

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

Fabien Deschamps,<sup>1,2</sup> Stéphane Guillot,<sup>1</sup> Marguerite Godard,<sup>2</sup> Muriel Andreani<sup>3</sup> and Kéiko Hattori<sup>4</sup>

<sup>1</sup>Laboratoire de Géodynamique des Chaînes Alpines, ISTERre, Université Grenoble I, 1381 rue de la Piscine, 38400 Grenoble Cedex 09, France;

<sup>2</sup>Géosciences Montpellier, CNRS/Université Montpellier 2, cc60, Place E. Bataillon, 34095 Montpellier, France; <sup>3</sup>Laboratoire de Sciences de la Terre, Université Claude Bernard Lyon I, 2 rue Raphaël Dubois, 69622 Villeurbanne, France; <sup>4</sup>Department of Earth Sciences, University of Ottawa, Ottawa, ON K1N 6N5, Canada

## 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

Serpentine 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). Serpentinities can hold on average 13 wt% H<sub>2</sub>O and may be stable down to depths of 170 km (Ulmer and Trommsdorff, 1995; Wunder and Schreyer, 1997); this makes serpentine a potentially important host of water in subducting lithosphere at mantle depths. 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

(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 (Ryan *et al.*, 1995; Leeman, 1996; Noll *et al.*, 1996), serpentinites contain high concentrations of fluid-mobile 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 prepara-

Correspondence: Dr Fabien Deschamps, Laboratoire de Géodynamique des Chaînes Alpines, Maison des Géosciences, 1381 Rue de la Piscine, 38400 Saint Martin d'Hères, France. Tel.: +33 (0)4 76 51 40 57; e-mail: fabien.deschamps@ujf-grenoble.fr

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 Moriri 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-serpentine 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-serpentine 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 low-grade 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-serpentine 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 Moriri 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).

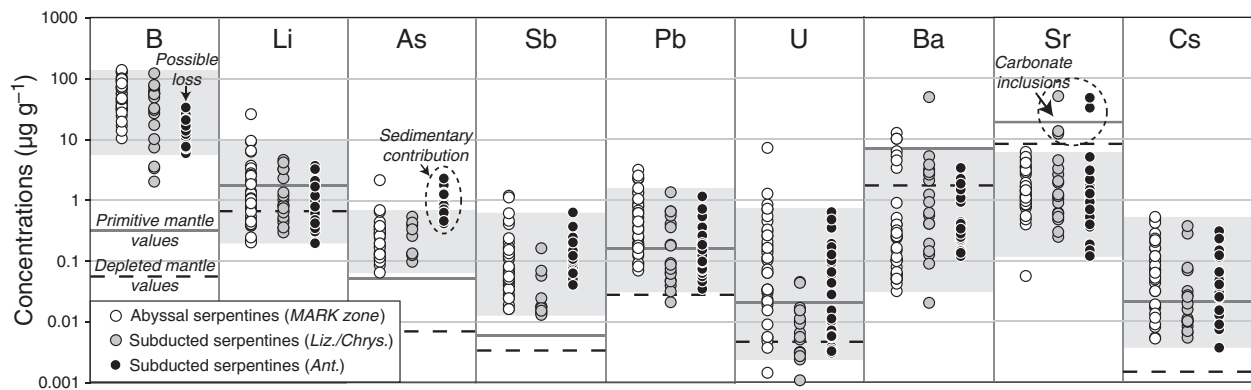
Abyssal serpentinites sampled at MARK (Andreani *et al.*, 2008) and in the Greater Antilles (Deschamps *et al.*, in preparation) are characterized by low bulk-rock concentrations of incompatible elements [e.g. Y, Zr, REE <1 × primitive mantle (PM); McDonough and Sun, 1995] and have similar compositions 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 serpentinite phases.

Rocks	Abyssal serpentinite		Subducted serpentinite		Subducted serpentinite	
Mineralogy	Chrysotile and lizardite		Chrysotile and lizardite		Antigorite	
Location	MARK		Greater Antilles		Greater Antilles	
Elements ( $\mu\text{g g}^{-1}$ )	Concentration (average, $\mu\text{g g}^{-1}$ ) ( $n = 27$ )		Concentration (average, $\mu\text{g g}^{-1}$ ) ( $n = 18$ )		Concentration (average, $\mu\text{g g}^{-1}$ ) ( $n = 34$ )	
		SD		SD		SD
B	47.77	26.97	41.25	32.27	14.27	7.10
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 serpentinites from ODP Site 920 (23°N, MARK Zone; white circles) and in subducted serpentinites 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 serpentinite phases analysed during this study.

