



Pressure–temperature estimates of the lizardite/antigorite transition in high pressure serpentinites

Stéphane Schwartz ^{a,*}, Stéphane Guillot ^a, Bruno Reynard ^b, Romain Lafay ^a, Baptiste Debret ^c, Christian Nicollet ^c, Pierre Lanari ^a, Anne Line Auzende ^d

^a *IsTerre, Université Grenoble 1, CNRS, F-38041 Grenoble, Cedex 9, France*

^b *Laboratoire de Géologie, Ecole Normale Supérieure de Lyon, CNRS, France, Site Monod, 15 parvis René Descartes, Lyon, F-69342, France*

^c *LMV, Université Blaise Pascal, CNRS, Clermont-Ferrand, France*

^d *IMPMC, Université Pierre et Marie Curie - Sorbonne Universités, 4 place Jussieu, Tour 23, 75252 Paris Cedex 05, France*

ARTICLE INFO

Article history:

Received 23 September 2012

Accepted 24 November 2012

Available online 5 December 2012

Keywords:

Serpentinite

Raman spectroscopy

Lizardite/antigorite transition

Western Alps

ABSTRACT

Serpentine minerals in natural samples are dominated by lizardite and antigorite. In spite of numerous laboratory experiments, the stability fields of these species remain poorly constrained. This paper presents petrological observations and the Raman spectroscopy and XRD analyses of natural serpentinites from the Alpine paleo-accretionary wedge. Serpentine varieties were identified from a range of metamorphic pressure and temperature conditions from sub-greenschist ($P < 4$ kbar, $T \sim 200$ – 300 °C) to eclogite facies conditions ($P > 20$ kbar, $T > 460$ °C) along a subduction geothermal gradient. We use the observed mineral assemblage in natural serpentinite along with the T_{max} estimated by Raman spectroscopy of the carbonaceous matter in associated metasediments to constrain the temperature of the lizardite to antigorite transition at high pressures. We show that below 300 °C, lizardite and locally chrysotile are the dominant species in the mesh texture. Between 320 and 390 °C, lizardite is progressively replaced by antigorite at the grain boundaries through dissolution–precipitation processes in the presence of SiO_2 enriched fluids and in the cores of the lizardite mesh. Above 390 °C, under high-grade blueschist to eclogite facies conditions, antigorite is the sole stable serpentine mineral until the onset of secondary olivine crystallization at 460 °C.

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

Serpentine minerals are phyllosilicates that contain up to 13 wt.% water and form during the hydration of basic to ultrabasic rocks. Hydration commonly takes place in an ocean spreading context, thus documenting chemical exchanges between the oceans and solid Earth (Alt and Shanks, 2003). Serpentinites are also common in blueschist to eclogite facies terranes of oceanic or mantle wedge origin (Hattori and Guillot, 2007). Due to the large metamorphic stability field of serpentinites, it is generally difficult to evaluate the P–T conditions to which they were subjected (e.g., Evans, 2004), but the associated metamorphic rocks permit approximations of the conditions. It is therefore important to accurately and rapidly characterize these common serpentine minerals. Serpentine minerals, which have the simplified structure formulae $(\text{Mg}, \text{Fe}^{2+})_3 \text{Si}_2\text{O}_5(\text{OH})_4$, are made of superposed 1:1 alternating tetrahedral and octahedral sheets. The different spatial arrangements of these layers result in three main serpentine minerals, i.e., lizardite, chrysotile and antigorite. The sheets form flat layers in lizardite, cylinders in chrysotile and corrugated modulated structures in antigorite (Wicks and O'Hanley, 1988). Serpentinites in

high-grade metamorphic terranes indicate that antigorite is the predominant species (Auzende et al., 2002, 2006; Debret et al., 2013; Evans and Trommsdorff, 1978; Groppo and Compagnoni, 2007; Guillot et al., 2009; Li et al., 2004; Mellini et al., 1987; Padron-Navarta et al., 2008; Scambelluri et al., 1995; Trommsdorff et al., 1998). Moreover, experimental studies confirm that antigorite is the stable serpentine mineral under high-pressure conditions (Bromiley and Pawley, 2003; Padron-Navarta et al., 2010; Reynard and Wunder, 2006; Ulmer and Trommsdorff, 1995; Wunder and Schreyer, 1997). Lizardite and chrysotile are the main varieties that are present in low-grade serpentinites from the oceanic lithosphere and from low-grade metamorphic ophiolites (Andréani et al., 2007; Evans, 2004). However, the transition from low-grade to high-grade metamorphic serpentine minerals is poorly constrained. Thermodynamic data predict that above 300 °C, the antigorite + brucite assemblage is more stable than lizardite, and chrysotile is absent (Evans, 2004). Moreover, the antigorite + brucite assemblage is often observed in natural samples, while the chrysotile + brucite assemblage is particularly abundant in retrogressed serpentinites (Baronnet and Belluso, 2002). Thus, further petrological investigations of natural serpentinite samples, where the P–T conditions are well-constrained, are required to refine the relative stability of each variety of serpentine over a wide range of metamorphic conditions. To definitively identify serpentine varieties, transmission electron microscopy (TEM)

