



# The water and fluid-mobile element cycles during serpentinite subduction. A review

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**Abstract:** The key role of serpentinites in the global cycles of volatiles, halogens and fluid-mobile elements in oceans and in subduction zones is now ascertained by many studies quantifying their element budgets and the composition of fluids they release during subduction. Geochemical tracers (*e.g.* B, As, Sb; stable B and radiogenic Sr and Pb isotopes) have also been employed to trace the provenance of serpentinites (slab or forearc mantle?) accreted to the plate interface of fossil subduction zones. In turn, this helps defining the tectonic processes, seismicity and mass transfer attending rock burial and exhumation within subduction zones. The results suggest that the sole use of geochemical data is insufficient to track the origin of subduction-zone serpentinites and the timing of serpentinization, whether oceanic or subduction-related. Integrated multidisciplinary studies of ophiolitic serpentinites show that pristine, oceanic, geochemical imprints (*e.g.* high <sup>11</sup>B, marine Sr isotopes, low As + Sb) become reset towards more radiogenic Sr, lower <sup>11</sup>B, and higher As + Sb *via* metasomatic exchange with crust-derived fluids during subduction accretion to the plate interface. The dehydration fluids released by serpentinite dehydration at various subduction stages and still preserved in these rocks as inclusions, carry significant amounts of halogens and fluid-mobile elements. The key compositional similarities of antigorite-breakdown fluids from different localities (Betic Cordillera, Spain; Central Alps, Switzerland) indicate that rocks record comparable subduction processes. We individuate the fluid-mediated exchange with sedimentary and/or crustal reservoirs during subduction as the key mechanism for geochemical hybridization of serpentinite. The antigorite dehydration fluids produced by hybrid serpentinites have high Cs, Rb, Ba, B, Pb, As, Sb and Li overlapping those of the arc lavas and representing the mixed serpentinite–sediment (crustal) component released to arcs. This helps discriminating the mass transfer processes responsible for *supra*-subduction mantle metasomatism and arc magmatism. The studied plate-interface hybrid serpentinites are also proxies of forearc mantle metasomatized by slab fluids. Based on the above observations, we propose that the mass transfer from slabs to plate interface and/or forearc mantle and the subsequent down-drag of this altered mantle to subarc depths potentially is a major process operating in subduction zones. The nominally anhydrous olivine, orthopyroxene, clinopyroxene and garnet produced by serpentinite dehydration host appreciable amounts of halogens and fluid-mobile elements that can be recycled in the deep mantle beyond arcs. Involvement of de-serpentinized residues in lower mantle metasomatism begins to be increasingly recognized by studies of ocean island basalts (OIB) and of B-bearing blue diamonds and by the isotopic serpentinite compositions presented here.

**Key-words:** serpentinite; dehydration; geochemistry; subduction; water-rock interaction; water cycle; boron; halogen; fluid-mobile elements.

## 1. Introduction

Today, serpentinites are considered as key players in the global volatile cycles in oceans and in subduction zones (Kendrick *et al.*, 2011, 2017; Deschamps *et al.*, 2013; Galvez *et al.*, 2013, 2016; Ryan & Chauvel, 2014; Barnes *et al.*, 2018). By transferring C–O–H components to subduction fluids, serpentinites enhance hydration and flux-melting of the *supra*-subduction mantle wedge and crustal accretion at convergent plate margins, all processes affecting the volatile return to the exosphere and keeping Earth habitable (Hattori & Guillot, 2003, 2007; Scambelluri *et al.*, 2004a;

Evans, 2010; Kendrick *et al.*, 2011; Alt *et al.*, 2013; Deschamps *et al.*, 2013; Evans *et al.*, 2013; Debret & Sverjensky, 2017; Barnes *et al.*, 2018). Moreover, the large pressure–temperature (*P–T*) stability field of serpentine, its high water content and its physical properties affect tectonics and intermediate-depth seismicity in subduction zones (Hacker *et al.*, 2003; Jung *et al.*, 2004; Hilairet *et al.*, 2007; Hirth & Guillot, 2013; Reynard, 2013; Proctor & Hirth, 2015; Ferrand *et al.*, 2017; Scambelluri *et al.*, 2017). Serpentinization is also relevant to the origin of life, as it releases *H*-rich fluids fuelling microbial life in oceanic and continental settings (Kelley *et al.*, 2005; Evans, 2010;

Ménez *et al.*, 2012; McCollom & Seewald, 2013). Reasonably, the chemical reactions enabling serpentinization and de-serpentinization processes are the most important ones in solid Earth.

Serpentinite attracted the attention of early 20th century geologists (Staub, 1922; Hess, 1955; De Roever, 1957; Bernoulli *et al.*, 2003; Moores, 2011) and of pioneering experimental petrologists, who investigated their role in orogenesis (Bowen & Tuttle, 1949; Raleigh & Paterson, 1965; Scarfe & Wyllie, 1967). Intensive research on serpentinite began in the mid-90s, when its abundance in oceans and its ability to trap and transfer volatiles to arcs was established by ocean drilling, experimental and field-based studies (Cannat *et al.*, 1995; Ulmer & Trommsdorff, 1995; Scambelluri *et al.*, 1995). Before these studies, serpentinites were poorly considered and much work was addressed on fresh mantle rocks and on deeply subducted coesite- and diamond-bearing ultrahigh-pressure rocks (Chopin, 2003). Nevertheless, earlier seminal research pointed out the importance of serpentinite by documenting: (i) its widespread occurrence in oceans (Bonatti, 1976); (ii) the genesis of eclogite-facies meta-peridotites by serpentinite dehydration (Evans & Trommsdorff, 1978); (iii) the potential role of serpentinized forearc mantle in transferring to subarc water and fluid-mobile elements found in arc lavas (Tatsumi, 1986). The Evans & Trommsdorff (1978) study is relevant to the present review, as it was the first to address the key role of serpentinite dehydration in the subduction-zone water cycle.

In the last two decades, ocean-drilling programs increasingly documented ultramafic exposures in (i) slow- and ultraslow-spreading oceans (Fig. 1a) (Dick *et al.*, 2003; Ildefonse *et al.*, 2007), in (ii) faults cutting the bending subducting plates at outer rises (Fig. 1b) and in (iii) the shallow forearc mantle (Ranero *et al.*, 2003; Alt & Shanks, 2006; Faccenda *et al.*, 2008). Deeper down in subduction zones, variations in  $P$  and  $S$  wave velocities and low  $V_p/V_s$  ratios of km-thick low-velocity zones located in-between the converging plates have suggested the extensive serpentinization of the subducting plate and of deep levels of the forearc mantle (Peacock, 1993; Bostock *et al.*, 2002; Van Keken *et al.*, 2002; Van Keken, 2003; Savov *et al.*, 2005b). An overview of serpentinite occurrence is reported in Fig. 1. Great relevance is now given to the subduction plate interface (Fig. 1c) where deformation, fluid and mass flow are channelized, and the buoyant uplift of high- (HP) and ultra-high-pressure (UHP) rocks occurs (Hermann *et al.*, 2000; Schwartz *et al.*, 2001; Gerya *et al.*, 2002; Hyndman & Peacock, 2003; Bebout, 2007; Angiboust *et al.*, 2012; Cannà *et al.*, 2016; Bebout & Penniston-Dorland, 2016; Sievers *et al.*, 2017). In such environments serpentinite can: (i) be part of tectonic mélanges atop the slab (Bebout, 2007); (ii) be the main lithology in kilometer slices of oceanic lithosphere detached from subducting slabs (Garrido *et al.*, 2005; Angiboust *et al.*, 2012); (iii) derive from hydration of forearc mantle (Fig. 1c) (Bostock *et al.*, 2002). Along with these discoveries, several works documented and modelled the serpentinite contribution to subduction and

exhumation tectonics and to geochemical recycling of volatile and fluid-mobile elements (FME; *e.g.* B, As, Sb, Pb) (Hermann *et al.*, 2000; Schwartz *et al.*, 2001; Gerya *et al.*, 2002; Rüpke *et al.*, 2004; Scambelluri *et al.*, 2004a, b; Marschall *et al.*, 2006; Bonifacie *et al.*, 2008; Faccenda *et al.*, 2008, 2012; Healy *et al.*, 2009; Barnes & Straub, 2010; John *et al.*, 2011; Kendrick *et al.*, 2011; Scambelluri & Tonarini, 2012; Marschall & Schumacher, 2012; Deschamps *et al.*, 2013; Reynard, 2013).

In the petrologic and geochemical perspective, serpentinites are major repositories of water, halogens, FMEs and noble gases acquired during oceanic alteration and by interaction with subduction fluids (Straub & Layne, 2003; Scambelluri *et al.*, 2004a, b; Barnes & Straub, 2010; Kodolányi *et al.*, 2012; Kendrick *et al.*, 2013; Cannà *et al.*, 2016; Barnes *et al.*, 2018). Once stored in serpentinite, these elements are released by prograde dehydration reactions (Hattori & Guillot, 2003; Kendrick *et al.*, 2011; Kodolányi & Pettke, 2011; John *et al.*, 2011; Deschamps *et al.*, 2013; Scambelluri *et al.*, 2015a). In this respect, the role of serpentinite in recycling FME during subduction is debated. Sediments and altered oceanic crust are identified as prime reservoirs for incompatible element delivery to arcs (Plank & Langmuir, 1993; Plank, 2014; Staudigel, 2014); it was also proposed that de-serpentinization fluids boost the wet melting of metasediments and the release of incompatible element by such rocks (Hermann *et al.*, 2006; Spandler & Pirard, 2013). Alternatively, shallow slab dehydration and sediment compaction can be accompanied by infiltration of crust-derived FME-rich fluids into the forearc mantle or in plate interface domains, facilitating peridotite hydration and metasomatism. Down-drag of this hydrated-metasomatized forearc mantle with the subducted lithosphere, or the diapiric ascent of buoyant inter-plate mélanges, transport the FME-enriched reservoirs into the sources of arc-magmas (*e.g.* Tatsumi, 1986; Hyndman & Peacock, 2003; Savov *et al.*, 2005a, 2007; Gerya *et al.*, 2006; Marschall & Schumacher, 2012; Ryan & Chauvel, 2014; Nielsen & Marschall, 2017; Ribeiro & Lee, 2017). The serpentinite capability of recording multiple interaction events with external fluids, as evidenced by increasing FME budgets and partial to complete reset of their isotopic signatures (Sr, Pb, O, Cl, B) makes this rock-type helpful to trace element recycling into the mantle and to unravel the evolution of exhumed HP–UHP terrains (Deschamps *et al.*, 2010; Barnes *et al.*, 2014; Cannà *et al.*, 2015, 2016; Scambelluri *et al.*, 2015b).

To test serpentinites as tracers of fluid activity in subduction zones and to define their role in subduction interface settings, here we review the occurrence, phase relations and composition of serpentinites from key geodynamic settings, completing this view with FME and B, Sr, Pb isotope analyses of Alpine HP–UHP serpentinites and of their dehydration products (meta-peridotite). We focus on the role of these rocks and of related serpentine breakdown fluids to envisage their contribution to metasomatic refertilization of the Earth's mantle.

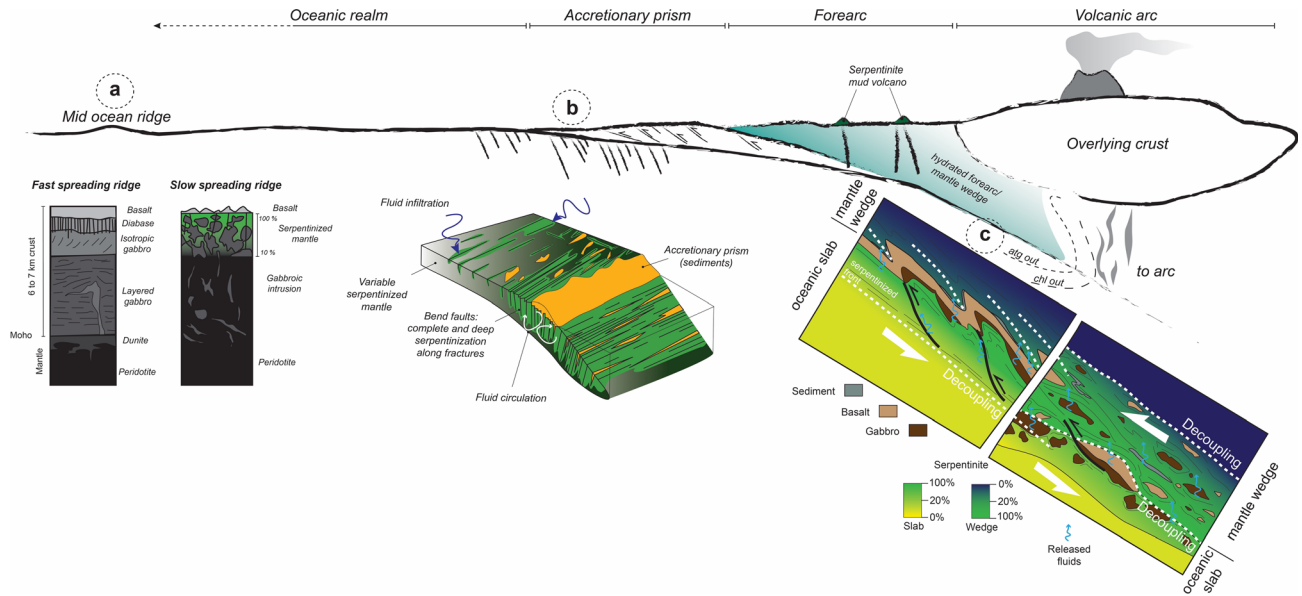


Fig. 1. General sketch showing the three main environments for serpentinite occurrence: (a) mid-ocean spreading ridges having different lithospheric structure depending on the fast (left column) *versus* slow-ultraslow (right column) spreading rate (after Dick *et al.*, 2006); (b) bend faults and forearc mantle (modified after Deschamps *et al.*, 2011); (c) subduction plate interface (modified after Guillot *et al.*, 2015).

