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

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## 23 **Abstract**

24

25         It is now recognized that the transition zone (TZ) is a significant repository for water.  
26 This means that other volatile species may also be stored in this region such as halogen  
27 elements. We have measured the solubility of fluorine in wadsleyite (Wd) and ringwoodite  
28 (Rw) under hydrous and anhydrous conditions at different pressures and temperatures,  
29 relevant for the transition zone. F contents are similar in Wd (665 to 1045 ppm F, up to 956  
30 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  
31 incorporated in the same manner as water in the major nominally anhydrous minerals of the  
32 TZ: ringwoodite and wadsleyite and that the transition zone could be a major reservoir for  
33 fluorine. In the framework of the “water filter model” proposed by Bercovici and Karato  
34 (2003), the contrast of volatile element contents between a depleted upper mantle and an  
35 enriched transition zone could be maintained over geological time scales. Previous estimates  
36 of the fluorine content of the Bulk Silicate Earth (BSE), such as 25 ppm by mass, have  
37 assumed a homogeneous mantle. Although we do not know whether the TZ is F saturated or  
38 not, we used our new experimental data and estimates of the lower mantle F content from  
39 ocean island basalts, to estimate a maximum BSE fluorine content of 59 ppm by mass for a  
40 hydrous, F-saturated TZ. This upper bound on the range of possible BSE F content  
41 emphasizes the challenges when explaining the origin of volatile elements in the Earth from a  
42 carbonaceous chondrite late veneer.

## 43 **1. Introduction**

44

45         The exceptional finding of a diamond inclusion made of hydrous ringwoodite (Pearson  
46 et al., 2014) has definitively proved that the mantle transition zone (410-660 km depth) is a

47 major deep repository for water. This discovery validates decades of experimental work  
48 devoted to the study of the solubility of water in the major nominally anhydrous silicate  
49 minerals of the transition zone, wadsleyite and ringwoodite (see the review after Smyth and  
50 Jacobsen, 2006). These two phases can host up to 3.3 wt % structural water equivalent  
51 (hydroxyl groups), through incorporation processes involving Mg vacancies for ringwoodite  
52 (Blanchard et al., 2009) and a combination of Mg and Si vacancies, depending on the water  
53 content, for wadsleyite (Blanchard et al., 2013). While the deep water cycle has been  
54 extensively studied these last decades, almost nothing is known about the behavior of the  
55 most abundant halogen element: fluorine. This element has been intensively studied for  
56 igneous processes (see the review after Pyle and Mather, 2009 and references therein),  
57 particularly for volcanic degassing (Schilling et al., 1980; Déruelle et al., 1992; Jambon et al.,  
58 1995). F affects directly the silicate melt properties such as magma viscosity (Dingwell and  
59 Mysen, 1985) or crystallization (Filiberto et al., 2012), and fluorine was for a long time  
60 believed to be stored in accessory phases such as phosphates, (apatite) or clinohumite or  
61 minor silicate minerals such as amphibole or phlogopite (Smith, 1981). Moreover, fluorine  
62 has been shown to be in slight excess in the bulk silicate Earth compared to Carbonaceous  
63 Chondrites (McDonough and Sun, 1995). These estimates are based on concentrations  
64 measured in natural basalts and peridotites. A direct consequence is that the resulting budget  
65 (25 ppm F in the BSE, after McDonough and Sun, 1995) is too high to fulfill a model based  
66 on a volatile-rich chondrite origin for the late veneer. Indeed, Marty (2012) has calculated that  
67 the contribution of 2% of carbonaceous chondrite material would fulfill the carbon and water  
68 abundances of the Earth. This would also fulfill the natural estimated abundances for heavy  
69 halogen elements (Cl, Br, I), but the abundance of F requires a much higher contribution of  
70 17%.

71 For these reasons it seems necessary to determine how F is stored within potential  
72 reservoirs of the mantle, and to consider whether the fluorine content in the BSE may have  
73 been over or underestimated. Therefore in an attempt to put constraints on the fluorine content  
74 in the upper mantle, fluorine concentrations have recently been measured in nominally  
75 anhydrous mantle minerals (Beyer et al., 2012; Mosenfelder and Rossman, 2013a, b). These  
76 studies have demonstrated that up to 47 ppm of fluorine can be incorporated in natural olivine  
77 and pyroxene. By comparison, experimental studies performed to determine fluorine  
78 solubility in these major mantle mineral phases yielded maximum contents of fluorine of  
79 4500 ppm to 1900 ppm in olivine (Bromiley and Kohn, 2007; Bernini et al., 2012), 626 ppm  
80 in pyroxenes (Dalou et al., 2012), and 1110 ppm in pyrope (Bernini et al., 2012). Like water,  
81 that is stored in silicate minerals as hydroxyl species, it has been proposed that the mantle  
82 fluorine budget can be entirely accommodated by these mineral phases (Beyer et al., 2012,  
83 Crépisson et al., 2014). Based on the observation of clumped fluoride-hydroxyl defects in  
84 pure-Mg olivine, the major upper mantle mineral, it is likely that fluorine and water cycles  
85 may be strongly coupled through the nominally anhydrous minerals (Crépisson et al., 2014).  
86 Like for water, F may be transferred at depth during subduction processes. For example,  
87 experimental studies indicate that a dense hydrous magnesium silicate phase - superhydrous  
88 phase B - stabilized at subduction zone conditions in the transition zone. This phase might  
89 incorporate significant amounts of fluorine and carry it down to the deep mantle (e.g. Hazen  
90 et al., 1997). By analogy with water, one may speculate that a significant repository for  
91 fluorine may exist in the transition zone (TZ). This is the hypothesis we would like to test in  
92 this study.

93 In this work, we measure the F solubilities in wadsleyite (Wd) and ringwoodite (Rw)  
94 to assess the F storage capacity of the TZ. Indeed, it is critical to know to which extent the

95 potential storage capacity of the transition zone may affect the global F budget and cycle,  
96 within a framework whereby F would be continuously brought in the TZ by subduction.

97

## 98 **2. Materials and methods**

99

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

113 Recovered samples were then embedded in crystal bond and mirror polished on one-  
114 side. The mineral phases were characterized using Scanning Electron Microscopy (SEM) at  
115 IMPMC-UPMC. Mineral identification was realized using Raman spectroscopy. The fine  
116 structure of the minerals, imaging, diffraction, and chemical measurements were performed  
117 with a JEOL 2100F transmission electron microscope (TEM) with a field emission gun, and

118 equipped with JEOL EDX detectors at IMPMC (UPMC). The acceleration voltage was at 200  
119 kV and we reached a resolution of 1.8 Å. The samples for TEM were prepared by Focused  
120 Ion Beam (FIB) with the dual beam Zeiss Crossbeam Neon 40 ESB at IMPMC (UPMC). The  
121 final lamella-thickness obtain is under 100 nm for suitable electron transparency. Major  
122 element compositions of the minerals were measured using electron microprobe analyses  
123 (EPMA) with an acceleration of 15 kV and 15 µm defocused beam at 10 nA on CAMECA-  
124 SX100 at CAMPARIS facility (UPMC, France).

