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High-pressure serpentinites, a trap-and-release system controlled by metamorphic conditions: Example from the Piedmont zone of the western Alps

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ABSTRACT

We provide new insights into the geochemistry of serpentinites from the Alpine orogenic wedge representing a paleo-subduction zone. These serpentinites are derived from similar oceanic protoliths, but they have experienced different metamorphic conditions related to three different structural levels of the paleo-subduction zone ((1) obducted: Chenaillet ophiolite, (2) accretionary wedge: Queyras Schistes lustrés complex and (3) serpentinite channel: Monviso ophiolite). Metamorphism undergone by these three units is well defined, increasing eastward from sub-greenschist to eclogite facies conditions, and allows us to examine trace element behavior from the oceanic ridge environment to subduction. Serpentinites first record moderate trace element enrichment due to seawater interaction resulting in the replacement of olivine and pyroxene by chrysotile and lizardite below 300 °C. In the sediment-dominated accretionary wedge, serpentinites are strongly enriched in fluid-mobile-elements (B, Li, As, Sb, and Cs) and act as a trapping system following the metamorphic gradient (from 300 to 390 °C) up to total replacement of the lizardite/chrysotile assemblage by antigorite. Under higher temperature conditions ($T>390$ °C), no enrichment was observed, and some fluid-mobile elements were released (B, Li, Cs, and Sr). Moreover, in the serpentinite channel ($T>460$ °C), most of the fluid-mobile elements are absent due to the scarcity of metasediments which prevent geochemical exchange between metasediments and serpentinites. This is also due to the onset of antigorite breakdown and the release of fluid-mobile elements. Thus, we emphasize that the geochemistry of Alpine serpentinites is strongly dependent on (1) the grade of metamorphism and (2) the ability of metasediments to supply fluid-mobile elements. We conclude that serpentinites act as a trap-and-release system for fluid-mobile elements in a subduction context.

1. Introduction

Serpentinites are recognized as an important pathway for water transport in settings ranging from oceanic spreading ridges to subduction zones and thus play an important role in the global geochemical cycle (Ulmer and Trommsdorff, 1995; Scambelluri et al., 2001; Rüpke et al., 2002; Hattori and Guillot, 2003, 2007; Deschamps et al., 2010). Serpentinites formed in abyssal environment which incude the serpentine species (lizardite (Lz), chrysotile (Ctl), and antigorite (Atg)) are characterized by strong enrichment in fluid-mobile elements (Thompson and Melson, 1970; Seitz and Hart, 1973; Moody, 1976; Bonatti et al., 1984; Deschamps et al., 2011, 2012; Pabst et al., 2011; Kodolányi et al., 2012), which are mainly due to fluid/rock interactions and hydrothermal activity occurring in slow-spreading ridge environments. During subduction, serpentinites undergo dehydration at roughly 650–700 °C (the so-called "*antigorite breakdown*", Ulmer and Trommsdorff, 1995; Wunder and Schreyer, 1997) allowing the release of water and fluid-mobile elements through the mantle wedge (Scambelluri and Philippot, 2001; Scambelluri et al., 2001, 2004; Hattori and Guillot, 2003; Deschamps et al., 2010; Kodolányi and Pettke, 2011; Vils et al., 2011). These fluids transported into the mantle wedge can contribute to the formation of arc magmas (Hattori and Guillot, 2003, 2007) and partly control their geochemical signatures. Recently, Deschamps et al. (2011) used Pb isotopes to show that over-enrichment in fluid-mobile elements in serpentinites can be related to early sediment dehydration during subduction. The timing and the modality of this geochemical exchange between serpentinites and metasediments remain unclear.

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In the western Alps, the Piedmont zone corresponds to the juxtaposition of different levels of a paleo-subduction zone. From the top to the bottom, we observe the following: (i) the obducted Chenaillet ophiolite; (ii) the Schistes lustrés complex dominated by oceanic sediments; and (iii) the Monviso ophiolite composed of mafic-to-ultramafic rocks related to the deeply subducted oceanic lithosphere. The present-day geometry corresponds to an orogenic wedge tilted to the west. The metamorphic P–T conditions increase eastward from sub-greenschist facies conditions to eclogite facies conditions (Goffé et al., 2004).

Sampling these different levels of the paleo-subduction zone offers the unique opportunity to trace the changes in the chemical composition of serpentinites along a low-temperature metamorphic gradient related to subduction dynamics. In this study, we present whole rock chemical analyses of serpentinites and associated sediments, as well as in situ analyses by laser ablation (LA) coupled with inductively coupled plasma (ICP) mass spectrometry (MS) (LA-ICP-MS) of serpentines. This approach allows: (i) tracing the geochemical evolution of serpentinites; (ii) constraining major and trace element behavior in relation to the structural level of the paleo-subduction zone; and (iii) deciphering the fluid exchange between serpentinites and metasediments during subduction processes.

