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The effect of fluorine on the stability of wadsleyite: Implications for the nature and depths of the transition zone in the Earth's mantle

Tobias Grützner[a,*], Stephan Klemme[a], Arno Rohrbach[a], Fernanda Gervasoni[a,b], Jasper Berndt[a]

[a] Institut für Mineralogie, Universität Münster, Corrensstrasse 24, 48149 Münster, Germany
[b] Faculdade de Ciências e Tecnologia, Universidade Federal de Goiás – UFG, Goiânia, GO, Brazil

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ABSTRACT

The Earth's mantle contains significant amounts of volatile elements, such as hydrogen (H), carbon (C) and the halogens fluorine (F), chlorine (Cl) and bromine (Br) and iodine (I). There is a wealth of knowledge about the global cycling of H and C, but there is only scant data on the concentrations of halogens in different Earth reservoirs and on the behavior of halogens during recycling in subduction zones. Here we focus on the storage potential of F in deeper parts of the Earth's mantle. The transition zone is a region in the Earth's mantle (410–660 km) known for its high water storage capacity, as the high pressure polymorphs of olivine, wadsleyite and ringwoodite are known to be able to incorporate several per-cent of water. In order to assess potential fractionation between water and F in the transition zone of the Earth's mantle, we set out to investigate the storage capacity of the halogen F in wadsleyite and olivine at transition zone conditions. Experiments were performed in a simplified mantle composition at temperatures from 1400 °C to 1900 °C and pressures from 17 up to 21 GPa in a multi anvil apparatus. The results show that F can shift the olivine–wadsleyite transition towards higher pressure. We find that F has an opposing effect to water, the latter of which extends the transition zone towards lower pressure. Moreover, the F storage capacity of wadsleyite is significantly lower than previously anticipated. F concentrations in wadsleyite range from 1470 ± 60 μg/g to 2110 ± 600 μg/g independent of temperature or pressure. The F storage capacity in wadsleyite is even lower than the F storage capacity of forsterite under transition zone conditions, and the latter can incorporate 3930 ± 140 μg/g F under these conditions. Based on our data we find that the transition zone cannot be a reservoir for F as it is assumed to be for water. Furthermore, we argue that during subduction of a volatile-bearing slab, fractionation of water from F will occur, where water enters preferentially the transition zone and F remains in the peridotite of the lowermost upper mantle.

1. Introduction

Volatiles are known to strongly affect fractional crystallization of magmas, viscosity of melts, and rheology of mantle minerals (e.g. Bell et al., 2004; Bolfan-Casanova, 2005; Peslier, 2010). It is, therefore, of great importance to understand the distribution, cycling and recycling mechanisms of water and other volatiles, such as N, C, and the halogens (F, Cl, Br and I) in the Earth's mantle.

Numerous studies focused on the deep water cycle and its role in Earth's mantle processes. This is justified by the fact that water is probably the most abundant and consequently also the most important volatile component in the deep Earth (e.g. Bolfan-Casanova, 2005; Hirschmann, 2006; Peslier, 2010; Hirschmann and Kohlstedt, 2012).

The Earth's transition zone at 410 to 660 km depth has the highest water storage capacity in the deep Earth. Inoue (1994) and Kohlstedt et al. (1996) could show that wadsleyite, the high-pressure polymorph of olivine stable between 410 km and 520 km can store up to 3.3 wt.% H_2O by replacing oxygen with OH-groups (Smyth, 1987, 1994). Ringwoodite, the second high-pressure polymorph of olivine, is stable in the lower transition zone at 520 km to 660 km. It can store up to 2.7 wt.% of H_2O (Kohlstedt et al., 1996; Bolfan-Casanova, 2000; Ohtani et al., 2000). It has been, therefore, assumed that the transition zone is a water-rich reservoir, which is fed mainly by recycled water from subduction zones (e.g. Bercovici and Karato, 2003; Smyth and Jacobsen, 2006). Ex-

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* Corresponding author.
E-mail addresses: tobias.gruetzner@wwu.de (T. Grützner), stephan.klemme@wwu.de (S. Klemme), arno.rohrbach@wwu.de (A. Rohrbach), gervasoni.fe@gmail.com (F. Gervasoni), jberndt@wwu.de (J. Berndt).

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perimental results at realistic transition zone temperatures and pressures from Demouchy et al. (2005) and Ohtani et al. (2000) indicate that the transition zone may not be saturated in water because the water storage capacity of the transition zone decreases dramatically with increasing temperature. Nevertheless water-rich natural ringwoodite (with 1.4 wt.% H_2O) has lately been found as an inclusion in a Brazilian diamond (Pearson et al., 2014). This finding confirms more than four decades of experimental work and indicates that the transition zone is indeed, at least in some regions, hydrous.

However, there are other important volatile elements such as carbon, sulfur, nitrogen or the halogens, which may have similar effects on the aforementioned mantle processes, but much less is known about the storage of these volatiles in the Earth's upper mantle and in the transition zone (e.g. Straub and Layne, 2003; Pyle and Mather, 2009; for halogens). Here we focus on Fluorine (F), which is probably the most abundant halogen in the Earth's mantle (McDonough and Sun, 1995) and with its ionic charge and radius F^- resembles OH^- (Shannon, 1976). It is anticipated that the Earth's mantle contains about 10 times more water than F (ca. 25 μg/g F vs. 50–200 μg/g H_2O in the primitive mantle; McDonough and Sun, 1995). Nevertheless, it has been argued that in subduction zones, 95% of the subducted F is transported down to mantle depths (Straub and Layne, 2003), where it is either stored in nominally F-free mantle minerals of the mantle wedge (e.g., Beyer et al., 2012, 2016; Grützner et al., 2017b) or it is transported into deeper parts of the mantle, perhaps even into the transition zone or the lower mantle (Grützner et al., 2017a).