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

131 Before any analysis, the largest crystals were selected with SEM cartographies. PIGE and  
132 ERDA measurements have been realized simultaneously with Particle Induced X-Ray  
133 Emission (PIXE) and Rutherford Backscattering Spectrometry (RBS) measurements, using a  
134  $3 \times 3 \mu\text{m}^2$  proton beam of 3 MeV for PIGE and a  $4 \times 16 \mu\text{m}^2$   $^4\text{He}$  beam of 3 MeV for  
135 ERDA. ERDA analyzes were performed on areas previously analyzed for F.

136         All measurements were performed by a scanning the beam on large selected areas  
137 from  $24 \times 50$  to  $150 \times 100 \mu\text{m}^2$ . Data acquisitions were performed with a beam current of 500-  
138 550 pA, during 1 or 2 hours depending on the concentrations. The combination of RBS and  
139 PIXE with ERDA and PIGE was useful to identify the analyzed crystals (Rw, Wd, Ol) and to  
140 detect any chemical heterogeneity such as NaF-rich fine intergrowths in the grain boundaries.

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

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

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

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

162 When ERDA is standard less (Raepsaet et al., 2008; Bureau et al., 2009; Withers et al.,  
163 2012), the quantification of fluorine requires the use of F-known content samples having a  
164 bulk composition similar to the samples (i.e. silicates). Therefore we have used the  
165 pantellerite KE12 (4200 ppm F and 5.32 wt% Na, Métrich and Rutherford, 1992) for PIGE  
166 calibration. We have preferred this standard instead of a  $\text{CaF}_2$  window or a maccusanite glass  
167 containing 1.33 wt% F and 3.11wt% Na (Pichavant et al., 1987), because the stopping power



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

171

172

### 173 **3. Results**

174

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

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

191 are incorporated in the crystal lattice. EDX analyses and elemental cartography performed  
192 using PIXE (Particle Induced X-Ray Emission) and PIGE (Particle Induced Gamma Ray  
193 Emission) do not indicate any chemical heterogeneity in the bulk crystals. Moreover, the Na/F  
194 ratios measured by PIGE in Rw and Wd is systematically  $\ll 1.21$  (NaF ratio), confirming that  
195 the detected F is corresponding to a structural concentration and not to the presence of any  
196 sub-micron NaF inclusions. Na contents are high, from 713 to 3230, however, such high Na  
197 contents have already been reported in wadsleyites (2100-2400 ppm, Gudfinnsson and Wood,  
198 1998) synthesized at 1600°C and 14.2 GPa. In these experiments Na<sub>2</sub>O was present in the  
199 starting materials (a glass) and was not in excess (0.42 wt.% Na<sub>2</sub>O).

200 Ol, Wd and Rw compositions range from Fo<sub>88</sub> to Fo<sub>97</sub> (with Fo defined as  
201  $100 \cdot (\text{Mg}/(\text{Mg}+\text{Fe}))$ ), while F contents, determined by PIGE, range from 323 to 410 ppm F for  
202 Ol, from 665 to 1045 ppm F for Wd and from 186 to 1235 ppm F for Rw (Table 1). The  
203 detection limit for F ranges from 37 to 123 ppm F for any investigated phase. The highest F  
204 contents are found in anhydrous Wd and Rw (Table 1). With the exception of run H3695, Wd  
205 and Rw F contents are higher than those of Ol (Table 1). Water contents measured by using  
206 Elastic Recoil Detection Analysis (ERDA), amount 428 H<sub>2</sub>O for Ol, whereas 864 to 956 ppm  
207 H<sub>2</sub>O are detected in Wd and 854 to 1404 ppm H<sub>2</sub>O are measured for Rw (Table 1).

208 When comparing different temperatures of synthesis, a slight decrease of F content is  
209 observed with increasing temperature in hydrous Rw. We do not have enough results to  
210 determine if a temperature effect would affect the F content of both Rw and Wd, similarly to  
211 what as it has been shown for water contents in Wd by Demouchy and co-workers (2005, see  
212 Fig 4). Figure 5 shows that the highest F contents are associated with quasi-anhydrous  
213 minerals when fluorine is examined as a function of H<sub>2</sub>O.

214

#### 215 **4. Discussion**

216 *4.1 Water and Fluorine in Ringwoodite and Wadsleyite*

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

222 We show an H<sub>2</sub>O solubility contrast for Ol (up to 428 ppm) compared with Wd and  
223 Rw (from 854 to 1404 ppm) with more water dissolved in the two high-pressure phases. This  
224 is in agreement with previous studies (e.g. Bolfan-Casanova et al., 2000; Ohtani et al., 2001;  
225 Demouchy et al., 2005;) but the amount of water measured in Wd and Rw from this study is  
226 one order of magnitude lower than previously reported solubilities for these phases (up to 3  
227 wt.% e.g. Smyth and Jacobsen, 2006). Such a significant reduction of OH incorporation is  
228 likely attributed to the presence of NaF salt which will reduce the H<sub>2</sub>O activity in the melt in  
229 equilibrium with the mineral phases. Previous studies have observed a significant decrease of  
230 OH incorporation in enstatite (2.5 GPa and 1150-1400°C), linked to the increase of NaCl or  
231 KCl content in starting materials (Stalder et al., 2008). An additional possibility might be a  
232 competition process between OH and F for incorporation in the mineral lattices of Wd and  
233 Rw. Indeed, a recent study combining infrared characterization of experimentally F- and OH-  
234 enriched olivines and first-principle calculations, Crépisson and co-workers (2014) have  
235 demonstrated a close association of fluoride, hydroxyl groups and Si vacancies. They found  
236 evidence for the presence of clumped fluoride-hydroxyl defects in the forsterite structure.  
237 Whereas in NaF-free systems the proposed H<sub>2</sub>O incorporation mechanism mostly involves  
238 Mg vacancies in forsterite (e.g. Balan et al., 2011) and in ringwoodite (Blanchard et al., 2009).  
239 Blanchard et al. (2013) have also provided evidence for the association of hydroxyl groups  
240 with Si vacancies in H<sub>2</sub>O-rich wadsleyites. Assuming that F and OH share the same vacancies

241 in Wd and Rw, and considering the slight F content decrease associated with increasing SiO<sub>2</sub>  
242 contents (Fig 6), we propose that F may at least partially be associated with Si vacancies. This  
243 suggests that H<sub>2</sub>O and F cycles are linked in the upper mantle and TZ, through Ol, Wd and  
244 Rw.