## 2. Serpentinite occurrence in modern geodynamic settings

Serpentinites occur at all plate margins: passive, divergent, convergent and transform (Guillot *et al.*, 2015). Extensional tectonics drives the near-surface exposure of the lithospheric mantle and enables low-temperature hydration of mantle peridotites by infiltrating ocean water. In subduction zones, large slices of serpentinitized oceanic mantle can accrete to the boundaries between converging plates (Angiboust *et al.*, 2012; Cannà *et al.*, 2016); this, together with forearc mantle hydration by uprising slab fluids, makes serpentinite a main lithology affecting behaviour of the subduction interface (Reynard, 2013). Therefore, the interplay between fluids and tectonics enhances mantle serpentinization in key geodynamic environments, weakens the intra-plate boundary structures and significantly impacts global tectonics.

At passive margins and in slow-ultraslow spreading oceans, the lithospheric mantle is uplifted near the seafloor along detachment faults. At both sides of the Atlantic and in the Red Sea, extensional faults accomplish rifting, exhumation and hydration of the subcontinental lithospheric mantle aside of extended continental margins (less than 10 km thick; Guillot *et al.*, 2015). In these settings, low  $P$ -wave velocities (5–8 km/s; Fig. 2a) suggest mantle serpentinization by seawater infiltration along the faults. Based on  $P$ -wave velocities, Guillot *et al.* (2015) estimated 15–100% serpentinization of a mantle layer up to 5 km-thick. The lithospheric structure of slow to ultraslow spreading ridges is very different from fast spreading ones, where a larger extent of asthenosphere upwelling produces a several kilometres-thick gabbroic and basaltic crust covering the mantle (Figs. 1a and 2b). In slow and ultraslow ridges, magmatism takes place on a lesser extent: the crustal layer is thinner and discontinuous,

and the gabbroic crust can be limited to kilometre-sized bodies intruding the mantle. In ridge and off-ridge domains of slow-spreading oceans, seafloor exposure of serpentinitized mantle can be as high as 25% of the surface area (Cannat *et al.*, 1995). Seawater-peridotite interaction in such settings leads also to carbonation, especially along detachment faults exhuming the deep oceanic crust to seafloor level (Früh-Green *et al.*, 2003; Kelley *et al.*, 2005).

The thick, fast-spreading oceanic crust prevents deep seawater infiltration and mantle serpentinization. Consequently, the presently subducted oceanic mantle is a preserved one, largely geochemically unaltered during drifting. Nonetheless, bending of subducting plates at trenches causes pervasive fracturing of the lithosphere (Fig. 1b), with faults cutting the bending plate down to the Moho (Ranero *et al.*, 2003). Seismic imaging suggests deep seawater infiltration along the bend faults, enhancing serpentinization of the lithospheric mantle. The extent and geometry of serpentinitized bend faults, their composition and their role in enhancing subduction-zone seismicity is debated (Peacock, 2001; Faccenda *et al.*, 2008, 2012). Though present-day subduction involves the fast-spreading Pacific lithosphere, past subduction led to consumption of slow-spreading oceans, as in the case of the Jurassic Tethys (*e.g.* Rampone & Hofmann, 2012), involved in the Alpine-Himalayan subduction and continental plate collision, and now exposed in Alpine-type HP and UHP ophiolites (Agard *et al.*, 2009; Manatschal & Müntener, 2009).

The supra-subduction forearc mantle is another key domain for serpentinization. The presence of mud volcanoes and conical seamounts offshore Japan indicates the buoyant uprise of serpentinite diapirs in the forearc mantle (Fryer *et al.*, 1999; Savov *et al.*, 2005b). Pebbles of mafic blueschists and of serpentinite with metamorphic olivine

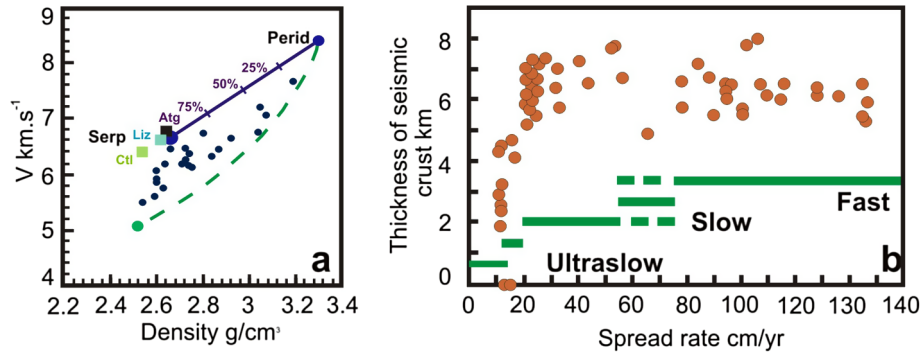


Fig. 2. (a) Seismic wave velocities in peridotite (Perid) and serpentinite (Serp; Atg, antigorite; Liz, lizardite; Chr, chrysotile) after Reynard (2013). The diagram also reports ultrasonic measurements of “end-member” rocks (large circles) and crystallographic measurements (empty squares, equation of state measurements; filled square, Brillouin spectroscopy on antigorite). In partially to fully serpentinitized peridotites, data (blue points) lie between linear Per-Atg (blue line) and non-linear Per-Chr-Liz (green dashed curve) velocity–density relationships. The lowest velocities are attributed to the structure of chrysotile that also results in high porosities and low densities.  $P$ -wave velocity in subduction-zone serpentinitized mantle (where antigorite is stable) is well described by the blue solid line between peridotite and antigorite serpentinite. Complex variations can occur in shallow contexts of oceanic, trench-faulting, and mantle wedge of intra-oceanic subduction where chrysotile may form. (b) thickness of the oceanic crust as a function of spreading rates (after Dick *et al.*, 2003).

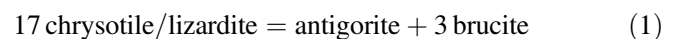
in mud volcanoes suggest this material was hydro-dynamically driven from the plate interface up to the surface (Maekawa *et al.*, 1992; Murata *et al.*, 2009; Pabst *et al.*, 2012). This evidence and the low  $V_p/V_s$  anomalies (Fig. 2a) point out serpentinitization of the plate interface and the forearc mantle of the Japan subduction zone (Van Keken, 2003). In the Cascadia subduction zone, Bostock *et al.* (2002) firstly documented the occurrence of low  $V_p/V_s$ , indicating intensive serpentinitization of the forearc mantle due to infiltration of slab fluids. In comparable settings, geophysical studies have documented the occurrence of free, pressurized pore fluids likely released from the downgoing slab (Audet *et al.*, 2009). Serpentinitization of the *supra*-subduction mantle by slab-derived saline fluids is also indicated by electric anomalies in the *supra*-subduction mantle (Reynard *et al.*, 2011; Reynard, 2016). As such, the forearc mantle represents a large water and FME reservoir: if dragged down to sub-arc depths it may recycle its water into the sources of arc magmas (Hattori & Guillot, 2003; Savov *et al.*, 2005b; Scambelluri & Tonarini, 2012; Ryan & Chauvel, 2014; Ribeiro & Lee, 2017). This view is contradicted by recent analysis of global seismic data and thermal models, suggesting that most mantle forearcs are dry due to slow dehydration kinetics of subducting plates (Abers *et al.*, 2017). Hot subduction zones, where slabs dehydration is faster, should be an exception (Abers *et al.*, 2017).

### 3. Petrology and phase relations of subducting serpentinite

The fate of serpentinite during subduction has been the subject of numerous articles dealing with specific aspects of serpentinite systems, such as petrology and phase relations (Evans & Trommsdorff, 1978, 1983; Scambelluri *et al.*, 1995; Ulmer & Trommsdorff, 1995, 1999; Wunder & Schreyer, 1997; Evans, 2004; Li *et al.*, 2004; Fumagalli & Poli, 2005; López Sánchez-Vizcaíno *et al.*, 2009; Rebay *et al.*, 2012; Debret *et al.*, 2013a; Padrón-Navarta *et al.*,

2013; Schmidt & Poli, 2014), fluid release and element recycling (Scambelluri *et al.*, 1997, 2001a, b, 2004a, b, 2016; Padrón-Navarta *et al.*, 2010; Lafay *et al.*, 2013; Debret *et al.*, 2013b, 2014a; Debret & Sverjensky, 2017), carbonation, decarbonation and redox state (Kerrick & Connolly, 1998; Andreani *et al.*, 2009; Debret *et al.*, 2014b; Collins *et al.*, 2015; Evans & Powell, 2015; Piccoli *et al.*, 2016; Scambelluri *et al.*, 2016; Debret & Sverjensky, 2017; Evans *et al.*, 2017). The subduction-zone evolution of serpentinite is bound to a sequence of temperature-dependent dehydration reactions with steep  $P$ – $T$  slopes (Fig. 3). The same reaction sequence (Fig. 3a) affects serpentinites metamorphosed along low  $P$ /high  $T$ , as well as high  $P$ /low  $T$  gradients: the association with blueschist- and eclogite-facies mafic rocks is therefore diagnostic for subduction-zone metamorphism of a given serpentinite (*e.g.* Scambelluri *et al.*, 1995; Rebay *et al.*, 2012; Debret *et al.*, 2013a). A recent thermodynamic calibration of the Al content of antigorite as a function of  $P$  and  $T$  in buffered assemblages has provided a first attempt at retrieving recrystallization conditions of serpentinites during prograde metamorphism (Padrón-Navarta *et al.*, 2013).

Experimental data and petrology of natural samples indicate that lizardite and chrysotile are the stable serpentine minerals below 300 °C (Evans, 2004; Schwartz *et al.*, 2013). Earlier data suggesting antigorite crystallization at 250 °C (O’Hanley, 1996) have been contradicted by Schwartz *et al.* (2013), who concluded that antigorite forms above 300 °C. According to Schwartz *et al.* (2013), antigorite and lizardite may coexist up to 380 °C above 0.9 GPa. Transition from chrysotile/lizardite to antigorite is the first transformation in serpentinite systems with increasing  $T$ . It can be driven by the water-conserving reaction:



occurring at 300 °C (Evans, 2004; Schwartz *et al.*, 2013), or by reactions involving a fluid phase, such as



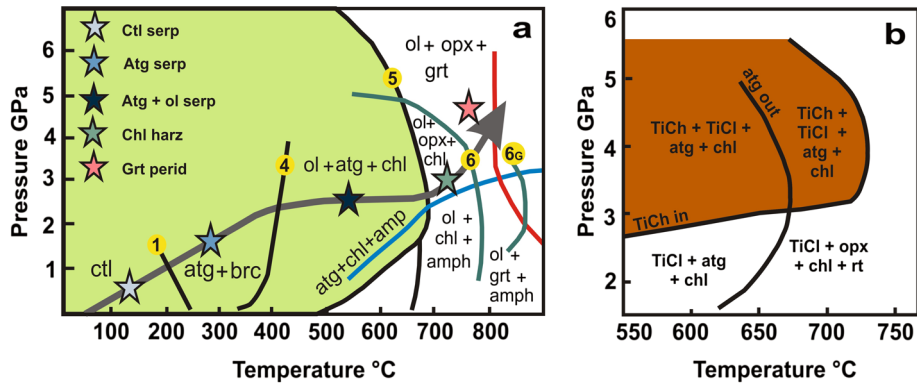
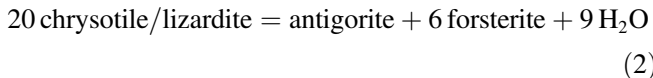
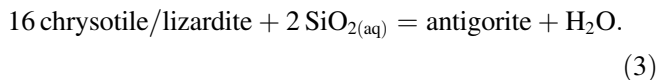


Fig. 3. (a)  $P$ - $T$  phase relations in serpentinite and in de-serpentinized peridotite. The numbers on each curve refer to the mineral reactions listed in text. The stars refer to different sample sets from various localities: they disclose the dehydration sequence recorded by subduction-zone serpentinites. The bold grey arrow represents a geothermal gradient estimated by Syracuse *et al.* (2010). (b)  $P$ - $T$  phase relations for Ti-bearing humite phases by Shen *et al.* (2015).



