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# From oceanic to continental subduction: Implications for the geochemical and redox evolution of the supra-subduction mantle

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## ABSTRACT

**Processes taking place in subduction zones are the main controller of the chemical cycle of volatile and incompatible elements in the Earth system. Metamorphic devolatilization reactions occurring during slab burial play a key role in the transfer of elements to the supra-subduction mantle, from forearc to sub-arc depth. Here, we discuss the elements released in fluids and melts from oceanic (i.e., sediments, altered oceanic crust, and hydrated lithospheric mantle) and continental slab materials during prograde subduction and the consequent implications in the chemical evolution of the supra-subduction mantle. We use bulk data and fluid and melt inclusions analyses to show and to constrain the mobility of elements from top to bottom in the subduction zone setting. The development of mélangé domains at the slab-mantle interface and its influence in the element cycle are also taken into account. Coupled with trace-element mobility, we review the redox evolution of slab materials during subduction and its implication in the redox conditions of the supra-subduction mantle due to fluid and melt infiltration down to sub-arc depth.**

## INTRODUCTION

Subduction processes are the main controller of the chemical cycle of volatile and incompatible elements in the Earth system (Stern, 2002; Elliott, 2004; Bebout, 2013; Schmidt and Poli, 2014; Hermann and Rubatto, 2014). The release of elements through dehydration and/or partial melting processes of the subducted materials is the main factor responsible for the metasomatism of the supra-subduction mantle. Generally, the subduction of oceanic lithosphere is promoted by its high density, thickness, and lower temperature with respect to the continental crust (e.g., Stern, 2002). However, the subduction of slices of continental crust up to ultra-high pressure (UHP) conditions is documented in several terranes by the discovery of UHP polymorphs such as coesite and diamond in gneisses or marbles (Chopin, 1984; Smith, 1984; Sobolev and Shatsky, 1990; Stöckhert et al., 2001). During the subduction path, slab rocks undergo chemical and physical transformations that are typical of high-pressure and low-temperature conditions, along a geotherm

gradient from ~5–10 °C/km up to 20 °C/km (Peacock, 1996; Syracuse et al., 2010; Van Keken et al., 2011). Devolatilization reactions are the main processes promoting the slab-to-mantle element transfer and strongly depend on temperature. The temperature gradient of the subducting slab is consequently a key parameter controlling chemical evolution of the slab materials and the release of elements in the supra-subduction mantle (e.g., Van Keken et al., 2011). A full understanding of these transfer processes requires suitable rock samples that record interactions between mantle peridotites and incoming subduction fluids from forearc to sub-arc depths. Such samples correspond to metasomatized peridotites cropping out in orogenic environments, which are associated with crust-derived rocks both equilibrated at HP and UHP. Moreover, the investigation of the fluid phases produced by subducted oceanic lithosphere (i.e., by antigorite breakdown) and continental crust (i.e., aqueous fluids and supercritical liquids) and their interaction with the supra-subduction mantle enables us to unravel the possible metasomatic processes down to depths corresponding to arc magma sources.

The purpose of this contribution is to characterize the different geochemical fingerprints of the subducted oceanic lithosphere and continental crust through an overview of their trace-element signature and isotopic imprint. Also, we will consider the chemistry of fluid inclusions in both oceanic HP serpentinites and metasediments as representative of the composition of fluid phases able to metasomatize the supra-subduction mantle. To complete the picture, we will also present trace-element and isotopic data of supra-subduction peridotites affected by fluid phases derived from the continental crust at HP and UHP from three unique localities: Ulten Zone (Italian Central Alps), Sulu (Eastern China), and Bardane (Western Gneiss Region). All these results will be discussed in the framework of recent data available on the oxidizing capability of slab-derived fluid phases and of the oxidation state of the supra-subduction mantle at sub-arc depth.

In this contribution, we will try to address some important questions that are still under debate by the scientific community:

- (1) How can the evolution of the subducting materials along the slab-mantle interface (from oceanic to continental crust) modify their geochemical features?

- (2) What is the role of subducted mineral assemblages as carriers of elements to depth?
- (3) How can such evolution influence the geochemical features of the supra-subduction mantle?
- (4) What is the redox state of the subducting lithosphere, and how does it evolve from oceanic to continental subduction?
- (5) How can the redox-state evolution influence the speciation of elements in the metasomatic fluids infiltrating the supra-subduction mantle?

## ■ GEOCHEMISTRY OF SUBDUCTING MATERIALS

Subduction input materials are mainly constituted by the oceanic lithosphere, subdivided, from top to bottom, in oceanic sediments, altered oceanic crust, and hydrated lithospheric mantle. During the formation of an ocean by rifting processes, slices of continental crust from the margins may also occur as extensional allochthons in the newly formed basin (Peron-Pinvidic and Manatschal, 2010; Lundin and Doré, 2011; Beltrando et al., 2014). In this context, the subduction of the oceanic lithosphere can be associated with subduction of slices of continental crust (Dal Piaz, 1999; Mohn et al., 2014). Moreover, when the oceanic materials are consumed and entirely buried at depth, the subsequent continent-continent collision allows the subduction of portions of continental crust. In the following sections, the key points concerning the geochemistry of the oceanic lithosphere and continental crust, as “input subduction materials,” are briefly described.

### Oceanic Lithosphere

Sedimentary materials on the ocean floor represent the result of the erosion of continents and of biogeochemistry and marine life. The chemical composition of these materials can be considered as a mixing between multiple end-members of sediments that strongly depend on their source, such as continental and volcanoclastic detritus, biogenic carbonate and opal, Fe-Mn oxides, siliceous materials, and many others. As proposed by Plank and Langmuir (1998) and recently updated by Plank (2014), detrital components can provide alkali elements (K, Rb, and Cs), B, Be, Pb, and high field strength elements (HFSE: Hf, Zr, Nb, Ta, and Ti), whereas biogenic phases and biological productivity strongly affect the Ba and Sr contents. Lithium and rare-earth elements (REEs) are typical of the upper continental crust or average shales, while U seems mainly linked to organic C-rich sediments. Another key feature of sedimentary materials is their enrichment in some fluid-mobile elements, such as As and Sb (Li, 1991; Plank and Ludden, 1992). As will be discussed in the next sections, these elements play an important role in understanding the chemical exchange between different geochemical reservoirs during the subduction of oceanic lithosphere (Hattori and Guillot, 2007; Deschamps et al., 2011; Scambelluri et al., 2014; Cannaò et al., 2015; Scambelluri et al., 2015; Cannaò et al., 2016). From an isotopic point of view, the sedimentary material is characterized by strong enrichment in radiogenic isotopes, such as high  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios

(0.7123 GLOSS II value) and Pb isotopes (e.g., Plank, 2014), due to the presence of micas that are the most important carrier of their parental elements Rb and Th-U, respectively. On the contrary, geochemical isotopic systematics of elements with high mantle affinity, such as Sm-Nd and Lu-Hf, are less radiogenic than mantle composition.

The oceanic crust forms at mid-ocean ridges by magmatism. Although quite homogeneous, its composition is related to the magma supply rates: In fast spreading ridges, magmas are generally more fractionated than those generated in slow spreading ridges (Perfit and Chadwick, 1998). Studies of the oceanic crust are accomplished through the collection of in situ drill cores, dredging of ocean floor, and by sampling and analyses of obducted ophiolitic sequences (e.g., Troodos in Cyprus and Samail in Oman). Based on major- and trace-element geochemistry analyses of these rocks, the average composition of the oceanic crust is typically mid-ocean ridge basalt (MORB), even if composition of MORB can vary substantially. The most important process able to strongly modify the elemental budget of the oceanic crust is the interaction with seawater or seawater-like fluids during hydrothermal alteration processes, contributing to the major addition of  $\text{H}_2\text{O}$  and  $\text{CO}_2$  via crystallization of secondary hydrous- and carbon-bearing minerals (Staudigel, 2003, and references therein). In terms of trace elements, the formation of these alteration minerals allows the storage of elements derived from the seawater and the underlying sedimentary package. In this way, the oceanic crust may display positive anomalies in alkali elements, such as Cs, Rb, and K, and enrichment in B, Ba, Th, U, and S (Alt and Teagle, 2003). Also Li is a good indicator of hydrothermal interaction with seawater-derived fluids (Vils et al., 2008). Moreover, enrichment of some immobile elements such as REEs has been identified in extremely altered basalts dredged from some seamounts (Staudigel et al., 1996).

During the alteration process at the oceanic stage, the oceanic crust is affected by partial to complete resetting of its isotopic signature, which may diverge significantly from its original mantle value. Modification of stable (e.g.,  $\delta^{18}\text{O}$ ,  $\delta\text{D}$ ,  $\delta^{13}\text{C}$ ,  $\delta^{11}\text{B}$ , and  $\delta^{37}\text{Cl}$ ) and radiogenic (e.g.,  $^{87}\text{Sr}/^{86}\text{Sr}$ ) isotopes may provide information about the oceanic alteration history of the crust. Subsequent subduction of these altered materials to mantle depth introduces significant geochemical anomalies with important consequence in the global element fluxes.

For the purpose of this review, we focus our attention on one of the most important isotopic systematics affected by alteration processes—the Sr ratio (Staudigel, 2003). Fresh crust shows the same Sr isotopic ratios of the depleted mantle ( $^{87}\text{Sr}/^{86}\text{Sr} = 0.7025$ ; Klein, 2003), whereas the Sr signature of the altered oceanic crust will be close to that of the interacting fluids, which is much more radiogenic (e.g., present-day seawater  $^{87}\text{Sr}/^{86}\text{Sr} = 0.7092$ ; Bruland et al., 2013). It is important to note that the Sr isotope ratio of seawater is affected by secular variation (McArthur et al., 2001). Due to the absence of isotopic fractionation during fluid production in subduction setting, the Sr isotopic signature of the fluids will be the same as that of the starting altered materials.

The lithospheric mantle is composed of depleted ultramafic rocks and therefore represents a poor geochemical reservoir (Niu, 2004). However, the

hydration of the ocean floor strongly modifies the initial chemical composition of mantle rocks, and consequently, it changes their role in the *subduction factory* concept (Tatsumi, 2005). The hydration of mantle peridotites, i.e., serpentinization, is characterized by the development of serpentine minerals (plus minor amounts of brucite, chlorite, talc, tremolite, and magnetite), at the expense of olivine and pyroxenes. Serpentinites are mainly formed at slow to ultra-slow spreading ridges due to the exposure of the mantle on the seafloor by the occurrence of normal faults related to the extension and thinning of the crust along major scarps and transform faults (Bonatti, 1976; Morishita et al., 2009). These structures promote the infiltration of fluids enhancing the alteration of mantle rocks. More than ten years ago, Ranero et al. (2003) indicated that the presence of strike-normal faults near the trench, due to the bending of the subducting plate, promotes the deep hydration of the mantle with subsequent enrichment in some sediment-like elements, such as Cs, As, and Sb (Deschamps et al., 2011; Cannà et al., 2016), with important implications in the subduction-related water cycle (Rüpke et al., 2004; Faccenda et al., 2009) and in the intermediate-depth seismicity (Ranero et al., 2005).

The presence of ~11%–15% of water into the crystal structure of serpentine minerals (e.g., chrysotile, lizardite, and antigorite) produces the most important chemical change in the oceanic lithospheric mantle prior to subduction. The geochemistry of serpentinites is quite homogeneous in terms of major elements, and the experimental study of Allen and Seyfried (2005) suggests that during seawater-peridotite interaction, the change in REE budget still reflects the geochemical imprint of the protolith. In this way, only the leftover trace-element contents will be affected by chemical depletion and/or enrichment, providing information about their geodynamic setting of formations (Deschamps et al., 2013). The entry of water in the crystal structure of serpentine minerals implies an increase of their molar volume, and therefore of the volume of the entire protolith (O'Hanley, 1992; Andreani et al., 2007), together with a decrease of density from 3.3 to 2.5 g/cm<sup>3</sup>. This change of the mineral structure allows serpentine, in all its forms, to increase its trace-element budget (Mével, 2003; Niu, 2004; Scambelluri et al., 2004, 2014; Boschi et al., 2008; Vils et al., 2008; Deschamps et al., 2012; Kodolányi et al., 2012). As pointed out by Poli and Schmidt (2002), a peculiar, but relevant, lithology as CO<sub>2</sub> “input material” is represented by ophiicarbonates. They consist of breccias of serpentinite clasts and micritic pelloids, cemented by a calcitic matrix, and often occur in ophiolite sequences (Schwarzenbach et al., 2013; Lafay et al., 2017). Despite their modest volume with respect to the rest of the oceanic lithosphere, they are able to transport high amounts of carbonates during subduction (Collins et al., 2015).