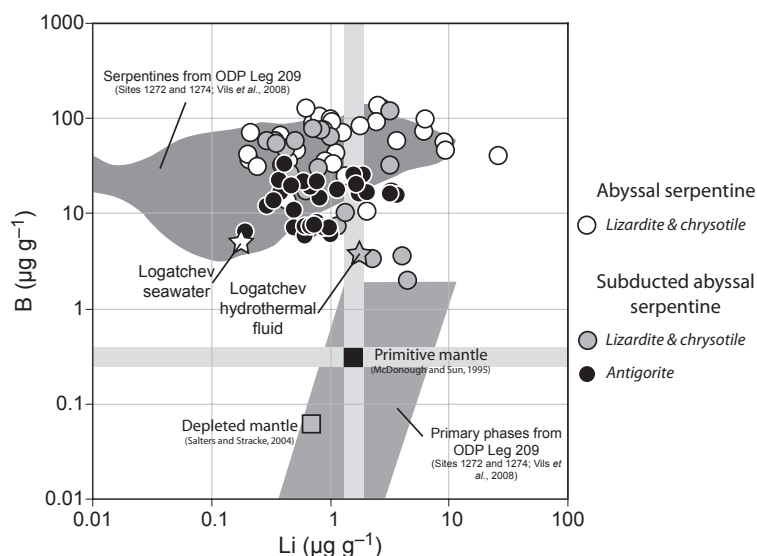
in preparation). This increase in FME occurs in most serpentinite minerals, whatever the mineral they replace (As, Sb, B and to a lesser extent Cs, U and Pb; Fig. 1), but FME concentrations remain very low in magnetite and Cr-spinel (F. Deschamps, unpublished data; Deschamps *et al.*, 2010).

### Origin and timing of fluid-mobile element enrichments

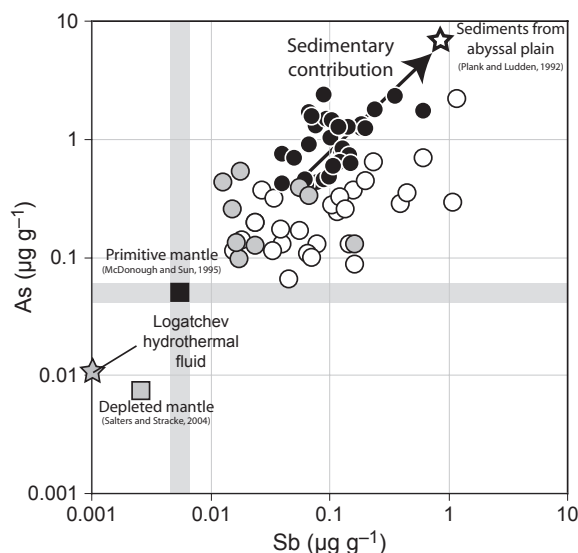
Abyssal peridotites are hydrated during their exposure to seawater on the seafloor or at shallow depths during ridge hydrothermal activity. Andreani *et al.* (2007) have demonstrated that MARK serpentinites were formed

after tectonically controlled penetration of seawater into mantle peridotites to depths of 3–8 km (Andreani *et al.*, 2007) at  $T < 300\text{--}350\text{ °C}$  (Allen and Seyfried, 2003). Abyssal serpentinites from MARK are characterized by significant enrichments in B (10.5–136  $\mu\text{g g}^{-1}$ ), Li (0.20–26.1  $\mu\text{g g}^{-1}$ ), As (0.07–2.16  $\mu\text{g g}^{-1}$ ), Sb (0.02–1.19  $\mu\text{g g}^{-1}$ ), U (up to 7  $\mu\text{g g}^{-1}$ ), Pb (up to 3  $\mu\text{g g}^{-1}$ ) and Cs (up to 0.52  $\mu\text{g g}^{-1}$ ) 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 serpentinites and fluids from the Logatchev hydrothermal field (Schmidt *et al.*, 2007) reveals that serpentinite is enriched in FME by 10–100 times compared with fluids. This implies extreme fluid/rock ratios, between  $\sim 20$  and up to  $10^6$ , during the hydration of abyssal serpentinites (Delacour *et al.*, 2008). B is enriched in all serpentinite 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 ( $\mu\text{g g}^{-1}$ ; modified from Vils *et al.*, 2008) for serpentinite 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 serpentinites 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).

