Earth and Planetary Science Letters 499 (2018) 173–184

Contents lists available at ScienceDirect

Earth and Planetary Science Letters

www.elsevier.com/locate/epsl

The influence of oceanic oxidation on serpentinite dehydration during subduction

Annette Bretscher, Joerg Hermann, Thomas Pettke *

University of Bern, Institute of Geological Sciences, Baltzerstrasse 1&3, CH-3012 Bern, Switzerland

ARTICLE INFO

Article history:
Received 1 February 2018
Received in revised form 12 July 2018
Accepted 12 July 2018
Available online xxxx
Editor: T.A. Mather

Keywords:
subduction
serpentinite
redox
metamorphic dehydration
mineral chemistry
oceanic alteration

ABSTRACT

Serpentinites are central to carry water and fluid-mobile elements down subduction zones. The breakdown of antigorite represents the most prominent aqueous fluid release, boosting fluid-mediated element cycling from the slab to the mantle wedge. At Cerro del Almirez, Spain, an antigorite dehydration reaction front is preserved in subducted serpentinites. Bulk rock and mineral major element chemistry linked to detailed petrography reveals that silicate mineral Mg# (100*[Mg/(Mg+Fe)]$_{\text{molar}}$) are higher than bulk rocks due to the presence of magnetite, and olivine Mg# are lower in Chl-harzburgite than in Atg-serpentinite. The amount of magnetite is lower in Chl-harzburgite (1.4 vol%) than in Atg-serpentinite (2.8 vol%), resulting in reactive bulk rock compositions with Mg# of 92.7 and 96.0, respectively. Pseudosection modelling employing these reactive bulk compositions yields a small temperature field at 670 °C, 1.6 GPa where Atg-serpentinite and Chl-harzburgite coexist at the same metamorphic conditions. Thus, the antigorite dehydration front represents a compositional boundary rather than a thermal front (isograd). We suggest that this compositional boundary represents an oxidation front established upon serpentinisation at the ocean floor. Previous studies have shown that with increasing extent of serpentinisation increasing amounts of magnetite are formed concomitant with an increase in the Mg# of coexisting silicates. During subduction of such heterogeneous ultramafic rocks antigorite dehydration will be a continuous reaction that can occur over up to ∼40 °C, controlled by variations in Mg# of the reactant silicates. The difference in the amount of magnetite between Atg-serpentinite and Chl-harzburgite is thus not related to a change in redox budget of subducting serpentinites at Almirez imposed by the antigorite dehydration reaction. Rather, mass balance considerations suggest that ferric iron from antigorite may actually be the most prominent contribution to the redox budget of the antigorite dehydration reaction. Our findings also imply that direct comparison between Atg-serpentinites and Chl-harzburgites to infer geochemical changes associated with prograde dehydration reactions may lead to erroneous conclusions, including estimates on element loss mediated by aqueous fluid escape and associated changes in redox budget based on Fe^{3+}/Fe_{tot}.

1. Introduction

Serpentinites play a major role in the fluid-mediated element cycling in subduction zones, owing to their capacity of carrying water and fluid mobile elements to subarc depths (e.g., Ulmer and Trommsdorff, 1995; Scambelluri and Philippot, 2001; Rüpke et al., 2004; Scambelluri et al., 2004, 2014; Hattori and Guillot, 2007; Kendrick et al., 2011, 2013; Deschamps et al., 2013). Upon serpentinite dehydration (antigorite-out and chlorite-out reactions) occurring somewhere between ∼50 and 150 km depth (e.g., Ulmer and Trommsdorff, 1999), up to 13 wt% H_2O (depending on the degree of initial hydration) along with fluid mobile elements are released (van Keken et al., 2011), to eventually trigger arc magmatism via fluid-fluxed melting in the overlying mantle wedge, and to affect rheological and seismic properties of the subducting slab and the slab to wedge interface (e.g., Spandler and Pirard, 2013; Konrad-Schmolke et al., 2016).