Hydration of the forearc mantle above the downgoing slab due to the uprising of slab-derived fluids may lead to the formation of supra-subduction serpentinites, such as in the Mariana forearc (Savov et al., 2007) or in now-exhumed mantle rocks (Hattori and Guillot, 2007). These serpentinites are characterized by enrichment in fluid-mobile elements, such as As, Sb, Cs, Pb, Th, U, and radiogenic Sr and Pb, with respect to the primitive mantle (PM) and abyssal serpentinites (Deschamps et al., 2012). In this respect, Peters et al. (2017) document that the use of U/alkali ratios may be a useful tool to unravel

oceanic versus forearc origin of serpentinized mantle rocks. This approach is based on the redox-sensitive behavior of U in the two different geological settings coupled with the alkali-enriched source of the fluids hydrating the forearc region. The downward dragging of these materials at depth by subduction forces makes these rocks “a new” input material in subduction zones (Scambelluri and Tonarini, 2012). The original trace-element budget of the abyssal serpentinites can be modified by the interaction with slab fluids already at shallow depth, in correspondence with the lizardite to antigorite transition (e.g., Deschamps et al., 2011), as well as during a second event of serpentinization of partially oceanic serpentinized rocks (Hattori and Guillot, 2007; Cannà et al., 2016). The typical sedimentary signature of these fluids allows serpentinites to increase their content of As and Sb, making these elements good candidates to track these processes (e.g., Hattori and Guillot, 2003).

As for the altered oceanic crust, the isotopic signature of the mantle rocks is reset due to hydration processes along the seafloor or in a forearc setting. In this way, the oceanic and forearc serpentinites will be characterized by different isotopic signatures (in particular for the <sup>87</sup>Sr/<sup>86</sup>Sr ratio and Pb isotopes) that will be similar to those of the oceanic seawater for abyssal serpentinites or similar to those of the metamorphic fluids in the case of forearc and/or subducted serpentinites (e.g., Hattori and Guillot, 2007; Deschamps et al., 2012; Cannà et al., 2016).

## Continental Crust

Concerning the subduction of continental crust, Hermann and Rubatto (2014) highlighted that felsic crust, which typically consists of orthogneisses and paragneisses, is the predominant lithotype in UHP terrains, with a good affinity to the upper-middle continental crust (see Rudnick and Gao, 2014). The main mineral assemblage is represented by phengite + coesite + kyanite + garnet + clinopyroxene, where phengite is the most important carrier of large ion lithophile elements (LILEs), volatile and fluid-mobile elements, followed by clinopyroxene. Apatite, rutile, zircon, and allanite and/or monazite are the accessory phases that play an important role in the cycle of elements such as Ti, P, Th, and LREE (more than clinopyroxene, Hermann, 2002; Hermann and Rubatto, 2009). The presence of aqueous-rich fluids deriving from the destabilization of phengite or uprising from the subducting oceanic lithosphere at T > 650–700 °C, can trigger the wet partial melting of the subducted continental crust with very important implications on the slab-to-mantle mass transfer (Nichols et al., 1994; Schmidt et al., 2004; Auzanneau et al., 2006; Hermann et al., 2006; Hermann and Spandler, 2007; Hermann et al., 2013). Due to the high stability of phengite at dry conditions during deep subduction (Domanik and Holloway, 1996), the continental crust can provide large amounts of hydrous melt extremely enriched in LILE (Hermann et al., 2013; Zheng and Hermann, 2014). The capability of continental rocks to store H<sub>2</sub>O is related to their composition in terms of MgO, K<sub>2</sub>O, and CaO, which in turn controls the stabilization of talc, phengite, and epidote and/or amphibole, respectively (Hermann, 2002; Ferrando, 2012).

The isotopic signature of the continental crust resembles that of the metasediments due to the high amount of minerals hosting Rb and Th-U, which decay during time in daughter  $^{87}\text{Sr}$  and radiogenic Pb isotopes ( $^{206}\text{Pb}$ ,  $^{207}\text{Pb}$ , and  $^{208}\text{Pb}$ ), respectively.

## ■ SLAB FINGERPRINT PRESERVED IN FLUIDS RELEASED TO THE MANTLE

### Fluids Produced by Oceanic Lithosphere versus Continental Crust: The Role of Phase Assemblages

To unravel the composition of the fluid phases released from the subducted oceanic lithosphere and continental crust to the supra-subduction mantle, we need to investigate their compositional evolution during subduction. The major- and trace-element concentration of slab-derived fluids strongly depends on their partitioning with stable assemblages. For this reason, in Figure 1, we report simplified phase diagrams for the different chemical constituents of the subducting slab (Fig. 1A: global subducted sediment [GLOSS]/continental crust; Fig. 1B: MORB +  $\text{H}_2\text{O}$ ; Fig. 1C: peridotite +  $\text{H}_2\text{O}$ ) and the elements released in the fluid phase after the complete breakdown of key hydrous minerals. The most representative reference works are reported in Table 1. Each pressure-temperature (P-T) diagram also reports the top-slab paths for hot and cold subduction zone (hot SZ and cold SZ, respectively) from Syracuse et al. (2010). The release of elements by mineral devolatilization in the following sections is described considering a static view of the subduction zone, with the hydrated lithospheric mantle at the bottom and the altered oceanic crust and metasediments lying above. Information about elements released from complex subduction setting, such as HP mélange, will be discussed in the next sections. Note that C-bearing phases are not considered in the following section, but we will treat their role in the redox evolution of the slab and supra-subduction mantle.

### *Metasediments*

Metasediments are a complex and very heterogeneous lithology, and a global overview of the amount of elements transported to depth by subduction is difficult to obtain. The global subducted sediment (GLOSS and GLOSS II, Plank and Langmuir, 1998; Plank, 2014) may be considered as a proxy of the average starting materials of what are now the metamorphosed sedimentary rocks. At relatively low temperature (<200 °C) and below 1 GPa, the compaction of sediments enhances the release of elements hosted in the pore fluids (Fig. 1A; B, As, Sb, and Cs; Moore and Vrolijk, 1992), which are subsequently released during the evolution of subduction. The main minerals in the GLOSS/continental crust system able to release considerable amounts of elements during prograde to peak subduction are, in order of destabilization, amphibole,

lawsonite, and phengite (and to a lesser extent biotite). Amphibole (glauco-phane) breakdown occurs at ~500 °C, at very different pressures, from 1.0 GPa to 2.5 GPa, depending if in warm or cold subductions, respectively. The released fluid phase should be enriched in Be, B, and LILE (and possibly As and Sb and halogens; Bebout et al., 2007). The destabilization of lawsonite occurs at different P-T conditions: at high thermal conditions it is similar to those of amphibole, but in cold subductions lawsonite is stable up to 2.8 GPa at a temperature of ~600 °C (Fig. 1A; Martin et al., 2014). Similarly to amphibole, the main trace elements released by lawsonite destabilization are Be, B, LILE, U, Th, and Ce (and possibly As and Sb; Bebout et al., 2007). Phengite is the key phase able to provide high amounts of trace elements (LILE, LREE, B, and Li) during its breakdown. In wet conditions, phengite-out reaction occurs at ~650–700 °C and 2.0 or 3.0 GPa, in warm and cold subduction thermal settings, respectively (Fig. 1A). At dry conditions and in a closed system, phengite is stable down to UHP and ~1000 °C in warm subductions; whereas in cold subduction settings, it can reach depths compatible with pressures of 10 GPa (or even more), before melting (Domanik and Holloway, 1996).

Figure 2A reports the trace-element patterns of some prograde and HP metasediments from Catalina Schist (California, USA), Cima di Gagnone (Central Alps), and Schistes Lustrés (Western Alps), normalized to the GLOSS II. These terranes are representative of warm (Catalina Schist) versus cold (Alpine suite) subduction zone thermal settings at different peak conditions. In the Catalina Schist, Bebout and Barton (1993) and Bebout et al. (1999) document the loss of B, Be, As, Sb, Cs, and N during metamorphic devolatilization from lawsonite-albite and lawsonite-blueschist to epidote-amphibolite and amphibolite facies (see also Fig. 3). Due to the relatively warm subduction path followed by the Catalina Schist unit, the release of these elements occurs at  $T > 350$  °C at ~1 GPa (Fig. 1A; Table 1). Examples of metasediments subducted at higher pressures along a cold subduction path are represented by paragneiss and micaschists from Cima di Gagnone (Central Alps), showing evidence of metamorphic peak conditions at ~2 GPa and 750 °C (Cannaò et al., 2015). These rocks are strongly depleted in fluid-mobile elements, such as Li, B, As, and Sb, and Zr-Hf, whereas they are enriched in Rb and K as well as LREE (and also U) due to the presence of stable white mica (mainly phengite) in the mineral assemblage. As shown in Figure 2A, compared to the Catalina Schist and the Cima di Gagnone metasediments, the Schistes Lustrés metasediments form the Western Alps do not display significant loss of elements from the sedimentary protoliths (Busigny et al., 2003; Chalot-Prat et al., 2003; Bebout et al., 2013). This could be due to the cold thermal regime of the fossil Alpine subduction zone with respect, for instance, to those of the Catalina Schist (e.g., Bebout et al., 2013). However, Lafay et al. (2013) and Cannaò et al. (2016) document depletion in some key fluid-mobile elements (As and Sb) in metasediments from the Queyras (Western Alps) and the Voltri Massif (Ligurian Western Alps), respectively (Fig. 3). Concerning this discrepancy, Busigny et al. (2003) proposed that the release of LILE and other incompatible elements may be controlled by the lithology of each sample, which, in turn, affects the devolatilization processes.





TABLE 1. TRACE ELEMENTS RELEASED DURING PROGRADE SUBDUCTION BY THE DIFFERENT SUBDUCTED LITHOLOGIES

Lithology	Elements	Temperature (°C)	Pressure (Gpa)	References	Terranes	
Marine sediments	B, As, Sb, Cs	<200	—	Moore and Vrolijk (1992)	Pore fluids	
	B, Cs	200–300	0.9–1.2	Bebout et al. (1999)	Catalina Schist	
	As, Sb	350–400	0.9–1.2	Bebout et al. (1999)	Catalina Schist	
	Rb, Cs, B	300	<1.0	Sadofsky and Bebout (2003)	Franciscan Complex	
	B, Li, Cs, Sr, As, Sb	350–400	0.9–1.5	Lafay et al. (2013)	Schistes Lustrés (Western Alps)	
	B	350–450	2.0	Bebout et al. (2013)	Western Alps	
	Sr, Li, B	300–400	0.9–1.2	Bebout et al. (2007)	Catalina Schist	
	B, As, Sb, Pb, Sr	300–400	0.9–1.2	Cannaò et al. (2016)	Voltri Massif (Ligurian Alps)	
	Li, B, Ba, As, Sb, Pb	300–400	0.9–1.2	Cannaò et al. (2015)	Cima di Gagnone (Central Alps)	
	REE, Sr, Pb, U, Th	550–600	<1.6	Spandler et al. (2003)	New Caledonia	
	Rb, Ba, Sr	<600	1.3–2.0	Arculus et al. (1999)	Raspas Complex (Ecuador)	
	K, Rb, Ba, Pb	<600–700	1.3–1.5	Becker et al. (2000)	Different terranes	
	Cs, Rb, Ba, K, B (?), High LREE/HREE, Sr	600–800	2.0–3.0	Vitale-Brovarone et al. (2014)	Alpine Corsica	
	LILE, B,	700–800	4.0	Kessel et al. (2005a)	Experiment	
LILE, LREE, HFSE, Li, Be, B, Pb, Th, U	900–1000	4.0	Kessel et al. (2005a)	Experiment		
Mafic oceanic crust	LILE, LREE, Li, Be, B, Nb, Ta, Pb, Th, U	800–900	6.0	Kessel et al. (2005a)	Experiment	
	LILE, LREE, Li, Be, B, HFSE, Pb, Th, U	1000–1200	6.0	Kessel et al. (2005a)	Experiment	
	Oceanic lithospheric mantle	B, Li, Cl, Sr	550–600	2.0–2.5	Scambelluri et al. (2001, 2004)	Erro-Tobbio (Ligurian Alps)/ Almirez (Betic Cordillera)
	B, As, Sb, Cs, Sr, Pb	600–700	1.7–2.0	Peters et al. (2017)	Almirez (Betic Cordillera)	
	Cs, Rb, Ba, U, Th, B, Pb, As, Sb, Li	700–800	2.3–3.0	Scambelluri et al. (2015)	Cima di Gagnone (Central Alps)	
	Li, B, Sr, Cs, Ba, Pb, Th, U	700–900	3.5–4.0	Spandler et al. (2014)	Experiment	
	Continental crust	Cs, Rb, Pb, Sr	700–750	4.0–4.3	Ferrando et al. (2009)	Dora-Maira
	Rb, Ba, K, Pb, Th, U, Sr, LREE	1000	5.0	Stepanov et al. (2016)	Kokchetav Massif	
	Cs, Rb, Ba, Pb, Th, U	600–650	2.2	Spandler et al. (2007)	Experiment	
	LILE, LREE, Pb, Th, U	750–1050	2.5–4.5	Hermann and Rubatto (2009)	Experiment	
Cs, Rb, Ba, K, Th, U	750–1000	2.5–4.5	Zheng and Hermann (2014)	Experiment		