occurring up to 380 °C (Evans, 2004), or *via*



Development of reaction (3) is suggested by the silica enrichment shown by many antigorite serpentinites with respect to chrysotile/lizardite ones, that likely results from exchange with sediment-derived subduction fluids (Lafay *et al.*, 2013; Schwartz *et al.*, 2013; Malvoisin, 2015). Overall, transition from chrysotile/lizardite to antigorite is also accompanied by water and fluid-mobile element loss from serpentinite (Kodolányi & Pettke, 2011). In general, chrysotile/lizardite together with subordinate magnetite, chlorite and minor brucite are related to low- $T$  hydration at shallow depth of oceanic and *supra*-subduction mantle. With increasing  $P$ - $T$  conditions, antigorite forms after chrysotile and lizardite, as shown by transmission electron microscopy (Mellini *et al.*, 1987) and by the occurrence of antigorite veins cutting through chrysotile/lizardite serpentine rocks (Fig. 3a; see also Schwartz *et al.*, 2013). The brucite-consuming reaction



produces the first metamorphic olivine stable with antigorite and a free fluid phase above 450 °C. Reaction (4) is recorded by many eclogite-facies Alpine serpentinites, which host additional high-pressure chlorite, diopside and titanian clinohumite (“Ti-clinohumite”) that crystallize as rock- and as vein-forming assemblages (Scambelluri *et al.*, 1997; Li *et al.*, 2004; Rebay *et al.*, 2012; Debret *et al.*, 2013a; Cannà *et al.*, 2016). Recent work shows that this first olivine-in reaction occurs *via* formation of a porous, talc-like intermediate reaction product (Plümper *et al.*,

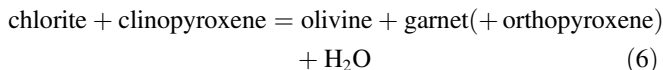
2017) that was firstly reproduced during high-pressure experiments (Perrillat *et al.*, 2005). This intermediate phase constitutes a highly porous medium that drains the fluid released by reaction (4), thus decreasing the local pore-fluid overpressure. In this new reaction frame, olivine is a late-stage product of reaction (4): it starts crystallizing as nanocrystalline olivine (500 nm) to evolve into vein-forming, eclogite-facies, coarse olivine crystals (Plümper *et al.*, 2017). The antigorite + olivine serpentinites form great part of the HP and UHP eclogitic materials exhumed into the Alpine belt and elsewhere. This is due to buoyancy and instability of antigorite + olivine-bearing serpentinites formed *via* reaction (4), which still host up to 10–11 wt% water. Full dehydration of HP antigorite serpentinites occurs *via* reaction



releasing up to 10% water by weight and transforming serpentinite back into a metaperidotite. This greatly affects the behaviour of ultramafic sections of the slab, of the plate interface and of the *supra*-subduction wedge, which sink into the mantle without much chance of exhumation. Just a few occurrences of meta-peridotites deriving from serpentinite dehydration were tectonically exhumed to the surface: these correspond to the Cerro del Almirez (Betic Cordillera, SE Spain; Trommsdorff *et al.*, 1998) and the Cima di Gagnone (Central Alps; Evans & Trommsdorff, 1978; Scambelluri *et al.*, 2014) localities. In such settings chlorite harzburgite and garnet peridotite are associated with crustal rocks that acted as the buoyant carriers of meta-peridotite to the surface (Hermann *et al.*, 2000).

Chlorite and Ti-clinohumite are other hydrous phases frequently coexisting with antigorite, olivine, diopside or tremolite and magnetite in HP and UHP assemblages. In natural rocks, both minerals survive the antigorite breakdown. In metamorphic chlorite harzburgite derived from dehydration of former serpentinite (Trommsdorff *et al.*,

1998; Fumagalli & Poli, 2005; Padrón-Navarta *et al.*, 2011; Scambelluri *et al.*, 2014), chlorite hosts the excess aluminium and enables further H<sub>2</sub>O storage in ultramafic systems. Its breakdown to garnet occurs above 800 °C *via* reaction



as suggested by experimental work (Fumagalli & Poli, 2005) and modelling of natural de-serpentinized peridotite (Scambelluri *et al.*, 2014). Several experimental works discussed the relevance of chlorite breakdown to garnet for fluid release at sub-arc depths (Fumagalli & Poli, 2005; Grove *et al.*, 2006; Till *et al.*, 2012). Besides releasing additional water, the chlorite dehydration reaction (Fig. 3a, reaction 6G) may intersect the water-saturated peridotite solidus (red curve in Fig. 3a) between 2 and 3.6 GPa, triggering dehydration melting of peridotite at sub-arc conditions (Grove *et al.*, 2006; Till *et al.*, 2012). This process was not observed in all experiments (Fumagalli & Poli, 2005) and was not yet detected in natural rocks (Scambelluri *et al.*, 2014).

Titanian clinohumite and titanian chondrodite (“Ti-chondrodite”) are humite-group minerals frequently present in ultramafic rocks. The humite-group minerals have general formula  $n(\text{M}_2\text{SiO}_4)\text{M}_{1-x}\text{Ti}_x(\text{OH},\text{F})_{2-2x}\text{O}_{2x}$ , where M corresponds to (Mg,Fe,Mn,Ni),  $n$  is 1 for norbergite, 2 for chondrodite, 3 for humite and 4 for clinohumite, and  $x \leq 0.5$  (Thompson, 1978; Veblen, 1991). They form a polysomatic series between norbergite and olivine, with different stacking sequences of olivine and norbergite (chondrodite has one olivine and one norbergite layer; clinohumite has three olivine and one norbergite layer; Thompson, 1978; Ehlers & Hoinkes, 1987). Ti-clinohumite and Ti-chondrodite have been found in antigorite + olivine bearing high-pressure serpentinites and in the associated metasomatized metagabbros (Scambelluri *et al.*, 1991; Scambelluri & Rampone, 1999; Li *et al.*, 2004; Rebay *et al.*, 2012; Shen *et al.*, 2014, 2015; Gilio, 2017; González-Jiménez *et al.*, 2017). In antigorite-bearing rocks Ti-clinohumite is an OH-bearing phase, whereas in rocks that experienced antigorite breakdown Ti-clinohumite uptakes substantial amounts of fluorine which expand its stability field by several hundreds of degrees (Engi & Lindsley, 1980; Trommsdorff & Evans, 1980; Evans & Trommsdorff, 1983; Ulmer & Trommsdorff, 1999). Shen *et al.* (2015) provided a new grid for the stability of Ti-clinohumite and Ti-chondrodite based on field observations and on a set of 11 experiments run at 2.5–5.5 GPa and 600–750 °C in a F-free natural system (Fig. 3b). The formation of Ti-chondrodite in serpentinite requires minimum pressures of about 2.6 GPa, whereas in Ti-rich systems it can form at considerably lower pressures. This experimental work very well matches the peak paragenesis in serpentinite from the UHP terrain of southwestern Tianshan (China; Shen *et al.*, 2014, 2015). Interestingly, Luoni *et al.* (2018) document the occurrence of peak UHP Ti-chondrodite veins in antigorite + olivine serpentinite

tectonically close to the coesite- and diamond-bearing Cignana UHP ophiolite (Western Alps).

## 4. Serpentinite compositions

Several review and research papers recently dealt with the role of serpentinite in volatile and FME cycling in oceans and subduction zones (Deschamps *et al.*, 2013; Kendrick *et al.*, 2013, 2017; Ryan & Chauvel, 2014; Peters *et al.*, 2017). Given the widespread occurrence of serpentinite in slabs, plate interface and forearcs, some of these studies have tried to identify geochemical tracers to relocate the exhumed HP–UHP serpentinites into the original subduction setting and to define timing of their accretion to the subduction plate interface (Hattori & Guillot, 2003; Deschamps *et al.*, 2012; Scambelluri & Tonarini, 2012; Lafay *et al.*, 2013; Scambelluri *et al.*, 2014; Cannà *et al.*, 2016). Notwithstanding the efforts, the overlap of the trace-element compositions of oceanic (abyssal), forearc and subduction-zone serpentinites hampered recognition of the tracer elements enabling to identify unequivocally the original formation setting of a given serpentinite (Peters *et al.*, 2017). A pure geochemical approach can work in specific cases; more generally, integration of geochemistry with field, textural and petrologic data is required. The approach is underway and later in this review we are going to examine some cases. The review on serpentinite geochemistry by Deschamps *et al.* (2013) offers a compilation of about 900 bulk-rock major and trace element analyses of serpentinite from various oceanic and subduction settings and provide some guidelines to interpret serpentinite compositions in terms of protolith rocks and formation environments. We anticipate here that Deschamps *et al.* (2013) point out that the fluid-mobile element enrichment in subducted serpentinites can reflect the influence of sediment derived fluids as the result of chemical interactions, probably within the subduction channel, and that “*serpentinites are considered as a reservoir of the FME in subduction zones and their role, notably on arc magma composition, is underestimated presently in the global geochemical cycle*”.

### 4.1. Oceanic serpentinite

In general, abyssal serpentinites do not record much variation in major-element composition with respect to their mantle protoliths. Their constant SiO<sub>2</sub>/(sum of oxides) suggests that on a broad range of serpentinization conditions major elements remain largely unchanged (Deschamps *et al.*, 2013, their Fig. 3a). Variations in CaO can be attributed to clinopyroxene serpentinization (Coleman & Keith, 1971; Janecky & Seyfried, 1986; Iyer *et al.*, 2008), though calcium loss from clinopyroxene may be counterbalanced by serpentinite carbonation (Bideau *et al.*, 1991). Other changes are related to SiO<sub>2</sub> increase in talc-bearing samples (Paulick *et al.*, 2006) and MgO loss due to seafloor weathering (Snow & Dick, 1995). As claimed by Deschamps *et al.* (2013), major elements are thus poor tracers of serpentinization environments and processes.

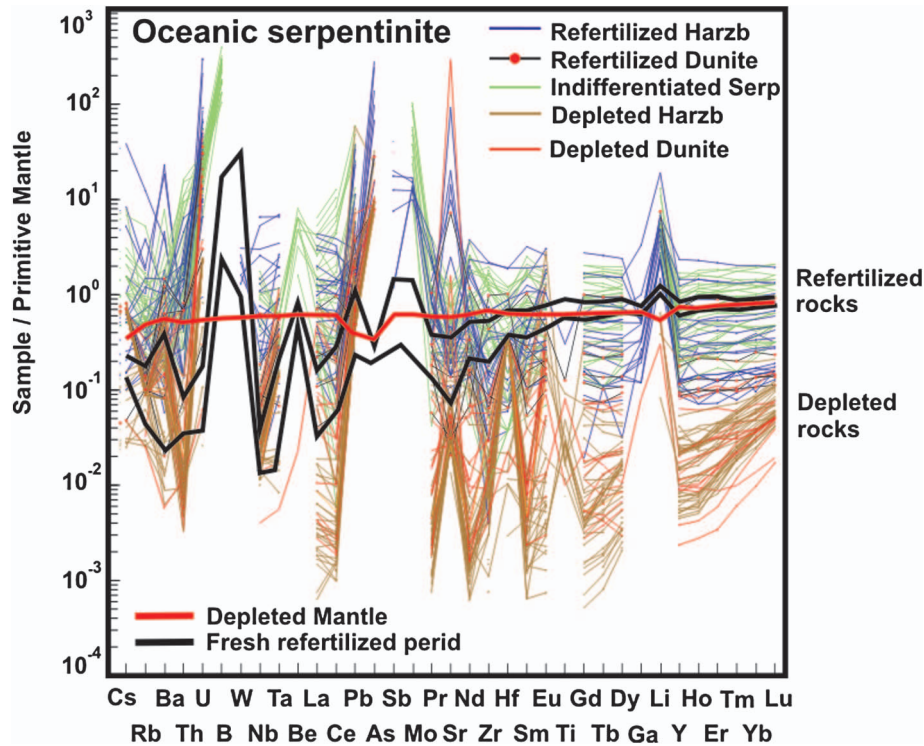


Fig. 4. Trace element composition of oceanic serpentinites. Data have been normalized to the Primitive Mantle (PM; McDonough & Sun, 1995). Serpentinite data are from the dataset by Deschamps *et al.* (2013) and Peters *et al.* (2017), which include data by Paulick *et al.* (2006), Delacour *et al.* (2008), Jöns *et al.* (2010), Augustin *et al.* (2012), Kodolányi *et al.* (2012), Boschi *et al.* (2013). The bold red pattern represents the depleted mantle by Salters & Stracke (2004) and the bold black lines represent the refertilized plagioclase-rich oceanic peridotite from Lanzo (data by Guarnieri *et al.*, 2012).