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

252

#### 253 *4.2 Fluorine in the transition zone*

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

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

274 It has been proposed that a neutral buoyant hydrous melt phase on the top of the TZ (410  
275 km depth) could control the distribution of incompatible elements within the upper mantle,  
276 acting as a chemical filter, the so-called "water-filter" model (Bercovici and Karato, 2003). In  
277 this model a high water content within the range 0.2 – 2 wt.% is assumed in the TZ, which is  
278 consistent with the 1 wt. % of water measured in a natural diamond inclusion of ringwoodite  
279 (Pearson et al., 2014). The water dissolved in the mantle would create a thin layer of melt at  
280 410 km depth, corresponding to the transformation of Wd into Ol and a hydrous melt (Fig 7).  
281 This dehydration melting would create a 10 km thick layer of molten silicate just above the  
282 410-km discontinuity that would retain most of the water together with incompatible  
283 elements. Since the melt is denser than the TZ minerals at these pressures it would remain  
284 stable. In this view of the mantle, the layer of melt would act as a filter by removing elements  
285 rising from the deep mantle and keeping the upper mantle chemically depleted and anhydrous  
286 (Bercovici and Karato, 2003). Following this model, the TZ is enriched in water and fluorine  
287 even when the upper mantle is depleted.

288

289        *4.3 The Fluorine budget in the Bulk Silicate Earth*

290

291            Our new experimental data allow us to estimate an upper bound for the BSE content of  
292 F assuming that the TZ is hydrous and saturated in F. We have calculated a maximum value  
293 for the BSE content of F assuming that the TZ is hydrous and saturated in F. We have used  
294 the F content of 16 ppm for the lower mantle, determined by (Beyer et al., 2012) from the  
295 concentrations of F measured in melt inclusions trapped in olivines from OIB products, when  
296 the degree of melting is of 2%. The crust is believed to contain 553 ppm F (Rudnick and Gao,  
297 2003), the depleted mantle (TZ excluded) is expected to host 12 ppm F (Beyer et al.,  
298 2012). This F content, inferred from its concentration in Ol and orthopyroxene in spinel  
299 lherzolites, is in good agreement with the F concentration proposed for the depleted MORB  
300 mantle (11 ppm F, Salters and Stracke, 2004). The calculated primitive OIB source is  
301 supposed to contain 16 ppm F (17 ppm including a contamination by 3% of recycled crust)  
302 based on the measurement of natural OIB volcanic samples (Beyer et al., 2012). In addition,  
303 OIBs are assumed to be not affected in their ascent through the TZ (Bercovici and Karato,  
304 2003). In order to calculate the maximum amount of F in the TZ, we have used an average  
305 pyrolite mineral assemblage model, together with the F contents obtained in our experiments  
306 for Wd and Rw of mantle composition (Mg# 0.90, Table 1). We assume a high F content for  
307 Rw and Wd as a first approximation for the upper limit of the F BSE content. This is based on  
308 the recent discovery of high water content (1.5 wt.%) in a ringwoodite trapped in a natural  
309 diamond (Pearson et al., 2014) and makes the assumption that the OH and F cycles are linked  
310 in silicate minerals. This assumption needs to be verified by further studies, such as  
311 partitioning measurements, and the maximum F content in the TZ may be reconsidered later.  
312 We have also assumed that F contents in clinopyroxene, garnet and Ca-perovskite are not  
313 significant.

314 We obtain a value of  $23.8 \times 10^{22}$  g F for the BSE corresponding to 59 ppm F (Fig 7).  
315 This high limit value is twice higher than the previous calculation of 25 ppm F after  
316 McDonough and Sun (1995), calculated from the Fluorine contents of MORBs and based on a  
317 homogeneous mantle. If the BSE contained this higher (59 ppm) amount of Fluorine, this  
318 would mean that about 70% of Earth's total fluorine budget would be currently stored in the  
319 transition zone. Assuming the present-day flux for F recycling into the mantle (John et al.,  
320 2011, fig. 7), more than 16 billion years would be necessary to fill the transition zone by  
321 subduction recycling if the TZ if it contained the maximum value of  $16.8 \times 10^{22}$  g of F. As  
322 discussed above, the fluorine content of the bulk silicate Earth is probably in the range 25 to  
323 59 ppm and most of the mantle's fluorine is probably stored in the transition zone. If all these  
324 assumptions are correct, it would mean that, F was stored in the TZ during the crystallization  
325 of the magma ocean during the Earth's differentiation in the Hadean. This is possible if we  
326 assume that the “water-filter” model (Bercovici and Karato, 2003) is an efficient process for F  
327 retention in the mantle and consequently a key control on the abundance of F in the Earth's  
328 crust.

329 The Earth is the result of possibly complex accretion and differentiation processes.  
330 The primordial building material for the Earth is still the matter of strong debates (e.g. Marty,  
331 2012; Javoy, 1995; Albarède, 2009) especially with respect to volatile elements. Considering  
332 the BSE contents in volatile elements after (McDonough and Sun, 1995) and comparing them  
333 with the abundances of the carbonaceous chondrites (CC: the most primitive materials), it has  
334 been shown that fluorine is slightly enriched compared to heavy halogen elements (Cl, Br, I)  
335 and noble gases. Indeed, if hydrogen, carbon and heavy halogen contents would be obtained  
336 after the addition of 2 % of a CC late veneer, it would be necessary to add 17% mass of a  
337 carbonaceous chondrite to reach the observed BSE fluorine amount (Marty, 2012). This  
338 would be even worse if the BSE would content more than 25 ppm. This also emphasizes

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

341

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

## 346 **5. Conclusion**

347

348 We have shown that the fluorine solubility in Wd and Rw is high at water contents,  
349 pressures and temperatures relevant to the TZ. Therefore, we suggest that F may be  
350 significantly stored together with water in the TZ. The association of F and H<sub>2</sub>O shows that  
351 their two geochemical cycles are associated at least through their incorporation in nominally  
352 anhydrous minerals. Assuming that 95% of the subducted F is recycled back to the mantle, a  
353 significant amount of F would reach the TZ where the slab is believed to be stagnant. In this  
354 way the TZ would be continuously supplied in F and water by subduction processes. In the  
355 frame of the “water-filter model” at the top of the TZ, both F and water contents may be  
356 chemically zoned in the mantle at a steady state. The global content of F in the bulk silicate  
357 Earth is probably underestimated. Assuming a hydrous, F-saturated TZ, we calculate an upper  
358 limit for the BSE F content of 59 ppm wt., higher than the previous estimate of 25 ppm by  
359 mass assuming a homogeneous mantle (McDonough and Sun, 1995). It is not know whether  
360 the TZ is F-saturated but given this uncertainty we propose that BSE fluorine content is better  
361 quoted as being in the range between 25 and 59 ppm by mass. If a significant amount of F is  
362 stored in the TZ, it puts constrains on the models proposed to explain the origin of volatile



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

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390 **References**

391

392 Albarède F., 2009. Volatile accretion history of the terrestrial planets and dynamic  
393 implications, *Nature*, 461, 7268, 1227-1233.