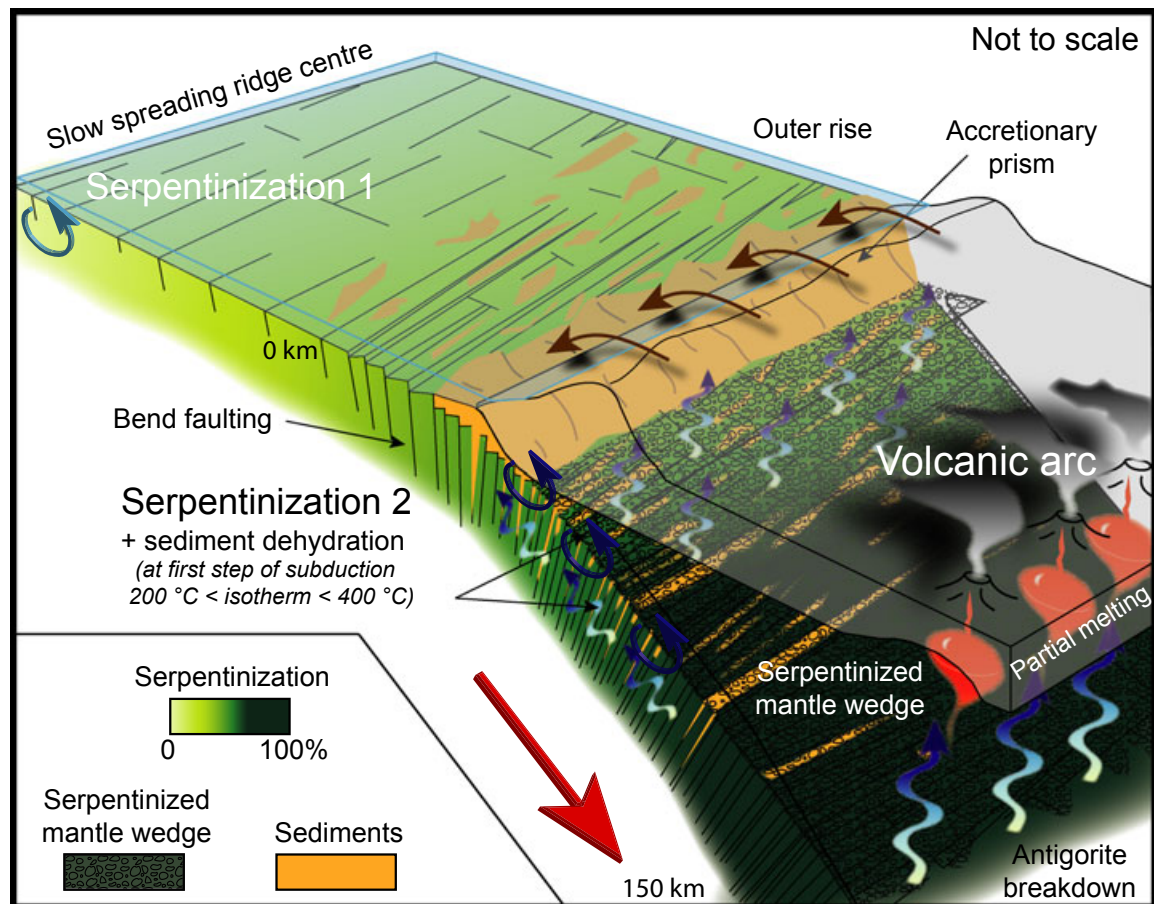


**Fig. 3** Plot of As vs. Sb concentrations in  $\mu\text{g g}^{-1}$  for serpentinite from abyssal serpentinites (MARK Zone; open circles) and Cuban and Dominican subducted serpentinites (grey circles are for lizardite/chrysotile-bearing samples and solid circles are for antigorite-bearing samples). 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 serpentinites (Lee *et al.*, 2008; Vils *et al.*, 2008).