* Corresponding author.

E-mail address: stephane.schwartz@ujf-grenoble.fr (S. Schwartz).

is usually required (Auzende et al., 2002; Boudier et al., 2010; Mellini et al., 1985). Indeed, serpentine grains are in some cases only a few microns in size and can display various habitus, which makes optical identification inaccurate. Vibrational Raman spectroscopy is also a powerful method for processing large numbers of complex samples, and numerous studies have been devoted to its use in serpentine characterization (Auzende et al., 2004; Bard et al., 1997; Groppo et al., 2006; Klopogge et al., 1999; Lewis et al., 1996; Rinaudo et al., 2003). In particular, the region of the OH stretching vibrational modes can be conveniently used to discriminate among the different varieties of serpentine (Auzende et al., 2004). The OH stretching modes in the high wavenumber range (approximately 3500 cm^{-1}) of the different serpentines are tentatively described in terms of the curvature of the layers, with potential applications for structural characterization by Raman spectroscopy. Raman spectroscopy permits the characterization of the phases at a micrometer scale of bulk samples or thin sections. To assess the reliability of Raman spectroscopy for identification purposes, we apply it to serpentines in a series of low to high pressure metamorphic serpentinite samples from the western Alps for which TEM characterization have been independently performed (Auzende et al., 2006). The serpentinites are also characterized by X-ray diffraction (XRD) in order to decipher the bulk serpentinite mineralogy.

2. Geological setting

Alpine evolution along the Eurasia-Africa boundary was initially dominated by plate divergence, which induced Mesozoic rifting and oceanic opening. Since Cretaceous time, the plate convergence has resulted in subduction and collision (Dumont et al., 2012; Rosenbaum and Lister, 2005). This study focuses on the Piedmont zone of the south-western Alps (Fig. 1a and b), which is composed of the association of units that originated in the distal European margin and from the nearby oceanic domain (Lemoine et al., 1987) and that were juxtaposed during the subduction and collision in Late Cretaceous to Tertiary times (Tricart, 1984). The Piedmont zone includes different levels of the paleo-subduction zone, preserving the low thermal gradient ($5\text{--}8\text{ }^{\circ}\text{C}/\text{km}$) associated with the subduction dynamics; moreover, it was partially overprinted by Alpine metamorphism conditions (Agard et al., 2002; Schwartz et al., 2001, 2007). At the top of the nappe pile, the Chenaillat massif corresponds to an obducted portion of the Tethyan oceanic lithosphere. This unit rests upon the Queyras Schistes lustrés (Fig. 1c), which represent a fossiliferous sedimentary accretionary wedge developed under blueschist facies conditions during the late Cretaceous–early Eocene subduction of the Tethyan Ocean (Schwartz et al., 2000, 2009; Tricart and Schwartz, 2006), as previously indicated by structural observations further to the north in the same Piedmont zone (Agard et al., 2001; Ganne et al., 2005). This domain derived from Mesozoic oceanic sediments that were primarily composed of marls, clays, and limestones (calcschists). These sediments were strongly deformed and metamorphosed during alpine subduction, and they outcrop today as foliated and polydeformed calcschists enclosing boudinaged meter- to kilometer-sized Jurassic ophiolites (Lagabrielle and Polino, 1988; Tricart and Lemoine, 1986). The P–T conditions increase toward the east, from low-temperature blueschist facies conditions (LT-blueschist) in western Queyras to the transitional conditions between high-temperature blueschist (HT-blueschist) and eclogite facies in eastern Queyras (Agard et al., 2001; Schwartz et al., 2009; Tricart and Schwartz, 2006). This blueschist domain is structurally above the Monviso eclogitic ophiolite. In this massif, the metasedimentary component is very small ($<20\text{ vol.}\%$) relative to the voluminous oceanic lithosphere (Schwartz et al., 2001). The serpentinite bodies are located along detachments and constitute a large volume of the eastern boundary of the massif (Angiboust et al., 2012; Schwartz et al., 2001). The Monviso ophiolite corresponds to the subduction channel (Guillot et al., 2009).