Oceanic serpentinites also inherit the REE compositions of their mantle protoliths. Figure 4 reports the trace-element compositions of numerous abyssal serpentinites from the large datasets by Deschamps *et al.* (2013) and Peters *et al.* (2017) normalized to the Primitive Mantle (PM, McDonough & Sun, 1995) (the dataset, in Table S1, includes analyses by Lagabrielle *et al.*, 1992; Parkinson & Pearce, 1998; Viti & Mellini, 1998; Anselmi *et al.*, 2000; Pearce *et al.*, 2000; Guillot *et al.*, 2001; Scambelluri *et al.*, 2001b; Chalot-Prat *et al.*, 2003; Garrido *et al.*, 2005; Savov *et al.*, 2005a, b, 2007; Aldanmaz & Koprubasi, 2006; Marchesi *et al.*, 2006, 2009; Paulick *et al.*, 2006; Hattori & Guillot, 2007; Delacour *et al.*, 2008; Pereira *et al.*, 2008; De Hoog *et al.*, 2009; Deschamps *et al.*, 2010, 2012; Jöns *et al.*, 2010; Saumur *et al.*, 2010; Ulrich *et al.*, 2010; Aziz *et al.*, 2011; Blanco-Quintero *et al.*, 2011; Augustin *et al.*, 2012; Kodolányi *et al.*, 2012; Boschi *et al.*, 2013; Lafay *et al.*, 2013; Andreani *et al.*, 2014; Cannà *et al.*, 2015, 2016; Table S1 is freely available in the Supplementary Material linked to this article on the GSW website of the journal: <https://pubs.geoscienceworld.org/eurjmin>). The compositions of unaltered, refertilized oceanic-type plagioclase peridotite (Lanzo, Western Alps; Guarnieri *et al.*, 2012), the depleted mantle (DM, Salters & Stracke, 2004). In Fig. 4 serpentinites are grouped according to (i) the degree of depletion of their mantle protoliths due to partial melting and (ii) subsequent enrichment by interaction with percolating MORB melts (Deschamps

*et al.*, 2013). The REE budgets and patterns of most oceanic serpentinites still reflect inheritance of the protolith compositions: these are below PM and DM in depleted harzburgite and dunite protoliths and above PM and DM in refertilized rocks. In Fig. 4 the poorly serpentinized and refertilized Lanzo peridotite (Guarnieri *et al.*, 2012) shows enrichment (1–30 times PM) in B, W, Be, Pb, Sb, Mo and Li, which can be attributed to a combination of melt–peridotite reaction and incipient serpentinization. Compared to the scarcely serpentinized peridotite from Lanzo, all oceanic serpentinites (especially the refertilized ones) display prominent spikes (10 to hundreds of times PM) in U, B, Pb, As, Sb, Mo, Sr, Li, and up to 10 PM enrichments in Cs, Rb, Ba, Th, Be, La, Ce (Fig. 4). Such FME anomalies can be largely attributed to serpentinization, as suggested by *in situ* trace-element analyses of serpentine in variably altered oceanic samples (Kodolányi *et al.*, 2012; Deschamps *et al.*, 2013).

Serpentinites are also halogen reservoirs, hosting up to 2000 ppm Cl (Anselmi *et al.*, 2000; Sharp & Barnes, 2004; Barnes & Sharp, 2006; Kodolányi & Pettko, 2011; Kendrick *et al.*, 2013), 204 ppm F (Stüber *et al.*, 1968; Mével, 2003), 1.3–24 ppm Br and 0.02–45 ppm I (Kendrick *et al.*, 2011, 2013). Figure 5 shows the Br/Cl and I/Cl ratios of serpentinites from present-day mid-ocean ridges, passive margins and forearcs, along with non-subducted ophiolitic serpentinites (Northern Apennine and Alps; data after John *et al.*, 2011; Kendrick *et al.*, 2013). While abyssal and passive-margin serpentinites display I/Cl and Br/Cl ratios



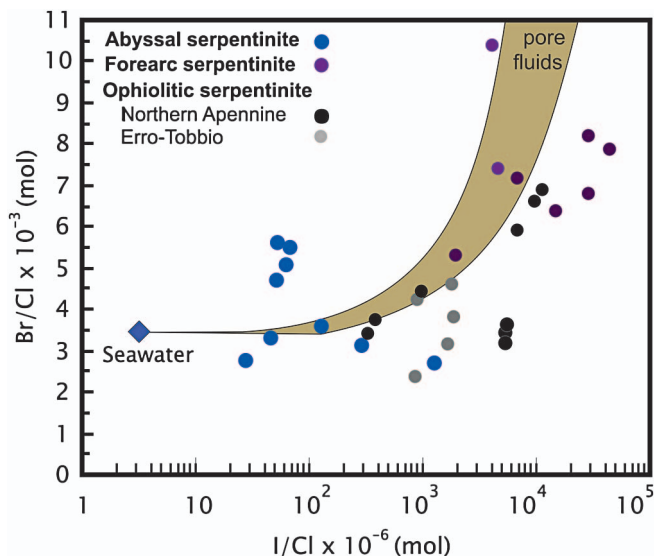


Fig. 5. The halogen composition of present-day abyssal and forearc serpentinite compared with ophiolitic non-subducted (Northern Apennine) and subducted serpentinite (Erro-Tobbio). Reference fields include the compositional range of sedimentary marine pore fluids and of seawater (after Kendrick *et al.*, 2013). Data by Kendrick *et al.* (2011, 2013) and John *et al.* (2011).

close to seawater, forearc serpentinites progressively shift their I/Cl and Br/Cl towards sedimentary pore fluids (Fig. 5). This is interpreted with an involvement of sedimentary components in slab fluids released into the forearc mantle wedge during sediment compaction at shallow depths. Interestingly, the Northern Apennine ophiolitic serpentinites that escaped subduction and the early chrysotile relics preserved in the subducted Erro-Tobbio unit show the same trend as the forearc serpentinites (Fig. 5). This feature points to the involvement of sedimentary marine pore fluids during shallow serpentinization of these ophiolitic mantle rocks (Kendrick *et al.*, 2013). These data lead to conclude that shallow hydration of Apennine and Alpine mantle rocks took place away from mid ocean ridges, in settings like outer rises, accretionary wedges and shallow forearc (Kendrick *et al.*, 2011, 2013; John *et al.*, 2011; Scambelluri & Tonarini, 2012). A contribution of pore fluids to the serpentinizing fluid is also supported by noble gas (He, Ar, Xe; Kendrick *et al.*, 2011) and Cl isotope data (Barnes & Sharp, 2006, 2017; John *et al.*, 2011; Barnes *et al.*, 2018).

All the above data point out that peridotite interaction with seawater and with shallow subduction fluids severely modifies the trace-element budget of the serpentinite materials processed in subduction zones.

#### 4.2. Subduction-zone serpentinite

The trace-element compositions of serpentinites from forearc and fossil subduction zone settings are shown in Fig. 6 together with the composition of present-day abyssal oceanic serpentinites (Fig. 4). Figure 6 shows a large overlap of the trace-element compositions of the different serpentinite types. A potential difference consists in the tendency of subduction-zone serpentinites to have higher FME

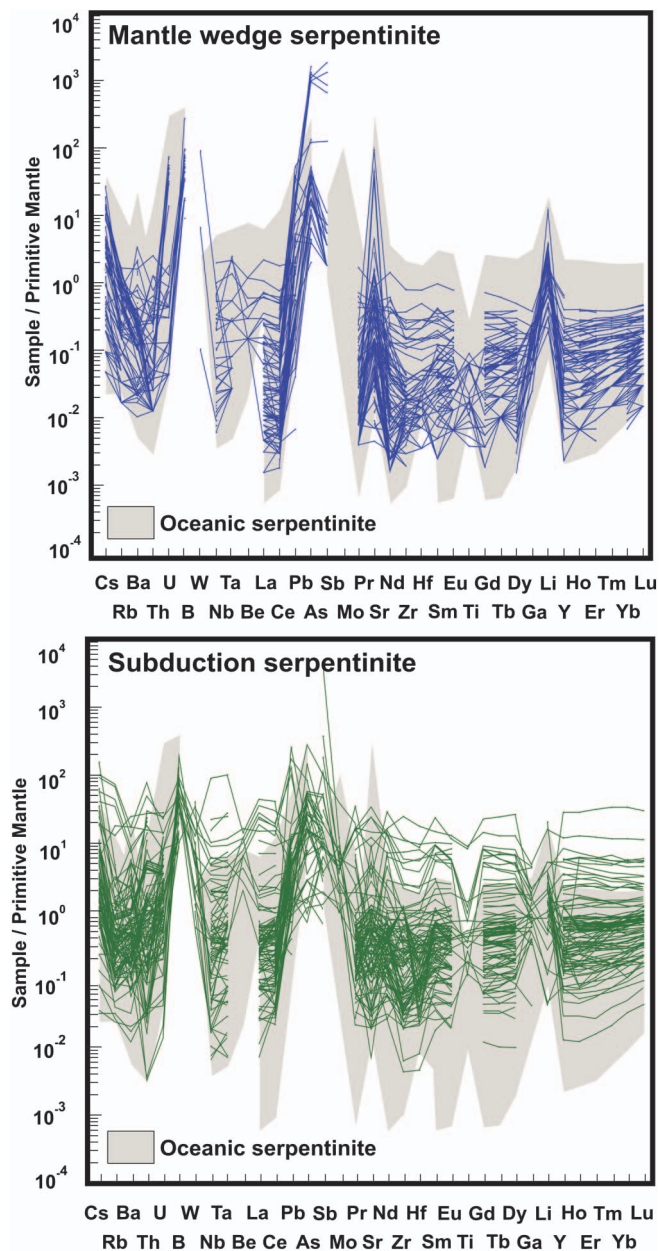


Fig. 6. Trace element compositions of mantle wedge and of subduction-zone serpentinite. The grey background field reports the compositions of oceanic serpentinites shown in Fig. 4. Data are from the dataset by Deschamps *et al.* (2013) and Peters *et al.* (2017), including data by Lagabrielle *et al.* (1992), Parkinson & Pearce (1998), Pearce *et al.* (2000), Scambelluri *et al.* (2001b), Guillot *et al.* (2001), Chalot-Prat *et al.* (2003), Garrido *et al.* (2005), Savov *et al.* (2005a, b, 2007), Aldanmaz & Koprubasi (2006), Marchesi *et al.* (2006, 2009), Hattori & Guillot (2007), Pereira *et al.* (2008), De Hoog *et al.* (2009), Ulrich *et al.* (2010), Deschamps *et al.* (2010, 2012), Saumur *et al.* (2010), Aziz *et al.* (2011), Blanco-Quintero *et al.* (2011), Kodolányi *et al.* (2012), Lafay *et al.* (2013), Cannào *et al.* (2015, 2016). Normalization to the Primitive Mantle (PM; McDonough & Sun, 1995).

contents (Cs, Rb, Ba, Th, Pb, As, Sb) than oceanic and forearc rocks. Relatively high contents in Pb and As also pertain to the forearc serpentinites. However, the simple comparison of serpentinite compositions may be indicative, not



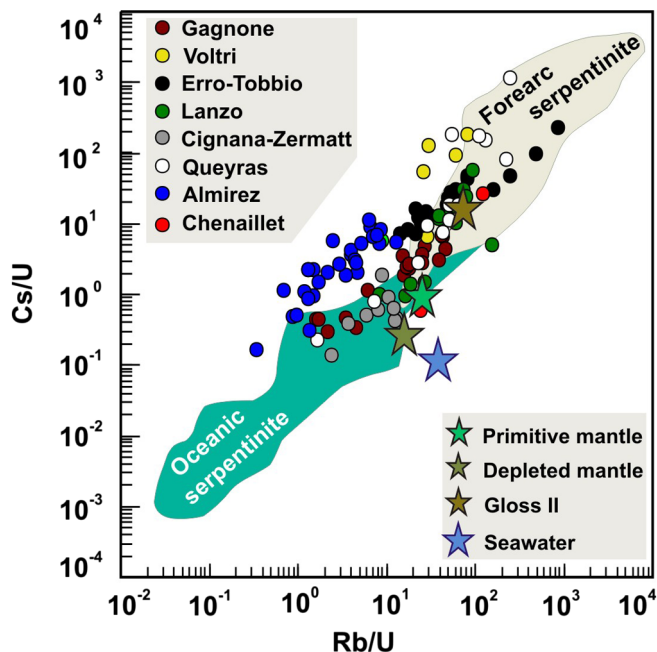


Fig. 7. Cs/U vs. Rb/U diagram reporting the compositional fields of oceanic and forearc serpentinites (redrawn after Peters *et al.*, 2017). Besides the original data by Peters *et al.* (2017) on Erro-Tobbio and Almiraz, also reported are the compositions of Gagnone (Scambelluri *et al.*, 2014; Cannà *et al.*, 2015), Queyras and Chenaillet (Lafay *et al.*, 2013) and Voltri (Cannà *et al.*, 2016).

diagnostic, of the formation environment and may lead to erroneous estimates of element gains and losses during subduction.

