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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 H₂O) and in Rw (186 to 1235 ppm F, up to 1404 ppm H₂O). 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, 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.

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; Déruelle 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 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, b). 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, SiO₂, FeO oxides, and (b) a mixture of natural pure San Carlos olivine (Fo₉₀) fine powders mixed with SiO₂. The addition of SiO₂ 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% H₂O. Mixtures were prepared in order to obtain bulk compositions of about Fo₉₀, 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).

Before any analysis, the largest crystals were selected with SEM cartographies. PIGE and ERDA measurements have been realized simultaneously with Particle Induced X-Ray Emission (PIXE) and Rutherford Backscattering Spectrometry (RBS) measurements, using a 3x3µm² proton beam of 3 MeV for PIGE and a 4x16 µm² ⁴He beam of 3 MeV for ERDA. ERDA analyzes were performed on areas previously analyzed for F.

All measurements were performed by a scanning the beam on large selected areas from 24x50 to 150x100 µm². Data acquisitions were performed with a beam current of 500-550 pA, during 1 or 2 hours depending on the concentrations. The combination of RBS and PIXE with ERDA and PIGE was useful to identify the analyzed crystals (Rw, Wd, Ol) and to detect any chemical heterogeneity such as NaF-rich fine intergrowths in the grain boundaries.

Data were first processed using the RISMIN (Daudin et al., 2003) to isolate any chemical heterogeneities and identify the desired crystals, This is possible thanks to the multi-

detection system: PIXE, RBS and PIGE allowing the comparison of elemental repartition in the investigated areas, i.e. Na versus F maps, but also Fe and Ca versus F maps, together with SEM pictures of the investigated areas. By comparing the repartitions of these elements we can identify and select (1) Wd, Ol and Rw areas (2) Na not contaminated areas. This is illustrated in the Figure 1 that describes the selection process for sample #3588.

After the selection of areas of interest, F and H contents were obtained using SIMNRA software (Mayer, 1997) when PIXE spectra were processed using GUPIXWIN (Campbell et al., 2005) software in order to get concentration with respect to elements of interest such as Fe.

PIGE analysis were performed thanks to the quantification of the 197 keV gamma ray emission resulting from $^{19}\text{F}(\text{p},\text{p}'\gamma)^{19}\text{F}$ reaction (Mosbah and Métrich, 1991, Jesus et al., 2000, Habrioux et al., 2012). Na was simultaneously quantified by this method using the 439 keV ray produced by the $^{23}\text{Na}(\text{p},\text{p}'\gamma)^{23}\text{Na}$ reaction. These conditions allow a depth of investigation of about 35 μm for F which is < to the larger size of the investigated crystals except for anhydrous F-bearing minerals. Indeed, when proton beam depth penetration in minerals can effectively reach up to 62 μm owing to the relatively low stopping power of protons, the gamma-ray emission from fluorine is induced only in the beginning of the path, as reaction cross-section falls close to zero for energies under 1.5 MeV as attested by a recent measurement reported in (Jesus et al., 2000).

When ERDA is standard less (Raepsaet et al., 2008; Bureau et al., 2009; Withers et al., 2012), the quantification of fluorine requires the use of F-known content samples having a bulk composition similar to the samples (i.e. silicates). Therefore we have used the pantellerite KE12 (4200 ppm F and 5.32 wt% Na, Métrich and Rutherford, 1992) for PIGE calibration. We have preferred this standard instead of a CaF_2 window or a maccusanite glass containing 1.33 wt% F and 3.11wt% Na (Pichavant et al., 1987), because the stopping power

of KE12 is similar to those of our samples. We have used more analysis performed on KE12 and on the Macusanite glass to validate the fluorine quantification. Results obtained for the pantellerite glass KE12 are ranging from 4187 to 4209 ppm F.