394 Balan E., Ingrin J., Delattre S., Kovács I., Blanchard M., 2011. Theoretical infrared spectrum  
395 of OH-defects in forsterite, *Eur. J. Mineral.*, 23, 285-292.

396 Bercovici D., Karato S., 2003. Whole-mantle convection and the transition-zone water filter,  
397 *Nature*, 425, 39-44.

398 Bernini D., Wiedenbeck M., Dolejš D., and Keppler H., 2012. Partitioning of halogens  
399 between mantle minerals and aqueous fluids: implications for the fluid flow regime in  
400 subduction zones, *Contrib. Mineral. Petrol.*, 165, 117-128.

401 Beyer C., Klemme S., Wiedenbeck M., Stracke A., Vollmer C., 2012. Fluorine in nominally  
402 fluorine-free mantle minerals: Experimental partitioning of F between olivine,  
403 orthopyroxene and silicate melts with implications for magmatic processes, *Earth Planet.  
404 Sci. Lett.*, 337-338, 1-9.

405 Blanchard M., Balan E., Wright K., 2009. Incorporation of water in iron-free ringwoodite: A  
406 first-principles study, *Am. Mineral.*, 94, 83-89.

407 Blanchard M., Roberge M., Balan E., Fiquet G., Bureau H., 2013. Infrared signatures of OH-  
408 defects in wadsleyite: A first-principles study, *Am. Mineral.*, 98, 2132-2143.

409 Bolfan-Casanova N., Keppler H., Rubie D. C., 2000. Water partitioning between nominally  
410 anhydrous minerals in the MgO–SiO<sub>2</sub>–H<sub>2</sub>O system up to 24 GPa: implications for the  
411 distribution of water in the Earth's mantle, *Earth Planet. Sci. Lett.*, 182, 209-221.

412 Bromiley D.W., Kohn S.C., 2007. Comparisons between fluoride and hydroxide  
413 incorporation in nominally anhydrous and fluorine-free mantle minerals. *Geochim.*  
414 *Cosmochim. Acta*, 71 Sup. A124.

415 Bureau H., Keppler H., Métrich N., 2000. Volcanic degassing of bromine and iodine:  
416 experimental fluid/melt partitioning data and applications to stratospheric chemistry,  
417 *Earth Planet. Sci. Lett.*, 183, 51-60.

418 Bureau H., Foy E., Raepsaet C., Somogyi A., Munsch P., Simon G., Kubsy S., 2010.  
419 Bromine cycle in subduction zones through in situ Br monitoring in diamond anvil cells,  
420 *Geochim. Cosmochim. Acta*, 74, 3839-3850.

421 Bureau H., Raepsaet C., Khodja H., Carraro A., Aubaud C., 2009. Determination of hydrogen  
422 content in geological samples using elastic recoil detection analysis (ERDA), *Geochim.*  
423 *Cosmochim. Acta*, 73, 3311-3322.

424 Campbell J.L., Maxwell J.A., Teesdale W.J., 2005. The guelph-pixe software package-II.  
425 *Nucl. Instrum. Methods B*, 95, 407-421.

426 Crépisson C., Blanchard M., Bureau H., Sanloup C., Withers A. C., Khodja H., Surblé S.,  
427 Raepsaet C., Béneut K., Leroy C., Giura P., Balan E., 2014. Clumped fluoride-hydroxyl  
428 defects in forsterite: Implications for the upper-mantle, *Earth Planet. Sci. Lett.*, 390, 287-  
429 295.

430 Dalou C., Koga K. T., Shimizu N., Boulon J., Devidal J.-L., 2012. Experimental  
431 determination of F and Cl partitioning between lherzolite and basaltic melt, *Contrib.*  
432 *Mineral. Petrol.*, 163, 591-609.

433 Daudin L., Khodja H., Gallien J.-P., 2003. Development of “position–charge–time” tagged  
434 spectrometry for ion beam microanalysis. *Nucl. Instrum. Methods Phys. Res. B*, 210,  
435 153–158.

436 Demouchy S., Deloule E., Frost D. J., Keppler H., 2005. Pressure and temperature-  
437 dependence of water solubility in Fe-free wadsleyite, *Am. Mineral.*, 90, 1084-1091.

438 Déruelle B., Dreibus G., Jambon A., 1992. Iodine abundances in oceanic basalts: implications  
439 for Earth dynamics, *Earth Planet. Sci. Lett.*, 108, 217-227.

440 Dingwell D. B. and Mysen B. O., 1985. Effects of water and fluorine on the viscosity of albite  
441 melt at high pressure: a preliminary investigation, *Earth Planet. Sci. Lett.*, 74, 266-274.

442 Filiberto J., Wood J., Dasgupta R., Shimizu N., Le L., Treiman A. H., 2012. Effect of fluorine  
443 on near-liquidus phase equilibria of a Fe–Mg rich basalt, *Chem. Geol.*, 312-313, 118-  
444 126.

445 Frost D. J., Langenhorst F., van Aken P. A., 2001. Fe–Mg partitioning between ringwoodite  
446 and magnesiowüstite and the effect of pressure, temperature and oxygen fugacity, *Phys.*  
447 *Chem. Miner.*, 28, 455-470.

448 Fukao Y., Widiyantoro S., Obayashi M., 2001. Stagnant slabs in the upper and lower mantle  
449 transition region, *Rev. Geophys.*, 39, 291–323.

450 Habrioux A., Surble S., Berger P., Khodja H., D’Affroux A., Mailley S., Gutel T., Patoux S.  
451 2012. Nuclear microanalysis of lithium dispersion in LiFePO<sub>4</sub> based cathode materials  
452 for Li-ion batteries. *Nucl. Instrum. Methods Phys. Res. B*, 290, 13–18.

453 Hazen R. M., Yang H., Prewitt C. T., Gasparik T., 1997. Crystal chemistry of superfluorous  
454 phase B (Mg<sub>10</sub>Si<sub>3</sub>O<sub>14</sub>F<sub>4</sub>); implications for the role of fluorine in the mantle, *Am.*  
455 *Mineral.*, 82, 647-650.

456 Hervig R.L., Bell D.R. 2005. Fluorine and hydrogen in mantle megacrysts. AGU, Fall  
457 Meeting 2005, abstract #V41A-1426.

458 Gudfinnsson G.H., Wood B.J., 1998. The effect of trace elements on the olivine-wadsleyite  
459 transformation, *Am. Mineral.*, 83, 1037-1044.

