



## Is the transition zone a deep reservoir for fluorine?



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### ABSTRACT

It is now recognized that the transition zone (TZ) is a significant repository for water. This means that other volatile species may also be stored in this region such as halogen elements. We have measured the solubility of fluorine in wadsleyite (Wd) and ringwoodite (Rw) under hydrous and anhydrous conditions at different pressures and temperatures, relevant for the transition zone. F contents are similar in Wd (665 to 1045 ppm F, up to 956 ppm H<sub>2</sub>O) and in Rw (186 to 1235 ppm F, up to 1404 ppm H<sub>2</sub>O). This suggests that F may be incorporated in the same manner as water in the major nominally anhydrous minerals of the TZ: ringwoodite and wadsleyite and that the transition zone could be a major reservoir for fluorine. In the framework of the “water filter model” proposed by Bercovici and Karato (2003), the contrast of volatile element contents between a depleted upper mantle and an enriched transition zone could be maintained over geological time scales. Previous estimates of the fluorine content of the Bulk Silicate Earth (BSE), such as 25 ppm by mass (McDonough and Sun, 1995), have assumed a homogeneous mantle. Although we do not know whether the TZ is F saturated or not, we used our new experimental data and estimates of the lower mantle F content from ocean island basalts to estimate a maximum BSE fluorine content of 59 ppm by mass for a hydrous, F-saturated TZ. This upper bound on the range of possible BSE F content emphasizes the challenges when explaining the origin of volatile elements in the Earth from a carbonaceous chondrite late veneer.

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### 1. Introduction

The exceptional finding of a diamond inclusion made of hydrous ringwoodite (Pearson et al., 2014) has definitively proved that the mantle transition zone (410–660 km depth) is a major deep repository for water. This discovery validates decades of experimental work devoted to the study of the solubility of water in the major nominally anhydrous silicate minerals of the transition zone, wadsleyite and ringwoodite (see the review after Smyth and Jacobsen, 2006). These two phases can host up to 3.3 wt% structural water equivalent (hydroxyl groups), through incorporation processes involving Mg vacancies for ringwoodite (Blanchard et al., 2009) and a combination of Mg and Si vacancies, depending on the water content, for wadsleyite (Blanchard et al., 2013).

While the deep water cycle has been extensively studied these last decades, almost nothing is known about the behavior of the most abundant halogen element: fluorine. This element has been intensively studied for igneous processes (see the review after Pyle and Mather, 2009 and references therein), particularly for volcanic degassing (Schilling et al., 1980; D eruelle et al., 1992; Jambon et al., 1995). F affects directly the silicate melt properties such as magma viscosity (Dingwell and Mysen, 1985) or crystallization (Filiberto et al., 2012), and fluorine was for a long time believed to be stored in accessory phases such as phosphates (apatite), or clinohumite or minor silicate minerals such as amphibole or phlogopite (Smith, 1981). Moreover, fluorine has been shown to be in slight excess in the bulk silicate Earth compared to Carbonaceous Chondrites (McDonough and Sun, 1995). These estimates are based on concentrations measured in natural basalts and peridotites. A direct consequence is that the resulting budget (25 ppm F in the BSE, after McDonough and Sun, 1995) is too high to

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**Table 1**  
Starting materials, experimental conditions and run products.

Sample	P (±1 GPa)	T (±50 °C)	Time (min)	Starting material	Description
San Carlos (SC) powder SCP					Mixture of natural olivine powder + SiO <sub>2</sub>
Synthetic Powder SP Samples					Mixture of SiO <sub>2</sub> + MgO + FeO of San Carlos composition
83(*)	15	1400	20	Pure SC	Wadsleyite
H3698(*)	22	1400	20	Pure SC	Ringwoodite
87_F(*)	14	1350	420	SCP + 5 wt% NaF	Wadsleyite (20 μm), enstatite, NaF
H3567(**)	20	1100	240	SCP + 5 wt% NaF	Ringwoodite (20 μm), stishovite, NaF
42_F(*)	14	1400	240	SP + 5 wt% NaF + 2 wt% Mg(OH) <sub>2</sub>	Olivine (70 μm), enstatite, NaF-bearing glass
88_F(*)	14	1400	360	SCP + 5 wt% NaF + 2 wt% Mg(OH) <sub>2</sub>	Olivine (80 μm), enstatite, NaF-bearing glass
40_F(*)	14	1100	240	SP + 5 wt% NaF + 2 wt% Mg(OH) <sub>2</sub>	Wadsleyite (80 μm), enstatite, NaF-bearing glass
H3588(***)	20	1100	240	SCP + 5 wt% NaF + 2 wt% Mg(OH) <sub>2</sub>	Ringwoodite (80 μm), stishovite, NaF-bearing glass
H3695(*)	22	1250	240	SCP + 5 wt% NaF + 2 wt% Mg(OH) <sub>2</sub>	Ringwoodite (60 μm), stishovite, NaF-bearing glass
H3695(*)	22	1250	240	SCP + 5 wt% NaF + 2 wt% Mg(OH) <sub>2</sub>	Ringwoodite (60 μm), stishovite, NaF-bearing glass
H3696(*)	22	1400	240	SCP + NaF 5 wt% + 2 wt% Mg(OH) <sub>2</sub>	Ringwoodite (60 μm), stishovite, NaF-bearing glass

(\*) Au–Pd capsule; (\*\*) Re-capsule; (\*\*\*) Pt capsule, NaF pure salt, Mg(OH)<sub>2</sub>, brucite, for all powders: (Mg + Fe)/Si = 1.76. Larger grain sizes in μm are given in brackets.

fulfill a model based on a volatile-rich chondrite origin for the late veneer. Indeed, Marty (2012) has calculated that the contribution of 2% of carbonaceous chondrite material would fulfill the carbon and water abundances of the Earth. This would also fulfill the natural estimated abundances for heavy halogen elements (Cl, Br, I), but the abundance of F requires a much higher contribution of 17%.