3. Results

Samples have been synthesized in multi-anvil press apparatuses from 14 to 22 GPa and from 1100°C to 1400°C (see Materials and methods). This temperature range is relevant for the transition zone and commonly used in experimental studies (e.g. Bolfan-Casanova et al., 2000; Demouchy et al., 2005; Smyth and Jacobsen, 2006). The run durations were ranging from 240 to 420 minutes, except for the references, Wd and Rw free of F and H (20 minutes). No chemical zonation was observed in the investigated crystals and we assume that samples were at chemical equilibrium. Recovered samples contain crystals of Ol, Wd, Rw, depending on the pressure coexisting with clinoenstatite or stishovite, interstitial NaF-rich silicate glass also enriched with respect to H (Table 2). Crystal areas ($20 \mu\text{m}^2$), are consistently smaller for anhydrous samples, than for hydrous samples, which are typically $\sim 40 \mu\text{m}^2$ in average (Fig 2). No particular textural difference or abrupt increase in the amount of quenched melt were observed between hydrous experiments performed at different temperatures.

Transmission Electron Microscopy (TEM) investigation of a thin section containing F-rich Rw (H3588) recovered using focused Ion Beam (FIB) shows that the structure revealed by selected area electron diffraction (SAED) is consistent with a pure single Rw crystal (Fig. 3). This observation also shows that no inclusion of salt or melt is present, and that F and water

are incorporated in the crystal lattice. EDX analyses and elemental cartography performed using PIXE (Particle Induced X-Ray Emission) and PIGE (Particle Induced Gamma Ray Emission) do not indicate any chemical heterogeneity in the bulk crystals. Moreover, the Na/F ratios measured by PIGE in Rw and Wd is systematically $\ll 1.21$ (Na/F ratio), confirming that the detected F is corresponding to a structural concentration and not to the presence of any sub-micron NaF inclusions. Na contents are high, from 713 to 3230, however, such high Na contents have already been reported in wadsleyites (2100-2400 ppm, Gudfinnsson and Wood, 1998) synthesized at 1600°C and 14.2 GPa. In these experiments Na₂O was present in the starting materials (a glass) and was not in excess (0.42 wt.% Na₂O).

Ol, Wd and Rw compositions range from Fo₈₈ to Fo₉₇ (with Fo defined as $100 \cdot (\text{Mg}/(\text{Mg}+\text{Fe}))$), while F contents, determined by PIGE, range from 323 to 410 ppm F for Ol, from 665 to 1045 ppm F for Wd and from 186 to 1235 ppm F for Rw (Table 1). The detection limit for F ranges from 37 to 123 ppm F for any investigated phase. The highest F contents are found in anhydrous Wd and Rw (Table 1). With the exception of run H3695, Wd and Rw F contents are higher than those of Ol (Table 1). Water contents measured by using Elastic Recoil Detection Analysis (ERDA), amount 428 H₂O for Ol, whereas 864 to 956 ppm H₂O are detected in Wd and 854 to 1404 ppm H₂O are measured for Rw (Table 1).

When comparing different temperatures of synthesis, a slight decrease of F content is observed with increasing temperature in hydrous Rw. We do not have enough results to determine if a temperature effect would affect the F content of both Rw and Wd, similarly to what as it has been shown for water contents in Wd by Demouchy and co-workers (2005, see Fig 4). Figure 5 shows that the highest F contents are associated with quasi-anhydrous minerals when fluorine is examined as a function of H₂O.

4. Discussion

4.1 Water and Fluorine in Ringwoodite and Wadsleyite

For volatile elements, solubility measurements, i.e. determination of the maximum content of the element in a matrix (silicates minerals, melts), have been used for decades to understand deep processes such as magma degassing, partial melting and physical properties or to assess to mantle storage. Thus determining the upper limits of volatile contents is key to making progress in the understanding of volatile element cycling into the Earth.