Subducted serpentinites have high levels of FME enrichment in B ( $2\text{--}120 \mu\text{g g}^{-1}$ ), Li ( $0.1\text{--}4.6 \mu\text{g g}^{-1}$ ), As ( $0.1\text{--}2.4 \mu\text{g g}^{-1}$ ), Sb ( $0.01\text{--}0.6 \mu\text{g g}^{-1}$ ), U (up to  $0.62 \mu\text{g g}^{-1}$ ), Pb (up to  $1.38 \mu\text{g g}^{-1}$ ) and Cs (up to  $0.36 \mu\text{g g}^{-1}$ ) compared with primitive mantle (McDonough and Sun, 1995; Table 1; Fig. 1). Note the high Sr concentrations in some subducted serpentinites (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 serpentinites is similar to that of MARK serpentinites (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:  $0.31\text{--}0.64 \mu\text{g g}^{-1}$ ; Sb:  $\approx 0.05 \mu\text{g g}^{-1}$ ) to antigorite serpentinites (As:  $0.64\text{--}3.74 \mu\text{g g}^{-1}$ ; Sb:  $0.09\text{--}0.14 \mu\text{g g}^{-1}$ ; Hattori and Guillot, 2007; Deschamps *et al.*, in preparation).

Micro-Raman spectroscopy in low-grade Cuban serpentinites shows two stages of serpentinization (Hattori and Guillot, 2007): a low-temperature serpentinization formed lizardite along cracks in olivine, and a later high-temperature serpentinization resulted in the development of antigorite in the matrix. The high As and Sb concentrations characterizing the antigorite-dominated 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,  $f\text{O}_2$  or  $f\text{S}$ : 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 ( $0.01 \mu\text{g g}^{-1}$ ; Schmidt *et al.*, 2007) than the As concentration in seawater ( $0.001 \mu\text{g g}^{-1}$ ; Correia *et al.*, 2010). However, sedimentary rocks commonly have high As contents ( $\geq 1 \mu\text{g g}^{-1}$ ; 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 high-

grade subducted serpentinites, As- and 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 fluids 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

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 epidote–blueschist transition between 350–400 °C and 0.9–1.2 GPa.

### Serpentinites: a sponge for fluid-mobile elements

Except for B, our results do not show evidence of loss of FME in serpentinites between the ridge and subduction environments. This result 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 abyssal serpentinites, whereas As and Sb are secondarily enriched (Figs 1 and 2). Only B shows evidence of depletion (65%) from low-grade 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.

