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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 H₂O) and in Rw (186 to 1235 ppm F, up to 1404 ppm H₂O). 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, SiO₂, FeO oxides, and (b) a mixture of natural pure San
102 Carlos olivine (Fo₉₀) fine powders mixed with SiO₂. The addition of SiO₂ 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% H₂O. Mixtures were prepared in
107 order to obtain bulk compositions of about Fo₉₀, 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 $4 \times 16 \mu\text{m}^2$ ^4He 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 24×50 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 μm 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 μm 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 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 Na₂O was present in the
199 starting materials (a glass) and was not in excess (0.42 wt.% Na₂O).

200 Ol, Wd and Rw compositions range from Fo₈₈ to Fo₉₇ (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 H₂O for Ol, whereas 864 to 956 ppm
207 H₂O are detected in Wd and 854 to 1404 ppm H₂O 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 H₂O.

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 H₂O 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 H₂O 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 H₂O 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 H₂O-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 SiO₂
242 contents (Fig 6), we propose that F may at least partially be associated with Si vacancies. This
243 suggests that H₂O 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 8.7×10^{14} g
268 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
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 23.8×10^{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 16.8×10^{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 H₂O 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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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 μm . 100*100 μm^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 μm for anhydrous Rw and about 40 μm 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 SiO₂ wt. % contents. The highest F contents are associated with the
551 lowest SiO₂ 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.

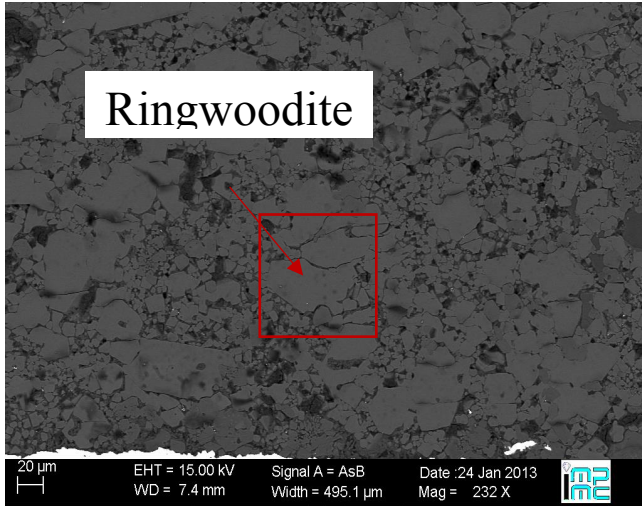
554 **Fig 7:**

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).