Roberge et al. (2015) were first to address the role of F in the transition zone. At relatively low temperatures ($T = 1100$–$1400\,°C$) they find surprisingly low water storage capacities in their experimental wadsleyite when compared to previous experimental results (Kohlstedt et al., 1996; Bolfan-Casanova, 2000; Demouchy et al., 2005; Ohtani et al., 2000). However, in a system that contains water and F, the storage capacities of both water and F in wadsleyite are similar which led Roberge et al. (2015) to conclude that the transition zone could be a reservoir for the storage of F, as it had been assumed for water (Roberge et al., 2015).

In this study we present new experimental results to investigate whether and how much F transition zone minerals can incorporate at transition zone P and T (1400 °C to 1900 °C and 17 GPa to 21 GPa). Moreover, we investigate the effect of T on the storage capacity of F in wadsleyite. Finally, we determine the effects of F on the P–T stability field of forsterite and wadsleyite, and consequently on the depths of the transition zone.

2. Methods

Experiments were performed in the system MgO–SiO_2–F_2 at P between 17–21 GPa and T of 1400 °C and 1900 °C. This dataset of experimental runs contains 4 experiments (M-83, 92, 97, 99) which are also briefly described in Grützner et al. (2017a).

2.1. Starting materials

The starting material was prepared from analytical grade oxides (MgO, Al_2O_3, SiO_2) and MgF_2 as a source of F. To release absorbed water and unwanted hydroxide components, the MgO starting material was fired in a Pt-crucible to 1000 °C for at least 2 h. The powders were then ground in an agate mortar under acetone for at least 1 h to obtain homogenous fine grained starting material mixtures. All starting materials were stored in a drying furnace at >100 °C to prevent the mixtures from absorbing moisture. The final starting mixture is $6MgO \cdot 3SiO_2 \cdot 1MgF_2$, or Forsterite + 25% MgF_2 in molar proportions.

2.2. Multi anvil experimental techniques

Experiments were performed in a 1000 t Walker-type multi anvil apparatus at the Institut für Mineralogie, University of Münster, using 10/4 multi anvil assemblies, in which the 10 refers to the edge length of the octahedron in mm and the 4 to the truncated edge lengths (mm) of the cubes. The multi-anvil assemblies consist of Cr-bearing MgO octahedra (Mino Ceramic Co, Japan), stepped $LaCrO_3$ heaters (Masuda Corporation, Japan) and pyrophyllite gaskets (Wonderstone Ltd, South Africa).

The starting material was sealed in Pt capsules, the latter of which were placed into crushable Al_2O_3 containers and finally placed in the center of the $LaCrO_3$ heater. In the 10/4 assemblies we used two 1.2 mm O.D. Pt-capsules with a length of 1.2 mm. These were placed on either side of the thermocouple. T was measured with $W_{97}Re_3$–$W_{75}Re_{25}$ thermocouples, centered between the two capsules. When running an experiment, first pressure was applied using a computer-controlled system and subsequently the experiments were heated up swiftly with a heating rate of about 600 °C/min and then kept constant for 1–4 h. T was controlled by a Eurotherm™ 2404-controller. T fluctuations during the run were within 10 °C. The 10/4 assembly was calibrated against the olivine–wadsleyite and wadsleyite–ringwoodite transitions at 14.2 and 20 GPa (1400 °C; Frost, 2003) in a Fe-free system and against ol–wd–rw phase transitions with varying Mg/Fe ratios at 14, 16 and 18 GPa (1400 °C; Frost, 2003; Wijbrans et al., 2016). All experiments were quenched rapidly by turning off the power supply and T fell from the run temperature to below 500 °C in less than 5 s.

2.3. Analytical methods

The experimental run products were characterized first using optical microscopy and a JEOL 6610LV scanning electron microscope equipped with an EDX system. To quantify the major element concentrations of the experimental products a JEOL JXA 8900 electron microprobe (EPMA) was used. Measurement conditions were typically 15 kV acceleration potential, 100 nA beam current and 10 μm beam diameter. Counting times were 20 s on the peak and 10 s on the background for all elements except F.

F concentrations in enstatite, forsterite and wadsleyite were analyzed with a synthetic multi-layered diffraction crystal (LDE). Counting times of 200 s were set on the F peak and 100 s on the background. Since there was no Fe in any starting material, the F-peak was not influenced by Fe $L\alpha_1$ and Fe $L\beta_1$ peaks (Witter and Kuehner, 2004), but slightly by the Mg $K\alpha$ II-peak at low F concentrations. Therefore, the left background measurement (−bg) was set 1.2 mm left to the peak, and the right background (+bg) 1.74 mm right to the peak. Standardization for F measurements was done using CaF_2 as reference material. For the standardization the −bg was set farther from the peak on −8.58 mm and the +bg on +2.0 mm as the peak broadens at higher F concentrations. A synthetic forsterite single crystal was used to monitor "true zero" F concentrations, in regards to potential negative net counts for F. These measurements did also show no effect on Mg and Si despite the high current. The detection limit for F during our EMPA measurements was 50 μg/g. Sample M-96 and M-99 were later re-analyzed together with reference material (Hbl Kakanui; Hbl Arenal) with 180 nA, 120 s on the peak, 60 s on bg+ and a 10 μm diameter beam, following the method of Zhang et al. (2015). These analyses were characterized by a detection limit for F of 20 μg/g and agree with our previous results within the uncertainties. Furthermore, the results of the two hornblende reference materials are in good agreement with previous measurements (Zhang et al., 2015), at 1631 ± 39 μg/g F (Hbl Kakanui) and 417 ± 23 μg/g F (Hbl Arenal).