A new approach in interpreting serpentinite compositions has been recently proposed by Peters *et al.* (2017), who show that using U versus alkalis and FME ratios enables distinction between abyssal and subduction-zone serpentinites (Peters *et al.*, 2017). Here we report the Cs/U and Rb/U ratios (Fig. 7) of a large compilation of oceanic and forearc serpentinites (Peters *et al.*, 2017), together with Alpine subduction-zone serpentinites and several global reservoirs. The oceanic serpentinites have high U contents, due to higher oxidation conditions affecting mantle rocks during serpentinization process in oceanic setting and are different from the forearc ones, having lower U and higher Cs, Rb (see Peters *et al.*, 2017). This alkali enrichment in the forearc serpentinites is interpreted as a consequence of infiltration of sedimentary fluids. Interestingly, the Alpine serpentinites, corresponding to oceanic mantle hydrated by seawater before subduction, plot in the forearc serpentinite field (Fig. 7). This feature, as emphasized by Peters *et al.* (2017) for a smaller number of Alpine serpentinite samples, points out that the fluid-mediated subduction zone processing of oceanic serpentinites can modify a set of fluid-mobile elements. Deschamps *et al.* (2010) achieved comparable results by analysing the trace-element compositions of serpentine pseudomorphs after mantle olivine and orthopyroxene in Himalayan serpentinites. They found that antigorite after olivine is enriched in As, Sb, B and U with respect to antigorite replacing orthopyroxene, showing higher Pb,

Cs, Li and Ba. This was related to two hydration episodes associated to a different mobility of the above elements during subduction: a stage of olivine serpentinization at low  $T$  which added As and Sb-rich slab fluids, followed by pyroxene serpentinization at higher  $T$ , adding Pb, Cs, Li and Ba (Deschamps *et al.*, 2010).

Therefore, although a difference between various serpentinite types can be shown based on bulk-rock compositions, assessing the environment where element enrichment/depletion occurred is not easy. The whole analysis is further complicated by superposed stages of oceanic and subduction-related hydration that affected most subduction-zone serpentinites. For this reason, an interdisciplinary approach combining field, textural and petrologic constraints together with bulk-rock and *in situ* fluid-mobile element analyses is now best suited to unravel timing, environment and element gains-losses that accompany hydration and dehydration of mantle rocks.

Halogens are released in the first 30 km subduction (up to 90% Cl loss) via the chrysotile-to-antigorite transition (Kodolányi & Pettke, 2011). Nevertheless, high-pressure serpentinites exhumed from greater depths still retain appreciable halogen concentrations (Scambelluri *et al.*, 2004a; Bonifacie *et al.*, 2008; John *et al.*, 2011; Kendrick *et al.*, 2011; Selverstone & Sharp, 2013; Barnes *et al.*, 2018). The extent of Cl recycling during serpentinite subduction is shown in Fig. 8 for the Erro-Tobbio and Almiraz samples, which experienced dehydration reactions (4) and (5), respectively (John *et al.*, 2011; Kendrick *et al.*, 2011). In general, Cl, Br and I concentrations in the above serpentinites decrease with dehydration progress: their loss from serpentinite is counterbalanced by fractionation in veins and in fluid inclusions, suggesting that these elements are released to fluids, with Br and I preferentially depleted relative to Cl (Kendrick *et al.*, 2011). Interestingly, the halogen composition of the Erro-Tobbio high-pressure antigorite, replacing shallow-level chrysotile (Fig. 8a), can be traced back to the original marine pore fluid signature. Overall, Fig. 8 shows that, despite halogen loss to fluids, the most dehydrated rocks still retain appreciable amounts of such elements, as indicated by bulk rock contents of up to 250 ppm Cl, 40–50 ppm F, 0.2 ppm Br, and 700 ppb I (John *et al.*, 2011; Kendrick *et al.*, 2011). These rocks can therefore introduce detectable halogen anomalies into the upper mantle.

#### 4.3. What gets in during subduction?

The recent production of trace element and isotopic data on serpentinites has set the basis for an inventory of elements gained by these rocks through the interaction with oceanic and subduction fluids, and for estimating their potential in global element cycling. The task now is assessing the timing of fluid-mobile element incorporation in serpentinite during multi-stage hydration and their original reservoirs. This inspired numerous recent studies integrating field, petrologic, and geochemical data which improved our knowledge of global element recycling and of subduction dynamics (John *et al.*, 2011; Kendrick *et al.*, 2011; Scambelluri &

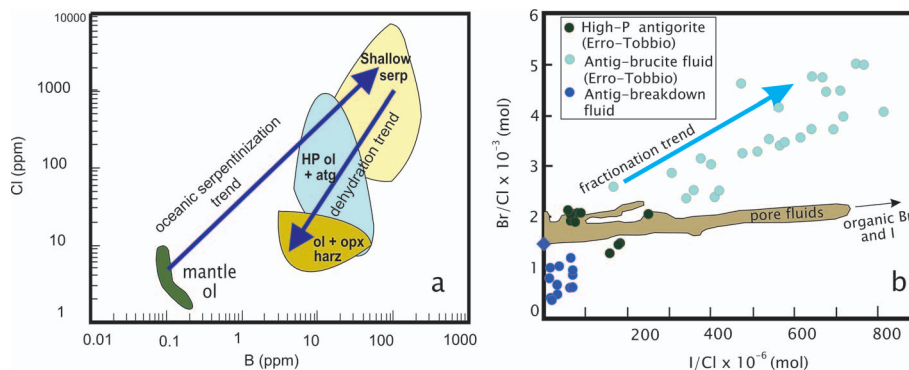


Fig. 8. (a) B vs. Cl composition of mantle olivine, early shallow serpentine and subduction-zone assemblages in high-pressure serpentinite formed by reaction (4) and in de-serpentinized peridotite formed by reaction (5). Data after Scambelluri *et al.*, 2004a. (b) Inset of halogen compositions of high-pressure antigorite and saline fluid inclusions from Erro-Tobbio (released from reaction (4) in Fig. 3) together with the compositions of the de-serpentinized peridotite and associated fluid inclusions (released from reaction (5) in Fig. 3). The field of sedimentary pore fluids is also reported. Drawn after Kendrick *et al.* (2011).

Tonarini, 2012; Deschamps *et al.*, 2013; Lafay *et al.*, 2013; Angiboust *et al.*, 2014; Barnes *et al.*, 2014; Scambelluri *et al.*, 2014; Cannà *et al.*, 2015, 2016; Peters *et al.*, 2017).

The above works define the elemental (*e.g.* B, Pb, Sr, As, Sb, Be, Li) and isotopic (B, Sr, Pb) tracers helpful to discriminate the serpentinization setting. For instance, the Alpine blueschist-facies serpentinite from the French Queyras and the eclogite-facies meta-peridotites from Cima di Gagnone (Central Alps) occur as blocks in metasedimentary accretionary complexes and are good candidates for testing element exchange between subducting serpentinite and sediments (Lafay *et al.*, 2013; Scambelluri *et al.*, 2014; Cannà *et al.*, 2015). The Queyras and Cima di Gagnone ultramafic rocks display enrichments in Cs, B, As, Sb, Li (Fig. 9). Lafay *et al.* (2013) showed that in the Queyras serpentinite a moderate initial trace-element enrichment acquired during oceanic serpentinization was followed by significant gain in FME carried by sediment-derived fluids during emplacement into the Alpine accretionary complex under greenschist- to blueschist-facies conditions. Lafay *et al.* (2013) also showed that, at higher-grade conditions and in serpentinite not embedded in metasediments, the FME enrichment was minor due to B, Li, Cs, Sr release to fluids upon antigorite dehydration. This emphasizes that the fluid-mobile element budgets of serpentinites depend on metamorphic grade and on interaction with sediment-derived fluids (Lafay *et al.*, 2013).

The Cima di Gagnone meta-peridotite gained FME during initial oceanic hydration and subsequent interaction with subduction fluids (Fig. 9). Similarity in U, Pb, B, Li, Sr composition of the Gagnone metaperidotites with present-day oceanic serpentinite suggests these elements were gained during oceanic serpentinization (Scambelluri *et al.*, 2014). However, high Be, As, Sb (Fig. 9) and radiogenic Sr and Pb isotope concentrations approaching the ones of associated metasediments (Cannà *et al.*, 2015) indicate exchange with sediment-derived fluids during coupling of the Gagnone serpentinized peridotite with sediments in the subduction zone. At this stage, the initial Jurassic marine

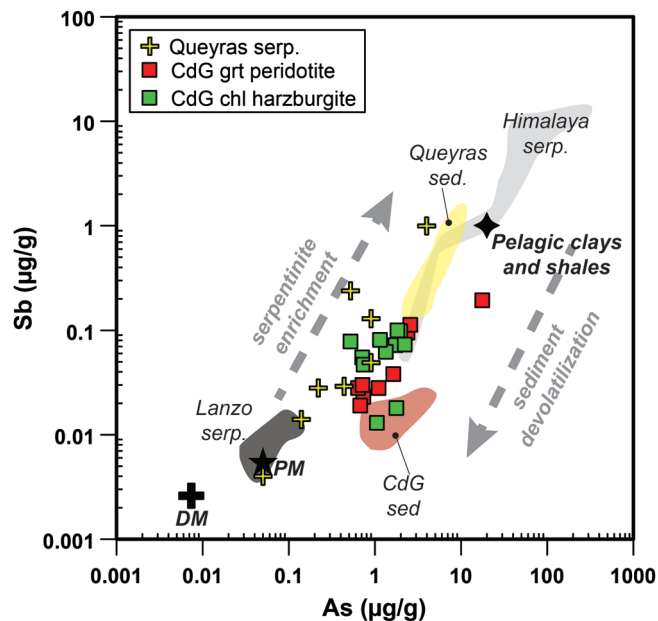


Fig. 9. As (µg/g) vs. Sb (µg/g) diagram showing the composition of Alpine ultramafic rocks from Queyras (Lafay *et al.*, 2013) and Cima di Gagnone (CdG; Scambelluri *et al.*, 2014; Cannà *et al.*, 2015). The fields of metasediments from the same localities and of oceanic (Lanzo; Debret *et al.*, 2013b) and wedge serpentinites (Himalaya; Hattori & Guillot, 2003) are shown for comparison. Devolatilization of sedimentary rocks can release these elements (grey arrow starting from oceanic pelagic clays and shale reservoirs; Li, 1991). Interaction of these fluids with serpentinite and meta-peridotite bodies within the Queyras and Cima di Gagnone mélanges leads to element storage in ultramafic rocks (grey arrow departing from the oceanic Lanzo serpentinite). It is important to note that ultramafic rocks from Cima di Gagnone might have partially lost As and Sb during antigorite dehydration. These are therefore minimum levels of enrichment for such rocks. Primitive and depleted mantle (PM and DM) are from McDonough & Sun (1995) and Salters & Stracke (2004).

Sr and Pb isotopic imprint of these rocks was reset towards metasedimentary values *via* the exchange with subduction fluids (Cannà *et al.*, 2015 their Fig. 5b and c). Since all

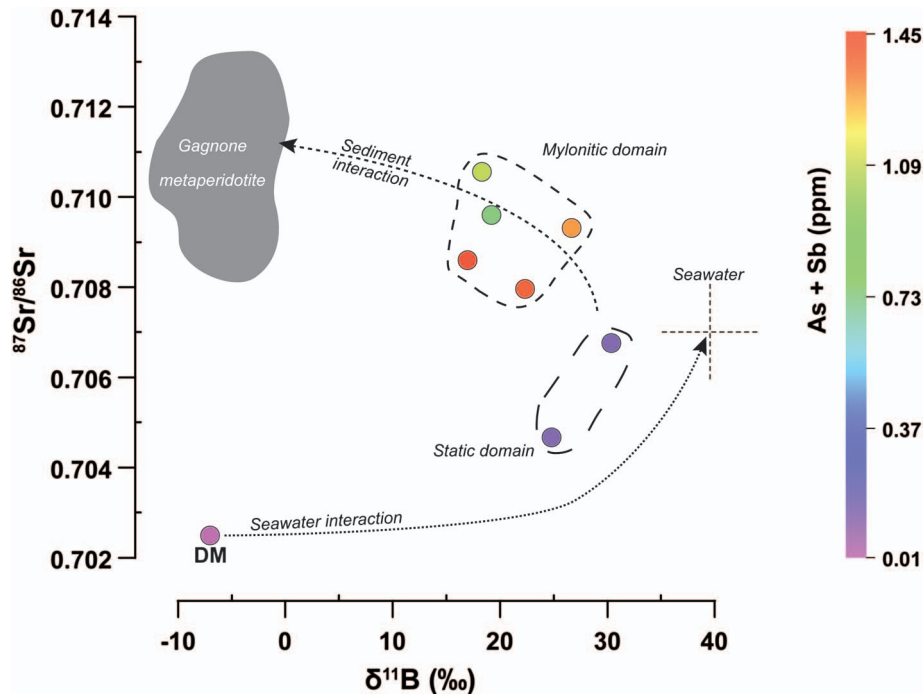


Fig. 10. Isotopic  $\delta^{11}\text{B}$  vs.  $^{87}\text{Sr}/^{86}\text{Sr}$  plus As + Sb content (ppm) of the Voltri undeformed and mylonitic serpentinites (dots; Cannà *et al.*, 2016), compared to the DM (Marschall *et al.*, 2017; Salters and Stracke, 2004), the Jurassic seawater (Smith *et al.*, 1995; Jones & Jenkyns, 2001) and the Cima di Gagnone metaperidotites (Cannà *et al.*, 2015). Interaction of the Voltri rocks with seawater during oceanic serpentinization shifted the  $\delta^{11}\text{B}$  and  $^{87}\text{Sr}/^{86}\text{Sr}$  isotopic composition towards seawater values, and caused slight enrichment in As and Sb. Interaction with sediment-derived fluid during subduction-zone deformation increased the  $^{87}\text{Sr}/^{86}\text{Sr}$  and As + Sb budget of serpentinites and partially reset their  $\delta^{11}\text{B}$ .

eclogite-facies minerals contain significant amounts of the above FME, the exchange with sediments must have predated eclogitization and antigorite dehydration in ultrabasic rocks (Scambelluri *et al.*, 2014; Cannà *et al.*, 2015).