2. Geological setting

The Piedmont zone of the internal part of the Western Alps (Fig. 1a) was formed by the juxtaposition of continental and oceanic units derived from the distal European margin and the oceanic domain (Lemoine et al., 1986). These units result from the closure of the Ligurian ocean, a part of the Tethys ocean, which occurred from the Late Cretaceous to the Oligocene (Handy et al., 2010). They represent a paleo-subduction zone deformed and metamorphosed under high-pressure and low-temperature conditions (HP-LT) during subduction from Northwest to Southeast. This paleo-subduction complex was exhumed and deformed during the Oligocene collision (Agard et al., 2002; Lardeaux et al., 2006; Tricart and Schwartz, 2006; Schwartz et al., 2009). The Piedmont zone is composed by the association of sediment, mafic and ultramafic lithologies related to the Tethyan oceanic lithosphere. From North to South the following units are outcropping in the piedmont zone: the Chenaillet ophiolite, the Schistes lustrés complex and the Monviso ophiolite. The Chenaillet ophiolite escaped high-pressure and low-temperature (HP-LT) metamorphism and represents a piece of the Tethyan ocean. Presently, the Chenaillet ophiolite lies on the Schistes lustrés complex. The Schistes lustrés complex corresponds to the sedimentary accretionary wedge derived from oceanic sediments (Lemoine et al., 1984). This complex is composed of a west-dipping, ten-kilometer thick nappe stack. Series within the Schistes lustrés complex are composed by heterogeneous metasediments (metamorphic marls, clays, and limestones) enclosing decametric-to-kilometric lenses of oceanic rocks (basalt, gabbro, serpentinite) (Tricart and Lemoine, 1991; Schwartz et al., 2009). The Schistes lustrés complex records blueschist facies conditions (Goffé et al., 2004) and was exhumed and tilted toward the west, generating extensional brittle structures during the Neogene (Tricart et al., 2004). The Monviso ophiolite is mainly composed of mafic and ultramafic rocks originating from the oceanic lithosphere that were strongly deformed and metamorphosed under eclogitic-facies conditions (Lombardo et al., 1978; Schwartz et al., 2000; Angiboust et al., 2011).

Previous studies (Agard et al., 2001; Goffé et al., 2004; Tricart and Schwartz, 2006; Schwartz et al., 2007, 2009; Angiboust et al., 2011) have identified several metamorphic units in the Piedmont zone (Fig. 1b). In this study, six metamorphic Grades have been defined. The Chenaillet ophiolite has recorded sub-greenschist-facies conditions ($200<T<300$ °C; $P<4$ kbar) and corresponds to Grade 0. In the Schistes lustrés complex, four Grades are distinguished, which record an increase of the P–T conditions eastward. In detail, the westward domain presents low-temperature blueschist-facies conditions ($300<T<350$ °C; $9<P<11$ kbar), this domain corresponds to Grade 1. The central domain records medium-temperature blueschist facies conditions, and it is divided into Grade 2 ($340<T<360$ °C; $10<P<12$ kbar) and Grade 3 ($360<T<390$ °C; $10<P<12$ kbar). The eastward domain has recorded high-temperature blueschist facies conditions ($390<T<480$ °C; $P>12$ kbar) and corresponds to Grade 4. In the Monviso ophiolite, all metamorphic assemblages are eclogitic ($T>460$ °C, $P>20$ kbar) and correspond to Grade 5.

In these six metamorphic grade domains, we collected a total of 18 samples including serpentinites and metasediments to investigate the geochemical evolution of serpentinites in each level of the paleo-subduction zone associated with the paleo-thermal gradient recorded during the subduction (Fig. 1b and c; Table 1).

3. Sample description

Eight metasediments (Fig. 1b) were collected, in a west–east transect, in Cretaceous calcareous-schists (Lemoine et al., 1984) derived from foraminifera oozes. Metasediments show lithologic variability owing to different clay versus carbonate fractions in their protoliths. The carbonate contents result from both biogenic production (pelagic foraminifera) and from detrital input (calciturbidites). Due to this high lithological heterogeneity, it is difficult to sample a single lithology all along the transect. The samples are strongly deformed, and the main schistosity is dominated by phengite, quartz, calcite and oxides. Glaucophane and pseudomorphs of lawsonite or zoisite are also present. In the Chenaillet ophiolite, the only sedimentary component corresponds to ophicalcite sediments. Because these sediments have a hydrothermal origin (Lemoine et al., 1983), we do not use them in this study.

Ten serpentinites were sampled from the studied area. Two come from Chenaillet ophiolite, four come from the Schistes lustrés complex and four come from the Monviso eclogitic unit (Fig. 1). These samples were systematically collected in preserved zones in the absence of retrogressed mineral phases. The serpentine mineral identification is described in detail in a companion paper (Schwartz et al., 2013) and was performed using optical and Raman spectroscopy (Table 1). All the serpentinites (Fig. 1b) display morphological oceanic features serpentinites with pseudomorphic textures (Wicks and Whittaker, 1977; Mével, 2003) (Fig. 2). These textures are the result of the remplacement of the primary assemblage (dominated by pyroxene and olivine) by serpentine. The replacement of olivine induces the formation of a mesh texture due to multiple hierarchic micro-fractures and formation of sub-grains. The replacement of pyroxene minerals during hydration of the oceanic lithosphere by oceanic water circulation induces the formation of bastite. The general serpentinization reaction can be expressed as: olivine + enstatite + H_2O = serpentine + magnetite ± brucite (Martin and Fyfe, 1970; Seyfried et al., 2007). Note that in all our samples no brucite was identified. The absence of brucite could be interpreted as the result of a lower degree of olivine hydration with respect to enstatite hydration precluding any release of Mg necessary for the brucite crystallization or alternatively that brucite is consumed during prograde reactions. Lizardite is the dominant phase in serpentinites and replaces the primary olivine and pyroxene, whereas chrysotile is present in veins cross-cutting the mesh texture. Magnetite is occurs as submillimetric veins surrounding mesh and bastite. A clear identification of serpentinite mineral texture provides important information on the nature of the initial peridotite.

Serpentinites ICH01 and ICH02 from Chenaillet (Grade 0) are not deformed, and their original texture is preserved (pseudomorphic texture), with fresh primary pyroxenes and olivines still visible. The samples are mainly dominated by lizardite, showing mesh and replacing, principally, primary olivine due to the circulation of hydrothermal fluids in an abyssal environment. Chrysotile veins crosscut the texture; they may be related to early fluids circulating during oceanic