460 Jambon A., Déruelle B., Dreibus G., Pineau F., 1995. Chlorine and bromine abundance in  
461 MORB: the contrasting behaviour of the Mid-Atlantic Ridge and East Pacific Rise and  
462 implications for chlorine geodynamic cycle, *Chem. Geol.*, 126, 101-117.

463 Javoy M., 1995. The integral enstatite chondrite model of the Earth, *Geophys. Res. Lett.*, 22,  
464 2219–2222.

465 Jesus A.P., Braizinha B., Ribeiro J.P., 2000. Excitation function and cross-sections of the  
466 reaction  $^{19}\text{F}(p,p'\gamma)^{19}\text{F}$ . *Nucl. Instrum. Methods Phys. Res. B*, 161-163, 186-190.

467 John T., Scambelluri M., Frische M., Barnes J. D., Bach W., 2011. Dehydration of subducting  
468 serpentinite: Implications for halogen mobility in subduction zones and the deep halogen  
469 cycle, *Earth Planet. Sci. Lett.*, 308, 65-76,

470 Khodja H., Berthoumieux E., Daudin L., Gallien J.-P., 2001. The Pierre Süe Laboratory  
471 nuclear microprobe as a multi-disciplinary analysis tool, *Nucl. Instrum. Methods Phys.*  
472 *Res. B* , 181, 83-86.

473 Marty B., 2012. The origins and concentrations of water, carbon, nitrogen and noble gases on  
474 Earth, *Earth Planet. Sci. Lett.*, 313-314, 56-66.

475 Mayer, M., 1997. SIMNRA User's Guide. Report IPP 9/113, Max-Planck-Institut für  
476 Plasmaphysik, Garching, Germany.

477 McDonough W. F., Sun S., 1995. The composition of the Earth, *Chem. Geol.*, 120, 223-253.

478 Métrich N., Rutherford M. 1992. Experimental-Study of Chlorine Behavior in Hydrous Silicic  
479 Melts. *Geochim. Cosmochim. Acta* 56, 607–616.

480 Mosbah M, Métrich N., 1991. PIGME fluorine determination using a nuclear microprobe with  
481 application to glass inclusions. *Nucl. Instrum. Methods Phys. Res. B*, 58, 227-231.

482 Mosenfelder J. L., Rossman G. R., 2013a. Analysis of hydrogen and fluorine in pyroxenes: I.  
483 Orthopyroxene, *Am. Mineral.*, 98, 1026-1041.

484 Mosenfelder J. L., Rossman G. R., 2013b. Analysis of hydrogen and fluorine in pyroxenes: II.  
485 Clinopyroxene , Am. Mineral., 98, 1042-1054.

486 Ohtani E., Toma M., Litasov K., Kubo T., Suzuki A., 2000. Stability of dense hydrous  
487 magnesium silicate phases and water storage capacity in the transition zone and lower  
488 mantle, Phys. Earth Planet. Inter., 124, 105-117.

489 Peacock S. A., 1990. Fluid Processes in Subduction Zones, Science, 248, 329-337.

490 Pearson D. G., Brenker F. E., Nestola, McNeill J., Nasdala L., Hutchison M. T., Matveev  
491 S., Mather K., Silversmit G., Schmitz S., Vekemans B., Vincze L., 2014. Hydrous  
492 mantle transition zone indicated by ringwoodite included within diamond, Nature, 507,  
493 221-224.

494 Pichavant M., Valencia-Herrera J., Boulmier S., Briquieu L., 1987. The Macusani glasses S.E.  
495 Peru : evidence of chemical fractionation in peraluminous magmas, in “Magmatic  
496 processes : physico-chemical principles. Geochem. Soc. 1, 359–373.

497 Pyle D. M. and Mather T. A., 2009. Halogens in igneous processes and their fluxes to the  
498 atmosphere and oceans from volcanic activity: A review, Chem. Geol., 263, 110-121.

499 Raepsaet C., Bureau H., Khodja H., Aubaud C., Carraro A. , 2008. Micro-ERDA  
500 developments in order to improve the water content determination in hydrous and  
501 nominally anhydrous mantle phases. Nucl. Instrum. Methods Phys. Res. B, 266, 1333–  
502 1337.

503 Ringwood A. E., A model for the upper mantle, J. Geophys. Res., 67, 857-867.

504 Rudnick R. L., Gao S., 2003. Composition of the Continental Crust, in Treatise on  
505 Geochemistry, Elsevier, 1-64.

506 Salters V. J. M., Stracke A., 2004. Composition of the depleted mantle, Geochem. Geophys.  
507 Geosystems, 5.

508 Schilling J.-G., Bergeron M. B., Evans R., Smith J. V., 1980. Halogens in the Mantle Beneath  
509 the North Atlantic, *Philos. Trans. R. Soc. London* 297, 147-178.

510 Smith J. V., 1981. Halogen and phosphorus storage in the Earth, *Nature*, 289, 762-765.

511 Smyth J.R, Jacobsen S.D., 2006. Nominally anhydrous Minerals and Earth's deep Water  
512 Cycle, in *Earth's Deep Water Cycle*, Ed. S. D. Jacobsen and S. Van der Lee Eds. AGU  
513 Monography, 1-11.

514 Stalder R., Kronz A., Simon K., 2008. Hydrogen incorporation in enstatite in the system  
515 MgO–SiO<sub>2</sub>–H<sub>2</sub>O–NaCl, *Contrib. Mineral. Petrol.*, 156, 653-659.

516 Straub, S.M., and Layne, G.D. 2003. The systematics of chlorine, fluorine, and water in Izu  
517 arc front volcanic rocks: Implications for volatile recycling in subduction zones. *Geochim.*  
518 *Cosmochim. Acta* 67, 4179–4203.

519 Withers A. C., Bureau H., Raepsaet C., Hirschmann M. M., 2012. Calibration of infrared  
520 spectroscopy by elastic recoil detection analysis of H in synthetic olivine, *Chem. Geol.*,  
521 334, 92-98.

522 **Figure captions**

523

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

529 **Fig. 2:** SEM pictures of hydrous and anhydrous ringwoodites showing the difference in  
530 crystal sizes: about 10  $\mu\text{m}$  for anhydrous Rw and about 40  $\mu\text{m}$  for hydrous Rw. Anhydrous F  
531 Rw, sample H3567 ; B Hydrous F Rw, sample H3696

532

533 **Fig. 3:**

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

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

538

539 **Fig. 4:**

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

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



545 **Fig. 5:**

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

549 **Fig. 6:**

550 F ppm wt. plotted versus SiO<sub>2</sub> wt. % contents. The highest F contents are associated with the  
551 lowest SiO<sub>2</sub> concentrations in ringwoodites possibly in wadsleyites. Assuming a similar  
552 incorporation processes for F in close association with OH in Wd and Rw, than in Ol, one  
553 may suggest an incorporation in Si vacancies. Symbols as in Figure 3.