The work on Gagnone and Queyras provided the geochemical background to unravel the fluid–rock interactions experienced by other Alpine serpentinites. The eclogite-facies serpentinite of the Voltri Massif consists of antigorite + chlorite + olivine + Ti-clinohumite + diopside + magnetite crystallized at 450–500 °C and 1.3–2.0 GPa (Cannà *et al.*, 2016). In Voltri, two different HP serpentinite domains were detected: undeformed and mylonitic. High-pressure mylonites wrap around undeformed HP serpentinite, eclogite and HP metaroddingite bodies (Scambelluri & Rampone, 1999). The undeformed serpentinite (Fig. 10, the blue-violet dots in the static domain) shows low As, Sb and B, O, Sr isotope composition pointing to serpentinization by Jurassic seawater ( $\delta^{11}\text{B}$  up to +30‰;  $\delta^{18}\text{O}$  4.5‰;  $^{87}\text{Sr}/^{86}\text{Sr}$  up to 0.70693; Cannà *et al.*, 2016). The mylonitic serpentinite (Fig. 10, the five large dots within the mylonitic domain) is slightly depleted in  $^{11}\text{B}$ , and is enriched in As, Sb and radiogenic Sr and Pb well matching the sediment-hosted Gagnone and Queyras ultramafic rocks. This points out that channelling of sediment-derived fluids along the mylonitic foliation caused partial resetting of the isotopic and trace-element oceanic signature of the mylonitic Voltri serpentinite. This process likely occurred when this serpentinite accreted to the plate-interface, above

and within oceanic sedimentary sequences (Cannà *et al.*, 2016).

## 5. Serpentine and element recycling

Having ascertained the capacity of serpentinite to uptake volatile and fluid-mobile elements during several hydration episodes, it is now of interest to examine how these elements behave during serpentinite dehydration and back-transformation into meta-peridotite at mantle depths. The above issues help constraining (i) element loss to subduction fluids linked to the genesis of arc crust and (ii) the deep recycling into the sources of ocean island basalts. If numerous papers provide evidence that serpentinite delivers water, halogens and FME to arcs (Hattori & Guillot, 2003; Savoy *et al.*, 2007; Barnes & Straub, 2010; Deschamps *et al.*, 2010; Scambelluri & Tonarini, 2012; Ryan & Chauvel, 2014; Ribeiro & Lee, 2017; Barnes *et al.*, 2018), a few papers deal with the composition of fluids produced by subduction breakdown of serpentinite (Scambelluri *et al.*, 2001a, 2004a, b, 2014; Spandler *et al.*, 2014) and only one paper deals with their recycling in the sources of ocean island basalt (OIB) (Kendrick *et al.*, 2017).

In the following section we conclude the serpentine subduction cycle, (i) by discussing the fluid released at subarc depths and retained by de-serpentinized meta-peridotite now exposed in orogenic belts, and (ii) by comparing the



compositions of such rocks with those of ocean island basalts, to provide hints on OIB sources.

### 5.1. Fluid-mediated recycling to arcs

The rock sources of subduction components transferred to arc magmas have long been debated. Though mafic crust and sediments are historically identified as major arc feeders since long (Plank & Langmuir, 1993; Elliott *et al.*, 1997; Plank, 2014), the hypothesis of water, halogen and FMEs delivery by serpentinite has gained ground (Hattori & Guillot, 2003; Scambelluri *et al.*, 2004a, b; Savov *et al.*, 2005a, b; Barnes & Straub, 2010; Scambelluri & Tonarini, 2012; Ryan & Chauvel, 2014; Barnes & Sharp, 2017; Barnes *et al.*, 2018). Moreover, since forearc and plate-interface serpentinites accept crust-derived elements, they can deliver fluids with mixed crust–serpentinite component (Scambelluri *et al.*, 2015a; Ribeiro & Lee, 2017). Central to this idea are geochemical studies of modern forearc serpentinites (Benton *et al.*, 2001; Savov *et al.*, 2005a, b, 2007; Alt & Shanks, 2006) and of their high-pressure equivalents (Hattori & Guillot, 2003; Deschamps *et al.*, 2013; Harvey *et al.*, 2014; Scambelluri *et al.*, 2014, 2015a; Peters *et al.*, 2017), together with geophysical studies of present-day subduction zones (Bostock *et al.*, 2002; Bostock, 2013). Debated key issues on mass transfer from subducting plates to arc magmas thus concern: (1) the volatile sources and (2) the transfer mechanism, whether by slab dehydration/melting beneath arc fronts, or by tectonic down-drag of metasomatized forearc mantle to subarc depths.

Regarding the first issue, though serpentinites carry water, halogens and FME (Ulmer & Trommsdorff, 1995; Scambelluri *et al.*, 2004a; John *et al.*, 2011; Kendrick *et al.*, 2011), direct evidence for their implication in hydration melting of the subarc mantle has long been elusive and, for this purpose, elemental boron and B isotopes can trace the process (Leeman, 1996; Tonarini *et al.*, 2011). At subarc depths, oceanic crust and sediments release fluids poor in  $^{11}\text{B}$  (the heavy B isotope) that cannot explain the  $^{11}\text{B}$  enrichment found in several volcanic arcs (Ishikawa & Nakamura, 1993, 1994; Peacock & Hervig, 1999). In contrast, the high  $^{11}\text{B}$  content of serpentinites makes a viable  $^{11}\text{B}$  source for subduction fluids. Figure 11 shows that numerous arc lavas tend to approach the  $^{87}\text{Sr}/^{86}\text{Sr}$  and  $^{11}\text{B}$ -rich composition of Alpine serpentinites and of their metamorphic veins, showing that serpentinite can supply the heavy B and water found in arc lavas (Scambelluri & Tonarini, 2012). The B systematics suggests, for instance, that fluids with up to 80% serpentinite component are added to the source of South Sandwich arc magmas (mixing line 1 in Fig. 11; Tonarini *et al.*, 2011). The interaction between serpentinites and sediment-derived fluids hybridizes the serpentinite composition. The dashed line connecting serpentinite and sedimentary end-members (Fig. 11, line 2–2') shows a possible range of serpentinite–sediment mixing. As serpentinite dehydrates at sub-arc depths, the resulting fluid acquires the serpentinite–sediment hybrid component found in arc lavas. Dehydration of Gagnone-like hybrid serpentinite can release fluids with negative  $^{11}\text{B}$  and high radiogenic Sr, which

mimic the composition of sedimentary reservoirs (Fig. 11). Exchange of such hybrid fluids with subarc mantle might generate arc lavas like the Andes, El Salvador and Kurile, where abundant sediments are subducted (line 3 in Fig. 11; Cannà *et al.*, 2015).

Complementary information on de-serpentinization fluids relies on studies of inclusions entrapping the antigorite-breakdown fluid released by natural rocks at eclogite-facies conditions. These inclusions were firstly discovered in chlorite harzburgites from Cerro del Almirez (Betic Cordillera; Trommsdorff *et al.*, 1998; Scambelluri *et al.*, 2001a) and, more recently, in chlorite harzburgite and garnet peridotite from Cima di Gagnone (Central Alps; Scambelluri *et al.*, 2015a). As discussed previously, before dehydration the serpentinized precursors of the Gagnone meta-peridotites experienced interaction with ocean waters and with crust-derived subduction fluids (Scambelluri *et al.*, 2014). Primary fluid-related inclusions derived from antigorite and chlorite breakdown, hosted in eclogitic rock-forming olivine and garnet, contain daughter microcrystals of silicates, Cl-bearing phases, sulphides and carbonates (Scambelluri *et al.*, 2015a). Their *in situ* LA-ICP-MS trace element analysis reveals two different inclusion types: type (A), hosted in olivine and strongly enriched in Cl, Cs, Pb, As, Sb (up to  $10^3$  times the PM), in Tl and Ba ( $\sim 10^2$  times PM), while Rb, B, Sr, Li, U are of the order of 10 times the PM; type (B) hosted in garnet, with lower FME contents and with enrichment patterns comparable to fluid type (A). Combined with bulk-rock and mineral trace element data, the inclusion compositions indicate that the trace element-enriched type (A) fluid derives from serpentine dehydration, whereas type (B) fluid with lower trace element budgets can relate with chlorite breakdown at higher  $P$ – $T$  conditions (Scambelluri *et al.*, 2015a).

The enrichment in large ion lithophile and in chalcophile elements of the Gagnone inclusions well reflects a fluid equilibrated with sediments, and the presence of the same elements in the inclusions and in coexisting eclogite-facies minerals reveals a recycling process. Starting from a serpentinized precursor, this process requires preferential partitioning of FMEs in the fluid phase and, to a lesser extent, into HP minerals forming the solid residues after antigorite and chlorite dehydration. Estimated fluid/solid partition coefficients are in the order of more than 100 and up to 20 thousand times the PM for Cs, Rb, Ba and of <10 for Th and U;  $K_{\text{D}(\text{fluid}/\text{olivine})} = 3$ –4 have been estimated for Li and B (Scambelluri *et al.*, 2015a). The compositions of type (A) inclusions bound to antigorite dehydration compare well with those of antigorite-breakdown inclusions in the Almirez chlorite harzburgite (Scambelluri *et al.*, 2004a, b; Bretscher, 2017), and with synthetic inclusions reproduced by antigorite dehydration experiments (Spandler *et al.*, 2014). The Almirez and Gagnone inclusions overlap and share common anomalies in Cs, Rb, Ba, B, Pb and La, suggesting that the exchange with sediment-derived subduction fluids was common to both localities. A sedimentary input in the Almirez ultramafic rocks was also envisaged by trace element (Marchesi *et al.*, 2013) and isotopic studies (Harvey *et al.*, 2014). This might explain the enrichment

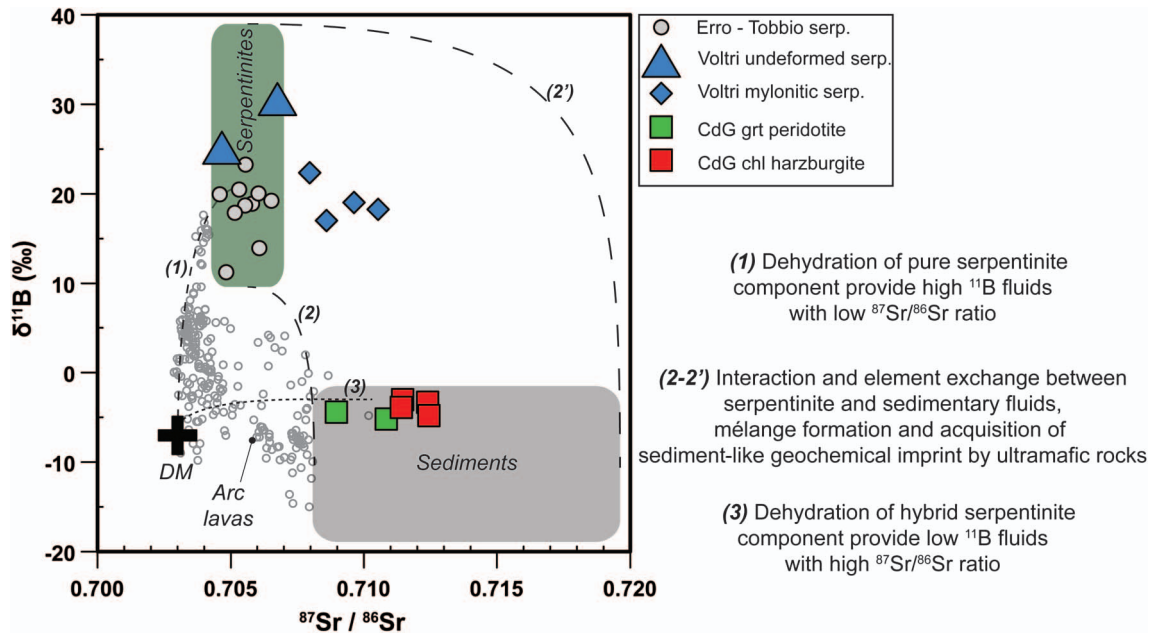


Fig. 11.  $\delta^{11}\text{B}$  vs.  $^{87}\text{Sr}/^{86}\text{Sr}$  diagram showing the serpentinite contribution to arc lavas. The mixing lines (2) and (2') show the range of isotopic compositions that can be acquired *via* fluid-mediated exchange between serpentinite and sedimentary reservoirs. Interaction of depleted mantle (DM) with fluids released by serpentinite poorly affected by sediment-derived fluids (*e.g.* Erro-Tobbio and Voltri undeformed) can produce a range of arc lava compositions following the dashed line 1. Interaction of DM with fluids released by serpentinite that intensively exchanged with sediment-derived fluids (Cima di Gagnone, CdG) can produce arc lava plotting along dashed line 3.

in crust-derived elements unusual in serpentinites formed by single-stage ocean-floor hydration, but increasingly found in ultramafic rocks involved in subduction-zone processes. The halogen analyses, available for Almirez inclusions only (Kendrick *et al.*, 2011), point out that the antigorite breakdown fluids become progressively depleted in Br and I relative to Cl as a result of halogen fractionation during antigorite breakdown (Fig. 8b).

