



Linking serpentinite geochemistry with tectonic evolution at the subduction plate-interface: The Voltri Massif case study (Ligurian Western Alps, Italy)

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Abstract

Recent geochemical work shows that subduction-zone serpentinites are repositories for fluid-mobile elements absorbed during interaction with sediment-derived fluids. Unraveling the geochemical fingerprint of these rocks helps to define timing of tectonic accretion of sediments along the subduction interface and the role of serpentinite in element recycling to volcanic arcs. Here we present the trace element and isotopic composition (B–O–H, Sr, Pb) of high-pressure serpentinites from the Voltri Massif (Ligurian Western Alps, Italy), to discuss their role as incompatible element carriers and their contribution to recycling of sediment-derived components in subduction zones.

The serpentinites presented here record metamorphic olivine growth during eclogite-facies metamorphism and show undeformed and mylonitic textures. Field relations show that undeformed rocks are enclosed in deformed ones and that no metasedimentary rocks are present nearby. Undeformed serpentinite has very high $\delta^{11}\text{B}_{\text{SRM951}}$ (from +26‰ to +30‰), low Sr and Pb isotope ratios ($^{87}\text{Sr}/^{86}\text{Sr} = 0.7053\text{--}0.7069$; $^{206}\text{Pb}/^{204}\text{Pb} = 18.131\text{--}18.205$) and low As and Sb contents (0.1 and 0.01 $\mu\text{g/g}$, respectively). Oxygen and hydrogen isotope compositions are +4.5‰ and –67‰, respectively. In contrast, mylonitic serpentinite shows lower $\delta^{11}\text{B}$ (from +22‰ to +17‰), significant enrichment in radiogenic Sr and Pb isotopes ($^{87}\text{Sr}/^{86}\text{Sr}$ up to 0.7105; $^{206}\text{Pb}/^{204}\text{Pb}$ up to 18.725), and enrichment in As and Sb (1.3 and 0.39 $\mu\text{g/g}$, respectively). $\delta^{18}\text{O}$ of the mylonitic serpentinites reaches values of +5.9‰, whereas δD is comparable with that of undeformed rocks (approximately –70‰). In mylonitic serpentinites, the B and Sr isotopic values and the fluid-mobile element (FME) concentrations are near those for the Voltri metasedimentary rocks (calc- and mica-schists). Pb systematics also reveal influx of a crust-derived component.

Our dataset shows that undeformed serpentinite still preserves an oceanic geochemical fingerprint, whereas mylonitic serpentinite is reset in its concentrations of FME and its B, Sr and Pb isotope compositions, due to interaction with sediment- and crust-derived fluids. The environment of this interaction is either compatible with (i) an outer-rise zone setting, with percolation of seawater-derived fluids enriched in sedimentary components into bending-related fault structures, or with (ii) subduction channel domains, where ascending sediment-derived slab fluids infiltrate slices of former oceanic serpentinite accreted to the plate interface domain. Influx of sediment-derived subduction fluids along major deformation zones in serpentinite modifies the element budget of the rocks, with important implications for element recycling and the tectonic history of serpentinite. The B, Sr and Pb isotopic systematics, coupled with FME concentration in serpentinites are particularly helpful

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geochemical tracers of interaction between different reservoirs in subduction-interface environments, and are more sensitive than the traditionally applied stable oxygen and hydrogen isotope compositions.

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1. INTRODUCTION

Subduction of hydrated oceanic plates leads to fluid release and fluid-mediated mass transfer from the downgoing slab into the overlying plate, affecting global element recycling and the chemical refertilization of the Earth's mantle (e.g. Stern, 2002; Tatsumi, 2005; Spandler and Pirard, 2013; Bebout and Penniston-Dorland, 2016). In the last twenty years an increasing number of petrologic and geochemical studies has highlighted the role of serpentinites as subduction reservoirs for water and carbon (e.g. Ulmer and Trommsdorff, 1995; Kerrick and Connolly, 1998; Collins et al., 2015; Scambelluri et al., 2016), halogens (Scambelluri et al., 2004a; Sharp and Barnes, 2004; Kendrick et al., 2011, 2013; John et al., 2011; Debret et al., 2014), nitrogen (e.g. Halama et al., 2014) and fluid-mobile elements (FME, Tenthorey and Hermann, 2004; Hattori and Guillot, 2003, 2007; Paulick et al., 2006; Scambelluri et al., 2001, 2004a,b, 2014, 2015; Kodolányi et al., 2012; Deschamps et al., 2010, 2011, 2012, 2013; Debret et al., 2013; Lafay et al. 2013; Barnes et al., 2014; Cannà et al., 2015). Stability of antigorite to pressures corresponding to 100–150 km depth in subduction zones extends the role of serpentinite as a carrier of volatiles, halogens and FME to subarc regions (see the discussions by Ulmer and Trommsdorff, 1995; Hattori and Guillot, 2003; Hacker, 2008; Scambelluri and Tonarini, 2012; Deschamps et al., 2013; Konrad-Schmolke and Halama, 2014).