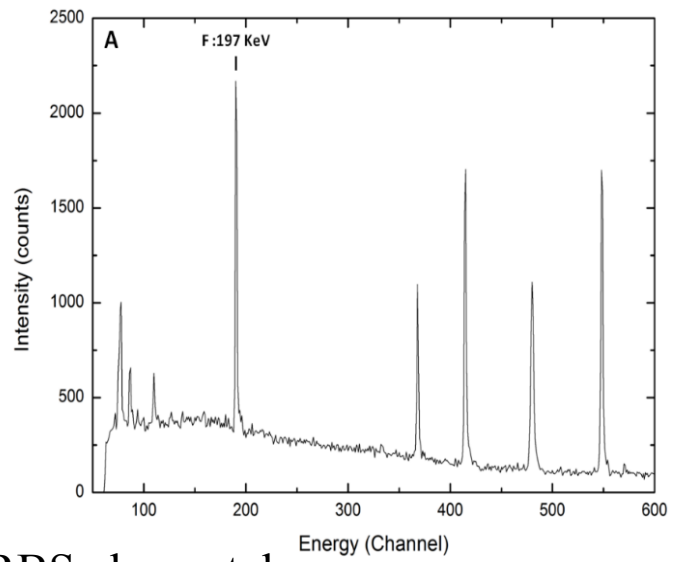
561

Fig 1

SEM picture of sample #3588



PIGE



PIXE, PIGE and RBS elemental

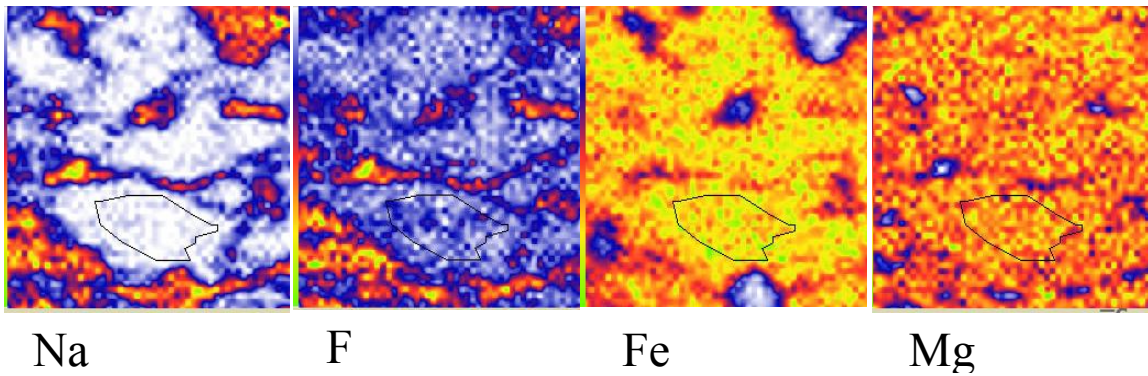


