Lithos 232 (2015) 23–34

Contents lists available at ScienceDirect

Lithos

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

Water in orthopyroxene from abyssal spinel peridotites of the East Pacific Rise (ODP Leg 147: Hess Deep)

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ARTICLE INFO

Article history:
Received 13 January 2015
Accepted 24 June 2015
Available online 30 June 2015

Keywords:
East Pacific Rise
Geothermometry
Infrared spectroscopy
Nominally anhydrous minerals
Orthopyroxene water content
Upper mantle

ABSTRACT

Abyssal spinel peridotites from Hess Deep, East Pacific Rise (ODP Leg 147) were investigated concerning their major, minor, and trace element mineral chemistry and the incorporation of structural water in orthopyroxene. The rocks are partially serpentinized harzburgites containing primary minerals of olivine, orthopyroxene, clinopyroxene, and spinel. Orthopyroxene is enstatitic with Mg# (Mg/(Mg + Fe)) between 0.90 and 0.92 and Al_2O_3 from 0.5 to 2.9 wt.%. The residual harzburgite experienced high degrees of melt removal in the spinel peridotite stability field. The average degree of partial melting was calculated to be 17.5% (range: 16.4–17.8%). Trace element data of ortho- and clinopyroxenes reflect this strong depletion, characteristic for the restitic nature of abyssal peridotites. Mantle re-equilibration temperatures around 1000 °C indicate that, after melt extraction and before exhumation to the ocean floor, the rocks experienced significant cooling in the spinel peridotite facies. Water contents of orthopyroxene range from 86 to 233 wt. ppm H_2O with an average concentration of 142 wt. ppm H_2O. These results represent the first data on water contents in the sub-pacific mantle obtained by direct measurements of sub-oceanic peridotite. The water contents are not related to mineral chemistry, stratigraphy, melting degree, mantle equilibrium conditions or oxidation state. Calculated post-melt peridotite water contents vary between 40 and 100 wt. ppm H_2O.

Compared to Mid-Atlantic Ridge peridotites, the East Pacific Rise samples of Leg 147 contain somewhat lower water concentrations than samples from Leg 153 and considerably higher contents than those of Leg 209 (Gose et al., 2009; Schmädicke et al., 2011). In Leg 147, the strongest OH absorbtion band occurs at 3420 cm^{-1}, wheras orthopyroxene from MAR peridotite (Legs 153 and 209) has its strongest absorbtion band at 3566 and 3522 cm^{-1}. The mantle equilibrium temperature of Leg 147 peridotites is lower than that of Leg 209 (~1250 °C) but close to that of Leg 153 samples (950–1000 °C). The high degree of partial melting of Leg 147 peridotite samples overlaps with the Leg 209 samples. In accordance to this data we conclude that in order to obtain relatively high water contents of up to 233 wt. ppm in depleted peridotite, after melt removal water must have re-entered the orthopyroxene structure. We suggest that re-equilibration of water contents took place under spinel-facies conditions before exhumation of the tectonite, since elevated temperatures enhance diffusion and elevated pressures facilitate hydrogen uptake. The extended time span between melt removal and uplift inferred from significant isobaric cooling of at least 200 K at spinel-facies depth facilitates re-equilibration of water contents and may explain the high concentrations. Exhumation from spinel-facies depth was fast and accompanied by further cooling such that re-equilibration to lower pressure assemblages and decompression-induced water loss were prevented.

1. Introduction

Most minerals of the Earth's upper mantle contain small amounts of hydrogen incorporated as protons attached to oxygen anions in the mineral structure, thereby forming hydroxyl defects (Bell and Rossman, 1992). The incorporation of protons, colloquially 'water', can be charge-compensated by either metal vacancies or coupled substitutions (Kohlstedt and Mackwell, 1999). Holding up to several hundred wt. ppm H_2O incorporated in its crystal structure, orthopyroxene as a nominally anhydrous mineral (NAM) is considered to be an important host for water in the upper mantle (Bell and Rossman, 1992; Grant et al., 2007; Hirschmann et al., 2005; Peslier, 2010). The amount of water in mantle minerals is of substantial importance influencing electrical conductivity, seismic, and rheological properties (e.g. Hirth and

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http://dx.doi.org/10.1016/j.lithos.2015.06.011

Kohlstedt, 1996; Karato, 1990). Also, water promotes mantle convection by reducing the viscosity and enhances melt production by lowering the solidus temperature (Asimow and Langmuir, 2003).