Figure 12 shows that, for a set of elements, the PM-normalized pattern of the Gagnone and Almirez inclusions fit the compositions of numerous arc lavas (data source in Kelemen *et al.*, 2014; Scambelluri *et al.*, 2015a; Bretscher, 2017). The overlap of analysed inclusions with arc lavas for Cs, Rb, Ba, B, Pb, As, Sb and Li visualises the mixed serpentinite–sediment component released to antigorite dehydration fluids. The subduction fluids produced by ultramafic rocks that experienced a larger interaction with sediment-derived fluids have higher budgets of LILE, chalcophile elements, Li and B (Scambelluri *et al.*, 2015a, b). Interestingly, the Almirez fluid inclusions plot in between the fluids hosted in olivine from chlorite harzburgites and in garnet from garnet peridotites. This strengthens the hypothesis of infiltration by sediment-derived fluids in Almirez, proposed by Marchesi *et al.* (2013) and Harvey *et al.* (2014).

The evidence presented here helps discriminating the mass-transfer processes leading to mantle metasomatism and arc magmatism. The Almirez and Gagnone meta-peridotites are equivalents of ultramafic rocks tectonically

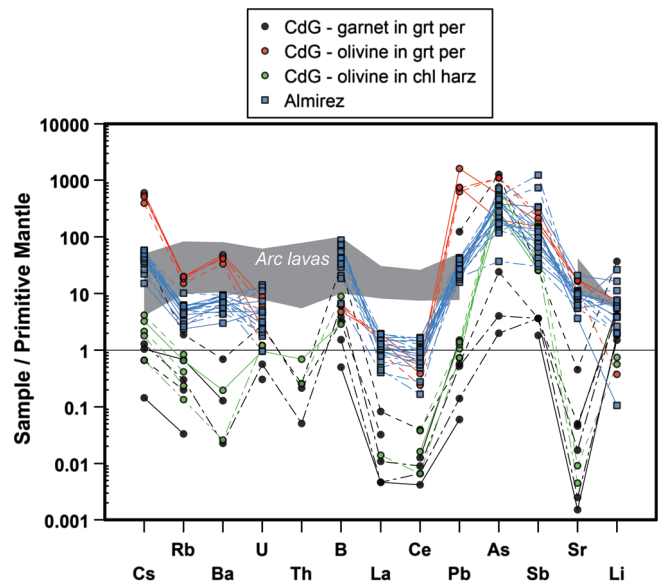


Fig. 12. Primitive-mantle (McDonough & Sun, 1995) normalized compositions of the olivine-hosted Gagnone inclusions related to antigorite breakdown (patterns with red and green dots; data after Scambelluri *et al.*, 2015a) compared to the antigorite-breakdown inclusions from Almirez (patterns with blue squares; data after Scambelluri *et al.*, 2004b; Bretscher, 2017). Also reported are the garnet-hosted inclusions from Gagnone (patterns with black dots; after Scambelluri *et al.*, 2015a). The grey area refers to arc lavas from Kermadec, Marianas, Scotia, Aleutian, Cascades, Costa Rica and Kamchatka (data source reported in Scambelluri *et al.*, 2015a).

embedded at the plate interface and/or in a subduction mélange, respectively. They may release fluids with mixed serpentinite–sediment component following a sequence of dehydration reactions consuming antigorite first and then chlorite (Fig. 13a). Alternatively, FME-enriched Gagnone meta-peridotites can be proxies of forearc mantle flushed by slab fluids during early subduction stages. In such a case (Fig. 13b), the altered forearc mantle (dotted layer above the plate interface) releases water and FMEs through the same reaction sequence as in Fig. 13a. As stated previously (Hattori & Guillot, 2003; Hyndman & Peacock, 2003; Savov *et al.*, 2005a, b; Scambelluri & Tonarini, 2012), mass transfer from slabs to plate interface and/or forearc mantle, and the subsequent down-drag of this altered mantle to subarc depths can be increasingly revealed by serpentinite geochemistry.

## 5.2. Recycling to OIB sources

If the impact of serpentinite on geochemical and tectonic cycles within the first hundred kilometres of subduction is increasingly studied, little is known of their fate beyond arc depths. This is essentially due to a paucity of de-serpentinized ultramafic rocks exhumed from such depths, Almirez and the Gagnone being the only known examples so far. The available studies clearly show that dehydration processes re-converting serpentinites into mantle rocks do not fully strip off water and FMEs from rocks: a significant fraction of FME and LILE still trapped in nominally anhydrous HP minerals (like olivine and orthopyroxene) after fluid extraction potentially introduces anomalies in the upper mantle (Scambelluri *et al.*, 2004a, 2014; John *et al.*, 2011; Kendrick *et al.*, 2011). The average trace-element composition of metamorphic olivine from the garnet peridotites and the available fluid/olivine partition coefficients (Tenthorey & Hermann, 2004; Scambelluri *et al.*, 2015a) were employed to estimate the trace element budget of a fully serpentinized protolith (12 wt% water). The element percentage still retained by the garnet peridotite after fluid extraction has been evaluated through a mass balance calculation (Table 1). The result indicates that after antigorite dehydration a significant part of the FME budget of the initial serpentinite is still trapped in the metaperidotites dehydration product, supporting the potential of such reservoir for geochemical input in the deep Earth's mantle. Moreover, recent data document addition of isotopically heavy boron to the mantle sources of carbonatites (Hulett *et al.*, 2016). Retention of boron anomalies in nominally anhydrous phases produced by de-serpentinization represents a viable mechanism for recycling B and other fluid-mobile elements into the Earth's lower mantle. This has been recently proposed in the case of super-deep B-bearing blue diamonds, hosting up to 10 ppm B potentially recycled by serpentinite precursors, and crystallized at minimum depths of 350–400 km down to 700 km (Smith *et al.*, 2018).

Seawater-derived element recycling throughout the Earth's mantle by serpentinite subduction has been recently proposed by Kendrick *et al.* (2017) after processing the water and halogen contents of >400 OIB glasses.

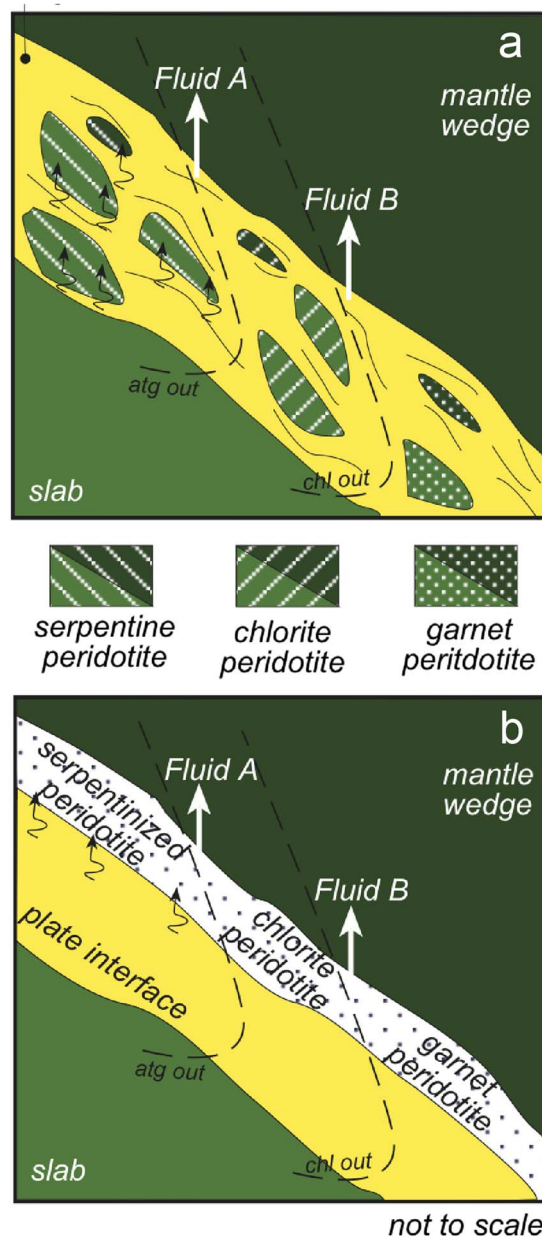


Fig. 13. Possible scenarios for stepwise fluid loss from subducting serpentinites like Gagnone. The cartoon shows release of type A and B fluids from mélange (plate a) and forearc mantle (plate b) settings as the result of antigorite- and chlorite-out reactions, respectively (after Scambelluri *et al.*, 2015a). (a) shows a subduction interface sedimentary mélange hosting ultramafic bodies (*e.g.* Gagnone). The different patterns indicate a possible provenance for the mélange blocks (light green from slab, dark green from mantle wedge). The prograde interaction of the serpentinized blocks with sediment-derived fluids (black arrows) allows full hydration, enrichment in FME and isotopic reset of the serpentinized blocks. The white dashed lines correspond to the dehydration breakdown of antigorite (atg) and chlorite (chl) in the ultramafic rocks: the antigorite out (atg out) reaction releases a first pulse of trace-element-rich fluid (Fluid A), followed by chlorite-breakdown (chl out) producing a pulse of a trace-element-poorer fluid (Fluid B). In (b), slab fluids infiltration into the forearc mantle produces hybrid serpentinite layers whose composition comparable to the Gagnone ultramafic rocks. During antigorite dehydration, type A and type B fluids are released (see Fig. 14) in a sequence. All figures are not to scale.



Table 1. Percent of elements retained/released during serpentinite dehydration.

	Olivine in grt peridotite <sup>‡</sup>	$K_{\text{fluid/ol}}^*$	$K_{\text{dfluid/rock}}^{\S}$	% of element retained in the metaperidotite		% of element released in the fluids	
	(ppm)	grt per	T&H (2004)	grt per	T&H (2004)	grt per	T&H (2004)
B	0.675	3	4	81	74	19	26
Li	2.315	4	100	74	8	26	92
Sb	0.030	90		9		91	
As	0.195	60	60	12	12	88	88
Rb	0.010		10		48		52
Sr	0.020	530	10	2	48	98	52
Y	0.002	80		10		90	
Nb	0.036	1.5		94		6	
Ba	0.023		30		22		78
La	0.002	830		1		99	
Ce	0.009	650		1		99	
Nd	0.004	40		18		82	
Dy	0.003	22		28		72	
Lu	0.001						
Ta	0.001						
Pb	0.056	440	250	2	3	98	97
Th	0.001		1.5		94		6
U	0.004	90	20	9	30	91	70

The calculation assumes 100% of serpentinitized ultramafic rocks (12 wt% of water).

<sup>‡</sup>Average olivine composition from Scambelluri *et al.* (2015a).

\* $K_{\text{ol/fluid}}$  of Cima di Gagnone garnet peridotite from Scambelluri *et al.* (2015a).

<sup>§</sup> $K_{\text{dfluid/rock}}$  from Tenthorey & Hermann (2004) – T&H (2004).

Traditionally, the geochemical fingerprint of OIBs is attributed to the presence in their mantle source of recycled oceanic crust (HIMU) and sediments (EM) (Workman *et al.*, 2006). Major outcome of Kendrick *et al.* (2017) work regards the unexpected enrichment in primary water and halogens in many analysed OIB glasses, this feature being a clear spike for deep recycling of dehydrated oceanic crust and of serpentinitized mantle in their source.

Further hints on the extent of recycling of formerly serpentinitized materials in OIBs can be given by the  $^{87}\text{Sr}/^{86}\text{Sr}$  vs.  $^{206}\text{Pb}/^{204}\text{Pb}$  diagram of Fig. 14, where Alpine ultramafic rocks recording exchange with sediments and crustal reservoirs are reported. Assuming that metamorphic dehydration does not affect radiogenic isotope fractionation, the isotopic ratios presented in Fig. 14 remained unchanged throughout the entire subduction pathway. Interestingly, such Alpine serpentinites display a range of isotopic values characteristic of OIB lavas so far attributed to recycled sediments (EM1–EM2). A global implication arising from this evidence is that serpentinites do not release the entire water, halogen and FME budget during dehydration in the first hundred kilometres of subduction: the residual budget affects the deep OIB mantle and indicate their potential influence on the cycles of water and halogens from shallow depths down to the OIB mantle.

