



The storage capacity of fluorine in olivine and pyroxene under upper mantle conditions

Tobias Grützner^{a,*}, Simon C. Kohn^b, David W. Bromiley^b, Arno Rohrbach^a,
Jasper Berndt^a, Stephan Klemme^a

^a *Institut für Mineralogie, Universität Münster, Corrensstrasse 24, 48149 Münster, Germany*

^b *School of Earth Sciences, Wills Memorial Building, Queen's Rd, University of Bristol, BS8 1RJ, UK*

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Abstract

We present new experimental results on the fluorine storage capacity of olivine and orthopyroxene in the Earth's mantle. Experiments were performed in the system $\text{MgO-SiO}_2 + \text{MgF}_2$ at temperatures between 1350 °C and 1700 °C and pressures up to 17 GPa. Electron microprobe measurements show that fluorine concentrations in olivine reach up to 5100 $\mu\text{g/g}$. The storage capacity of fluorine in olivine shows only a small pressure dependence but a strong temperature dependence with a positive correlation between increasing temperature and fluorine storage capacity. Fluorine concentrations found in enstatite are one order of magnitude smaller and reach up to 670 $\mu\text{g/g}$. Our data show that concentrations of fluorine in fluorine-saturated olivine are in the same range as water concentrations in olivine. Nevertheless, fluorine and water solubility in olivine show opposing behavior with increasing pressure and temperature. The fluorine solubility in olivine increases with increasing temperature but is not much affected by pressure. In contrast, water solubility in olivine has previously been shown to decrease with increasing temperature and increase with increasing pressure. Our experiments show that nominally fluorine-free minerals like forsterite and enstatite are capable of storing the entire fluorine budget of the upper mantle, without the need to invoke accessory phases such as apatite or amphibole.

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1. INTRODUCTION

The influence of volatile elements on mantle melting, which ultimately leads to the eruption of magma on the surface, has long been recognized. Furthermore, volatile elements are known to strongly affect fractional crystallization of magmas, viscosity of melts, and rheology of mantle minerals. Numerous studies have focused on water and its role in Earth's mantle processes (e.g. Bell et al., 2004; Bolfan-Casanova, 2005; Peslier, 2010). 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). Water may be stored in the mantle in OH-bearing minerals such as amphibole, mica or apatite and a significant amount of water can also be stored in nominally anhydrous minerals (NAMs) like olivine, pyroxene, spinel and garnet (e.g. Rauch and Keppler, 2002; Stalder and Skogby, 2002; Zhao et al., 2004; Hirschmann et al., 2005; Stalder et al., 2005, 2008; Grant et al., 2006, 2007; Bali et al., 2008; Tenner et al., 2009, 2012; Ardia et al., 2012). Deeper in the transition zone of the mantle, wadsleyite and ringwoodite can host up to 3.3 wt.% of water (e.g. Inoue, 1994; Kawamoto et al., 1996; Demouchy and Mackwell, 2003; Smyth et al.,

* Corresponding author.

E-mail address: tobias.gruetzner@wwu.de (T. Grützner).

2006; Mosenfelder et al., 2011; Pearson et al., 2014). However, there are other important volatile elements such as carbon, sulfur, nitrogen and 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 mantle.

To partially address these matters, we set out to examine the storage potential of the halogen fluorine (F) in the Earth's mantle. F 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). F is known to strongly affect melt structure and viscosity but also plays an important role during fractionation of crustal magmas (e.g. Dingwell and Mysen, 1985; Edgar and Pizzolato, 1995). Furthermore, F is one of the most abundant gaseous components released from active volcanoes (Schilling et al., 1980; Symonds et al., 1994; Pyle and Mather, 2009 and references therein) but very few studies have been undertaken to study the influence of halogens on mantle processes (Schilling et al., 1980; Edgar et al., 1994; Edgar and Pizzolato, 1995; Hauri, 2002; Klemme, 2004; Hauri et al., 2006). Recently, however, interest in mantle halogens has been rejuvenated and several studies have presented experimental and analytical results on the role of halogens in Earth's mantle processes (Beyer et al., 2012, 2016; Filiberto et al., 2012; Bernini et al., 2013; Debret et al., 2013; Fabbriozio et al., 2013; Mosenfelder and Rossman, 2013a, 2013b; Wu and Koga, 2013; Crépeisson et al., 2014; Warren and Hauri, 2014; Joachim et al., 2015; Roberge et al., 2015; Rosenthal et al., 2015; Adam et al., 2016; Bénard et al., 2017).