Fig 2

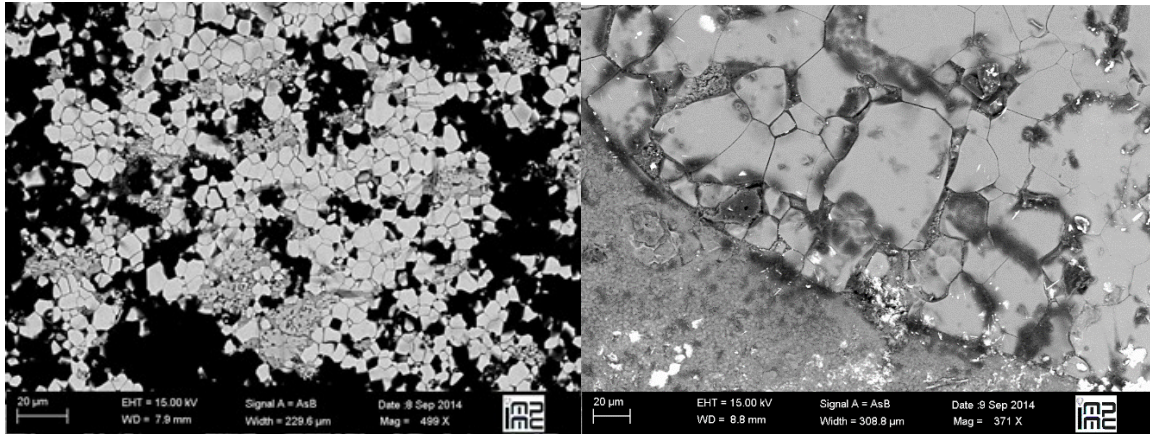


Fig 3

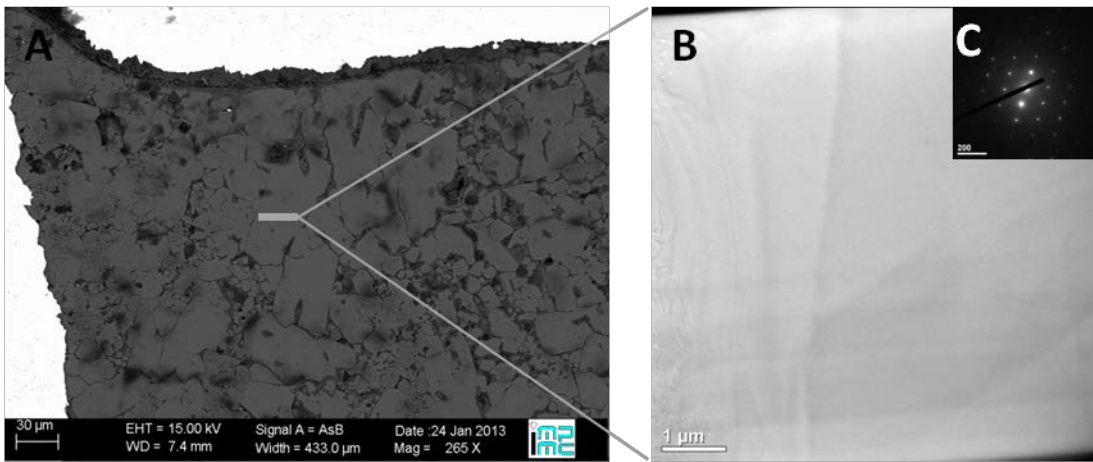


Fig 4

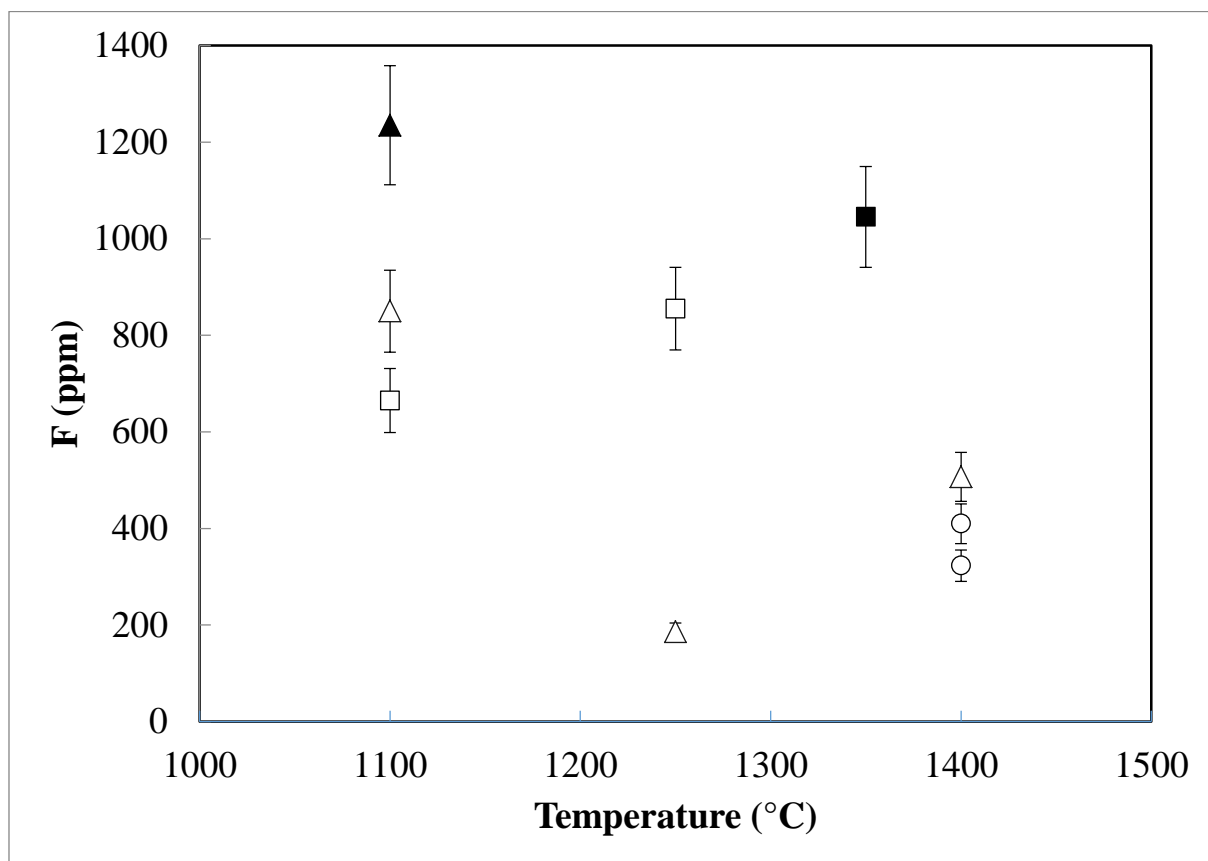