### References

Allen, D.E. and Seyfried Jr, E., 2003. Compositional controls on vent fluids

- from ultramafic-hosted hydrothermal systems at mid-ocean ridges: an experimental study at 400 °C, 500 bars. *Geochim. Cosmochim. Acta*, **67**, 1531–1542.
- Andreani, M., Mével, C., Boullier, A.-M. and Escartin, J., 2007. Dynamic control on serpentine crystallization in veins: constraints on hydration processes in oceanic peridotites. *Geochem. Geophys. Geosyst.*, **8**, Q02012, 24pp., doi: 10.1029/2006GC001373.
- Andreani, M., Godard, M. and Mével, C., 2008. An in-situ trace elements study of serpentinites from the MARK area (ODP site 920, 23°N). *Geochim. Cosmochim. Acta*, **72**, A26.
- Auzende, A.-L., Devouard, B., Guillot, S., Daniel, I., Baronnat, A. and Lardeaux, J.-M., 2002. Serpentinites from Central Cuba: petrology and HRTEM study. *Eur. J. Mineral.*, **14**, 905–914.
- Bebout, G.E., 2007. Metamorphic chemical geodynamics of subduction zones. *Earth Planet. Sci. Lett. Front.*, **260**, 373–393.
- Bebout, G.E., Ryan, J.G., Leeman, W.P. and Bebout, A.E., 1999. Fractionation of trace elements by subduction-zone metamorphism – effect of convergent-margin thermal evolution. *Earth Planet. Sci. Lett.*, **171**, 63–81.
- Bebout, G.E., Bebout, A.E. and Graham, C.M., 2007. Cycling of B, Li, and LILE (K, Cs, Rb, Ba, Sr) into subduction zones: SIMS evidence from micas in high-P/T metasedimentary rocks. *Chem. Geol.*, **239**, 284–304.
- Benton, L.D., Ryan, J.G. and Tera, F., 2001. Boron isotopes systematics of slab fluids as inferred from a serpentine seamount, Mariana forearc. *Earth Planet. Sci. Lett.*, **187**, 273–282.
- Bonatti, E., Lawrence, J.R. and Morandi, N., 1984. Serpentinization of oceanic peridotites: temperature dependence of mineralogy and boron content. *Earth Planet. Sci. Lett.*, **70**, 88–94.
- Cannat, M., Mével, C., Maia, M., Deplus, C., Durand, C., Gente, P., Agrinier, P., Belarouchi, A., Dubuisson, G., Humler, E. and Reynolds, J., 1995. Thin crust, ultramafic exposures, and rugged faulting patterns at the Mid-Atlantic Ridge (22°–24°N). *Geology*, **23**, 49–52.
- Carlson, R.L., 2001. The abundance of ultramafic rocks in Atlantic Ocean crust. *Geophys. J. Int.*, **144**, 37–48.
- Correia, C.L.T., Gonçalves, R.A., Azevedo, M.S., Vieira, M.A. and Campos, R.C., 2010. Determination of total arsenic in seawater by hybrid generation atomic fluorescence spectrometry. *Microchem. J.*, **96**, 157–160.
- Delacour, A., Früh-Green, G.L., Frank, M., Gutjahr, M. and Kelley, D.S., 2008. Sr- and Nd-isotope geochemistry of the Atlantis Massif (30°N, MAR):