We show an H₂O solubility contrast for Ol (up to 428 ppm) compared with Wd and Rw (from 854 to 1404 ppm) with more water dissolved in the two high-pressure phases. This is in agreement with previous studies (e.g. Bolfan-Casanova et al., 2000; Ohtani et al., 2001; Demouchy et al., 2005;) but the amount of water measured in Wd and Rw from this study is one order of magnitude lower than previously reported solubilities for these phases (up to 3 wt.% e.g. Smyth and Jacobsen, 2006). Such a significant reduction of OH incorporation is likely attributed to the presence of NaF salt which will reduce the H₂O activity in the melt in equilibrium with the mineral phases. Previous studies have observed a significant decrease of OH incorporation in enstatite (2.5 GPa and 1150-1400°C), linked to the increase of NaCl or KCl content in starting materials (Stalder et al., 2008). An additional possibility might be a competition process between OH and F for incorporation in the mineral lattices of Wd and Rw. Indeed, a recent study combining infrared characterization of experimentally F- and OH-enriched olivines and first-principle calculations, Crépeisson and co-workers (2014) have demonstrated a close association of fluoride, hydroxyl groups and Si vacancies. They found evidence for the presence of clumped fluoride-hydroxyl defects in the forsterite structure. Whereas in NaF-free systems the proposed H₂O incorporation mechanism mostly involves Mg vacancies in forsterite (e.g. Balan et al., 2011) and in ringwoodite (Blanchard et al., 2009). Blanchard et al. (2013) have also provided evidence for the association of hydroxyl groups with Si vacancies in H₂O-rich wadsleyites. Assuming that F and OH share the same vacancies

in Wd and Rw, and considering the slight F content decrease associated with increasing SiO₂ contents (Fig 6), we propose that F may at least partially be associated with Si vacancies. This suggests that H₂O and F cycles are linked in the upper mantle and TZ, through Ol, Wd and Rw.

F solubilities measured in Rw (186-1235 ppm) and in Wd (665-1045 ppm) are similar for both phases and higher than any F concentrations measured in natural NAMs of the upper mantle. A comparison with previous experimental studies is moreover difficult because experimental conditions are not consistent between studies (pressures, bulk compositions, starting materials). Very high F contents experimentally obtained in olivines (e.g. in the 2-4 GPa pressure range: 1715 ppm F, Crépisson et al., 2014), would suggest a possible pressure effect on F solubility.

4.2 Fluorine in the transition zone

From the lithophile behavior of F (McDonough and Sun, 1995) and based on previous studies (Beyer et al., 2012), it has been proposed that nominally anhydrous silicate phases (such as olivine and pyroxene Px) might accommodate the bulk F content of the whole upper mantle in regards to their high modal proportion in the mantle. However, the F contents measured in upper mantle natural Ol and Px are < 100 ppm (Hervig and Bell, 2005; Beyer et al., 2012; Mosenfelder and Rossman 2013a, b). Here we show that Wd and Rw are potentially important F-bearing minerals, and that the TZ is a good candidate for its storage for two reasons: (1) fluorine may have been trapped very early in the TZ when the mantle was crystallizing from the magma ocean; (2) fluorine may be regularly supplied to the TZ through subduction. Indeed, a regular water supply is expected from the slabs. F is lithophile compared to Cl, Br and I, which are hydrophilic (e.g. Bureau et al., 2000; 2010), therefore

when most of the heavy halogen elements and a significant part of water are likely devolatilized from the slab during dehydration processes, most of the F may remain in the slabs en route to the TZ. Subduction would thus drive an annual global flux of 8.7×10^{14} g H_2O (Peacock, 1990) and of $9.9\text{--}10 \times 10^{12}$ g F to the Earth's interior (John et al., 2011). Large amounts of F and water are expected to be recycled back to the mantle (95% F and 87% water respectively, Peacock, 1990; John et al., 2011). Hydrous phases may transport F efficiently to the TZ (e.g. Hazen et al., 1997). Once the subducted slab reaches the TZ, the storage of F and water would be enhanced by the tendency of many slabs to deflect horizontally, and to remain permanently or temporarily at the 660-km discontinuity (e.g. Fukao et al., 2001).