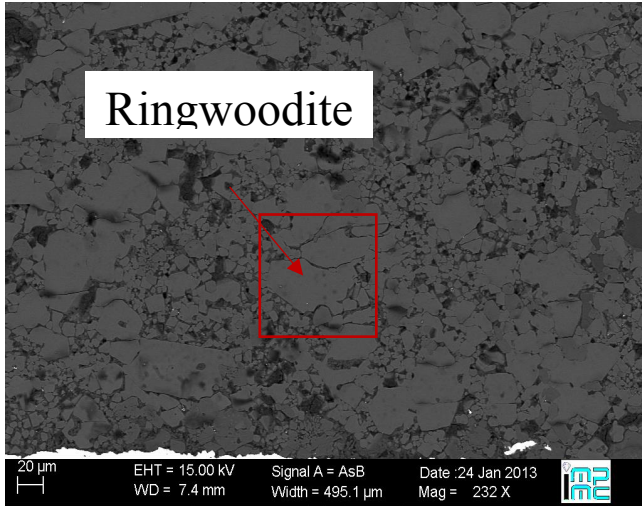
554 **Fig 7:**

555 Schematic section of the interior of the Earth showing F storage and fluxes. Yellow arrows  
556 show F and H fluxes: estimated fluxes of HF released to the atmosphere (Pyle et Mather,  
557 2009) and subducted F (John et al., 2011) and H (Straub and Layne, 2003) fluxes.  
558 Distribution of F in the mantle is from this study. In this model the TZ is enriched both in F  
559 and H. T This region of the mantle may control the distribution of these two volatile elements  
560 via the "water filter" model (Bercovici and Karato, 2003).

