Fig. 3 Plot of As vs. Sb concentrations in $\mu g \, g^{-1}$ for serpentine from abyssal serpentinites (MARK Zone; open circles) and Cuban and Dominican subducted serpentinites (grey circles are for lizardite/chrysotile-bearing samples and solid circles are for antigorite-bearing samples). Note the higher As content in antigorite-bearing samples (solid circles); see text for explanation. Compositions of primitive mantle (black square) and depleted mantle (grey square) are from McDonough and Sun (1995) and Salters and Stracke (2004), respectively. Logatchev hydrothermal fluid (grey star) composition is from Schmidt *et al.* (2007). The average composition of sediments from the Argo abyssal plain (Site 765; Plank and Ludden, 1992) is represented by the white star.

enriched in seawater and hydrothermal fluids. This decoupled behaviour of B and Li is typical of abyssal serpentines (Lee *et al.*, 2008; Vils *et al.*, 2008).

Subducted serpentines have high levels of FME enrichment in B (2-120 $\mu g g^{-1}$), Li (0.1–4.6 $\mu g g^{-1}$), As $(0.1-2.4 \mu g g^{-1})$, Sb $(0.01-0.6 \mu g g^{-1})$, U (up to $0.62 \mu g g^{-1}$), Pb (up to $1.38 \ \mu g \ g^{-1}$) and Cs (up to $0.36 \ \mu g$ g⁻¹) compared with primitive mantle (McDonough and Sun, 1995; Table 1; Fig. 1). Note the high Sr concentrations in some subducted serpentines (Fig. 1), which are best explained by the presence of carbonate grains disseminated in the serpentine phase. Except for As and Sb, the FME composition of subducted serpentines is similar to that of MARK serpentines (Figs 1 and 3). As and, to a lesser extent, Sb are enriched in antigorite in subducted serpentinites compared with lizardite and chrysotile in abyssal and subducted serpentinites. The bulk-rock composition also shows this increase in As and Sb concentrations from lizardite/chrysotile serpentinites (As: $0.31-0.64 \mu g g^{-1}$; Sb: $\approx 0.05 \mu g g^{-1}$) to antigorite serpentinites (As: 0.64– $3.74 \mu g g^{-1}$; Sb: 0.09– $0.14 \mu g g^{-1}$; Hattori and Guillot, 2007; Deschamps et al., in preparation).

Micro-Raman spectroscopy in lowgrade Cuban serpentinites shows two stages of serpentinization (Hattori and Guillot, 2007): a low-temperature serpentinization formed lizardite along cracks in olivine, and a later hightemperature serpentinization resulted in the development of antigorite in the matrix. The high As and Sb concentrations characterizing the antigoritedominated serpentinites are likely related to this second stage of serpentinization, while antigorite is formed after lizardite/chrysotile. This secondary enrichment may result from the preferential incorporation of As and Sb into antigorite due to a change in local pH, fO2 or fS: such variations in the local conditions of alteration would destabilize accessory phases such as sulphides, arsenides or Fe oxides and thus favour the release of chalcophile elements. Model calculations (Klein et al., 2009) show the intimate connection of partitioning and oxidation state of iron with temperature and water/rock ratio during serpentinization, notably for the

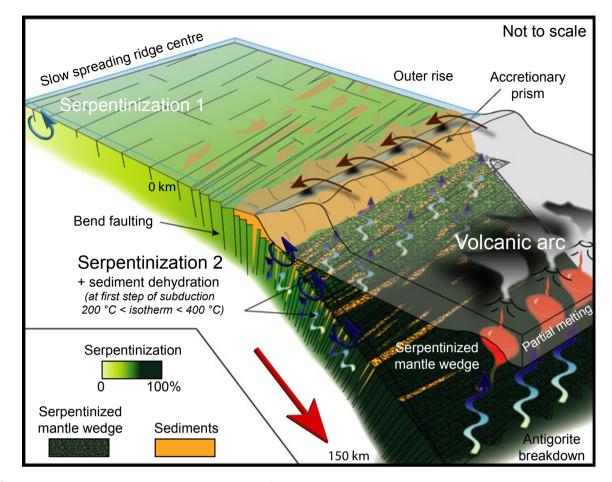


Fig. 4 Sketch illustrating the two-step serpentinization of abyssal peridotites. The first serpentinization takes place at or close to a slow-spreading ridge, whereas the second serpentinization is related to (i) bending faults when the slab is subducted or (ii) mechanical mixing between metasediments and serpentinites in the subduction channel. In this context, the contribution of sediments is marked by high As–Sb concentrations in subducted serpentinites. Thus, serpentinites act as sponges from the ridge until their dehydration, incorporating great amounts of fluid-mobile element (FME). They are a temporary reservoir and can efficiently transfer significant quantities of FME and a sedimentary geochemical signature from shallow to great depths in the mantle, down to the antigorite breakdown isograd.

stability of Fe-Ni-O-S phase assemblages. However, previous studies (Hattori et al., 2005; Deschamps et al., 2010) and our unpublished data on the trace element compositions of iron oxides demonstrate that Fe-rich phases cannot explain the whole-rock budget of As and Sb. Moreover, if chalcophile elements are redistributed from iron oxides and sulphides/arsenides to antigorite during the transformation from lizardite/chrysotile to antigorite, the bulk-rock composition should remain the same. We observe higher bulk concentrations of As and Sb in rocks dominated by antigorite (Hattori and Guillot, 2007; Deschamps et al., in preparation). Therefore, we propose that As and Sb in the serpentine originated from an external source.