- implications for fluid fluxes and lithospheric heterogeneity. *Chem. Geol.*, **254**, 19–35.
- Deschamps, F., 2010. *Caractérisation in situ des Serpentinites en Contexte de Subduction: de la Nature à l'expérience*. Unpublished doctoral dissertation, Université Joseph Fourier, Grenoble, 402 pp.
- Deschamps, F., Guillot, S., Godard, M., Chauvel, C., Andreani, M. and Hattori, K., 2010. *In situ* characterization of serpentinites from forearc mantle wedges: timing of serpentinization and behavior of fluid-mobile elements in subduction zones. *Chem. Geol.*, **269**, 262–277.
- Dobson, D.P., Meredith, P.G. and Boon, S.A., 2002. Simulation of subduction zone seismicity by dehydration of serpentine. *Science*, **298**, 1407–1410.
- Evans, B.W., 1977. Metamorphism of Alpine peridotite and serpentinite. *Annu. Rev. Earth Planet Sci.*, **5**, 397–447.
- García-Casco, A., Torres-Roldán, R.L., Millán, G., Monié, P. and Schneider, J., 2002. Oscillatory zoning in eclogitic garnet and amphibole, northern serpentinite melange, Cuba: a record of tectonic instability during subduction? *J. Metamorphic Geol.*, **20**, 581–598.
- García-Casco, A., Torres-Roldán, R.L., Iturralde-Vinent, M.A., Millán, G., Nunez Cambra, K., Lázaro, C. and Rodríguez Vega, A., 2006. High pressure metamorphism of ophiolites in Cuba. *Geol. Acta*, **4**, 63–88.
- García-Casco, A., Iturralde-Vinent, M.A. and Pindell, J., 2008. Latest Cretaceous collision/accretion between the Caribbean Plate and Caribéana: origin of metamorphic terranes in the Greater Antilles. *Int. Geol. Rev.*, **50**, 781–809.
- Garrido, C.J., López Sánchez-Vizcaino, V., Gómez-Pugnaire, M.T., Trommsdorff, V., Alard, O., Bodinier, J.-L. and Godard, M., 2005. Enrichment of HFSE in chlorite-harzburgite produced by high-pressure dehydration of antigorite-serpentinite: implications for subduction magmatism. *Geochem. Geophys. Geosyst.*, **6**, Q01J15, 15pp., doi: 10.1029/2004GC000791.
- Guillot, S., Hattori, K.H., de Sigoyer, J., Nägler, T. and Auzende, A.-L., 2001. Evidence of hydration of the mantle wedge and its role in the exhumation of eclogites. *Earth Planet. Sci. Lett.*, **193**, 115–127.
- Hattori, K.H. and Guillot, S., 2003. Volcanic fronts form as a consequence of serpentinite dehydration in the forearc mantle wedge. *Geology*, **31**, 525–528.
- Hattori, K.H. and Guillot, S., 2007. Geochemical character of serpentinites associated with high- to ultrahigh-pressure metamorphic rocks in the Alps, Cuba, and the Himalayas: recycling of elements in subduction zones. *Geochem. Geophys. Geosyst.*, **8**, Q09010, 27pp., doi: 10.1029/2007GC001594.
- Hattori, K.H., Takahashi, Y., Guillot, S. and Johanson, B., 2005. Occurrence of arsenic (V) in forearc mantle serpentinites based on X-ray absorption spectroscopy study. *Geochim. Cosmochim. Acta*, **69**, 5585–5596.
- Iturralde-Vinent, M.A., 1998. Sinopsis de la constitución geológica de Cuba. *Acta Geol. Hisp.*, **33**, 9–56.
- Jiao, W., Silver, P.G., Fei, Y. and Prewitt, C.T., 2000. Do intermediate- and deep-focus earthquakes occur on preexisting weak zones? An examination of the Tonga subduction zone. *J. Geophys. Res.*, **105**, 28125–28138.
- Kirby, S.H., Engdahl, E.R. and Denlinger, R., 1996. Intermediate-depth intraslab earthquakes and arc volcanism as physical expressions of crustal and uppermost mantle metamorphism in subducting slabs. In: *Subduction: Top to Bottom*, Vol. 96 (G.E. Bebout, ed), pp. 195–214. Geophysical Monographs Series, AGU, Washington, DC.
- Klein, F., Bach, W., Jöns, N., McCollom, T., Moskowitz, B. and Berquó, T., 2009. Iron partitioning and hydrogen generation during serpentinization of abyssal peridotites from 15°N on the Mid-Atlantic Ridge. *Geochim. Cosmochim. Acta*, **73**, 6868–6893.