Fig 5

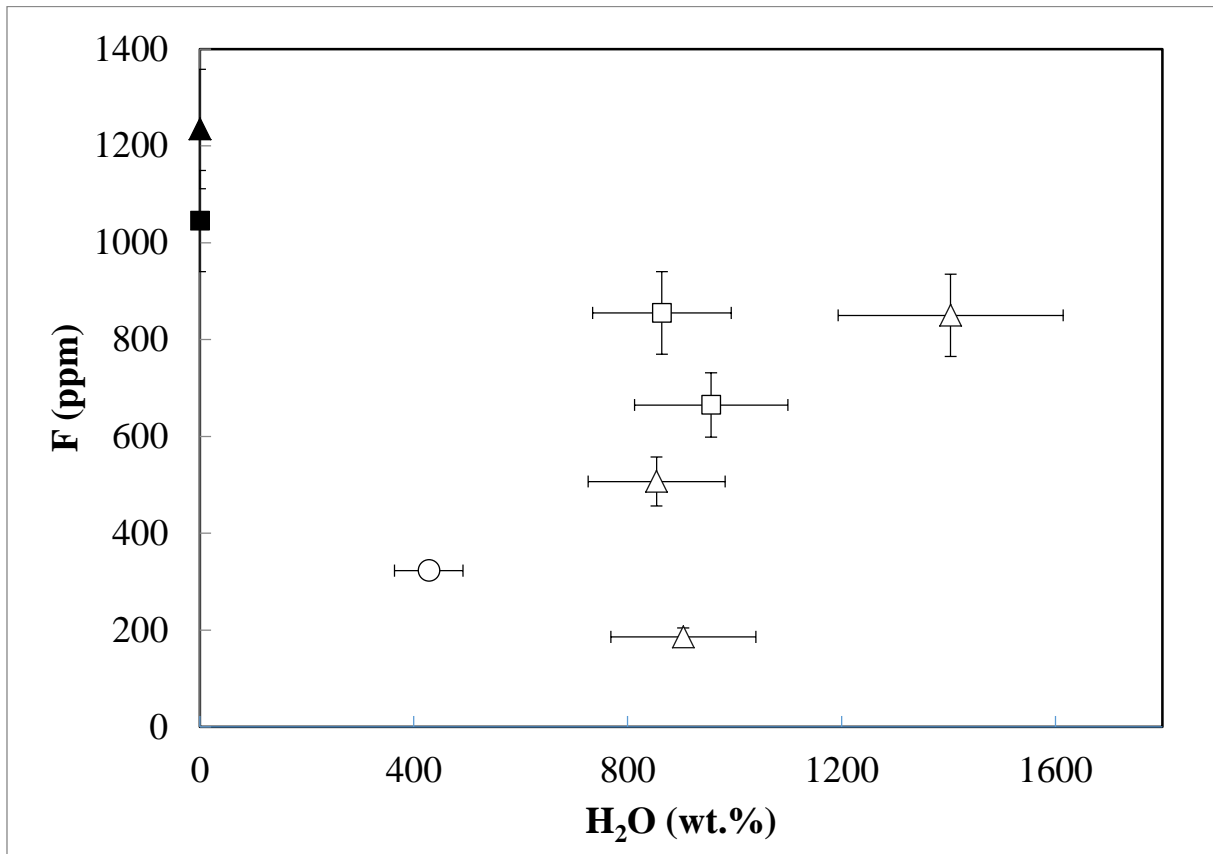


Fig 6

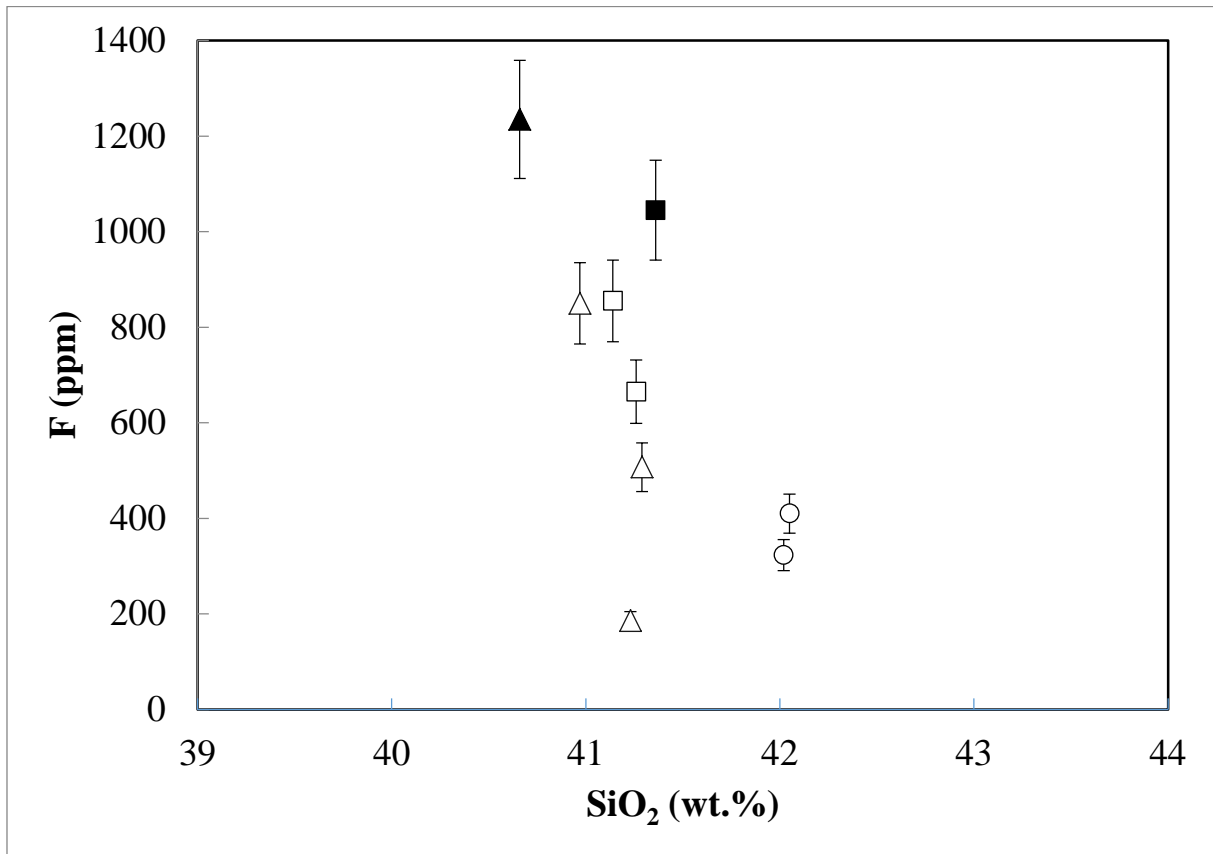


Fig 7