It has been proposed that a neutral buoyant hydrous melt phase on the top of the TZ (410 km depth) could control the distribution of incompatible elements within the upper mantle, acting as a chemical filter, the so-called “water-filter” model (Bercovici and Karato, 2003). In this model a high water content within the range 0.2 – 2 wt.% is assumed in the TZ, which is consistent with the 1 wt. % of water measured in a natural diamond inclusion of ringwoodite (Pearson et al., 2014). The water dissolved in the mantle would create a thin layer of melt at 410 km depth, corresponding to the transformation of Wd into Ol and a hydrous melt (Fig 7). This dehydration melting would create a 10 km thick layer of molten silicate just above the 410-km discontinuity that would retain most of the water together with incompatible elements. Since the melt is denser than the TZ minerals at these pressures it would remain stable. In this view of the mantle, the layer of melt would act as a filter by removing elements rising from the deep mantle and keeping the upper mantle chemically depleted and anhydrous (Bercovici and Karato, 2003). Following this model, the TZ is enriched in water and fluorine even when the upper mantle is depleted.

4.3 The Fluorine budget in the Bulk Silicate Earth

Our new experimental data allow us to estimate an upper bound for the BSE content of F assuming that the TZ is hydrous and saturated in F. We have calculated a maximum value for the BSE content of F assuming that the TZ is hydrous and saturated in F. We have used the F content of 16 ppm for the lower mantle, determined by (Beyer et al., 2012) from the concentrations of F measured in melt inclusions trapped in olivines from OIB products, when the degree of melting is of 2%. The crust is believed to contain 553 ppm F (Rudnick and Gao, 2003), the depleted mantle (TZ excluded) is expected to host 12 ppm F (Beyer et al., 2012). This F content, inferred from its concentration in Ol and orthopyroxene in spinel lherzolites, is in good agreement with the F concentration proposed for the depleted MORB mantle (11 ppm F, Salters and Stracke, 2004). The calculated primitive OIB source is supposed to contain 16 ppm F (17 ppm including a contamination by 3% of recycled crust) based on the measurement of natural OIB volcanic samples (Beyer et al., 2012). In addition, OIBs are assumed to be not affected in their ascent through the TZ (Bercovici and Karato, 2003). In order to calculate the maximum amount of F in the TZ, we have used an average pyrolite mineral assemblage model, together with the F contents obtained in our experiments for Wd and Rw of mantle composition (Mg# 0.90, Table 1). We assume a high F content for Rw and Wd as a first approximation for the upper limit of the F BSE content. This is based on the recent discovery of high water content (1.5 wt.%) in a ringwoodite trapped in a natural diamond (Pearson et al., 2014) and makes the assumption that the OH and F cycles are linked in silicate minerals. This assumption needs to be verified by further studies, such as partitioning measurements, and the maximum F content in the TZ may be reconsidered later. We have also assumed that F contents in clinopyroxene, garnet and Ca-perovskite are not significant.

We obtain a value of 23.8×10^{22} g F for the BSE corresponding to 59 ppm F (Fig 7). This high limit value is twice higher than the previous calculation of 25 ppm F after McDonough and Sun (1995), calculated from the Fluorine contents of MORBs and based on a homogeneous mantle. If the BSE contained this higher (59 ppm) amount of Fluorine, this would mean that about 70% of Earth's total fluorine budget would be currently stored in the transition zone. Assuming the present-day flux for F recycling into the mantle (John et al., 2011, fig. 7), more than 16 billion years would be necessary to fill the transition zone by subduction recycling if the TZ if it contained the maximum value of 16.8×10^{22} g of F. As discussed above, the fluorine content of the bulk silicate Earth is probably in the range 25 to 59 ppm and most of the mantle's fluorine is probably stored in the transition zone. If all these assumptions are correct, it would mean that, F was stored in the TZ during the crystallization of the magma ocean during the Earth's differentiation in the Hadean. This is possible if we assume that the “water-filter” model (Bercovici and Karato, 2003) is an efficient process for F retention in the mantle and consequently a key control on the abundance of F in the Earth's crust.