- Krebs, M., Maresch, W.V., Schertl, H.-P., Münker, C., Baumann, A., Draper, G., Idelman, B. and Trapp, E., 2008. The dynamics of intra-oceanic subduction zones: a direct comparison between fossil petrological evidence (Rio San Juan Complex, Dominican Republic) and numerical simulation. *Lithos*, **103**, 106–137.
- Lee, C.-T.A., Oka, M., Luffi, P. and Agranier, A., 2008. Internal distribution of Li and B in serpentinites from the Feather River Ophiolite, California, based on laser ablation inductively coupled plasma mass spectrometry. *Geochem. Geophys. Geosyst.*, **9**, Q12011, 14pp., doi: 10.1029/2008GC002078.
- Leeman, W.P., 1996. Boron and other fluid-mobile elements in volcanic arc lavas: Implications for subduction processes. In: *Subduction top to bottom* (G.E. Bebout, J. Platt, D.W. Scholl and S. Kirby, eds.), *American Geophysical Union Geophysical Monograph*, **96**, 269–276.
- Li, X.-P., Rahn, M. and Bucher, K., 2004. Serpentinites of the Zermatt-Saas ophiolite complex and their texture evolution. *J. Metamorphic Geol.*, **22**, 159–177.
- Marschall, H.R., Altherr, R. and Rüpke, L., 2007. Squeezing out the slab – modelling the release of Li, Be and B during progressive high pressure metamorphism. *Chem. Geol.*, **239**, 323–335.
- McDonough, W.F. and Sun, S.-S., 1995. The composition of the Earth. *Chem. Geol.*, **120**, 223–253.
- Mével, C., 2003. Serpentinization of abyssal peridotites at mid-ocean ridges. *CR Géosci.*, **335**, 825–852.
- Millán, G., 1997. Geología del macizo metamórfico del Escambray. In: *Estudios Sobre Geología de Cuba* (G.F. Furrázola Bermúdez and K.E. Núñez Cambra, eds), pp. 271–288. Centro Nacional de Información Geológica, La Habana, Cuba.
- Nedimović, M.R., Bohnenstiehl, D.R., Carbotte, S.M., Canales, J.P. and Dziak, R.P., 2009. Faulting and hydration of the Juan de Fuca plate system. *Earth Planet. Sci. Lett.*, **284**, 94–102.
- Niu, Y., 2004. Bulk-rock major and trace element compositions of abyssal peridotites: implications for mantle melting, melt extraction and post-melting processes beneath Mid-Ocean Ridges. *J. Petrol.*, **45**, 2423–2458.
- Noll Jr, P.D., Newsom, H.E., Leeman, W.P. and Ryan, J.G., 1996. The role of hydrothermal fluids in the production of subduction zone magmas: evidence from siderophile and chalcophile trace elements and boron. *Geochim. Cosmochim. Acta*, **60**, 587–611.
- Paulick, H., Bach, W., Godard, M., De Hoog, J.C.M., Suhr, G. and Harvey, J., 2006. Geochemistry of abyssal peridotites (Mid-Atlantic Ridge, 15°20'N, ODP Leg 209): implications for fluid/rock interaction in slow spreading environments. *Chem. Geol.*, **234**, 179–210.
- Peacock, S., 2001. Are the lower planes of double seismic zones caused by serpentinite dehydration in subducting oceanic mantle? *Geology*, **29**, 299–302.
- Pearce, N.J.G., Perkins, W.T., Westgate, J.A., Gorton, M.P., Jackson, S.E., Neal, C.R. and Chenery, S.P., 1997. A compilation of new and published major and trace element data for NIST SRM 610 and NIST SRM 612 glass reference materials. *Geostand. Newslett. J. Geostand. Geoanal.*, **21**, 115–144.
- Perrillat, J.-P., Daniel, I., Koga, K.T., Reynard, B., Cardon, H. and Crichton, W.A., 2005. Kinetics of antigorite dehydration: a real-time X-ray diffraction study. *Earth Planet. Sci. Lett.*, **236**, 899–913.
- Plank, T. and Ludden, J.N., 1992. Geochemistry of sediments in the Argo abyssal plain at Site 765: a continental margin reference section for sediment recycling in subduction zones. In: *Proceedings of the Ocean Drilling Program, Scientific Results, Vol. 123* (F.M. Gradstein, J.N. Ludden and the Shipboard Scientific Party, eds), pp. 167–189. College Station TX, (Ocean Drilling Program).