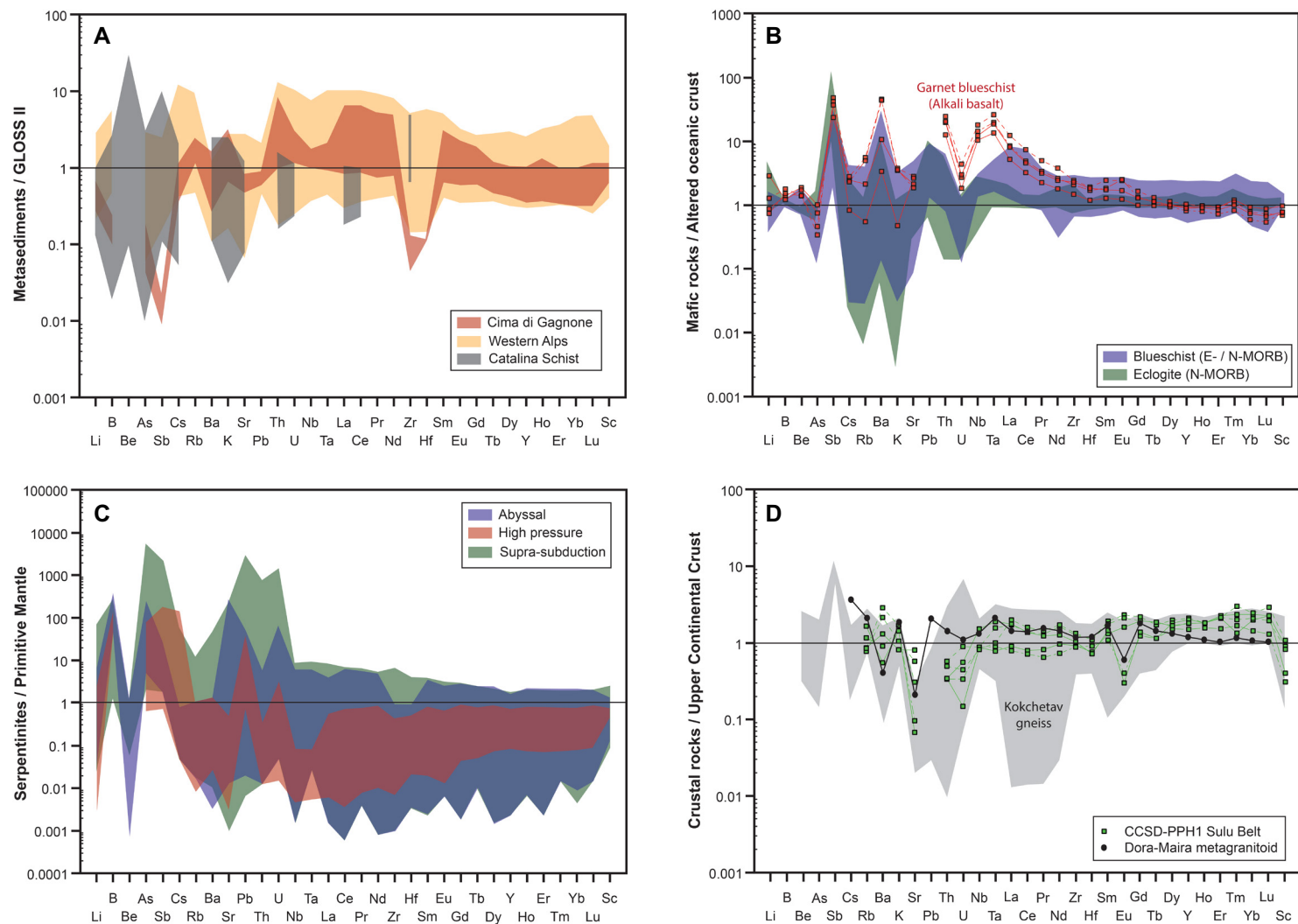
Abbreviations: HFSE—high field strength element; LILE—large ion lithophile element; LREE—light rare-earth element; HREE—heavy rare-earth element; REE—rare-earth element.

### Metabasalts

In a MORB + H<sub>2</sub>O system (Fig. 1B; modified from Schmidt and Poli, 2014), the minerals able to transport at great depth significant amounts of trace and volatile elements are amphibole, lawsonite, phengite (in K-bearing system), together with chlorite, chloritoid, and epidote. As for the sedimentary system, the thermal setting of the subduction zone is crucial for the stability of lawsonite. In warm subduction zones, its breakdown reaction may occur at low temperature (400 °C) and pressure (1.0 GPa), whereas in cold subduction zones, its destabilization occurs at ~600 °C and 2.5 GPa (Fig. 1B; Schmidt and Poli, 1994). This is one of the most important reactions in a mafic system able to release considerable amounts of aqueous fluids enriched in incompatible elements (Be, B, Ba, U, Th, Ce, and Pb) and LREE at depth (e.g., Bebout et al., 2007; Vitale-Brovarone et al., 2014). Sodium-amphibole stability is P-dependent, occurring at ~2.0–2.5

GPa, for T ranging between 400 and 700 °C. Even if the amphibole/liquid partition coefficient for incompatible and LILE during amphibole formation in magmatic process is very low (Tiepolo et al., 2007), the formation of secondary amphibole on the ocean floor is associated with the incorporation of a relatively high amount of incompatible elements and halogens (e.g., Debret et al., 2016). The trace elements released in this reaction are similar to those for the sedimentary system (Figs. 1A and 1B). Also, Debret et al. (2016) document partial release of halogens and boron during prograde amphibole transformation from low-pressure polytype to glaucophane at ~1 GPa and 300–400 °C. Therefore, the real budget of element transfer to depth during complete amphibole dehydration may be influenced by these early stages of release.

At conditions of 550–600 °C and 1.0–2.5 GPa, chlorite destabilizes, releasing mainly Li, Cl, and B in the fluid phase (Fig. 1B). For Al-rich protoliths, at higher temperature and pressure conditions (600–650 °C; 2.5–4.0 GPa), the subduction



**Figure 2.** Trace-element composition of subduction input materials. (A) Metasediments normalized to global subducted sediment (GLOSS II) (Plank, 2014). Cima di Gagnone from Cannaò et al. (2015); Western Alps from Bebout et al. (2013) and Lafay et al. (2013); Catalina Schist from Bebout et al. (1999). (B) High-pressure mafic rocks normalized to altered oceanic crust (Onishi and Sandell, 1955; Smith et al., 1995; Kelley et al., 2003). Blueschist and eclogite rocks from Becker et al. (2000), Spandler et al. (2004), and John et al. (2010). (C) Abyssal, subducted, and supra-subduction serpentinites normalized to primitive mantle (McDonough and Sun, 1995). Abyssal serpentinite from Paulick et al. (2006) and Kodolányi et al. (2012); subducted serpentinites from Lafay et al. (2013), Debret et al. (2013), and Cannaò et al. (2016); supra-subduction serpentinites from Ishii et al. (1992), Lagabrielle et al. (1992), Parkinson and Pearce (1998), Pearce et al. (2000, 2005), Guillot et al. (2001), Savov et al. (2005, 2007), Hattori and Guillot (2003, 2007), Marchesi et al. (2006, 2009), Saumur et al. (2010), Deschamps et al. (2012), Blanco-Quintero et al. (2011), and Kodolányi et al. (2012). (D) Continental crust normalized to upper continental crust (Rudnick and Gao, 2014). Dora-Maira from Ferrando et al. (2009); Kokchetav gneiss from Stepanov et al. (2014); Chinese Continental Scientific Drilling Pre-Pilot Hole 1 (CCSD-PPH1) of the Sulu Belt from Zhang et al. (2005).

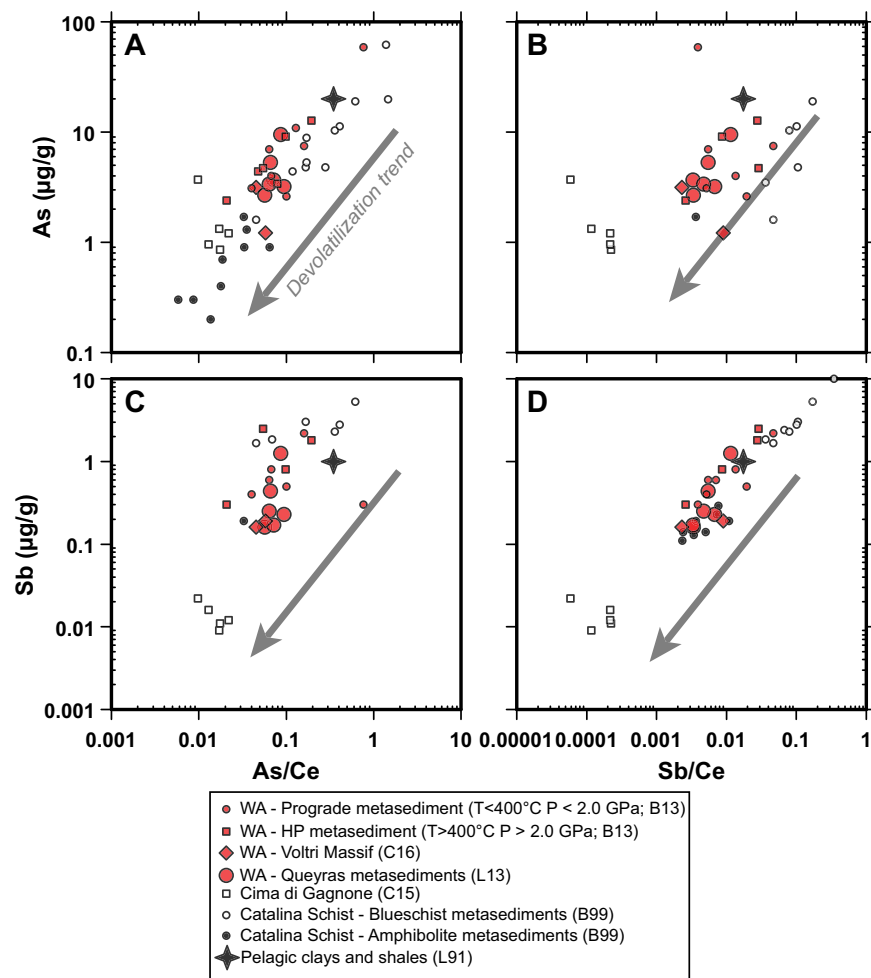


Figure 3. (A–D) As and Sb versus As/Ce and Sb/Ce diagrams for metasedimentary rocks from Western Alps (WA; B13: Bebout et al., 2013; L13: Lafay et al., 2013; C16: Cannaò et al., 2016), Catalina Schist (B99: Bebout et al., 1999) and Cima di Gagnone (C15: Cannaò et al., 2015), compared with pelagic clays and shales (L91: Li, 1991). The gray arrow shows the devolatilization trend due to As and Sb loss during early prograde subduction processes.

path reaches the breakdown of chloritoid, which is able to release trace elements such as Be, B, and Rb (Xiao et al., 2016). At similar pressures but at  $T = 650\text{--}750\text{ }^{\circ}\text{C}$ , epidote (zoisite) breakdown provides significant amounts of Sr, Pb, and Ce (and light rare-earth elements [LREEs]; e.g., Xiao et al., 2016). Recent experimental studies by Carter et al. (2015) propose that  $\text{Fe}^{3+}$ -bearing epidote may be stable at higher temperature (up to  $900\text{ }^{\circ}\text{C}$ ) at 3 GPa, controlling the release of LREE and Th to the fluid phase. The destabilization of phengite corresponds to the partial melting condition of mafic systems at water-saturated conditions and occurs at relatively HT-HP ( $>700\text{ }^{\circ}\text{C}$  and  $>2\text{ GPa}$ ). During this process, phengite transfers large quantities of trace elements in the melt phase

(LILE, LREE, and B). Similarly to what happens in the metasedimentary system, minor accessory phases are able to play an important role in the partitioning of Ti, Nb, Ta (rutile), LREE, Th, Sr, Pb (allanite), P, LREE, Th, U (apatite), and Zr, Hf (zircon) (Hermann, 2002; Zack et al., 2002; Rubatto and Hermann, 2003; Spandler et al., 2003; Klimm et al., 2008). Recently, Tsay et al. (2017) proposed that the addition of various ligands into the fluid phase, such as Cl and F, might affect the solubility of elements thus controlling their partitioning and mobility.

Figure 2B portrays the trace-element composition of blueschist- and eclogite-facies mafic rocks from several metamorphic terranes (Raspas Complex, Western Alps, and New Caledonia; data from Becker et al., 2000; Spandler et al.,



2004; John et al., 2010) normalized to the altered oceanic crust (AOC; Smith et al., 1995; Onishi and Sandell, 1955; Kelley et al., 2003). It must be specified that the composition of AOC could be extremely variable, depending on the alteration degree of the original protolith. In order to better unravel the potential trace-element release from subducted oceanic mafic crust affected by the major dehydration process within the downgoing slab (the blueschist-eclogite transition; Peacock, 1993), in Figure 2B, we consider rocks showing affinity with the enriched and normal MORB (enriched [E]- and normal [N]-MORB, respectively), as well as alkali basalt. Blueschist mafic rocks display a relatively narrow pattern of element concentration variability for Li, B, Be, and As together with the REE. The concentration of these elements is close to 1 × AOC up to 10 × AOC values. The most incompatible and fluid-mobile elements show a wide range of concentrations, with Cs, Rb, K, and U characterized by negative anomalies, and Sb, Ba, Pb, and Th showing an opposite behavior. Mafic rocks re-equilibrated under eclogite-facies conditions show similar trace-element patterns even if they are characterized by the depletion in almost all elements (except Sb, Pb, and Th). Garnet-bearing blueschist mafic rocks showing affinity with alkali basalt are strongly enriched in LREE and LILE reflecting the high modal amount of phengite and amphibole in the mineral assemblages. This lithology is expected to introduce high amounts of incompatible elements into depth during phengite and amphibole destabilization.