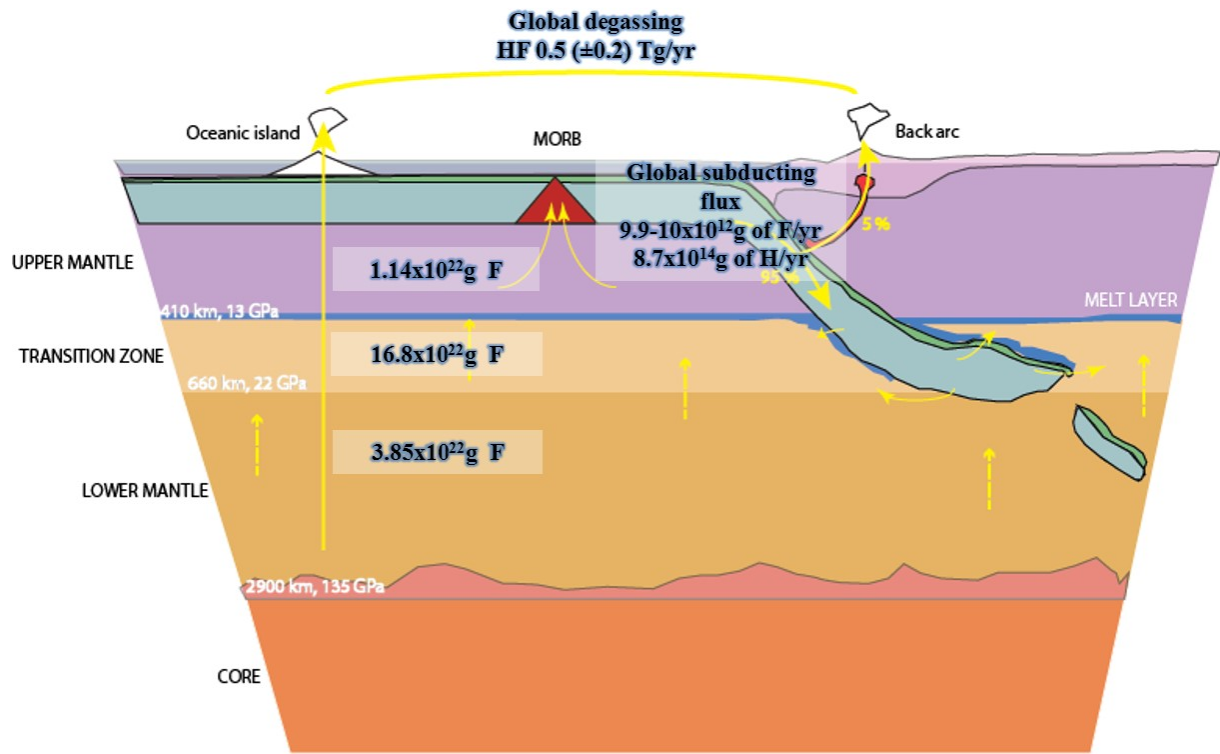


Table 1: Starting materials, experimental conditions and run products

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.