- Ranero, C., Villaseñor, A., Morgan, J.P. and Weinrebe, W., 2005. Relationship between bend-faulting at trenches and intermediate-depth seismicity. *Geochem. Geophys. Geosyst.*, **6**, Q12002, 25pp., doi: 10.1029/2005GC000997.
- Rüpke, L.H., Morgan, J.P., Hort, M. and Connolly, J.A.D., 2002. Are the regional variations in Central American arc lavas due to differing basaltic versus peridotitic slab sources of fluids? *Geology*, **30**, 1035–1038.
- Rüpke, L.H., Morgan, J.P., Hort, M. and Connolly, J.A.D., 2004. Serpentine and the subduction zone water cycle. *Earth Planet. Sci. Lett.*, **223**, 17–34.
- Ryan, J.G., Morris, J., Tera, F., Leeman, W.P. and Tsvetkov, A., 1995. Cross-arc geochemical variations in the Kurile arc as a function of slab depth. *Science*, **270**, 625–627.
- Salters, V.J.M. and Stracke, A., 2004. Composition of the depleted mantle. *Geochem. Geophys. Geosyst.*, **5**, Q05B07, 27pp., doi: 10.1029/2003GC000597.
- Saumur, B.-M., Hattori, K.H. and Guillot, S., 2010. Contrasting origins of serpentinites in a subduction complex, northern Dominican Republic. *Geol. Soc. Am. Bull.*, **122**, 292–304.
- Savage, J.C., 1969. The mechanics of deep-focus faulting. *Tectonophysics*, **8**, 115–127.
- Scambelluri, M., Müntener, O., Hermann, J., Piccardo, G.B. and Trommsdorff, V., 1995. Subduction of water into the mantle: history of an alpine peridotite. *Geology*, **23**, 459–462.
- Scambelluri, M., Piccardo, G.B., Philippot, P., Robbiano, A. and Negretti, L., 1997. High salinity fluid inclusions formed from recycled seawater in deeply subducted alpine serpentinite. *Earth Planet. Sci. Lett.*, **148**, 485–499.
- Scambelluri, M., Bottazzi, P., Trommsdorff, V., Vannucci, R., Hermann, J., Gómez-Pugnaire, M.T. and López-Sánchez Vizcaino, V., 2001a. Incompatible element-rich fluids released by antigorite breakdown in deeply subducted mantle. *Earth Planet. Sci. Lett.*, **192**, 457–470.
- Scambelluri, M., Rampone, E. and Piccardo, G.B., 2001b. Fluid and element cycling in subducted serpentinite: a trace-element study of the Erro-Tobbio high pressure ultramafites (Western Alps, NW Italy). *J. Petrol.*, **42**, 55–67.
- Scambelluri, M., Müntener, O., Ottolini, L., Pettke, T.T. and Vannucci, R., 2004a. The fate of B, Cl and Li in the subducted oceanic mantle and in the antigorite breakdown fluids. *Earth Planet. Sci. Lett.*, **222**, 217–234.
- Scambelluri, M., Fiebig, J., Malaspina, N., Müntener, O. and Pettke, T., 2004b. Serpentinite subduction: implications for fluid processes and trace-element recycling. *Int. Geol. Rev.*, **46**, 595–613.
- Schmidt, M.W. and Poli, S., 1998. Experimentally based water budget for dehydrating slabs and consequences for arc magma generation. *Earth Planet. Sci. Lett.*, **163**, 361–379.
- Schmidt, K., Koschinsky, A., Garbe-Schönberg, D., Carvalho, (de) L.M. and Seifert, R., 2007. Geochemistry of hydrothermal fluids from the ultramafic-hosted Logatchev hydrothermal field, 15°N on the Mid-Atlantic Ridge: temporal and spatial investigation. *Chem. Geol.*, **242**, 1–21.
- Schneider, J., Bosch, D., Monié, P., Guillot, S., García-Casco, A., Lardeaux, J.M., Torres-Roldan, R.L. and Millan Trujillo, G., 2004. Origin and evolution of the Escambray Massif (Central Cuba): an example of HP/LT rocks exhumed during intraoceanic subduction. *J. Metamorphic Geol.*, **22**, 27–247.
- Sharp, Z.D. and Barnes, J.D., 2004. Water-soluble chlorides in massive seafloor serpentinites: a source of chloride in subduction zones. *Earth Planet. Sci. Lett.*, **226**, 243–254.
- Smedley, P.L. and Kinniburgh, D.G., 2002. A review of the source, behaviour and distribution of arsenic in natural waters. *Appl. Geochem.*, **17**, 517–568.
- Somin, M.L. and Millán, G., 1981. *Geology of the Metamorphic Complexes of Cuba*. Nauka Press, Moscow, USSR, 218 pp. (in Russian).
- Spear, F.S., 1993. Metamorphic phase equilibria and pressure-temperature-time paths. *Mineral. Soc. Am. Mon. Ser.*, **799** p. Washington D.C.
- Stanek, K.P., Maresch, W.V., Grafe, F., Grevel, C.H. and Baumann, A., 2006. Structure, tectonics, and metamorphic development of the Sancti Spiritus Dome (eastern Escambray massif, Central Cuba). *Geol. Acta*, **4**, 151–170.
- Tenthorey, E. and Hermann, J., 2004. Composition of fluids during serpentinite breakdown in subduction zones: evidence for limited boron mobility. *Geology*, **32**, 865–868.
- Ulmer, P. and Trommsdorff, V., 1995. Serpentine stability to mantle depths and subduction-related magmatism. *Science*, **268**, 858–861.
- Vils, F., Pelletier, L., Kalt, A., Müntener, O. and Ludwig, T., 2008. The lithium, boron and beryllium content of serpentinized peridotites from ODP Leg 209 (Sites 1272A and 1274A): implications for lithium and boron budgets of oceanic lithosphere. *Geochim. Cosmochim. Acta*, **72**, 5475–5504.
- Wunder, B. and Schreyer, W., 1997. Antigorite: high-pressure stability in the system MgO-SiO<sub>2</sub>-H<sub>2</sub>O (MSH). *Lithos*, **41**, 213–227.

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).

Please note: Wiley-Blackwell are not responsible for the content or functionality of any supporting materials supplied by the authors. Any queries (other than missing material) should be directed to the corresponding author for the article.