Hydrated mantle rocks are among the simplest rock compositions to study metamorphic dehydration reactions when compared to metapelitic or metamafic rocks. In mafic and pelitic rocks, there is a large variation in bulk rock composition, especially in the Mg# (100*[Mg/(Mg + Fe)]$_{\text{molar}}$, where all Fe is considered to be Fe^{2+}), leading to continuous dehydration reactions over large temperature intervals (Thompson, 1976). In contrast, hydrated mantle rocks such as serpentinites have a limited compositional range and Mg# is nearly constant at 90 (Niu, 2004). Because of this high Mg#,

---

* Corresponding author.
E-mail address: pettke@geo.unibe.ch (T. Pettke).

https://doi.org/10.1016/j.epsl.2018.07.017

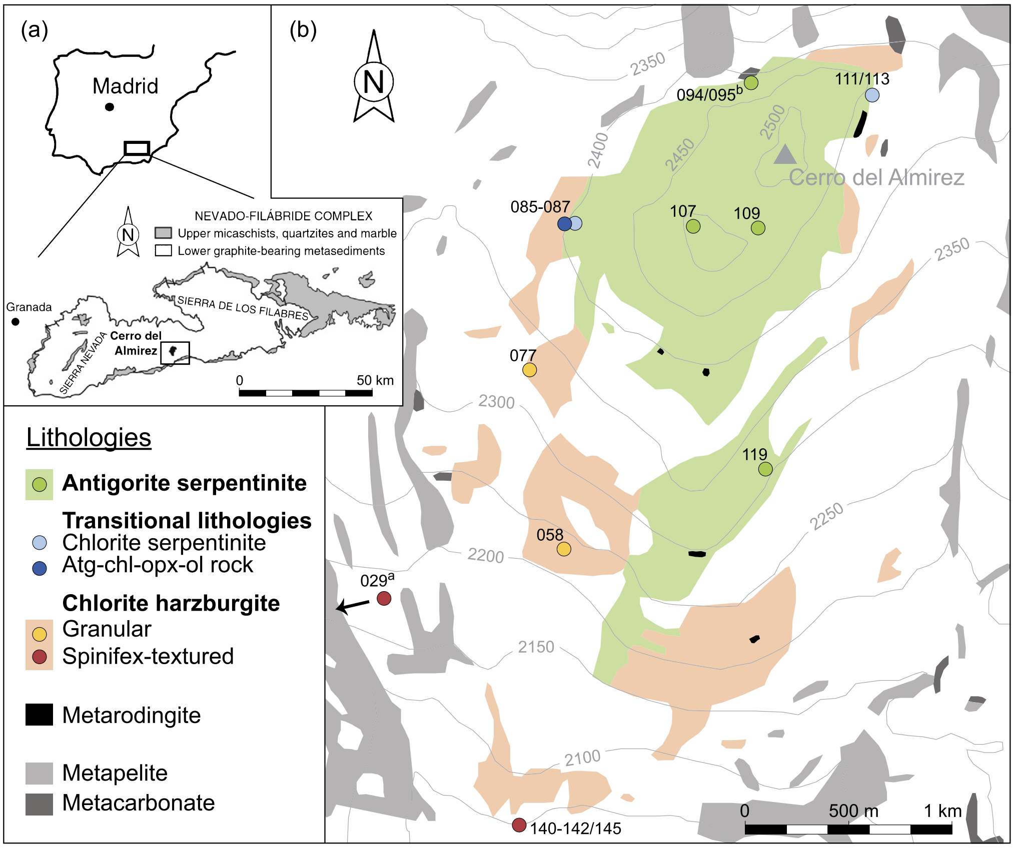

Fig. 1. (a) Geological overview map. The Nevado-Filábride Complex in the Betic Cordillera (southern Spain) with the location of Cerro del Almirez ultramafic body (taken from Marchesi et al., 2013). (b) Geological outcrop map of the main ultramafic body at Cerro del Almirez (coloured lithologies: Atg-serpentinites, transitional lithologies and Chl-harzburgites) and associated metarodingites and metasediments (redrawn from Schönbächler, 1999). Colour-coded dots and numbers represent ultramafic rocks investigated in detail in this study (Alm06-XXX). The Chl-harzburgite sample Alm06-029 was taken from one of the two minor Chl-harzburgite bodies located to the west of the main body. Samples taken from boulders are marked with a "b" in the exponent.