2. HOW MUCH F DOES THE EARTH'S MANTLE CONTAIN?

Geochemical estimates of F in bulk silicate Earth (BSE) are 15–26 $\mu\text{g/g}$ (McDonough and Sun, 1995), and 11 $\mu\text{g/g}$ in the depleted MORB mantle, based on similar geochemical behavior of F and P (Saal et al., 2002; Salters and Stracke, 2004). However, Hervig and Bell (2005) presented the first SIMS measurements of F in olivines from mantle xenoliths that show remarkably high F concentrations in olivine (F = up to 240 $\mu\text{g/g}$). More recent studies by Beyer et al. (2012) and Mosenfelder and Rossman (2013a) showed that the mantle olivines studied contained up to 30 $\mu\text{g/g}$ F. Klemme (2004) observed F-rich blebs in subduction zone related mantle xenoliths which were interpreted as immiscible F-rich melts. Several recent studies addressed the partitioning of Cl and F between mantle minerals and melts or hydrous fluids (Beyer et al., 2012, 2016; Dalou et al., 2012; Bernini et al., 2013; Fabbriozio et al., 2013; Crépeisson et al., 2014; Adam et al., 2016; Bénard et al., 2017), with the general result that F is generally less incompatible than OH^- in olivine and pyroxenes. Furthermore, a few studies equilibrated olivine with F-bearing hydrous fluids at high pressures and high temperatures. These experiments show that olivine can incorporate several thousand $\mu\text{g/g}$ F (Dalou et al., 2012; Bernini et al., 2013).

In this study we focus on the storage potential of F in olivine and orthopyroxene. To that effect, we experimentally equilibrated forsterite and enstatite with F-rich melts. The experimental results define the maximum storage capacity for F in nominally F-free minerals of the upper mantle. As the experiments were conducted at different pressures and temperatures, we also investigated the effect of temperature (T) and pressure (P) on F saturation in olivine and pyroxene.

3. METHODS

Experiments were performed using several different chemical compositions at pressures ranging from 0.1 MPa (atmospheric pressure) up to 17 GPa, and temperatures at between 1350 and 1700 °C. Starting materials were prepared from analytical grade oxides (MgO , SiO_2) and MgF_2 . To release absorbed water, hydroxides or carbonate, the MgO starting material was fired in a Pt-crucible to 1000 °C for at least 2 h and then kept in a drying furnace at 110 °C. The starting material powders were ground in an agate mortar under acetone to obtain homogenous mixtures. All starting materials were stored in a drying furnace at 110 °C. Table 1 lists the major element composition of the starting materials.

3.1. Experimental techniques

3.1.1. High temperature furnace

Experiments at atmospheric pressure (1 atm) were conducted in a vertical furnace (Gero, Germany) at temperatures between 1350 and 1500 °C in Münster. All 1 atm experiments were run with sealed Pt capsules: the starting material was pressed into 2 mm O.D. Pt capsules with a length of 3–4 mm and welded shut using an arc-welder (Lampert PUK, Germany).

3.1.2. Piston Cylinder (PC)

Experiments at pressures between 0.5–2 GPa and 1350–1600 °C were conducted in identical Boyd & England-type piston cylinder apparatus (Boyd and England, 1960) at the Universities of Bristol and at the University of Münster. The $1/2$ piston cylinder assemblies consisted of concentric cylinders of talc, Duran[®] or Pyrex glass, a thin graphite heater, and an inner cylinder made from crushable alumina. The temperatures were monitored with $\text{W}_{97}\text{Re}_3\text{-W}_{75}\text{Re}_{25}$ thermocouples and controlled by a Eurotherm[™]-controller. The temperatures were accurate within 10 °C.

For experiments conducted in Münster, a pressure correction of –13% was applied to the nominal pressure due to friction of the talc-Pyrex assemblies, which was calibrated using the quartz-coesite transition (Bose and Ganguly, 1995a) and the $2\text{MgCr}_2\text{O}_4 + \text{SiO}_2 = \text{Mg}_2\text{SiO}_4 + \text{Cr}_2\text{O}_3$ reaction (Klemme and O'Neill, 1997). The quoted pressures are correct within 0.1 GPa. The starting material was encapsulated into Pt capsules of the same size which was used for the high temperature furnace experiments. Similar procedures were employed at Bristol University.

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