3. Sampling strategy

The Chenaillat–Queyras–Monviso transect is a unique natural laboratory for observing mineral changes in serpentinite along an increasing metamorphism gradient. However, there are no directly applicable thermal calibrations in serpentinites; therefore, we propose to estimate the thermal conditions by applying the method of Raman spectroscopy of carbonaceous material (RSCM) to the metasediments associated with the serpentinites to obtain the T_{max} experienced by the serpentinites. A thermal transect is realized, according to 25 metasediment samples from the Chenaillat to the Monviso (Fig. 1a, Table 1). These sediments are Cretaceous calcschists derived from foraminifera oozes (Deville et al., 1992). The lithology of each sample is not homogeneous due to variation in carbonate-clay proportions. Moreover, the carbonate contents result both from biogenic production (pelagic foraminifera) and from detrital input (calciturbidites). The samples are strongly deformed, and the main schistosity is dominated by phengite, quartz, calcite and oxides. Glauconite and pseudomorphs of lawsonite and zoisite are also present. Along this thermal transect, 8 serpentinites have been studied (Fig. 1a). The serpentinite samples were taken from the cores of hecto-metric serpentinite bodies; these bodies (100 m) were embedded in the metasediments from which the metasediment samples were acquired. These serpentinites escaped alpine deformations and preserved oceanic mesh textures. Sample ICH2 comes from the ophiolitic Chenaillat massif. This sample records a low degree of metamorphic conditions, with sea-floor metamorphism (Mével et al., 1978) overprinted by sub-greenschist facies conditions ($P < 4\text{ kbar}$; $T \sim 200\text{--}300\text{ }^{\circ}\text{C}$; Goffé et al., 2004) related to alpine metamorphism. Sample CR02 comes from the Cristillan massif at the western boundary of the Schistes lustrés complex in the LT-blueschist domain (Fig. 1). Two samples come from the medium-temperature blueschist domain (MT-blueschist) of the Schistes lustrés complex: RQ23 from the Rocca Nera massif and RQ16 from the Eychassier massif. Samples BB01 (Bric Bouchet massif) and RQ01 (Traversette massif) come from the HT-blueschist domain of the Schistes lustrés complex. The samples Vi01 and Vi02 come from the Monviso eclogitic ophiolite.

4. Temperature estimates from Raman spectroscopy of carbonaceous material (RSCM)

4.1. Analytical conditions

Raman spectroscopy on carbonaceous material (RSCM) is based on the quantitative degree of graphitization of the organic material during regional metamorphic processes. The graphitization phenomenon corresponds to the solid-state transformation of organic matter into carbonaceous material. The structure of carbonaceous matter is not sensitive to the retrograde history related to the exhumation of metamorphic rocks. The progressive graphitization process can be used to estimate the peak temperature (T_{max}) reached by a given sample (Beyssac et al., 2002, 2003). The degree of graphitization appears to be independent of the metamorphic pressure, although a minimum pressure is required for the graphitization process to take place (Quirico et al., 2009). This thermometer is based on the quantification of the degree of ordering of the carbonaceous material, using the R2 area ratio between the G, D1 and D2 bands ($R2 = D1/[G + D1 + D2]$) extracted from the Raman spectra (Beyssac et al., 2002). The R2 ratio is linearly correlated with the T_{max} of the metamorphic cycle ($T_{\text{max}}(^{\circ}\text{C}) = -445 \times R2 + 641$). This correlation may be used as a thermometer with an intrinsic error calibration of $50\text{ }^{\circ}\text{C}$ due to the petrological data used for calibration and a precision of approximately $15\text{ }^{\circ}\text{C}$ (Beyssac et al., 2007).

Raman spectroscopy was performed at the ENS-Lyon using a Horiba Jobin-Yvon LabRam HR800 apparatus. The excitation was provided by an argon laser with a wavelength of 514 nm . An Olympus™ BX30 open microscope equipped with a $\times 100$ objective lens was

Download English Version:

<https://daneshyari.com/en/article/4716260>

Download Persian Version:

<https://daneshyari.com/article/4716260>

[Daneshyari.com](https://daneshyari.com)