The Earth is the result of possibly complex accretion and differentiation processes. The primordial building material for the Earth is still the matter of strong debates (e.g. Marty, 2012; Javoy, 1995; Albarède, 2009) especially with respect to volatile elements. Considering the BSE contents in volatile elements after (McDonough and Sun, 1995) and comparing them with the abundances of the carbonaceous chondrites (CC: the most primitive materials), it has been shown that fluorine is slightly enriched compared to heavy halogen elements (Cl, Br, I) and noble gases. Indeed, if hydrogen, carbon and heavy halogen contents would be obtained after the addition of 2 % of a CC late veneer, it would be necessary to add 17% mass of a carbonaceous chondrite to reach the observed BSE fluorine amount (Marty, 2012). This would be even worse if the BSE would contain more than 25 ppm. This also emphasizes

the fact that the origin of F in the Earth is difficult to explain with the simple accretion of CI chondrites during the differentiation stage.

Our measurements show that a significant amount of fluorine could be stored in the transition zone, and we suggest that the global F budget of the Earth may have been underestimated. More experimental data are necessary to constrain the fluorine cycle and storage in the Earth.

5. Conclusion

We have shown that the fluorine solubility in Wd and Rw is high at water contents, pressures and temperatures relevant to the TZ. Therefore, we suggest that F may be significantly stored together with water in the TZ. The association of F and H₂O shows that their two geochemical cycles are associated at least through their incorporation in nominally anhydrous minerals. Assuming that 95% of the subducted F is recycled back to the mantle, a significant amount of F would reach the TZ where the slab is believed to be stagnant. In this way the TZ would be continuously supplied in F and water by subduction processes. In the frame of the “water-filter model” at the top of the TZ, both F and water contents may be chemically zoned in the mantle at a steady state. The global content of F in the bulk silicate Earth is probably underestimated. Assuming a hydrous, F-saturated TZ, we calculate an upper limit for the BSE F content of 59 ppm wt., higher than the previous estimate of 25 ppm by mass assuming a homogeneous mantle (McDonough and Sun, 1995). It is not known whether the TZ is F-saturated but given this uncertainty we propose that BSE fluorine content is better quoted as being in the range between 25 and 59 ppm by mass. If a significant amount of F is stored in the TZ, it puts constraints on the models proposed to explain the origin of volatile

elements in the Earth. We also suggest that the actual BSE content estimated for the heavy halogen elements chlorine, bromine and iodine may need to be revised, because these elements would also likely been stored in the mineral assemblage of the TZ, but their real contents in deep minerals remain unknown. A real progress in the understanding of the origin of volatile elements requires the determination of precise budgets for these elements in the whole Earth.

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Figure captions

Fig.1: Sample #3588 of ringwoodite: SEM picture, PIGE spectrum showing the F peak located at 197 keV. Larger grain sizes are of about 80 μm . 100*100 μm^2 maps of element repartition in the selected area of interest, corresponding to one large crystal of ringwoodite: Fe from PIXE, Na and F from PIGE, Mg from RBS. Hot spots in the maps are corresponding to interstitial NaF-bearing silicate glasses.

Fig. 2: SEM pictures of hydrous and anhydrous ringwoodites showing the difference in crystal sizes: about 10 μm for anhydrous Rw and about 40 μm for hydrous Rw. Anhydrous F Rw, sample H3567 ; B Hydrous F Rw, sample H3696

Fig. 3:

A) SEM image of ringwoodite sample H3588. The thick grey line shows the position where a FIB section has been dig.

B) Bright field image and the corresponding diffraction pattern C) of the Rw crystal investigated. No evidence of nano-inclusion is observed.