Experiments have shown that the amount of incorporated water in orthoenstatite is positively correlated to pressure. Under water-saturated conditions, a maximum water content of 867 ± 35 wt. ppm H_2O is reached at 75 kbar and 1100 °C before declining again towards higher pressures (Rauch and Keppler, 2002). Between 10 and 100 kbar increasing temperatures also enhance water solubility in orthopyroxene (Mierdel and Keppler, 2004). Furthermore it has been demonstrated experimentally that trivalent cations such as aluminum, chromium, or ferric iron enhance hydrogen incorporation by coupled substitutions (Stalder, 2004). However, the simultaneous presence of various trivalent cations reduces the solubility of hydrogen by the formation of anhydrous Tschermaks-analogue components (Stalder et al., 2005), a process that is more readily performed at high pressures (Prechtel and Stalder, 2012).

An important question is, whether natural mantle minerals retain their original water concentration during uplift from the upper mantle to the Earth's surface or lose water due to decompression. In contrast to the fast dehydration kinetics of olivine (Mackwell and Kohlstedt, 1990), which may lead to decompression-induced water loss as documented by olivine grains with hydrogen contents decreasing from core to rim (Peslier and Luhr, 2006; Peslier et al., 2015), loss of hydrogen in pyroxenes is generally slower (Ingrin et al., 1995; Stalder and Skogby, 2002). Although the oxidation of iron serves as an important hydrogen extraction mechanism (Skogby and Rossman, 1989), other trivalent cations such as aluminum and chromium, which are abundant in natural orthopyroxenes, reduce hydrogen mobility considerably, such that hydrogen diffusion presumably depends on the ratio of these trivalent elements (Stalder and Behrens, 2006).

Another comparative investigation of natural orthopyroxene and olivine of spinel peridotite xenoliths from Simcoe (USA) and Mexico revealed consistent and reproducible water contents in orthopyroxene but highly variable contents in coexisting olivine (Peslier and Luhr, 2006; Peslier et al., 2002). This was ascribed to hydrogen loss in olivine during ascent. Orthopyroxene grains of the same sample showed no signs of water loss as demonstrated by the lack of hydrogen diffusion profiles in the single grains. Moreover, loss of hydrogen was excluded for orthopyroxene, since water contents could be correlated to various chemical parameters such as whole rock Al_2O_3 or Fe^{3+} content in spinel, which are not disturbed by xenolith uplift (Peslier et al., 2002). Thus, the authors concluded that orthopyroxene in contrast to olivine is rather immune to water loss during xenolith transport, implying that they preserve their original mantle water (Peslier and Luhr, 2006).

A recent paper by Warren and Hauri (2014) confirms these findings. They analyzed and compared water concentrations in peridotites from various locations using SIMS (secondary ion mass spectrometry) and concluded that olivines in orogenic and abyssal peridotites have diffusively lost water as demonstrated by disequilibrium between olivine and coexisting pyroxenes, which in contrast preserved their high-temperature water contents.