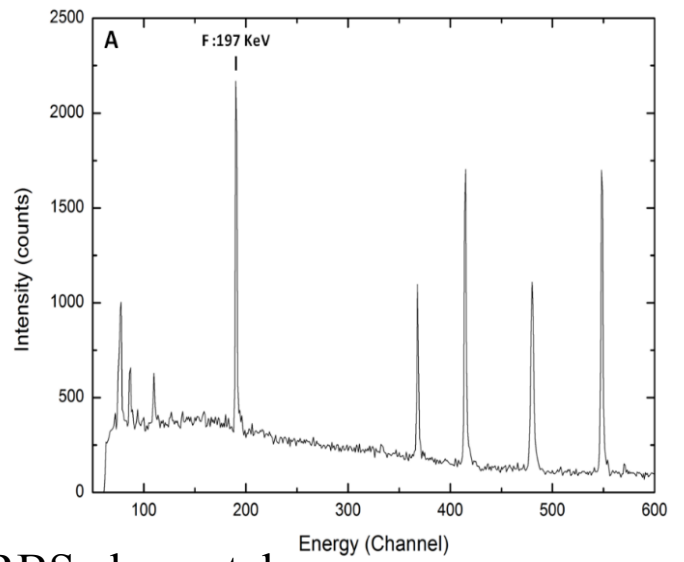
561

Fig 1

SEM picture of sample #3588



PIGE



PIXE, PIGE and RBS elemental

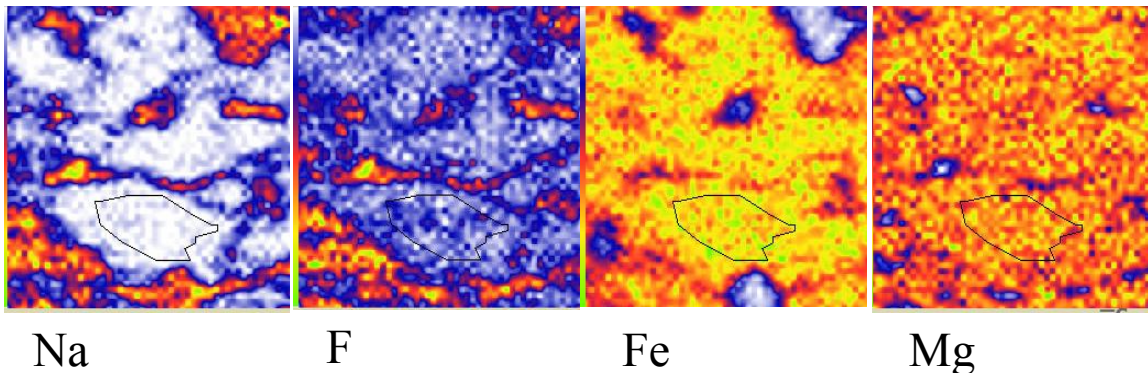


Fig 2

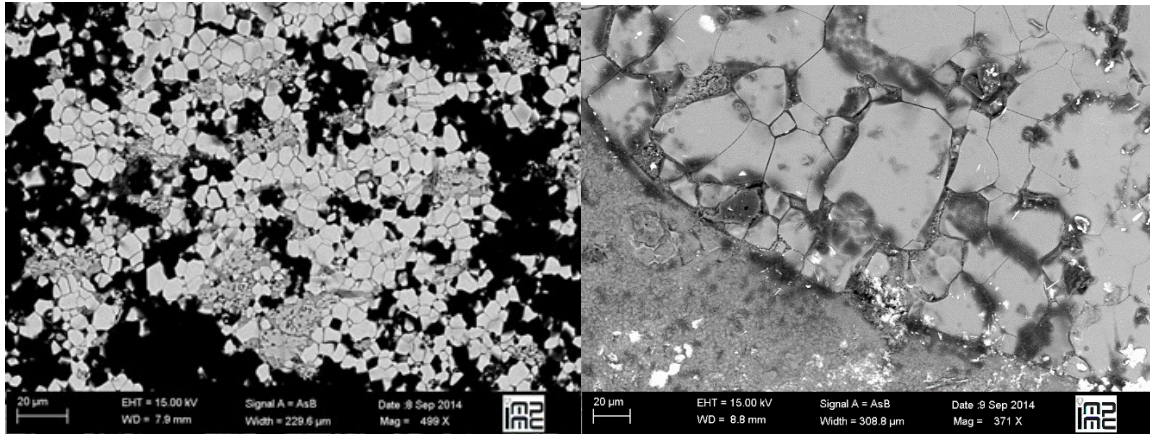


Fig 3

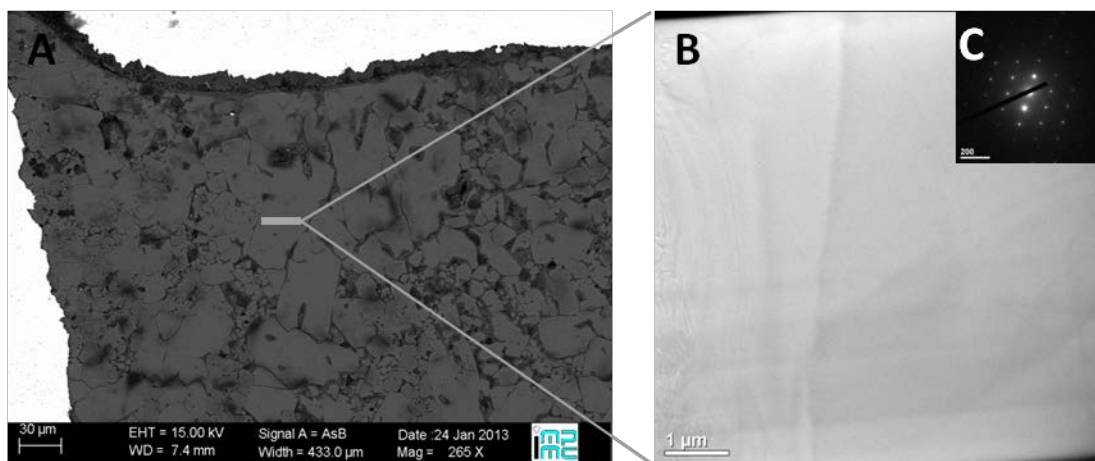


Fig 4

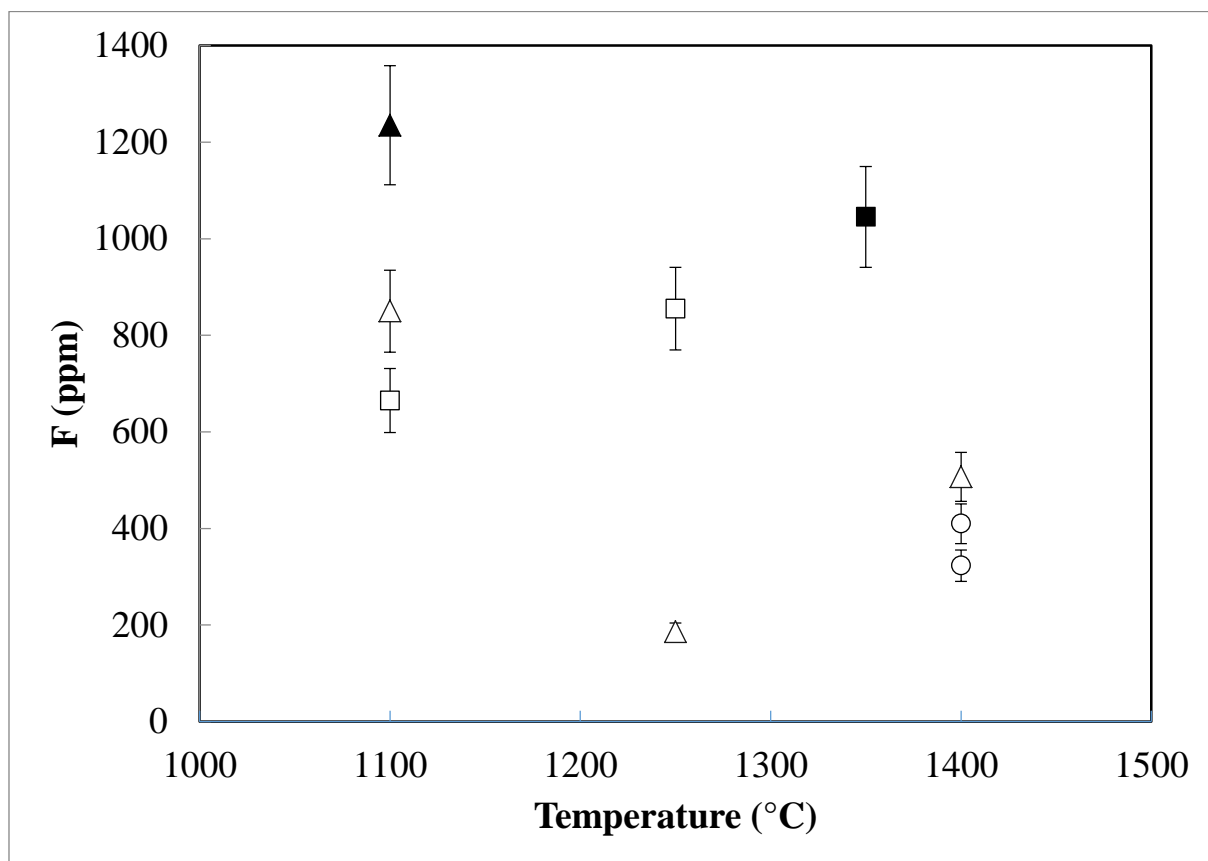


Fig 5

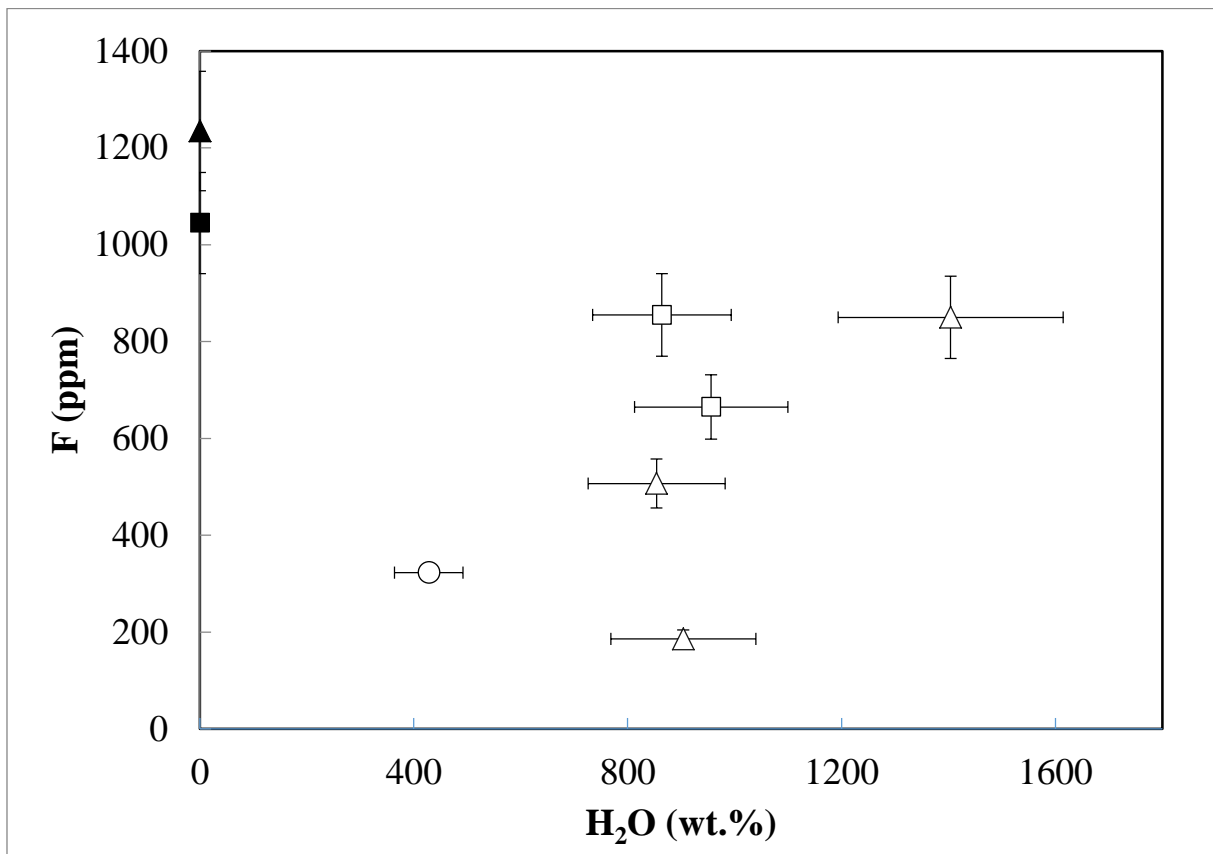
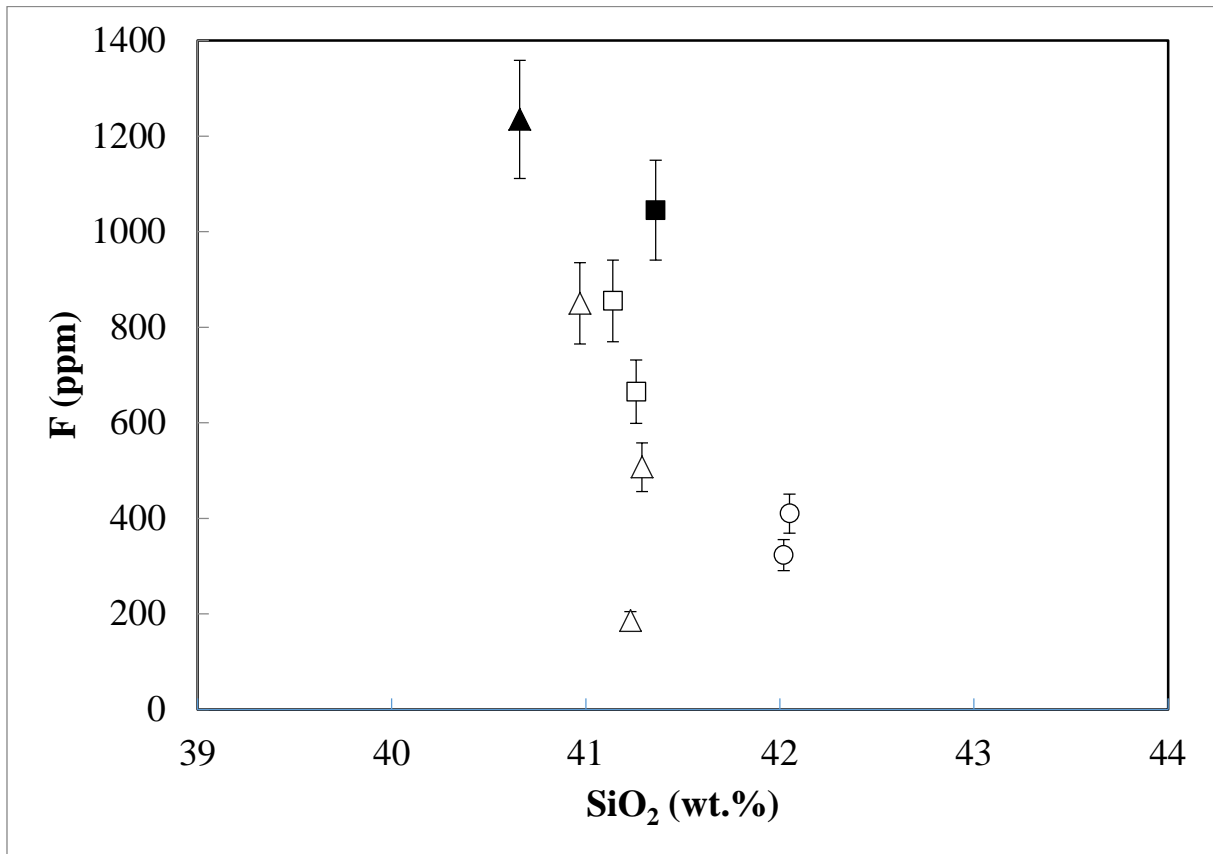


Fig 6







**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 <sub>2</sub>
Synthetic Powder SP					Mixture of SiO <sub>2</sub> + 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 $\mu$ m), enstatite, NaF
H3567(**)	20	1100	240	SCP+ 5 wt.% NaF	Ringwoodite (20 $\mu$ m), stishovite, NaF
42_F(*)	14	1400	240	SP + 5 wt.% NaF + 2 wt.% Mg(OH) <sub>2</sub>	Olivine (70 $\mu$ m), enstatite, NaF-bearing glass
88_F(*)	14	1400	360	SCP + 5 wt.% NaF + 2 wt.%Mg(OH) <sub>2</sub>	Olivine (80 $\mu$ m), enstatite, NaF-bearing glass