For these reasons it seems necessary to determine how F is stored within potential reservoirs of the mantle, and to consider whether the fluorine content in the BSE may have been over or underestimated. Therefore in an attempt to put constraints on the fluorine content in the upper mantle, fluorine concentrations have recently been measured in nominally anhydrous mantle minerals (Beyer et al., 2012; Mosenfelder and Rossman, 2013a, 2013b). These studies have demonstrated that up to 47 ppm of fluorine can be incorporated in natural olivine and pyroxene. By comparison, experimental studies performed to determine fluorine solubility in these major mantle mineral phases yielded maximum contents of fluorine of 4500 ppm to 1900 ppm in olivine (Bromiley and Kohn, 2007; Bernini et al., 2012), 626 ppm in pyroxenes (Dalou et al., 2012), and 1110 ppm in pyrope (Bernini et al., 2012). Like water, that is stored in silicate minerals as hydroxyl species, it has been proposed that the mantle fluorine budget can be entirely accommodated by these mineral phases (Beyer et al., 2012; Crépisson et al., 2014). Based on the observation of clumped fluoride-hydroxyl defects in pure-Mg olivine, the major upper mantle mineral, it is likely that fluorine and water cycles may be strongly coupled through the nominally anhydrous minerals (Crépisson et al., 2014). Like for water, F may be transferred at depth during subduction processes. For example, experimental studies indicate that a dense hydrous magnesium silicate phase – superhydrous phase B – stabilized at subduction zone conditions in the transition zone. This phase might incorporate significant amounts of fluorine and carry it down to the deep mantle (e.g. Hazen et al., 1997). By analogy with water, one may speculate that a significant repository for fluorine may exist in the transition zone (TZ). This is the hypothesis we would like to test in this study.

In this work, we measure the F solubilities in wadsleyite (Wd) and ringwoodite (Rw) to assess the F storage capacity of the TZ. Indeed, it is critical to know to which extent the potential storage capacity of the transition zone may affect the global F budget and cycle, within a framework whereby F would be continuously brought in the TZ by subduction.

## 2. Materials and methods

F-bearing olivine, wadsleyite and ringwoodite were synthesized from two different powders: (a) a mixture of MgO, SiO<sub>2</sub>, FeO oxides, and (b) a mixture of natural pure San Carlos olivine (Fo<sub>90</sub>) fine powders mixed with SiO<sub>2</sub>. The addition of SiO<sub>2</sub> provides slight excess of silica (Mg/Si atomic ratio = 1.76) in order to promote the formation of a silicate melt in equilibrium with the crystals that can incorporate the excess of fluorine and water (Demouchy et al., 2005). F was added as a salt: NaF (up to 5 wt% in the bulk), whereas water was added as brucite in order to get a total amount of 2 wt% H<sub>2</sub>O. Mixtures were prepared in order to obtain bulk compositions of about Fo<sub>90</sub>, corresponding to the pyrolitic composition after Ringwood (1962). Wadsleyite, ringwoodite and olivine were synthesized in a multi-anvil press at pressures between 14 and 22 GPa and in the temperature range 1100 °C to 1400 °C. Typical run durations were between 30 minutes and 9 hours in either Re, Pt or Au–Pd capsules (Table 1). Experiments were performed at LMV Clermont-Ferrand and BGI Bayreuth following the procedures detailed in Frost et al. (2001), Demouchy et al. (2005).

Recovered samples were then embedded in crystal bond and mirror polished on one-side. The mineral phases were characterized using Scanning Electron Microscopy (SEM) at IMPMC-UPMC. Mineral identification was realized using Raman spectroscopy. The fine structure of the minerals, imaging, diffraction, and chemical measurements were performed with a JEOL 2100F transmission electron microscope (TEM) with a field emission gun, and equipped with JEOL EDX detectors at IMPMC (UPMC). The acceleration voltage was at 200 kV and we reached a resolution of 1.8 Å. The samples for TEM were prepared by Focused Ion Beam (FIB) with the dual beam Zeiss Crossbeam Neon 40 ESB at IMPMC (UPMC). The final lamella-thickness obtain is under 100 nm for suitable electron transparency. Major element compositions of the minerals were measured using electron microprobe analyses (EPMA) with an acceleration of 15 kV and 15 μm defocused beam at 10 nA on CAMECA-SX100 at CAMPARIS facility (UPMC, France).

Fluorine and hydrogen contents were measured using ion beam analysis at the nuclear microprobe of the LEEL, CEA, Saclay, France (Khodja et al., 2001). F was measured using Particle Induced Gamma Ray Emission (PIGE) following the procedure described in Crépisson et al. (2014). Hydrogen was measured using Elastic Recoil Detection Analysis (ERDA) using the procedure described in Raepsaet et al. (2008), Bureau et al. (2009), Withers et al. (2012).

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