phase relations in serpentinites have often been approached in the simplified $MgO–SiO_2–H_2O$ (MSH) system (e.g., Ulmer and Trommsdorff, 1999; Wunder and Schreyer, 1997), resulting in univariant (discontinuous) dehydration reactions. However, results obtained from experimental petrology using a natural serpentinite composition (e.g., Ulmer and Trommsdorff, 1995) and, specifically, on the effect of Mg# on serpentine dehydration (Padrón-Navarta et al., 2010), as well as calculations on the increase of serpentine stability by incorporation of Al (Padrón-Navarta et al., 2013) all indicate that small variations of bulk rock compositions may influence the positions and temperature intervals of dehydration reactions.

Variations in bulk rock composition of mantle rocks are mainly driven by melt depletion trends, leading to reduction in Al and Ca and a small increase in Mg# (e.g., Niu, 2004). It has been proposed that the major element bulk rock composition of hydrated mantle rocks largely corresponds to its precursor peridotite except for addition of carbonates and H_2O and possible loss of CaO in case of carbonate-free serpentinites (e.g., Niu, 2004). However, ocean floor hydration of peridotites can significantly modify the distribution of major elements between minerals, including the formation of magnetite, hydrous silicates such as brucite [$(Mg,Fe)(OH)_2$] and chlorite, and sometimes carbonates (e.g., Kodolányi et al., 2012) and therefore generates significant heterogeneity at mm to km scales along with orders of magnitude variations in trace element signatures (e.g., Bonatti et al., 1984; Kodolányi et al., 2012; Niu, 2004; Paulick et al., 2006; Savov et al., 2005).

In this paper we address the question to what extent chemical variations induced by serpentinisation and oxidation at the seafloor influence metamorphic dehydration reactions during subduction. We investigated the well-studied locality at Cerro del Almirez (Betic Cordillera, S-Spain), where a contact between Atg-serpentinite and Chl-harzburgite is preserved in subducted ultramafic rocks. This field occurrence has thus become the type locality to study the petrology (Padrón-Navarta et al., 2010; Trommsdorff et al., 1998), and the evolution of chemistry and parameters (e.g., redox, element mobility in antigorite dehydration fluid) across the antigorite-out reaction by a simple comparison between reactant Atg-serpentinites and product Chl-harzburgites (e.g., Alt et al., 2012, 2013; Debret et al., 2014, 2015; Garrido et al., 2005; Harvey et al., 2014; Marchesi et al., 2013; Padrón-Navarta et al., 2010, 2011; Scambelluri et al., 2004). We performed detailed petrography, bulk rock and mineral chemistry and combined this with thermodynamic modelling, in order to evaluate the role of changing magnetite contents acquired during oceanic serpentinisation of the mantle rocks on the nature of the reaction front at high pressures from Atg-serpentinite to Chl-harzburgite at Cerro del Almirez.

2. Geological setting

The hydrous mantle rock units at Cerro del Almirez belong to the Nevado-Filábride Complex, the lowermost tectonometamorphic unit of the Internal Zone of the Betic Cordillera (southern Spain; Fig. 1), being part of the Betic Ophiolite Association that represents exhumed slices of the Piemont-Ligurian Ocean (Puga et al., 1999; Trommsdorff et al., 1998). The Almirez Atg-serpentinites and Chl-harzburgites occur intercalated with metasediments (quartzite, micaschist, marble) and, locally, orthogneiss (Schönbächler, 1999).