In contrast to this evidence, Spandler et al. (2003) document insignificant element mobility during prograde metamorphism from lawsonite-blueschist to eclogite facies in HP metabasalts from New Caledonia. These authors provide evidence that the trace elements released during blueschist mineral breakdown reactions are retained in the newly formed major and accessory minerals, such as epidote, phengite, garnet, rutile, and zircon. This implies that eclogitic minerals still retain significant amounts of elements leading to the release of huge quantities of aqueous fluids depleted in trace elements (Spandler et al., 2003).

### **Serpentinities**

In the hydrous peridotite system (Fig. 1C), serpentine is the most important mineral capable of trapping, transporting, and releasing volatiles and key trace elements at great depth (Ulmer and Trommsdorff, 1995; Scambelluri and Philippot, 2001; Scambelluri et al., 2001, 2004, 2007, 2014, 2015). The phase transition from lizardite and/or chrysotile to antigorite at  $T < 300$  °C and low  $P$ , is associated with the partial release of Li, Cl, B, Sr, As, and Sb from the system, due to changes in the mineral structure and the loss of ~2 wt% of water (Kodolányi and Pettke, 2011). During the olivine-in reaction (400–500 °C; 0.5–2.5 GPa), these elements are lost (Deschamps et al., 2011; Lafay et al., 2013) even if metamorphic olivine is still able to retain a significant amount of them (e.g., B, As, and Sb, Tenthorey and Hermann, 2004; Scambelluri et al., 2014). The complete breakdown of antigorite is mainly temperature dependent (Ulmer and Trommsdorff, 1995; Wunder and Schreyer, 1997) and occurs at  $T$  between 600 and 700 °C, in relation to its Al content (Padrón-Navarta et al., 2013). Due to the “sponge-like” behavior charac-

terizing serpentine (e.g., Deschamps et al., 2011; Lafay et al., 2013; Cannaò et al., 2015, 2016), the fluid-mediated mass transfer processes, occurring during prograde subduction in a top slab mélange setting, as well as in peridotites from a supra-subduction setting, allow serpentinites to be enriched in exogenous elements (LILE, LREE, and fluid-mobile element). All these elements will then be released upon complete antigorite destabilization.

In addition to serpentine, chlorite and amphibole are also able to release some trace elements after their breakdown. Chlorite destabilization occurs at higher temperature (700–800 °C) and in the presence of garnet may provide high LREEs and heavy rare-earth elements (HREEs) in the fluid phase coupled with Cl and Li. Calcic amphibole can be present in the HP mineral assemblage of subduct-derived metaperidotite (i.e., the product of complete dehydration of serpentinite precursor; Scambelluri et al., 2014) and represents the last hydrous phase enriched in incompatible elements, able to release B, As, Sb, LILE, and Pb (and potentially halogens). As for the other systems, its stability is mainly  $P$ -dependent (2.5–3.0 GPa) at  $T$  up to 900–1000 °C (Fumagalli and Poli, 2005). Among accessory phases, the most important ultramafic systems are the humite-type minerals (clinohumite, humite, chondrodite, and norbergite). It is indeed well known that the stability of clinohumite increases with the increase of its  $F/OH$  ratio, acting as carrier of volatiles and halogens into the deeper parts of the mantle (Engi and Lindsley, 1980; Trommsdorff and Evans, 1980; Evans and Trommsdorff, 1983; Weiss, 1997; Stalder and Ulmer, 2001; López Sánchez-Vizcaino et al., 2005; Hermann et al., 2007; John et al., 2011). The new experimental data by Grützner et al. (2017) suggest that  $F$ -bearing humites could be stable even at conditions corresponding to the transition zone (up to 1800 °C at 17 GPa).

In Figure 2C, the primitive mantle (PM) normalized (McDonough and Sun, 1995) trace-element patterns of subducted HP serpentinites and from supra-subduction settings are compared with those of abyssal serpentinites. Abyssal serpentinites, before subduction, may be enriched in halogens (not shown in the plot; Kendrick et al., 2011, 2013, 2017; John et al., 2011) and B, As, Sb, Sr, U, and Li (Paulick et al., 2006; Delacour et al., 2008; Vils et al., 2008; Kodolányi and Pettke, 2011; Augustin et al., 2012). Boron and As are the only elements always above the PM values, whereas Be shows a negative anomaly and is always below the PM value as well as other LILEs (Cs, Rb, and Ba). During subduction, serpentinites maintain the trace-element budget acquired from oceanic serpentinization (cf. purple and yellow patterns of Fig. 2C) and thus are even more enriched in As, Sb, and Cs. Also supra-subduction serpentinites record enrichment in these elements, reaching absolute values of As, Sb, Pb, Th, and U  $> 1000$  × PM. The previously mentioned characteristics are likely acquired during the fluid-mediated mass transfer at the slab-mantle interface, between serpentinites and the other slab reservoirs (altered oceanic crust and/or sediments). This exchange allows HP and supra-subduction serpentinites to acquire hybrid and unusual geochemical signature also in terms of B, Sr, and Pb isotopic compositions (e.g., Deschamps et al., 2011, 2012; Lafay et al., 2013; Cannaò et al., 2015, 2016). Evidence of these interactions is well recorded in several Alpine mélange-type terranes and seems to have occurred during their prograde subduction (Lafay et al., 2013; Cannaò et al., 2015, 2016).

### Continental Crust

The main difference between the oceanic lithosphere and the continental crust in terms of dehydration during prograde subduction is that sediments and altered oceanic crustal rocks progressively lose H<sub>2</sub>O during their burial, due to water-conservative metamorphic reactions taking place within the slab (e.g., Schmidt and Poli, 2014). At the same time, beyond the antigorite and chlorite breakdown (and phase-A at low T), H<sub>2</sub>O can be stored only in continental crust lithologies (in phengite, talc, and amphibole). In particular, Hermann (2002) suggested that the hydration of dry continental crust by metamorphic slab fluids is able to stabilize phengite at the expense of K-feldspar, as documented, for example, in the Dora-Maira Massif (Biino and Compagnoni, 1992; Compagnoni et al., 1995; Ferrando et al., 2009). Similarly, chloritization of granitic rocks and formation of talc and phlogopite in Mg-rich system are processes that provide a significant amount of water even in continental rocks at H<sub>2</sub>O-undersaturated conditions (Schertl and Schreyer, 2008). In this way, the continental crust may also become an important reservoir for H<sub>2</sub>O. Subduction of portions of continental crust is able to reach UHP conditions in a cold subduction thermal setting prior to phengite-dehydration melting. In this way, deep element transfer from continental crust allows the release of a high amount of LILE and incompatible elements to the supra-subduction region.

The most famous terranes where exhumation of UHP continental crust occurs are the Kokchetav Massif (Northern Kazakhstan), Dora-Maira (Western Alps), and Sulu Belt (Eastern China). As shown in Figure 2D, the gneiss from Kokchetav (Stepanov et al., 2014) normalized to the upper continental crust (UCC, Rudnick and Gao, 2014) displays quite uniform middle-heavy rare-earth element (M-HREE) patterns ranging from 1 to 3 times the UCC values (except for Sm with a slight negative anomalies). On the other hand, the compositional range of the LREE is much more widespread, with a strong negative anomaly down to two orders of magnitude with respect to the UCC. This high variability in the LREE budget is related to the amount of white mica present in the gneisses coupled with the complete dissolution of monazite and allanite during melt production in the most restitic portion of the rocks (Stepanov et al., 2014). Strontium, Pb, and Th show a similar trend to that of the LREE, whereas U may reach up to 10 times the UCC value. The LILE pattern is scattered, with negative anomalies in Cs and Ba and positive anomalies for Rb and K. Antimony is always positive up to one order of magnitude higher than the UCC value, whereas As and Be range from 2 to 0.2 times the UCC values (Fig. 2D). No data about Li and B are available in the literature. The metagranite from Dora-Maira (Ferrando et al., 2009) normalized to the UCC shows relative depletion in M- and HREE and almost flat LREE pattern with a negative Eu anomaly (Fig. 2D), with concentrations always above those of the UCC. Lead and Th are slightly enriched, and U is close to the UCC value. Barium and Sr display negative anomalies, whereas other LILEs appear enriched. Continental crustal rocks from the Sulu Belt display almost flat REE patterns, with no significant depletion in LREE in some samples. A negative Eu anomaly is present for a couple of samples. Uranium, Th, and Sr show a relatively wide range of variation and values always below the UCC, whereas the

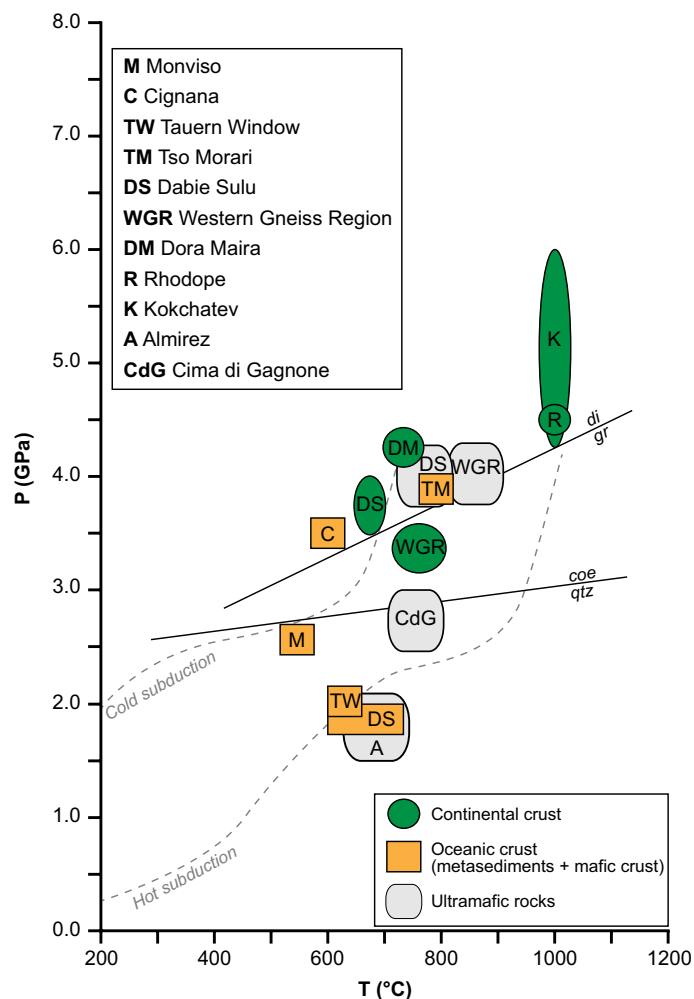
other LILE are mostly above UCC. No data for Li, B, Be, As, and Sb from these two massifs are currently available in literature.

Overall, it seems that the gneiss from Kokchetav massif is much more depleted in LREE. This is probably due to the partial melting that occurred during their subduction and exhumation history, as testified by the presence of multiple melt inclusions in garnet (Stepanov et al., 2014, 2016). Nevertheless, their LILE concentrations are still comparable with those of the UCC. Compared to the Kokchetav Massif, the gneiss and metagranite from Sulu and Dora-Maira do not show evidence of partial melting consistent with the relative enrichment in LILE characterized by the occurrence of stable phengite in these rocks.

### Slab-Derived Fluid Composition: Evidence from Fluid/Melt Inclusions

The occurrence of fluid/melt or multiphase solid inclusions in the newly formed metamorphic anhydrous minerals, such as garnet or omphacite in eclogites and olivine and enstatite in serpentinites, witnesses the entrapment of fluid or melt phases (or supercritical liquids above the second critical end-point) produced by the dehydration reactions previously described. A P-T compilation of HP and UHP terranes where fluid/melt inclusions have been characterized is displayed in Figure 4. The laser ablation analyses of these inclusions allow the determination of their compositions in terms of trace elements. In Figure 5, we report natural and experimental trace-element data of aqueous fluids, supercritical liquids, and melt inclusions occurring in eclogite-facies rocks representing the different input subduction zone components, normalized to the PM values (Fig. 5A: continental crust and/or sediments; Fig. 5B: oceanic crust; Fig. 5C: ultramafic rocks).