The concentration of As in ridge hydrothermal fluids is 10 times higher $(0.01 \mu g g^{-1}$; Schmidt *et al.*, 2007) than the As concentration in seawater $(0.001 \mu g g^{-1}; Correia et al.,$ 2010). However, sedimentary rocks commonly have high As contents (≥1 µg g⁻¹; Smedley and Kinniburgh, 2002). We propose that the As in antigorite is mainly derived from sediments. The secondary enrichment of As and Sb observed in antigorite cannot occur at, or close to, the mid-ocean accretion zone because sediments represent a very minor component of the lithosphere at ridges. As higher concentrations of As and Sb are only observed in highgrade subducted serpentinites, Asand Sb-rich fluids originating from subducted sediments likely penetrated into the downwelling abyssal serpentinites.

Interactions between serpentinites and sediments are greatly facilitated by the tectonic context of subduction zones (Fig. 4), and thus two scenarios could be envisaged to explain the serpentinite/sediment/fluid interactions. (i) Faulting in the early stages of subduction favours the accumulation of sediments and the infiltration of fluids bearing this sedimentary signature into the slab: normal faults that formed earlier at spreading ridges are likely to be reactivated when the serpentinized oceanic lithosphere enters into the subduction zone, and

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new bending normal faults may also form at the outer rise/trench zone (Savage, 1969; Kirby et al., 1996; Jiao et al., 2000; Peacock, 2001; Ranero et al., 2005; Nedimović et al., 2009). (ii) Sediment-derived fluids infiltrate the serpentinized oceanic lithosphere along major faults in the accretionary prism or percolate through the serpentinites along the subduction channel, where sediments and serpentinites are more or less intimately mixed. We observe the As-Sb over-enrichment after the recrystallization of lizardite/chrysotile into antigorite, which implies that it occurred at least around isotherms 300–380 °C (Schwartz et al., submitted). The occurrence of As- and Sb-rich antigorite is in agreement with the data of Bebout et al. (1999), which showed that As and Sb are released from metasediments at the lawsonite-blueschist to epidoteblueschist transition between 350-400 °C and 0.9-1.2 GPa.

Serpentinites: a sponge for fluidmobile elements

Except for B, our results do not show evidence of loss of FME in serpentinites between the ridge and subducenvironments. This contradicts the common assumption that FME are mobile in fluids at high temperatures. Cs, like B, is easily removed by fluids at low T (200-300 °C) from metasedimentary rocks, whereas As and Sb will be released at higher T (350-400 °C; Bebout et al., 1999) when antigorite becomes stable (Wunder and Schreyer, 1997). Yet, in spite of the transition from chrysotile/ lizardite to antigorite in subducted serpentinites when temperature increases, Li, Pb, U, Ba Sr and Cs concentrations remain similar to those observed in abvssal serpentinites. whereas As and Sb are secondarily enriched (Figs 1 and 2). Only B shows evidence of depletion (65%) from lowgrade subducted serpentines to antigorite (Fig. 2); such loss has already been observed in Mariana forearc serpentinites by Benton et al. (2001) as well as in metasediments (Bebout et al., 1999). It can be explained (i) by a reequilibration with a B-depleted fluid during the already discussed As-Sb secondary enrichment or (ii) by an increase in temperature at the lizardite-antigorite transition, similar to that observed in metasediments around 250–300 °C (Bebout *et al.*, 1999). Because B and Li preserve their decoupled behaviour whatever the grade of metamorphism (Fig. 2), we favour the second hypothesis.

With the exception of As, Sb and B, most FME have similar concentrations in the serpentine phases of abyssal and subducted serpentinites. This observation suggests that these elements are not mobile in serpentinites during phase transitions, in contrast with the devolatilization of FME observed during prograde metamorphism of subducted sedimentary rocks (Bebout *et al.*, 1999, 2007) and of altered oceanic crust (Bebout, 2007; Marschall *et al.*, 2007).

Serpentine phases, and therefore serpentinites, act as a sponge in subduction zone environments (Fig. 4). They can incorporate large amounts of FME in their crystal structure near ridges and in subduction zones. The high degree of FME enrichment suggests that serpentinization at spreading ridges occurs under very high fluid/rock ratios. Subsequently, serpentinites undergo a second stage of serpentinization marked by the lizardite-antigorite transition. This second event involves loss of B but additional incorporation of FME, especially As and Sb, which are released from sedimentary rocks. We propose that serpentinites act as a temporary reservoir, which will transport from shallow depths to great depths (between 100 and 170 km, depending on the geothermal gradient) in the sub-arc mantle not only large amounts of FME, typical of abyssal serpentinite compositions, but also the As-Sb sedimentary signature acquired during the onset of subduction.

Acknowledgements

The study was supported by PROCOPE grants and CNRS INSU programmes. We thank Simone Pourtales, Olivier Bruguier and Jean-Luc Devidal for analytical assistance. We are grateful to Horst Marschall, Marco Scambelluri, Antonio García-Casco and Alfred Kroener for their constructive reviews that helped to improve the manuscript.

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Received 22 March 2010; revised version accepted 31 January 2011

Supporting Information

Additional Supporting Information may be found in the online version of this article:

Appendix S1. Trace element compositions were acquired using a ThermoFinnigan Element 2 HR-ICP-MS with a single collector double-focusing sector field Element XR (eXtended Range) coupled with laser ablation (LA) system at Géosciences Montpellier (University Montpellier 2, France).

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