The results from laboratory experiments and the study of natural mantle rocks suggest that orthopyroxene can be considered a useful indicator for the content of water and its distribution in the Earth's upper mantle. Most samples investigated so far are derived from the subcontinental mantle (Bell and Rossman, 1992; Rossman, 1996; Peslier et al., 2002; Bell et al., 2004; Grant et al., 2007; Sundvall and Stalder, 2011; Peslier et al., 2012). Information on the sub-oceanic mantle is limited to few investigations of abyssal peridotites from Gakkel Ridge, the South-West Indian Ridge (SWIR), and the Mid-Atlantic Ridge (MAR): While orthopyroxenes from Gakkel Ridge analyzed by FTIR contain between 25 and 60 ppm H_2O (Peslier et al., 2007), the water contents of SWIR orthopyroxenes analyzed by SIMS vary between 9 and 198 ppm H_2O, not including two highly altered samples with values of 289 and 378 wt. ppm H_2O (Warren and Hauri, 2014). Samples derived from two locations at the MAR also analyzed by FTIR reveal highly different water contents. Orthopyroxenes from depleted MAR peridotites sampled near 23°N reveal high water contents of 170–260 wt. ppm H_2O (Gose et al., 2009) resembling values obtained from continental mantle samples. In contrast, MAR peridotites from near 15°N contain extremely water-poor orthopyroxene accommodating about 15 wt. ppm water (Schmädicke et al., 2011). The data were interpreted to reflect primary upper mantle concentrations not being influenced by decompressional water loss (Gose et al., 2011). However, differences in the degree of partial melting could not explain the contrasting water contents between the two locations which instead may have resulted from different mantle residence times, i.e. the time span between melt removal and exhumation (Schmädicke et al., 2011). This model is supported by significantly differing post-melting mantle equilibrium temperatures comparing Leg 153 (950–1000 °C) and Leg 209 (~1250 °C) peridotites. In the case of Leg 153, isobaric cooling by ≥300 K, from melting temperature to the subsequent mantle equilibrium temperature, requires a relatively long mantle residence time enabling water contents to re-equilibrate (Schmädicke et al., 2011).

To further evaluate the thesis of water contents being influenced by different mantle residence times, in this study a set of harzburgites from the fast-spreading East Pacific Rise (EPR) sampled during the Ocean Drilling Program (ODP) Leg 147 cruise is examined. The samples are analyzed for major and trace elements, water in orthopyroxene, and equilibrium temperatures and melting history are modeled. A main objective of this study is to evaluate if water contents of orthopyroxene relate to specific geologic variables such as mineral chemistry, degree of melt removal, or temperature and pressure re-equilibration conditions reflecting the subsequent, pre-exhumation state of the mantle source region. The findings are compared to abyssal peridotites drilled along the slow-spreading Mid-Atlantic Ridge (Legs 153 and 209) and the South-West Indian Ridge.

2. Geological setting and samples

As a former triple junction between the Cocos-Nazca-Ridge and the EPR, the Hess Deep exposes dismembered crustal sections created by a fast-spreading center (65 km/m.y.; Lonsdale, 1988) on the ocean floor and represents a tectonic window to the lithosphere. The crustal sections at Leg 147 sites 894 (2°18.0′N, 101°31.5′W) and 895 (2°16.6′N, 101°26.7′W) were generated at the former ridge axis and are between 0.3 and 1.0 million years old (Lonsdale, 1988). Hess Deep is the deepest part of a westward-propagating rift valley opening up the Eastern flank of the equatorial EPR in advance of the propagating Cocos-Nazca spreading center. The western end of the rift valley is located 30 km from the EPR axis, where the crust is broken by two 5 km wide grabens that again join a few kilometers further east. As the rift valley extends eastward, it broadens to 20 km and deepens to over 5400 m below sea level (mbsl). Its uplifted shoulders rise to depths less than 2200 mbsl. Approximately 70 km east of the EPR axis, the Cocos-Nazca spreading center begins to build a volcanic ridge in the rift valley (Lonsdale, 1988). Site 895 is located along the slope south of the intra rift crest. The site consists of six holes, 895A through 895F, penetrating a total of 272.9 m and recovering 64.56 m of rock (Gillis et al., 1993). The recovered ultramafic rocks predominantly consist of dunite and harzburgite, and intercalated, less abundant mafic rocks such as gabbro, olivine gabbro, and troctolite (Fig. 1). These shallow mantle lithologies are interpreted as representing the upper mantle just below the mantle-crust-boundary, i.e. the petrologic Mohorovičić discontinuity (Gillis et al., 1993). The intrarift-ridge represents a tectonic block of largely plutonic rocks with a complex internal structure including dikes of gabbros and massive serpentinized peridotites, exposed and locally uplifted during the opening of the rift (Dick and Natland, 1996). These serpentinized peridotites directly lying on the seafloor provide insights into mantle dynamic processes. Late stage melt migration can