Multiphase solid inclusions from Dora-Maira whiteschist (Ferrando et al., 2009) and melt inclusions from gneisses of the Kokchetav massif (Stepanov et al., 2016) may be considered as proxies of the compositional evolution recorded by fluids in metasediments during their subduction to UHP, with enrichment in the most incompatible trace elements. The fluid inclusions within the garnet in the whiteschist from the Dora-Maira UHP unit are representative of the fluid released during the peak condition via the reactions: phlogopite + kyanite + talc = garnet + phengite + fluid and kyanite + talc = garnet + coesite + fluid (Ferrando et al., 2009). This fluid is strongly enriched in LILE and U, relatively enriched in Ba and Th, and is depleted in HFSE. Inclusions hosted in garnet from the Kokchetav UHP gneiss represent the product of partial melting at 4.5 GPa and ~1000 °C. During this process, LILE, LREE, Th, and U are released in the melt phase. As shown in Figure 5A, these different inclusions show visible differences in their LILE and LREE concentrations, as well as in U and Th. These are related to the presence of stable phengite in the mineral assemblage of the Dora-Maira rocks, which partitions most of the LILE. Melt inclusions from the Kokchetav rocks derive from the partial melting induced by the destabilization of phengite. For comparison, in Figure 5A, we also reported the composition of experimental aqueous fluids and hydrous melts (Spandler et al., 2007; Hermann and Rubatto, 2009; Zheng and Hermann, 2014). These are similar to natural fluid/melt inclusions in terms of element mobility, showing

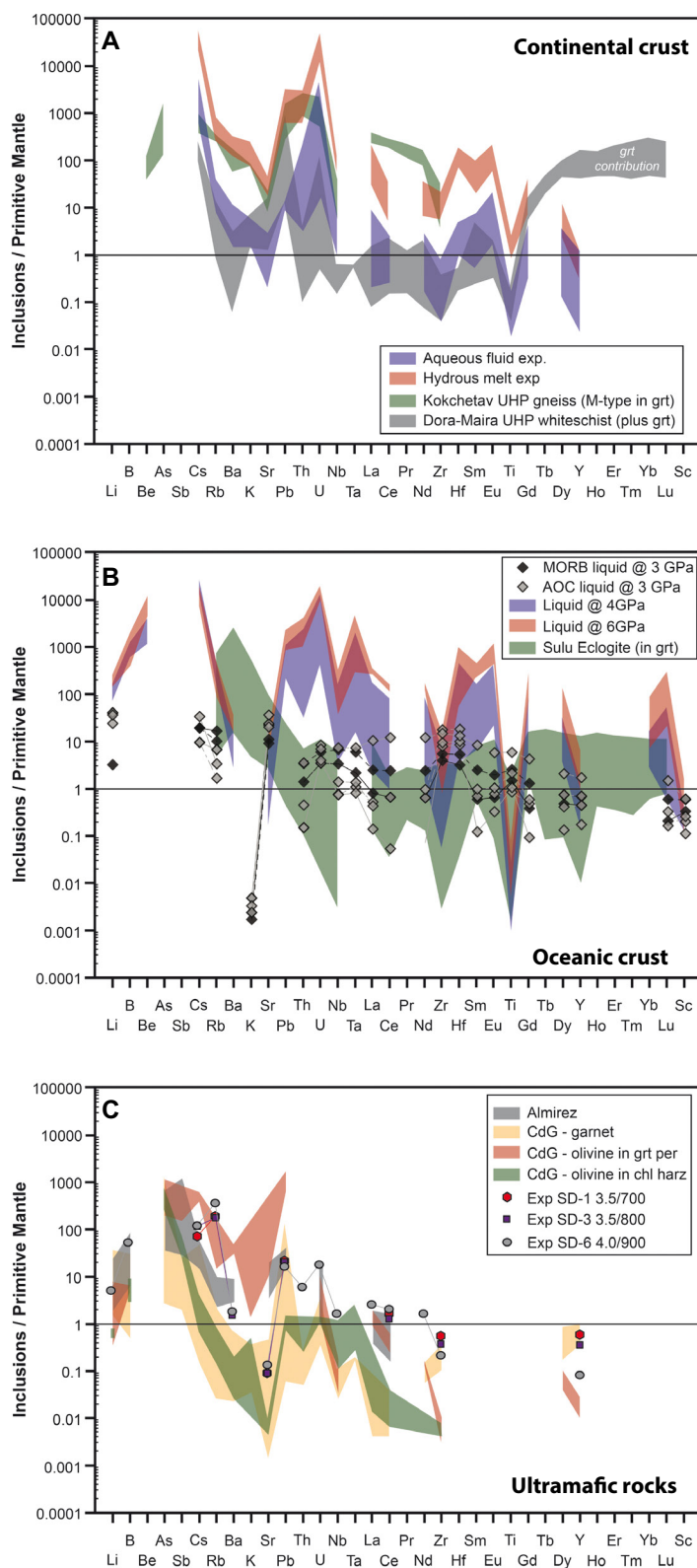


**Figure 4. Pressure-temperature (P-T) conditions of high-pressure and ultrahigh-pressure complex subdivided in oceanic crust (metasediments + eclogite, orange areas), ultramafic rocks (gray areas), and continental crust (green areas) based on fluid/melt inclusions occurrence (modified from Frezzotti and Ferrando, 2015).**

enrichment in LILE, Pb, Th, and U. The main difference is that these elements are much more concentrated in the hydrous melt than in the aqueous fluids, in agreement with the ability of hydrous melts to mobilize trace elements as discussed by Hermann et al. (2006). Again, it should be noted that no data about Li, Be, and Sb concentrations in fluid/melt inclusions in sediment/continental crust occur in the literature as of now.

Concerning the oceanic crust (Fig. 5B), the multiphase solid inclusions hosted in garnet of the UHP eclogite from Sulu (China; Gao et al., 2012, 2013) show enrichment in Rb, Ba, K, and Sr coupled with variable enrichment in Pb, Th, and U, depletion in HFSE and more enrichment in LILE than LREE. These inclusions are interpreted to be the product of the dehydration melting of eclogite during phengite breakdown. The trace-element signatures of K-free MORB-derived supercritical liquids and melts were determined experimentally for T ranging between 700 and 1200 °C and P = 4–6 GPa (Kessel et al., 2005a, 2005b). Both supercritical liquids (LT) and melts (HT) are enriched in B, Li, LILE, and LREE. The supercritical liquids at 6 GPa show a relatively narrow range of trace-element concentrations in relation to the temperature variation. Conversely, in the supercritical liquids at lower pressure (4 GPa), the trace-element concentrations are much more temperature dependent, suggesting an increase of the fluid/solid partition coefficient with increasing temperature for the analyzed elements. Recently, Carter et al. (2015) experimentally documented the element release by MORB and AOC system ( $K_2O$  wt% is the main difference) at 3 GPa and T ranging from 750 to 1000 °C. Their results show several discrepancies compared to previous studies, in particular due to abundant residual epidote storing Th and LREE. The increase of the LILE content in the melt with temperature is always related to the partial destabilization of phengite. Other experimental studies focused on understanding the mobility and fractionation of REE in aqueous fluids during the slab dehydration at 2.6 GPa and T from 600 to 800 °C, were carried out by Tsay et al. (2014; not shown in figure 5B). These authors document the increase in the REE contents of the aqueous fluid with the increase of temperature, also promoted by the presence of additional ligands such as  $Cl^-$ ,  $F^-$ ,  $CO_3^{2-}$  and  $SO_4^{2-}$ . A different behavior is recorded by HREE and HFSE. Crystallization of garnet and accessory minerals, such as zircon and rutile, during the opening of HP veins in eclogites promotes the partitioning of HREE and HFSE, respectively. Such a partitioning leads to low mobility of these elements in the fluid phase during the dehydration of the oceanic crust (Rubatto and Hermann, 2003). To date, no data about fluid mobile As and Sb are documented in literature.

Figure 5C shows the composition of multiphase solid and aqueous fluid inclusions hosted by olivine and garnet in metaperidotites from Cerro del Almirez (Betic Cordillera) and Cima di Gagnone (CdG, Central Alps) HP and UHP ultramafic rocks. They represent the product of partial (Almirez) to complete (CdG) dehydration of serpentinites and serpentinized peridotites (Evans and Tromsdorff, 1978; Scambelluri et al., 2014). These data are compared with the experimental study performed by Spandler et al. (2014). The fluid inclusions hosted in metamorphic olivine are believed to represent the fluid composition produced by the antigorite breakdown, whereas the fluid inclusions hosted in garnet represent the remnants of the fluids released after the chlorite-out reaction (see also Fig. 1C; Scambelluri et al., 2015). The full trace-element composition of fluid inclusions from Almirez is reported in Peters et al. (2017, and references therein) showing enrichment in Li, B, As, Sb, Pb, Th, and LILE and LREE are close to  $1 \times PM$ . Multiphase solid inclusions hosted in the metamorphic olivine of the chlorite harzburgite from CdG show comparable



**Figure 5.** Trace-element patterns of natural and experimental fluid/melt inclusions normalized to primitive mantle (McDonough and Sun, 1995) for (A) continental crust (Dora-Maira: Ferrando et al., 2009; Kokchetav: Stepanov et al., 2016); aqueous fluid experiment (Spandler et al., 2007, and Zheng and Hermann, 2014); hydrous melt experiment (Hermann and Rubatto, 2009); (B) oceanic crust (eclogite in Sulu terrane: Gao et al., 2013); liquid experiment (Kessel et al., 2005a); mid-ocean ridge basalt (MORB) and altered oceanic crust (AOC) experiment (Carter et al., 2015); and (C) ultramafic rocks (Cima di Gagnone [CdG]: Scambelluri et al., 2015; Almirez: Peters et al., 2017); experimental results (Exp SD) from Spandler et al. (2014) at different pressure (3.5–4.0 GPa) and temperature (700–900 °C) conditions. UHP—ultrahigh-pressure.

enrichment in B but, overall, a decrease in all other trace elements such as LILE down to  $1 \times$  PM or even below. On the contrary, the same inclusions hosted in olivine from the garnet peridotites display strong enrichments in As, Sb, and LILE. The trace-element budget of the fluid produced by the chlorite dehydration at higher temperature is represented by the yellow field in Figure 5C. This fluid is less enriched in incompatible elements with respect to those of the olivine inclusions but still preserves B, As, and Sb contents higher than those of the PM. It is interesting to note that previous trace-element and isotopic studies on these localities provided the evidence that Almirez and Cima di Gagnone ultramafic rocks were affected by a different grade of interaction with sediment-derived fluids during prograde subduction (Marchesi et al., 2013; Harvey et al., 2014; Cannaò et al., 2015). This process may explain the enrichment in incompatible and fluid-mobile elements shown by these fluids. Here, we want to highlight that, to date, the pure geochemical signatures of abyssal serpentinite component transported at depth are still missing due to the sponge-like behavior of serpentinitized mantle rocks during subduction processes (e.g., Deschamps et al., 2011; Cannaò et al., 2016).

From an experimental point of view, Spandler et al. (2014) showed that the trace elements released during UHP serpentinite dehydration at 3.5 GPa and 700–800 °C consist of Li, B, LILE, LREE, and U in the fluid phase. Chlorite dehydration, at higher P-T conditions (4.0 GPa and 900 °C), produces fluids with high LREE and HREE and Ce/Y ratios, due to retention of HREE and Y in the newly formed garnet.

## ■ REDOX EVOLUTION DURING SUBDUCTION

When we consider geochemical fluxes at subduction zones, we must pay attention to elements that are sensitive to the redox conditions of the system (e.g., Fe, C, S, Mn, P, and U). These elements occur in different oxidation states and in variable concentrations within the slab lithologies and may be released after a change in their oxidation state during subduction (Evans, 2012). As an example, carbon is transported into subduction zones as an organic component (valence 0) in marine sediments or as carbonates (valence 4+) in altered oceanic basalts and/or veins in serpentinitized mantle. During subduction, dissolution of carbonates by fluids produced by dehydration reactions enables the transport of carbonate and bicarbonate ions (valence 4+) in fluid inclusions trapped by eclogite minerals into depths (Frezzotti et al., 2011). Also the occurrence of  $\text{CH}_4$  (valence 4-) in fluid inclusions preserved in subducted eclogites (Fu et al., 2003) further indicates that redox processes define the speciation of carbon (in these examples), as well as of other redox-sensitive elements in complex systems. The case of carbon speciation in subducted rocks and/or fluids is emblematic, since its valence state is likely governed (buffered) by the oxidation state of the host system. Subducted oceanic crust (eclogite) and serpentinites contain considerable amounts of iron so that the equilibria between ferric ( $\text{Fe}^{3+}$ ) and ferrous ( $\text{Fe}^{2+}$ ) iron in mineral assemblages are considered to buffer the oxygen fugacity ( $f\text{O}_2$ ) and the valence state of carbon. On the other hand, the C species in subduction fluids may control the oxidation

state of their hosting phase assemblages by redox reactions during degassing, dehydration, melting, and fluid/rock interactions. In other words, the dilemma of “what controls what” can be overcome only by considering the degree of fluid/rock interaction.

The oxidizing or reducing capacity of a rock is determined by the amount and by the oxidation state of redox-sensitive elements present (Evans, 2006). As a consequence, the  $f\text{O}_2$ , expressed as  $\Delta\text{FMQ}$  ( $\log f\text{O}_2[\text{sample}] - \log f\text{O}_2[\text{fayalite-magnetite-quartz}]$ ) to compare with different P-T equilibration conditions of the mineral assemblages), is likely very inhomogeneous in a subducting slab, reflecting the different bulk chemical-mineralogical compositions of the slab lithologies (Tumiati et al., 2015). Figure 6 attempts to picture this concept summarizing most of the data available in the literature. As we have seen previously, abyssal serpentinites represent the hydration of oceanic peridotites by seafloor hydrothermal and seawater alteration. According to Deschamps et al. (2013) and references cited in their work, these rocks record  $\Delta f\text{O}_2$  in the range between FMQ-2 and FMQ. Subducted serpentinites, originating either from abyssal peridotites or from the oceanic-continent transition zone, look slightly more reduced, with  $\Delta f\text{O}_2$  between FMQ-2 and FMQ-1. Prograde metamorphism of subducted serpentinites triggers the antigorite breakdown, with consequent  $\text{H}_2\text{O}$  release and growth of  $\text{Fe}^{2+}$ -bearing orthopyroxene, chlorite, and olivine. The crystallization of hematite in harzburgites studied by Debret et al. (2015) yields to a  $f\text{O}_2$  increase in the slab up to  $\Delta\text{FMQ} = +4$ . Finally, the antigorite-free subducted lithospheric mantle at depths of 150–350 km is generally more reduced (FMQ-2 to FMQ-3) even if more oxidized when compared with the surrounding mantle (Foley, 2011).