Fig. 4:

F content in ppm wt. plotted versus temperature. A slight decrease of F content is observed with the temperature increase for Rw whereas it seems to have no effect on the F content of Wd.

Circles: Ol, squares: Wd, triangles : Rw. Black symbols are for anhydrous samples, open symbols are for hydrous samples.

Fig. 5:

F ppm wt. plotted versus water ppm wt. contents. The highest F contents are associated with quasi anhydrous minerals, but a slight increase of fluorine content is associated to an increase of water in Rw. Symbols as in Figure 3.

Fig. 6:

F ppm wt. plotted versus SiO₂ wt. % contents. The highest F contents are associated with the lowest SiO₂ concentrations in ringwoodites possibly in wadsleyites. Assuming a similar incorporation processes for F in close association with OH in Wd and Rw, than in Ol, one may suggest an incorporation in Si vacancies. Symbols as in Figure 3.

Fig 7:

Schematic section of the interior of the Earth showing F storage and fluxes. Yellow arrows show F and H fluxes: estimated fluxes of HF released to the atmosphere (Pyle et Mather, 2009) and subducted F (John et al., 2011) and H (Straub and Layne, 2003) fluxes. Distribution of F in the mantle is from this study. In this model the TZ is enriched both in F and H. T This region of the mantle may control the distribution of these two volatile elements via the "water filter" model (Bercovici and Karato, 2003).

Fig 1

SEM picture of sample #3588

PIGE

PIXE, PIGE and RBS elemental

Fig 2

Fig 3

Fig 4

Fig 5

Fig 6

Fig 7

Table 1: Starting materials, experimental conditions and run products

Sample	P ($\pm$ 1GPa)	T ($\pm$ 50°C)	Time min	Starting Material	Description
San Carlos (SC) powder SCP					Mixture of natural olivine powder +SiO ₂
Synthetic Powder SP					Mixture of SiO ₂ + MgO + FeO of San Carlos composition
<i>Samples</i>					
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 μ m), enstatite, NaF
H3567(**)	20	1100	240	SCP+ 5 wt.% NaF	Ringwoodite (20 μ m), stishovite, NaF
42_F(*)	14	1400	240	SP + 5 wt.% NaF + 2 wt.% Mg(OH) ₂	Olivine (70 μ m), enstatite, NaF-bearing glass
88_F(*)	14	1400	360	SCP + 5 wt.% NaF + 2 wt.%Mg(OH) ₂	Olivine (80 μ m), enstatite, NaF-bearing glass
40_F(*)	14	1100	240	SP + 5 wt.% NaF + 2 wt.% Mg(OH) ₂	Wadsleyite (80 μ m), enstatite, NaF-bearing glass
H3588(***)	20	1100	240	SCP + 5wt.% NaF + 2 wt.% Mg(OH) ₂	Ringwoodite 80 μ m), stishovite, NaF-bearing glass
H3695(*)	22	1250	240	SCP + 5 wt.% NaF + 2 wt.% Mg(OH) ₂	Ringwoodite (60 μ m), stishovite, NaF-bearing glass
H3695(*)	22	1250	240	SCP + 5 wt.% NaF + 2 wt.% Mg(OH) ₂	Ringwoodite (60 μ m), stishovite, NaF-bearing glass
H3696(*)	22	1400	240	SCP + NaF 5 wt.% + 2 wt.% Mg(OH) ₂	Ringwoodite (60 μ m), stishovite, NaF-bearing glass

(*) Au-Pd capsule, (**) Re-capsule, (***) Pt capsule, NaF pure salt, Mg(OH)₂, brucite, for all powders : (Mg+Fe)/Si= 1.76. Larger grain sizes in μ m are given in brackets

Table 2: Representative analyses of experimental run products and starting natural composition