The presence of hydrated (serpentinized) layers atop the slab and in the hanging wall mantle infiltrated by slab-derived fluids is promoted by geophysical imaging (Bostock et al., 2002; van Keken et al., 2011), numerical models (e.g. Gerya and Stöckhert, 2002; Agard et al., 2009; Malatesta et al., 2012a) and field observations (e.g. Blanco-Quintero et al., 2011; Deschamps et al., 2012). The amount and thickness of hydrated and serpentinized materials in such environments depends on the thermal regime of the subduction zone and on the architecture of the plate interface (mega-slices of slab materials *vs.* subduction mélange; e.g. Guillot et al., 2015; Bebout and Penniston-Dorland, 2016). Clearly, the physical properties of serpentinite at convergent plate boundaries are relevant to the formation of low-viscosity channels where deformation is strongly focussed and where exhumation of high-pressure rocks is boosted by serpentinite rheology and buoyancy (2.75 g/cm³ density compared with mantle density of 3.5 g/cm³; e.g. Hermann et al., 2000; Gerya and Stöckhert, 2002; Agard et al., 2009; Reynard, 2013; Guillot et al., 2015).

One way to ascertain the processes governing the formation and behavior of plate interfaces is through field-based analysis of high-pressure metamorphic rocks. In this respect, serpentinite provides information on fluid-

mediated exchange with chemically contrasting rocks during tectonic accretion to subduction interface environments. For this purpose, the Alpine chain hosts the largest exposures of exhumed serpentinites in close association with eclogite-facies mafic and metasedimentary rocks, all representative of subducted fossil oceanic lithosphere. For the Western Alps, Lafay et al. (2013) demonstrated that prograde, blueschists-facies meta-sedimentary accretionary complexes enclose km-scale serpentinite lenses enriched in fluid-mobile Cs, Rb, As, Sb, Pb and Sr due to exchange with sediment-derived fluids during early subduction stages. Similarly, the ultramafic blocks hosted in the subduction mélange of Cima di Gagnone (Swiss Central Alps), became enriched during subduction in Cs, B, As, Sb, and in radiogenic Sr and Pb by interaction with host metasedimentary rocks (Scambelluri et al., 2014, 2015; Cannà et al., 2015). For Alpine serpentinites from the Punta Rossa unit (Aosta Valley), Barnes et al. (2014) suggested the influx of sediment-derived fluids, leading to re-equilibration of stable O, H and Cl isotopes and to enrichment in Pb, Ba, Cs and U. Taken together, all of these lines of evidence indicate that serpentinites can serve as valuable tracers of the exchange of FME between different geochemical reservoirs and can transport element anomalies obtained by this exchange to great depths in subduction zones (e.g. Ryan et al., 1995; Hattori and Guillot, 2003; Scambelluri et al., 2004b; Tonarini et al., 2011; Deschamps et al., 2011).

Despite the role of serpentinites as sinks for FME and radiogenic isotopes, geochemical data for these rocks are still somewhat sparse. Here, we report whole-rock trace element, stable B–O–H and radiogenic Sr, Pb isotope analyses of high-pressure ophiolitic serpentinites from the Voltri Massif (Ligurian Western Alps). Our goals are to further define their role as subduction repositories for sediment-derived elements and isotopes, using their geochemical fingerprint to trace their tectonic subduction history. For these reasons we also analyzed two samples of metasedimentary rocks described by Federico et al. (2004) showing evidence of high silica content in phengite minerals as index of eclogite-facies recrystallization: they are used here as representative end-members for the metasedimentary fluids source. We show that the Voltri serpentinites, despite presently being quite distant from the high-pressure metasediments, record influx of sediment-derived fluids along major deformation zones during early stages of their subduction history.

2. GEOLOGICAL BACKGROUND AND FIELD RELATIONSHIPS

The study area is situated near the Village of Vara (Voltri Massif), at the eastern end of the Western Alps

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