The subducted oceanic crust is depicted in Figure 6 as simplified blueschist to eclogite mafic rocks (blending blue and purple). Slab blueschist from South Tianshan (Li et al., 2016) and eclogite from North Qilian (Cao et al., 2011) in China record values of  $\Delta\text{FMQ}$  from 0 to +4 and from  $\text{FMQ}<0$  to  $\text{FMQ}+2.5$ , respectively.

Many more complications arise when we consider the slab-mantle interface. Mélange complexes are the result of deformation, boudinage, and chemical re-homogenization among the various lithologies derived from both slab and mantle scraps. The fluid-present high strain rates promote rock hybridization, which may act as chromatographic filtering, fixing, or releasing elements at variable P-T conditions (Schmidt and Poli, 2014). In this frame, slices from the slab and from the supra-subduction mantle embedded in this subduction mélange appear variously oxidized, likely due to the different fluid/rock ratio experienced. The  $\Delta\text{FMQ}$  of blueschists and serpentinites ranges from -1 to +1 (Deschamps et al., 2013; Li et al., 2016), while hydrated eclogites reach up to +4.5 (Mattinson et al., 2004). The highest  $f\text{O}_2$  variation is recorded by metapelitic rocks because they are characterized by variable bulk compositions. Eclogite-facies carbonate and calc-silicate rocks from Lindås Nappe and Bergen Arcs (Norway) show  $f\text{O}_2$  from  $\text{FMQ}+2$  to  $\text{FMQ}+4$  (Donohue and Essene, 2000; Boundy et al., 2002). Mn-bearing quartzite and metacherts range from  $\text{FMQ}+1$  (Frezzotti et al., 2014) to  $\text{FMQ}+12$  (Tumiati et al., 2015). As already pointed out by Evans (2012) and demonstrated by Malaspina et al. (2009b)



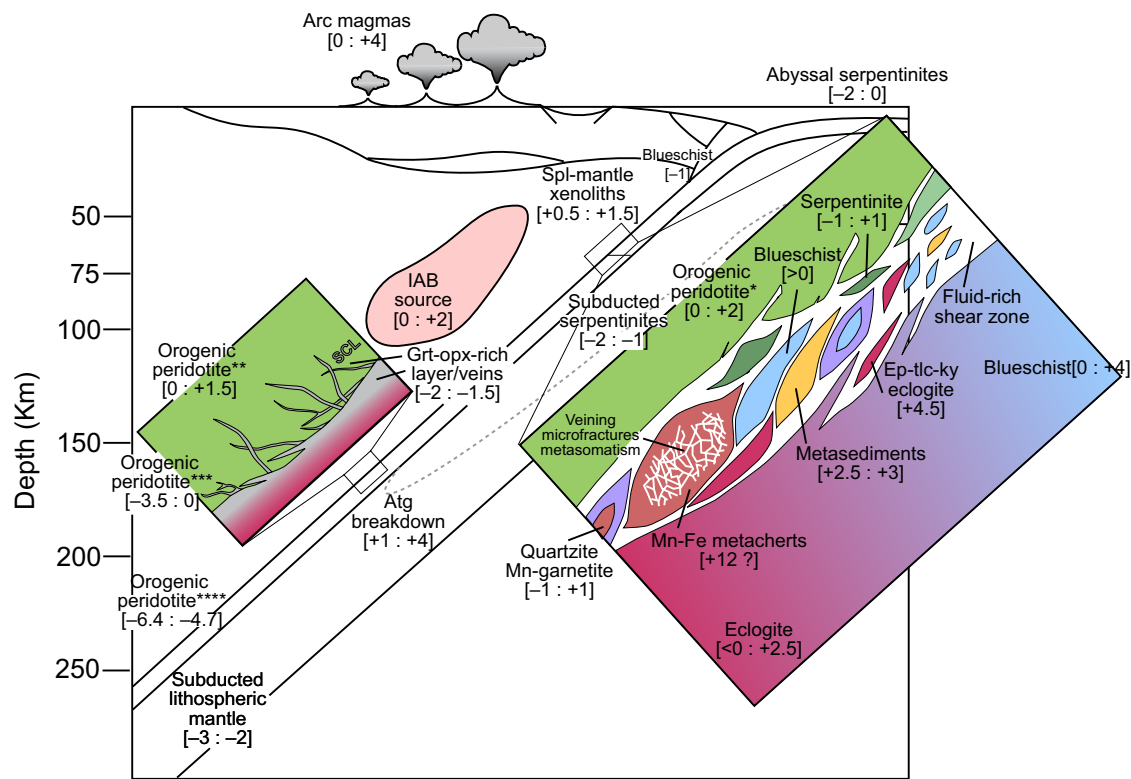


Figure 6. Schematic cartoon showing various redox conditions of subducted oceanic lithosphere and supra-subduction mantle. Numbers in brackets are the values of  $\Delta FMQ$ . For comparison, the oxygen fugacities of arc magmas (Rohrbach et al., 2005; Carmichael et al., 2006; Evans et al., 2008) and island arc basalt (IAB) sources (Ballhaus, 1993; Parkinson and Arculus, 1999) are also reported. References: abyssal and subducted serpentinites (Deschamps et al., 2013), antigorite breakdown (Debret et al., 2015), subducted lithospheric mantle (Foley, 2011), accretionary prism blueschists (Zanchetta et al., 2018), slab blueschists and eclogites (Cao et al., 2011; Li et al., 2016); mélange lithotypes: serpentinites (Deschamps et al., 2013), blueschists (Li et al., 2016), metasediments (Donohue and Essene, 2000; Boundy et al., 2002), ep-tlc-ky eclogites (Mattinson et al., 2004), Mn-Fe metacherts (Tumiati et al., 2015), quartzite and Mn-garnetite (Frez-zotti et al., 2014); slab-mantle interface: grt-opx-rich layer/veins (Malaspina et al., 2017); supra-subduction mantle: spl-mantle xenoliths (Brandon and Draper, 1996; Parkinson and Arculus, 1999; Peslier et al., 2002); \*—orogenic peridotite from Ulten Zone (Malaspina et al., 2009a), grt-opx-rich layer/veins (Malaspina et al., 2017); \*\*—orogenic peridotite from Sulu (Malaspina et al., 2009b); \*\*\*—orogenic peridotite from Bardane (Malaspina et al., 2010; Rielli et al., 2017); \*\*\*\*—orogenic peridotite from Ugelvik (Rielli et al., 2017). SCL—supercritical liquid.

and Tumiati et al. (2015), the oxidized or reduced nature of a rock, particularly in geodynamic environments where different bulk compositions and metasomatic chemical variations occur (e.g., subduction mélange), cannot be described by the commonly used intensive variables  $fO_2$  or  $\mu O_2$ . Such variables are in fact by definition independent on the relative proportion of the phases in a rock (Frost, 1991). The estimate of an oxygen mass balance is therefore mandatory to evaluate the oxidation state of an equilibrium phase assemblage.

### SLAB-TO-MANTLE MASS TRANSFER: TRACE ELEMENTS AND REDOX BUDGET

One of the most important pieces of evidence of the deep element recycling at subduction zones is the production of arc lavas relatively enriched in water, LILE, and to a lesser extent also in LREE, compared to the oceanic crust formed at mid-ocean ridges (Pearce et al., 2005). Such enrichment is called the “slab signature” (Tatsumi and Eggins, 1997). Moreover, the  $H_2O$  content and slab-derived fluid mobile elements of lavas and melt inclusions from arc vol-

canoes can be linearly correlated with their  $Fe^{3+}/\Sigma Fe$ , indicating that the oxidation state of such magmas is closely related to subduction fluid influx in their source (Kelley and Cottrell, 2009). If pure water is not likely an efficient carrier of  $Fe^{3+}$  (Schneider and Eggler, 1986), solute-rich slab-derived fluids could be potentially able to mobilize  $Fe^{3+}$  (Kelley and Cottrell, 2009) as they do for other trivalent fluid-immobile elements such as REE (Kessel et al., 2005a, 2005b; Tsay et al., 2014).

Several models have been proposed to explain how these geochemical signatures may be transferred from the slab to the arc lava sources in the mantle wedge (Tatsumi, 1986; Malaspina et al., 2006a, 2006b; Bebout, 2007; Hack and Thompson, 2011; Behn et al., 2011; Marschall and Schumacher, 2012; Till et al., 2012; Tumiati et al., 2013; Cannào et al., 2015; Pirard and Hermann, 2015; Scambelluri et al., 2015). The formation of subduction channels play an important role for mass transfer at subduction zones between the subducting slab and the overlying mantle by percolation of slab fluids (Cloos, 1982; Bostock et al., 2002; Gerya et al., 2002). At pressures up to 3 GPa, the slab-mantle interface corresponds to a mélange zone (e.g., Bebout, 2007), where high fluid fluxes

allow chemical exchange within the mélange materials forming hydrated and low-viscosity layers atop the subducting plate, with a hybrid geochemical signature (Bebout, 2007; Bostock, 2013).

The experimental work of Pirard and Hermann (2015) suggests that, at higher pressures, the direct transport of hydrous silicate-rich liquids by focused flow is the fastest and suitable mechanism of mass transfer through the mantle wedge able to supply the required geochemical signatures found in arc lavas worldwide. On the contrary, the percolation of supercritical liquids (*l.s.*) in mantle wedge peridotites by porous flow processes leads to the formation of several hydrous phases, such as amphibole and phlogopite (Zanetti et al., 1999; Scambelluri et al., 2006), which are able to incorporate significant quantities of trace elements, thus modifying the original slab signature (Pirard and Hermann, 2015). The SiO<sub>2</sub>-enriched composition of supercritical liquids makes them very reactive with the overlying mantle, leading to the possible formation of metasomatic orthopyroxenite layers (Malaspina et al., 2006b; Endo et al., 2015).

Alternatively to the conventional model of mass transfer described above, Nielsen and Marschall (2017) propose that the slab signature may be transferred to arc lavas by mixing the solid components along the slab-mantle interface (see also Marschall and Schumacher, 2012; Cruz-Urbe et al., 2018), rising in the denser mantle as cold diapirs. Therefore, altered oceanic lithosphere, ophicarbonates, hybrid rocks from mélange zones, and hydrated peridotites drive the cold plume in the mantle wedge (Tumiati et al., 2013). The interaction between melts produced by the uprising cold plume and the mantle wedge may provide the fractionated trace-element signatures shown by arc volcanic rocks (Marschall and Schumacher, 2012; Spandler and Pirard, 2013; Nielsen and Marschall, 2017).

The mechanism of fluid-mediated redox budget transfer from the subducting plate to the overlying mantle, and then to the source regions of arc lavas in the mantle wedge, is still debated and poorly constrained. As discussed by Evans (2012), the oxidized forms of iron, sulfur, and carbon are potentially the agents able to transfer O<sup>2-</sup> to the mantle, depending on their solubility in slab-derived fluid phases. Sulfur is probably the best carrier of redox budget (up to  $1.6 \times 10^{12}$  mol yr<sup>-1</sup> from calculations by Evans, 2012) able to largely oxidize the Fe<sup>2+</sup> of mantle mineral assemblages. Its transfer from the slab to the mantle is likely fluid mediated, since anyhdrite can be easily solubilized in saline fluids (Newton and Manning, 2005). Sulfate minerals are common daughter crystals in saline fluid inclusions of eclogite veins and coesite-bearing schists in the Western Alps (Philippot and Selverstone, 1991; Philippot et al., 1995), and in multiphase solid inclusions in UHP rocks from different terranes (see Table 1 of Frezzotti and Ferrando, 2015). If slab-derived fluids are able to transport sulfates in the overlying mantle, their reduction to sulfides will oxidize the Fe<sup>2+</sup>-bearing minerals with a ratio of 1:8, if the oxygen fugacity of the mantle is below the sulfide-sulfur oxide buffer (Kelley and Cottrell, 2009). Also carbon can be a carrier of redox budget when transferred from the subducting plate to the overlying mantle after dissolution of carbonates in subduction fluids. Natural, theoretical, and experimental works demonstrated that both carbonates and CO<sub>2</sub> can be solubilized in HP fluids (Newton and Manning,

2002; Caciagli and Manning, 2003; Dolejš and Manning, 2010; Frezzotti et al., 2011; Ferrando et al., 2017; Tumiati et al., 2017). The conversion from CO<sub>2</sub> to C in the mantle gives a potential redox budget flux in the order of 10<sup>11</sup> mol year<sup>-1</sup>, inducing the oxidation of the sub-arc mantle (Evans, 2012). The solubility of Fe<sup>3+</sup> in subduction zone fluids is not well known, even if the solute content of deep slab fluids may contain high Fe<sup>3+</sup> concentrations also after the interaction with the host mineral during the crystallization of the daughter phases (Campione et al., 2017; Malaspina et al., 2017).