## 6. Perspectives

Knowledge of serpentinite evolution from oceans to subduction zones underwent rapid development in the last decade, especially concerning the geochemical studies, the estimates

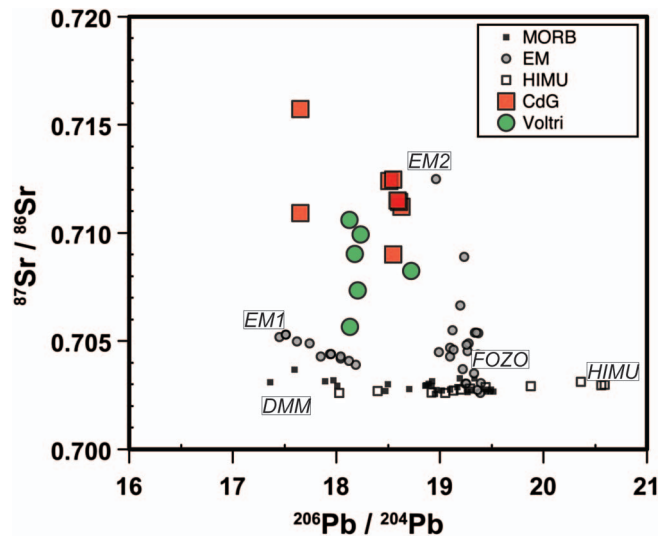


Fig. 14.  $^{206}\text{Pb}/^{204}\text{Pb}$  vs.  $^{87}\text{Sr}/^{86}\text{Sr}$  diagrams of Alpine ultramafic rocks compared with mantle reservoirs and OIBs. The diagram is redrawn after Kendrick *et al.* (2017, and reference therein) and reports present day values. Principal mantle end-members for OIB (depleted MORB mantle, DMM; Enriched Mantle 1 and 2, EM1 and EM2; high- $\mu$  – HIMU – all characterized by high U/Pb) and the focus zone (FOZO) are also reported (after Kendrick *et al.*, 2017). The isotopic compositions of the Voltri serpentinites and of de-serpentinitized peridotites from Gagnone (data after Cannà *et al.*, 2015, 2016) potentially represent new contaminants of the type 2 enriched mantle (EM2).

of fluid-mobile trace element budgets of these rocks and their phase relations at changing  $P$ – $T$  conditions. This well integrates with studies of the physical properties of

serpentine minerals (Sect. 2) and the impact of de-serpentinization reactions on subduction-zone seismicity. Recently, nano olivine has been shown to form as high-pressure dehydration product of antigorite (Plümper *et al.*, 2017). This can induce a decrease in viscosity and lead to localized shear instabilities, thus providing insights into the genesis of seismic tremors in hydrated, low-velocity plate interface domains (Green *et al.*, 2015; Plümper *et al.*, 2017). For a proper discussion of relationships between serpentinite dehydration and seismicity, we refer to Jung *et al.* (2004), Green *et al.* (2015), Proctor & Hirth (2015), Gasc *et al.* (2017) and Ferrand *et al.* (2017). Here we aim at addressing new petrologic-geochemical research trends and major topics worth investigation.

### 6.1. Rock structures and fluid flow

Because early oceanic signatures are retained in rock domains unaffected by large finite strain, future investigations should be carried out in deformed *versus* undeformed serpentinite within key rock units (*e.g.* Cannà *et al.*, 2016), in order to clarify how strain localization promotes fluid channeling and resetting of initial geochemical signatures of serpentinites. In this regard, the mechanisms of fluid access and of fluid/mineral reaction are yet to be defined and represent a research frontier. In general, the fluid pathways into serpentinizing rocks are associated to tectonic fracturing and shearing of oceanic and *supra*-subduction mantle. Fluid influx has also been linked to volume change during serpentinization, leading to crack propagation, enhanced fluid access, dissolution of unstable minerals and serpentine precipitation (Jamtveit *et al.*, 2009; Kelemen & Hirth, 2012; Plümper *et al.*, 2012). However, crack infilling by serpentine substantially clogs the pores and inhibits fluid flow. Tutolo *et al.* (2016) proposed that fluid access into these rocks occurs through nano-scale micropores and defects inside serpentine minerals, which represent a significant fraction of the rock porosity. Permeability changes during deformation, metamorphism and fluid-controlled mineral dissolution play a key control on fluid stagnation *versus* fluid channelling and on development of reaction fronts and element transport into serpentinite and mantle domains being serpentinized (Kelemen & Matter, 2008; Malvoisin, 2015; Leclère *et al.*, 2018). The above studies steer current research towards an understanding of fluid circulation patterns and reaction kinetics and stimulate scientists to refine textural observations from micro- to nanoscales, so to identify the mechanisms driving to large-scale fluid flow in serpentinite. This analysis must be coupled with other fine-scale observations showing the details of fluid production and how high fluid pressures locally built up in dehydrating rock domains can decrease during channelized fluid flow (John *et al.*, 2012; Plümper *et al.*, 2017; Taetz *et al.*, 2017). Defining the above features can improve our understanding of the physical mechanism controlling open-system fluid influx in the oceanic lithosphere and in the mantle wedge (*e.g.* Malvoisin, 2015; Malvoisin *et al.*, 2015), whether punctuated and temporally associated to

dehydration pulses, or continuous and due to migration of fluids from far dehydration fronts.

### 6.2. Carbon storage and release

Oceanic and subduction-zone serpentinites are also relevant for storing carbon and releasing carbonic fluids. Carbonation of shallowly exposed oceanic mantle and permanent C storage in ophicarbonate rocks are common to modern and past oceans and to continental settings, where they occur *via* low-*T* interaction of aqueous-carbonic fluids with serpentinized peridotites (Kelemen & Matter, 2008; Etiope & Sherwood Lollar, 2012). The behaviour of subduction-zone serpentinite is equally important, yet more complex. On one hand, by releasing aqueous fluids upon dehydration, they enhance C release from nearby carbonate-rich rocks and formation of aqueous-carbonic (COH) fluids (*e.g.* Caciagli & Manning, 2003; Gorman *et al.*, 2006; Ague & Nicolescu, 2014; Piccoli *et al.*, 2016). On the other hand, back-reaction of COH fluids with serpentinite and associated mafic rocks promotes carbonation and long-term C re-storage into newly formed carbonates (Piccoli *et al.*, 2016; Scambelluri *et al.*, 2016; Piccoli & Vitale Brovarone, 2018). Moreover, serpentinites and peridotite serpentinization can promote reducing conditions and C recycling in two alternative ways: by converting carbonate minerals into graphite and thereby leading to long-term C storage (Malvoisin *et al.*, 2012; Galvez *et al.*, 2013); or by favouring the genesis of mobile C-bearing species such as CH<sub>4</sub> (Vitale Brovarone *et al.*, 2017). As future perspective, addressing the interplay of processes controlling C mobility (decarbonation, COH-fluid genesis) or storage (carbonation, graphite precipitation) in subduction-zone serpentinite is crucial for quantifying C speciation in subduction-zone fluids, the long-term C cycling in subduction zones and, consequently, the CO<sub>2</sub> and CH<sub>4</sub> emissions to atmosphere by arc volcanic fronts (Berner *et al.*, 1983; Malaspina & Tumiati, 2012; Dasgupta, 2013; Collins *et al.*, 2015; Kelemen & Manning, 2015).

### 6.3. Redox state

Carbon speciation in rocks and fluids strongly depends on redox conditions. As previously discussed, serpentine strongly contributes to water release from slabs to arc magmas (Fig. 11; see also Scambelluri & Tonarini, 2012), which commonly display Fe<sup>3+</sup>/Fe<sub>tot</sub> higher than MORB and OIB basalts because of addition to their mantle sources of fluids carrying oxidised species, like H<sub>2</sub>O, CO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub> and sulfate (Arculus, 1994; Kelley & Cottrell, 2009; Malaspina *et al.*, 2009, 2010; Evans & Tomkins, 2011; Evans & Powell, 2015; Evans *et al.*, 2017). In turn, the speciation of subduction fluids is controlled by the variable oxidation state of the source rocks (Tumiati *et al.*, 2015; Debret & Sverjensky, 2017; Evans *et al.*, 2017; Cannà & Malaspina, 2018; Tumiati & Malaspina, 2019). Because serpentinite is the rock that primarily controls the release of slab fluids, efforts have been recently done to determine the redox state of serpentinized rocks and fluids by means of (i) direct measurements of the Fe<sup>3+</sup> content of bulk rocks and serpentine (Andreani

*et al.*, 2013; Debret *et al.*, 2014b, 2015; Evans *et al.*, 2017) and (ii) theoretical calculations (Debret & Sverjensky, 2017). The results show a range of values for the redox conditions of subduction-zone rocks (slab,  $-1$  to  $4.5$   $\Delta$ FMQ; mantle wedge,  $-3.5$  to  $-1.5$   $\Delta$ FMQ) and for the oxidation capability of fluids. This can lead us to much better constrain the volatile mass transfer in subduction zones, the bulk oxygen budget and the type of C-bearing minerals in the mantle wedge. These investigations need further support by direct measurements of the oxidation state of slab fluids, either preserved as inclusions in rocks (Campione *et al.*, 2017; Malaspina *et al.*, 2017), or produced experimentally. Compared to  $\text{Fe}^{3+}$  measurement in solids, the study of fluid-related inclusions is more challenging because it requires *in situ* high-resolution techniques such as transmission electron microscopy coupled with electron energy loss spectroscopy (EELS). Such an approach enabled Malaspina *et al.* (2017) to measure the  $\text{Fe}^{3+}$  concentration in micrometre-sized inclusion infillings (spinel = 12%  $\text{Fe}^{3+}$  of total iron, amphibole = 30%  $\text{Fe}^{3+}$ , chlorite and phlogopite = 70%  $\text{Fe}^{3+}$ ) and to calculate the oxygen mass balance of fluids with respect to the host rock. The results show that the fluid precipitates are more oxidised than the host rocks, even after possible post-entrapment modifications (Campione *et al.*, 2017) and that this fluid conveys oxidised components into the mantle.

Future development of the above investigations and analytical techniques will enable to address the mechanisms driving of fluid and element storage and release by rocks which dominate the water cycles in oceans and subduction zones. Addressing the above issues will help defining volatile speciation in de-serpentinization fluids, their contribution to global volatile recycling into the mantle and, importantly, the mechanism of reactive fluid migration in solid, porous rock media.

## 7. Conclusions

We have presented evidence of the key role of serpentinites in recycling volatiles, halogens and fluid-mobile elements from the Earth's surface reservoirs into the mantle at subduction zones. Their trace-element budget is either acquired during interaction of the oceanic mantle with seawater-derived fluids, or during evolution along the subduction plate interface.

Numerous works documenting the fluid-mobile element (*e.g.* B, As, Sb) and isotopic (*e.g.* B, Sr) composition of oceanic, forearc and subduction-zone serpentinites try to identify provenance of serpentinites now exposed in orogenic belts. However, a provenance study just based on geochemical data is not fully reliable: detailed field, textural and petrologic information are a necessary complement of the geochemical characterization of these rocks. For example, the field-based interdisciplinary studies of serpentinite slices accreted to the fossil Alpine subduction interface help constraining the fluid-mediated geochemical fluxes in and out this domain. The Alpine serpentinites can contain undeformed relict cores with inherited oceanic geochemical

signatures (*e.g.* high  $^{11}\text{B}$ , marine Sr isotopes, low As and Sb) embedded in subduction-related foliations showing resetting of the original oceanic imprint towards more radiogenic Sr, lower  $^{11}\text{B}$ , and higher As and Sb. These studies thus disclose the geochemical reworking of pristine, oceanic, geochemical imprints *via* the exchange with crust-derived fluids along the subduction plate interface.

The de-serpentinization fluids released at various stages, and still preserved in these rocks as inclusions, carry significant amounts of halogens and fluid-mobile elements. The antigorite-breakdown fluids produced in different localities share compositional similarities suggesting that these rocks record comparable processing. We show that the fluid-mediated exchange with sedimentary and/or crustal reservoirs during subduction leads to hybridization of the serpentinite and to release of high Cs, Rb, Ba, B, Pb, As, Sb and Li fluids overlapping the arc lavas. These fluids can represent the mixed serpentinite–sediment component released to arcs upon antigorite dehydration. This evidence helps discriminating the mass-transfer processes responsible for *supra*-subduction mantle metasomatism and arc magmatism. Fluid and element transfer from slabs to plate interface and/or forearc mantle, and the subsequent down-drag of this altered mantle to subarc depths, should be re-evaluated as major processes operating in subduction zones.

If the role of serpentinites as trace element carriers in the upper mantle is now clarified by many studies, their involvement in lower-mantle metasomatism begins to be recognized. The nominally anhydrous olivine, ortho-, clino-pyroxene and garnet forming the high-pressure rock residues after serpentinite dehydration still host appreciable amounts of halogens and fluid-mobile trace elements. In practice, de-serpentinization does not release to fluid its entire elemental budget: de-serpentinized ultramafic rocks can transfer halogen and FME anomalies to the deep mantle beyond arcs. As shown by the water and halogen-rich composition of OIB glasses (Kendrick *et al.*, 2017), by the isotopic compositions of serpentinites presented here (Fig. 14), and by the B content of ultradeep blue-diamonds (Smith *et al.*, 2018), the presence of de-serpentinized materials can be identified in the lower mantle and might well be increasingly documented in the near future.

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