40_F(*)	14	1100	240	SP + 5 wt.% NaF + 2 wt.% Mg(OH) <sub>2</sub>	Wadsleyite (80 $\mu$ m), enstatite, NaF-bearing glass
H3588(***)	20	1100	240	SCP + 5wt.% NaF + 2 wt.% Mg(OH) <sub>2</sub>	Ringwoodite 80 $\mu$ m), stishovite, NaF-bearing glass
H3695(*)	22	1250	240	SCP + 5 wt.% NaF + 2 wt.% Mg(OH) <sub>2</sub>	Ringwoodite (60 $\mu$ m), stishovite, NaF-bearing glass
H3695(*)	22	1250	240	SCP + 5 wt.% NaF + 2 wt.% Mg(OH) <sub>2</sub>	Ringwoodite (60 $\mu$ m), stishovite, NaF-bearing glass
H3696(*)	22	1400	240	SCP + NaF 5 wt.% + 2 wt.% Mg(OH) <sub>2</sub>	Ringwoodite (60 $\mu$ m), 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  $\mu$ m are given in brackets

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

Sample		Oxides %wt (% rel)												
		SiO <sub>2</sub>	FeO	MnO	Al <sub>2</sub> O <sub>3</sub>	Na <sub>2</sub> O	MgO	CaO	TiO <sub>2</sub>	Total	Mg #	H <sub>2</sub> 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. H<sub>2</sub>O 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.