In geodynamic settings where a high fluid/rock ratio is expected, such as subduction mélanges, oxygen is likely transported along fractures and veins, possibly through mechanisms of dissolution-precipitation of O-enriched oxides and silicates (Tumiati et al., 2015) or by advective processes (Marschall and Schumacher, 2012; Tumiati et al., 2013; Nielsen and Marschall, 2017). On the other hand, fluid percolation at low fluid/rock ratios occurs when the metasomatic fluid phases produced at UHP (silica-saturated supercritical liquids) interact with peridotitic rocks at the slab-mantle interface (Fig. 6). In such occurrences, O<sub>2</sub> cannot be considered a perfectly mobile component, as defined by Korzhinskii (1959, 1965), because most of the redox reactions take place between solid oxides and silicates. Based on this principle, the quantity of inert components (e.g., FeO then forming Fe<sub>2</sub>O<sub>3</sub> and vice versa) has a fundamental role, and the molar quantity of exchanged oxygen (nO<sub>2</sub>) must be considered as an independent state variable. A recent study by Malaspina et al. (2017) reports the oxygen mass balance of crust-derived fluids preserved in multiphase solid inclusions from hybrid garnet orthopyroxenites of Maowu, a well-known example of metasomatic layers at the slab/mantle interface (Malaspina et al., 2006b; Chen et al., 2017). Because mass transfer is supported by chemical gradients, in this case by gradient in nO<sub>2</sub>, a metasomatic front may develop from an oxidized slab, contributing to 200 mol m<sup>-3</sup> of excess O<sub>2</sub> to the overlying mantle (10 mol m<sup>-3</sup> O<sub>2</sub>), passing through a transitional layer of hybrid rocks (gray field in Fig. 6) with the same excess of oxygen. On the contrary, the redox budget of the crust-derived fluids (multiphase inclusions) records more oxidized conditions than the host rock, reaching up to 400 mol m<sup>-3</sup> of nO<sub>2</sub> (Malaspina et al., 2017). This suggests that even if the solubility of Fe<sup>3+</sup> in subduction fluid phases is not well known, C-S-free aqueous fluids still remain potential carriers of oxidized components when they escape the slab-mantle interface.

## ■ METASOMATISM AND IMPLICATIONS FOR THE REDOX STATE OF THE SUPRA-SUBDUCTION MANTLE

Information on deep metasomatism of the supra-subduction mantle can be gained by the study of UHP terranes that contain felsic rocks associated with metasomatized garnet peridotites. Such associations represent an ideal context to study the element exchange between crustal and mantle rocks at pressures corresponding to sub-arc depths. Even if the origin of many HP-UHP orogenic peridotites is still under debate, examples of supra-subduction peridotites dragged by the subducting continental crust crop out in the Ulten Zone (Italian Central Alps), in the Western Gneiss Region (Norway), in the Massif Central

and South Carpathian Variscides, in the Bohemian Massif, and in the Chinese Sulu Belt (Bodinier and Godard, 2013, and references therein). Most of these garnet peridotites provide evidence of recycling in the mantle of slab-derived fluids by the occurrence of primary multiphase solid inclusions, which have been attributed to silicate-rich supercritical liquids (van Roermund et al., 2002; Malaspina et al., 2006b; Vrijmoed et al., 2006; Scambelluri et al., 2008; Malaspina et al., 2010; Malaspina and Tumiati, 2012; Frezzotti and Ferrando, 2015). The trace-element pattern of the fluids that potentially leave the slab-mantle interface (the “residual fluid” of Malaspina et al., 2006b) is characterized by an enrichment of LREE and a selective enrichment in LILE, with spikes of Cs, Ba, and Pb relative to Rb and K. The pattern of this “residual fluid,” reported in Figure 7 (Maowu fluid inclusions), resembles the LILE-enriched trace-element pattern of arc lavas, attributed to the addition of a “subduction component” that derives from the subducted sediments. Figure 7 also shows, for comparison, the incompatible trace-element pattern of peridotites from the Ulten Zone (Italian Alps), a known example of supra-subduction mantle peridotites metasomatized by crust-derived fluid phases at eclogite-facies conditions (Tumiati et al., 2003, 2007; Scambelluri et al., 2006). The patterns reported in Figure 7 record the transformation of lithospheric spinel lherzolites into garnet + amphibole and amphibole peridotites during a continuous P-T history (see also Nimis and Morten, 2000; Tumiati et al., 2003). They show a peculiar “W-type” signature with strong enrichment in Cs, Ba, Pb, and U with respect to Rb, K, and Th, coupled with moderate enrichment in Li (Fig. 7). The pattern of the “residual

fluid” is also compared with that of pseudosecondary multiphase inclusions found in the garnet peridotites from Sulu, again another famous example of metasomatized supra-subduction mantle. Such inclusions were considered to represent a fluid phase that infiltrated the mantle after an earlier metasomatism by alkaline melt (Malaspina et al., 2009a). These inclusions have trace-element compositions surprisingly similar to the ones of Maowu (Fig. 7), pointing to a genetic relation with the two fluids. The similarity between the fluids trapped in the inclusions of both Maowu and Sulu peridotites and the metasomatic pattern recorded by the Ulten peridotites strongly suggests that these kinds of fluids may be effective metasomatic agents in the lithospheric supra-subduction mantle, once they escape the slab-mantle interface.

Crust-derived fluid metasomatism is also recorded by ultradeep majorite-bearing peridotites and websterites from Fjórtoft Island (Bardane, Western Gneiss Region). As demonstrated by Scambelluri et al. (2010), the mineral paragenesis re-equilibrated during deep Caledonian subduction is enriched in LREE, LILE (Pb, U, and Th), and light elements (Li and B). In particular, phlogopite and clinopyroxene and also majoritic garnet filling veins formed by percolating fluids at 6.5–7.0 GPa are the LREE and LILE repositories (Scambelluri et al., 2008). This indicates a common genesis from incompatible element-enriched subduction fluids that flushed the Bardane websterite (Scambelluri et al., 2010).

The Sr isotopic composition of these peridotites helps to further constrain the origin of fluids responsible for their metasomatism. The  $^{87}\text{Sr}/^{86}\text{Sr}$  of the Sulu garnet peridotites, the Maowu garnet orthopyroxenite, Ulten zone

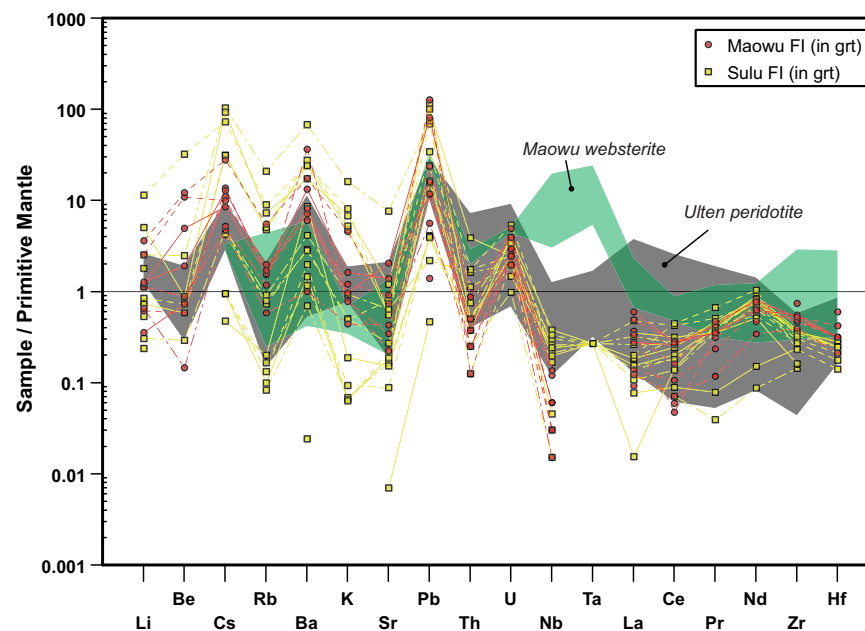


Figure 7. Primitive mantle (McDonough and Sun, 1995) normalized trace-element patterns of metasomatized supra-subduction zone mantle rocks (Ulten: Scambelluri et al., 2006; Maowu: Malaspina et al., 2006b) and fluid inclusions (FI) from Sulu (Malaspina et al., 2009a) and Maowu (Malaspina et al., 2006b).

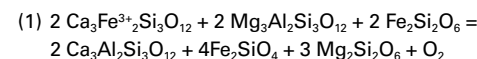
peridotites, and some of the peridotites from Norway reported in the literature point to a crust-derived metasomatism. As portrayed in Figure 8, they show enrichment in the radiogenic component, ranging from 0.7072 to 0.7076 for the Maowu orthopyroxenites (Jahn et al., 2003) and from 0.7085 to 0.7095 for the Sulu peridotites (Yang and Jahn, 2000). The peridotites from the Ulten zone show radiogenic  $^{87}\text{Sr}/^{86}\text{Sr}$  signatures ranging from 0.7050 to 0.7074 (Tumiati et al., 2003), as well as some of the garnet peridotites from Norway (up to 0.7130; Spengler et al., 2009). These ranges provide evidence of the resetting of the original mantle isotopic signature (of 0.7025) toward crustal values (dashed dark blue field in Fig. 8). Together with Sr isotopes, Nd systematic also shows evidence of crustal contamination for some terranes, showing negative  $\epsilon_{\text{Nd}}$  ranging from  $-4.2$  to  $-7.1$  for Maowu rocks, from  $-9.0$  to  $-9.7$  for Sulu peridotites, and down to  $-8.1$  for the Ulten peridotites.

### The Oxidation State of (Portions of) the Metasomatized Supra-Subduction Mantle

The three examples of mantle-derived garnet peridotites and websterites from Ulten, Sulu, and Bardane presented in the previous section also experienced metasomatism by  $\pm\text{C}$ -bearing subduction fluid phases, up to 200 km depth. Ulten garnet peridotites were metasomatized by slab-derived fluids, which enhanced the crystallization of pargasitic amphibole and dolomite (Sapienza et al., 2009; Malaspina and Tumiati, 2012). Sulu peridotites record a multistage metasomatism by alkali-rich silicate melt, and a subsequent influx of a slab-derived incompatible element and silicate-rich fluid, which crystallized phlogopite and magnesite (Malaspina et al., 2009b). Websterites from Bardane preserve remnants of crust-derived fluids that precipitated graphite/diamond + dolomite/magnesite + Cr-spinel + phlogopite/K-amphibole in multiphase inclusions hosted by majoritic garnet (van Roermund et al., 2002; Scambelluri et al., 2008; Malaspina et al., 2010). As we will see later, an apparent correlation between the composition of the metasomatic agent (C- and alkali-bearing) and the fluid-induced oxidation of the peridotite mineral assemblage may occur.

The interpretation of the oxygen fugacities retrieved from mantle rocks is still a subject of debate. Even though the works by Canil (2002) and Lee et al. (2005) emphasize a homogeneity in the redox state of the convective asthenosphere, including subduction zone environments, systematic  $f\text{O}_2$  estimates for mantle xenoliths from different geological settings, both in the spinel and garnet facies, indicate that the upper mantle is zoned (Daniels and Gurney, 1991; Ballhaus and Frost, 1994; Ballhaus, 1995; Woodland and Koch, 2003; Frost and McCammon, 2008). In addition, there are a number of studies in the literature that reveal lateral  $f\text{O}_2$  variations related to different tectonic settings. These are summarized in Figure 9 (references are reported in the figure caption), where the range of oxygen fugacities ( $\Delta\text{FMQ}$ ) for spinel and garnet peridotites from various tectonic settings (black lines) are plotted as a function of equilibration pressure. These studies are in contrast to the “oxidized” nature of the mantle wedge, derived from oxygen thermobarometry of arc lavas (yellow lines) or from models of IAB sources (blue square).