Sample		Oxides %wt (% rel)												
		SiO ₂	FeO	MnO	Al ₂ O ₃	Na ₂ O	MgO	CaO	TiO ₂	Total	Mg #	H ₂ O ppm (ppm)	F ppm (ppm)	Na ppm (ppm)
<i>References</i>														
San Carlos	Ol	40.34	9.22	0.13	0.01	0.01	49.8	0.08	0.01	99.72	0.90	-	-	-
83	Wd	41.55 (0.09)	9.21 (0.10)	0.12 (0.04)	0.11 (0.02)	0.02 (0.02)	48.48 (0.29)	0.02 (0.03)	0.01 (0.01)	99.63 (0.38)	0.90	-	0	0
H3698	Rw	41.50 (0.31)	9.70 (0.14)	0.12 (0.05)	0.04 (0.04)	0.01 (0.01)	48.79 (0.27)	0.07 (0.02)	0.01 (0.02)	100.39 (0.38)	0.90	-	0	0
<i>Anhydrous</i>														
87_F	Wd	41.24 (0.30)	9.02 (0.19)	0.12 (0.03)	0.09 (0.02)	0.82 (0.09)	48.80 (0.48)	0.02 (0.01)	0.00 (0.00)	100.11 (0.49)	0.91	-	1045 (2)	3145 (2)
H3567	Rw	39.58 (0.11)	11.53 (0.47)	0.13 (0.04)	0.05 (0.04)	0.41 (0.06)	45.67 (0.17)	0.02 (0.01)	0.03 (0.03)	97.42 (0.18)	0.88	-	1235 (5)	2123 (7)
<i>Hydrous</i>														
42_F	Ol	35.41 (3.83)	9.69 (1.87)	0.01 (0.01)	0.05 (0.03)	0.78 (0.33)	54.02 (1.36)	0.01 (0.01)	0.01 (0.01)	99.98 (0.71)	0.93	nd	410 (41)	3230 (323)
88_F	Ol	41.78 (0.27)	3.44 (0.25)	0.10 (0.03)	0.06 (0.02)	0.12 (0.04)	53.86 (0.26)	0.01 (0.01)	0.02 (0.02)	99.39 (0.27)	0.97	428 (65)	323 (32)	713 (71)
40_F	Wd	41.66 (0.34)	8.62 (0.2)	0.04 (0.02)	0.05 (0.01)	0.24 (0.08)	49.91 (0.81)	0.01 (0.01)	0.01 (0.02)	100.54 (0.54)	0.90	956 (132)	665 (67)	2573 (258)
H3588	Rw	40.49 (0.55)	7.67 (0.07)	0.04 (0.04)	0.07 (0.00)	0.09 (0.04)	49.97 (0.42)	0.00 (0.01)	0.03 (0.02)	98.36 (0.30)	0.90	1404 (197)	850 (85)	2503 (250)
H3695	Rw	41.19 (0.29)	10.71 (0.18)	0.10 (0.00)	0.01 (0.01)	0.34 (0.16)	47.64 (0.19)	0.01 (0.00)	0.02 (0.02)	100.02 (0.41)	0.89	904 (127)	186 (19)	1025 (103)
H3696	Rw	40.42 (0.03)	10.61 (0.11)	0.09 (0.02)	0.02 (0.01)	0.39 (0.03)	46.47 (0.14)	0.01 (0.01)	0.00 (0.00)	98.01 (0.04)	0.89	854 (128)	507 (51)	1473 (147)

Oxides wt.% are from EMPA. H₂O ppm from ERDA F ppm and Na ppm from PIGE. Ol= olivine. Wd= wadsleyite. Rw =ringwoodite. Gl= glass. Mg#= Mg/(Mg+Si); uncertainties are given in brackets

Highlights

1. Almost nothing is known about fluorine deep geochemical cycle.
2. Fluorine and water cycles may be closely related in the mantle.
3. Fluorine contents can be significant in wadsleyite and ringwoodite.
4. Large amounts of fluorine may be stored in the transition zone
5. This may provide constraints on the origin of fluorine in the Earth.