Lithos 178 (2013) 96–127

Contents lists available at ScienceDirect

Lithos

journal homepage: www.elsevier.com/locate/lithos

Invited review article

Geochemistry of subduction zone serpentinites: A review

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ARTICLE INFO

Article history:
Received 5 October 2012
Accepted 31 May 2013
Available online 11 June 2013

Keywords:
Subducted serpentinites
Mantle wedge serpentinites
Abyssal peridotites
Serpentine phases
Subduction zones
Geochemistry

ABSTRACT

Over the last decades, numerous studies have emphasized the role of serpentinites in the subduction zone geodynamics. Their presence and role in subduction environments are recognized through geophysical, geochemical and field observations of modern and ancient subduction zones and large amounts of geochemical database of serpentinites have been created. Here, we present a review of the geochemistry of serpentinites, based on the compilation of ~900 geochemical data of abyssal, mantle wedge and exhumed serpentinites after subduction. The aim was to better understand the geochemical evolution of these rocks during their subduction as well as their impact in the global geochemical cycle.

When studying serpentinites, it is essential to determine their protoliths and their geological history before serpentinization. The geochemical data of serpentinites shows little mobility of compatible and rare earth elements (REE) at the scale of hand-specimen during their serpentinization. Thus, REE abundance can be used to identify the protolith for serpentinites, as well as magmatic processes such as melt/rock interactions before serpentinization. In the case of subducted serpentinites, the interpretation of trace element data is difficult due to the enrichments of light REE, independent of the nature of the protolith. We propose that enrichments are probably not related to serpentinization itself, but mostly due to (*sedimentary-derived*) fluid/rock interactions within the subduction channel after the serpentinization. It is also possible that the enrichment reflects the geochemical signature of the mantle protolith itself which could derive from the less refractory continental lithosphere exhumed at the ocean–continent transition.

Additionally, during the last ten years, numerous analyses have been carried out, notably using in situ approaches, to better constrain the behavior of fluid-mobile elements (FME; e.g. B, Li, Cl, As, Sb, U, Th, Sr) incorporated in serpentine phases. The abundance of these elements provides information related to the fluid/rock interactions during serpentinization and the behavior of FME, from their incorporation to their gradual release during subduction. Serpentinites are considered as a reservoir of the FME in subduction zones and their role, notably on arc magma composition, is underestimated presently in the global geochemical cycle.

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0024-4937/$ – see front matter
http://dx.doi.org/10.1016/j.lithos.2013.05.019

1. Introduction

Serpentinites (hydrated ultramafic rocks) and the processes of serpentinization have attracted much attention over the last two decades, and interest in these rocks continues unabated. It has recently been posited that the occurrence of serpentinites, specifically in subduction zones, could have important implications for the Earth's dynamic and global geochemical cycle (e.g. Hattori and Guillot, 2003; Hilairet et al., 2007). However, deciphering the origin of the serpentinites and the causalities of serpentinization remains a challenge as the onset of this particular process mostly occurs at the seafloor (near mid-ocean ridges, MOR) and continues during subduction of abyssal serpentinites and peridotites; moreover mantle wedge serpentinites are produced by fluids released from the subducting slab. A large number of high quality bulk rock compositions, as well as in situ geochemical data on serpentine phases, have now become available and hence correspond to a fully representative set of serpentinite compositions worldwide (see references through the text; Section 2.4). In this context, the present manuscript attempts to review the available geochemical data of abyssal peridotites and subduction zone-related serpentinites, including subducted and metamorphosed serpentinites and mantle wedge–forearc serpentinites. This review paper will emphasize the role of serpentinites on chemical cycling in subduction zones, and in doing so perhaps broach new concerns for the forthcoming studies.

This paper aims: (i) to review and to provide comprehensive geochemical compositions of serpentinites, as well as serpentine phases, in order to depict the influence and significance of protolith; (ii) to evaluate the role of fluid-mobile element (FME) compositions as tracers of fluid/rock interactions in geodynamic contexts and processes (temperature (T), pressure (P), redox conditions); and finally, (iii) to discuss the active role of serpentinites upon the global geochemical cycle in subduction zones. Notably, we summarize observations about interactions between various lithologies in the subducted slab and serpentinites into the subduction channel, and the fluids and fluid-mobile elements released during their metamorphism. We are fully aware about the non-exhaustive review of this synthesis and we refer the reader to the many outstanding studies cited below.

1.1. Subduction zones

Subduction zones are one of the most challenging geological contexts in Earth sciences. Since the first reference to these particular environments six decades ago (Amstutz, 1951), numerous studies have been undertaken in order to constrain their geophysical and geochemical signatures (see Stern, 2002, for a review). Subduction zones and oceanic convergent boundaries represent a total length of around 67,500 km (Bird, 2003; Lallemand, 1999). As a weak and buoyant mineral, and its broad P–T stability field, a serpentine mineral can play a key role in the dynamics of subduction zone, notably on the triggering of earthquakes, exhumation of HP to UHP rocks, and probably initiation of subduction itself (Hirth and Guillot, 2013). One of the most important features of subduction zones is the recycling of hydrated lithologies back into the mantle, the so called "subduction factory" (Tatsumi, 2005). This recycling mechanism has important consequences into the global geochemical cycling as well as on the dynamics of the Earth. Due to the downgoing movement of the hydrated oceanic lithosphere and its heating related to prograde metamorphism, fluids are progressively released from the slab. These fluids are considered to trigger partial melting within mantle wedge leading to arc magmatism (e.g. Green, 2007; Tatsumi et al., 1986). In this context, subduction-related metamorphism will play a major role in the dynamics, chemistry and rheology of subduction zones. Numerous studies were conducted in order to determine the water budget of the subducting lithosphere and the timing of water released (e.g. Rüpke et al., 2002; Schmidt and Poli, 1998; Van Keken et al., 2011). Dehydration mostly occurs during the first 100 to 170 km of subduction, depending on the geothermal gradient, and is related to the stability of key hydrous phases such as amphiboles (Pawley and Holloway, 1993; Poli and Schmidt, 1995) and serpentines (Ulmer and Trommsdorff, 1995; Wunder and Schreyer, 1997; Fig. 1a).

1.2. Water: an important component in subduction zone

Water is one of the most important components in subduction zone and its geochemical cycle. Water can be transported, and recycled, at different depths when it is stored into subducted sediments, and to a lesser extent in the oceanic lithosphere. Under the effect of subduction-related prograde metamorphism, water can also be released into the overlying mantle wedge and react with mantle peridotites to form hydrous minerals. Water is present in different forms: (1) molecular (H_2O) in magmas and/or silicate fluids released from the slab, (2) hydroxyl (OH^-) as part of hydrous phases (e.g. chlorite, amphibole, serpentine), (3) hydrogen as point defects in nominally