For HP-UHP peridotite mineral assemblages,  $f\text{O}_2$  can be evaluated from several equilibria involving  $\text{Fe}^{3+}$ -garnet components, where  $\text{Fe}^{3+}$  occurs in octahedral coordination. For the olivine + orthopyroxene +  $\text{Fe}^{3+}$ -garnet assemblage, two of these reactions are represented by:



and



Equilibrium (1) by Luth et al. (1990) has been experimentally tested by Stagno et al. (2013) at  $P > 5$  GPa, while equilibrium (2) was calibrated by Gudmundsson and Wood (1995) and is valid at pressures below 5 GPa (Stagno et al., 2013). At high pressures, oxygen fugacity is therefore traditionally determined from the  $\text{Fe}^{3+}$  contents of garnet in equilibrium with olivine and orthopyroxene. The green (and gray) lines portrayed in Figure 9 are the  $\Delta\text{FMQ}$  ranges cal-

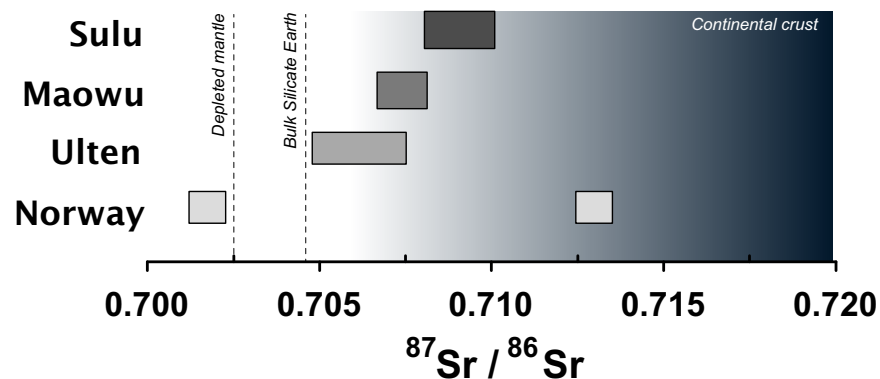


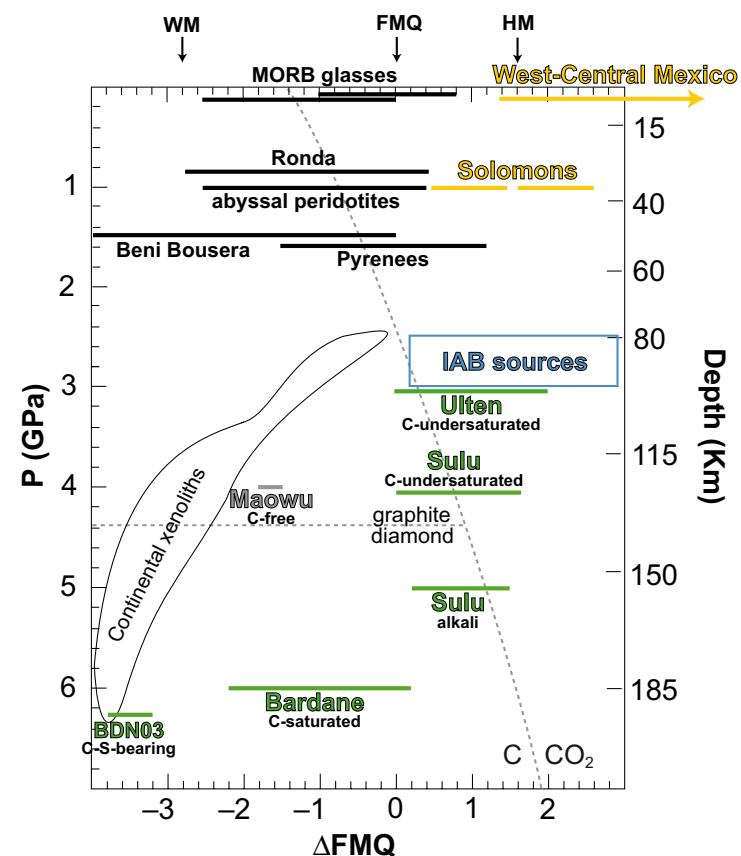
Figure 8.  $^{87}\text{Sr}/^{86}\text{Sr}$  isotopic ratio of mantle rocks from supra-subduction setting. Sulu from Yang and Jahn (2000); Maowu from Jahn et al. (2003); Ulten from Tumiati et al. (2003); Norway from Spengler et al. (2009). Depleted mantle from Rehkämper and Hofmann (1997); bulk silicate earth from Salters and Stracke (2004). The dark blue field represents the typical range of  $^{87}\text{Sr}/^{86}\text{Sr}$  signature of the continental materials.

Figure 9. Ranges and average values of  $\Delta FMQ = (\log fO_2 \text{ sample} - \log fO_2 \text{ FMQ})$  for the Ulten, Maowu, Sulu, and Bardane garnet peridotites plotted as a function of pressure (data from Malaspina et al., 2009b, 2010, 2017; BDN03 is from Rielli et al., 2017). They are compared with selected examples of glasses and peridotites from various tectonic settings, equilibrated at similar temperature conditions: mid-ocean ridge basalt (MORB) glasses (Christie et al., 1986; Bézos and Humler, 2005), oceanic mantle lithosphere (Bryndzia and Wood, 1990), and peridotite massifs (Woodland et al., 1992, 2006) (black lines); garnet peridotite xenoliths from sub-cratonic mantle (Woodland and Koch, 2003) (white area). Note the negatively correlated trend between supra-subduction garnet peridotites (green lines), arc lavas from west-central Mexico (Carmichael et al., 2006), and from Solomon (Rohrbach et al., 2005) (yellow lines), and island arc basalt (IAB) sources (Ballhaus, 1993; Parkinson and Arculus, 1999), which is grossly parallel to the  $\Delta FMQ$  decrease of continental xenoliths with depth. The CCO oxygen buffer ( $C = O_2 + CO_2$ ), calculated at an average  $T = 900 \text{ }^\circ\text{C}$  and the graphite-diamond transition at the temperature conditions of M3-3 stage of Bardane peridotites ( $1000 \text{ }^\circ\text{C}$ ), are also indicated for reference. WM—wüstite-magnetite; FMQ—fayalite-magnetite-quartz; and HM—hematite-magnetite buffers.

culated from  $Fe^{3+}$  measurements of garnets from supra-subduction orogenic peridotites, in relation to the metasomatic phase assemblages formed: C-free (Maowu), C-undersaturated (Ulten and Sulu), alkali-bearing (Sulu), C-S-saturated (Bardane), slab-derived fluids. Lee et al. (2005) interpreted the high barometric  $fO_2$  of arc lavas as resulting from the evolution of magmas during their ascent, emplacement, and/or magmatic differentiation. These authors have also suggested that the generally higher  $fO_2$  of mantle xenoliths from the arc lithosphere compared with the convective mantle at similar pressures (Christie et al., 1986; Bryndzia and Wood, 1990; Bézos and Humler, 2005) is likely due to continuous metasomatic fluid influx in these mantle rocks during their long residence time in the sub-arc lithosphere. Even if the dispute about the process responsible for the relative oxidation of the mantle at subduction zones and the actual oxidizing ability of slab-derived metasomatic fluids is still going on, the metasomatized mantle apparently looks more “oxidized.”

Interestingly, the  $fO_2$  calculated for the garnet + orthopyroxene  $\pm$  olivine assemblage of the C-free metasomatic orthopyroxenites from Maowu (gray line in Fig. 9) shows much lower values with respect to that of supra-subduction C-bearing peridotites equilibrated at similar pressures. The data compilation reported in Figure 9 therefore suggests that carbon- (and sulfur-; Rielli et al., 2017) rich fluids may play an important role in the oxidation of iron-bearing garnets in mantle peridotites.

Besides the direct involvement of carbon and sulfur in fluid-mediated redox reactions in the mantle, we must consider that the increase of  $Fe^{3+}$  in garnet from mantle peridotites is not always correlated with the increase of the whole-rock  $Fe_2O_3$ , but could also be the consequence of the partitioning of  $Fe^{3+}$  from clinopyroxene into garnet (Canil and O'Neill, 1996; Woodland and Peltonen, 1999; Woodland and Koch, 2003; Rohrbach et al., 2007, 2011; Woodland, 2009). A recent work by Aulbach et al. (2017) also reports a strong negative correlation of  $Fe^{3+}/\Sigma Fe$  in garnet with the jadeite content in coexisting clinopyroxene. This has been again interpreted as partitioning of  $Fe^{3+}$  from garnet into jadeite-rich clinopyroxene with consequences in the  $fO_2$  calculations from garnet-only-bearing assemblages. Moreover, because redox reactions depend on the abundance of redox-sensitive elements, and on the moles of oxygen



exchanged in the redox equilibria, the determination of the oxidation state of metasomatized garnet peridotites is a demanding task because clinopyroxene, amphibole, and phlogopite, in addition to garnet (and/or spinel), incorporate both ferric and ferrous iron (Malaspina et al., 2012, 2017).

Finally, another important underestimated aspect related to the metasomatic oxidation of garnet peridotites is the role of alkali elements, particularly of  $Na_2O$ . Clinopyroxene in metasomatized garnet peridotites may be enriched in  $Fe^{3+}$  as aegirine component (Woodland, 2009; Aulbach et al., 2017) and potentially become the major  $Fe^{3+}$  host when the peridotites are metasomatized by  $Fe_2O_3$ - and alkali-rich fluid phases, as was exactly what happened to Sulu peridotites during the first stage of metasomatism by alkali-rich melts (Fig. 9; Malaspina et al., 2012). This suggests that if net bulk oxidation can be demonstrated, carbon-, sulfur-, and also alkali-bearing slab-derived metasomatic agents may be potential carriers of  $S^{6+}/S^{3-}$ ,  $C^{4+}$ , and  $Fe^{3+}$  capable of oxidizing the overlying mantle.



## ■ CONCLUDING REMARKS

Based on the questions addressed in the beginning of this review, some concluding remarks are listed below.

- (1) Geophysical imaging of subduction zones (e.g., Bostock et al., 2002) documents an important front of hydration in the supra-subduction mantle region, due to the uprise of fluids released from sediments and subducted oceanic crust. The hydration mechanism of the supra-subduction mantle produces different plate interface style settings depending on the thermal state of the subduction zone. This also plays an important role in the geochemical imprint of the hydrated mantle and its possible contribution to arc magmatism (Marschall and Schumacher, 2012; Spandler and Pirard, 2013). The released fluids developing *mélange* terrains promote the formation of “hybrid” rocks, which are able to selectively exchange trace elements with other slab reservoirs. The hybridization process may lead to a chemical transformation both in terms of major elements (e.g., formation of lawsonites, chlorite schists, and tourmaline-rich blackwalls; see Marschall et al., 2006; Marschall and Schumacher, 2012; Vitale Brovarone et al., 2014) and/or of trace elements. In top slab *mélange*, the prograde fluid-mediated chemical exchange between slices of slab and wedge-derived rocks and slab fluids can be tracked using fluid-mobile elements (e.g., As and Sb) and isotopic tracers (B, Sr, and Pb). This process may yield to oddities in the geochemical signature of mantle rocks.
- (2) The major- and trace-element concentration of slab-derived fluids strongly depends on their partitioning with stable phase assemblages, which in turn depend on the thermal regime of subduction (Fig. 1). Phengite is the most important phase controlling the partitioning of LILE and LREE in K-bearing systems and is stable up to 200 km depth along cold subduction paths. In addition, accessory minerals such as allanite, monazite, zircon, and rutile, which are ubiquitous in different slab lithologies, play an important role in the storage of HFSE but also LREE and U-Th. The stability of garnet as a product of metamorphic reactions controls the partitioning of HREE. The release of incompatible elements, particularly of LILE and LREE, is modulated by the modal amount of key phases, such as phengite, in the slab rocks and by their stability, which depends on the occurrence of free H<sub>2</sub>O, which lowers their solidus temperature (Fig. 1).
- (3) The geochemical modification of the supra-subduction mantle wedge strongly depends on the magnitude of trace-element supply by fluids/melts. At relatively low pressures (up to 3 GPa, i.e., antigorite breakdown), the subducted lithosphere releases large quantities of H<sub>2</sub>O and forms *mélange* layers characterized by high fluid/rock ratios. In this framework, elements are likely transported along fractures and veins (Fig. 6), possibly through mechanisms of dissolution-precipitation or by advective processes. At higher pressures ( $P > 3$  GPa), fluid percolation at low fluid/rock ratios (porous or focused flow) is mediated by Si-saturated supercritical liquids interacting with peridotitic rocks at the slab-mantle interface. In such occurrences, focused flow is the fastest and most suitable mechanism of mass transfer through the mantle wedge capable of supplying the required geochemical signatures found in arc lavas.
- (4) The redox state of the subducting lithosphere is intrinsically heterogeneous due to the different lithologies bearing different amounts of redox-sensitive elements (Fe, Mn, C, and S) and different fluid/rock ratios experienced (Fig. 6). The estimate of an oxygen mass balance is mandatory to evaluate the oxidation state of the slab equilibrium phase assemblages. Nevertheless, one of the most important pieces of evidence of the deep redox budget recycling at subduction zones is the production of arc lavas with Fe<sup>3+</sup>/ΣFe linearly correlated with the H<sub>2</sub>O content and slab-derived fluid mobile elements. This evidence indicates that the oxidation state of arc magmas is closely related to the transfer of Fe<sup>3+</sup>, C<sup>4+</sup>, and/or S<sup>6+</sup> in their source by slab-derived metasomatic agents.
- (5) The redox-state evolution of slab and supra-subduction lithologies may influence the speciation of elements in the metasomatic fluids infiltrating the overlying mantle. The valence state of carbon and sulfur and the speciation of their compounds are governed by the rock system, i.e., by the equilibria among mineral assemblages containing redox-sensitive major elements (e.g., Fe and Mn). Alternatively, the carbon and/or sulfur species in subducted rocks and deep fluids control the oxidation state of the host system by redox reactions during fluid/rock interactions (e.g., Fig. 9). Whether the redox state of the system is buffered by the rock or by C-S-bearing fluids depends on the fluid/rock ratios. At high ratios, such as *mélange* layers, fluids control the redox state of the system, and oxygen can be considered perfectly mobile. At low ratios, such as during porous flow of metasomatic agents at UHP, the mantle rock controls the speciation of redox-sensitive metasomatic components, and oxygen is considered inert. Finally, another important aspect related to the metasomatic-related oxidation of the mantle wedge is the role of alkali elements, particularly of Na<sub>2</sub>O, which favors the incorporation of Fe<sup>3+</sup> in peridotite clinopyroxene as aegirine component. This suggests that if net bulk oxidation can be demonstrated, C-, S-, and even alkali-bearing slab-derived metasomatic agents may oxidize the overlying mantle.

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