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# Xenon and iodine behaviour in magmas

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27

## Abstract

28

29 Iodine (I) and xenon (Xe) are two key elements that trace Earth's differentiation (e.g. atmosphere  
30 formation) and dynamics (e.g. volcanism and recycling at subduction zones). Iodine and Xe  
31 abundances are linked through the decay of the extinct  $^{129}\text{I}$  that produced  $^{129}\text{Xe}$ , which is today  
32 depleted in the Earth's atmosphere compared to the composition of the solar system (i.e.  
33 chondrites). Iodine and Xe cycles and storage in the deep Earth are almost unknown, which is in  
34 large part due to the fact that their behaviour in magmas and fluids, key agents of mass transfer  
35 through planetary envelopes, are poorly known. Here, the solubility of Xe and I in melts is  
36 measured under high pressure ( $P$ ) and temperature ( $T$ ) conditions using large volume presses, and  
37 Xe and I behaviour in melts and fluids is monitored *in situ* under high  $P$ - $T$  conditions using resistive  
38 heating diamond anvil cells combined with synchrotron x-ray fluorescence (XRF) and Raman  
39 spectroscopy. Xenon, I and H ( $\text{H}_2\text{O}$ ) contents were measured in quenched glasses by particle x-ray  
40 Emission (PIXE) and Elastic Recoil Detection Analysis (ERDA). Solubility, speciation and  
41 degassing processes are investigated for two different compositions: haplogranitic melt (HPG  
42 analogue for crustal melts) and basaltic melts (MORB and IAB). Experimentally measured  
43 solubilities for both elements are much higher than their natural abundances in terrestrial magmas.  
44 Xenon solubility at 3.5 GPa reaches 4.00 wt.% in HPG and 0.40 wt.% in basalts. Iodine solubility  
45 is 0.46 wt.% at 0.4 GPa on average in HPG, and reaches 1.42 wt.% in basalts at 2 GPa. The *in situ*  
46 Raman spectroscopic study shows that I forms I-I bonds in hydrous high P fluids/melts unlike Xe  
47 that was previously shown to oxidize in high P melts. The XRF monitoring of I and Xe partitioning

48 between aqueous fluids and silicate melts during decompression (i.e. water degassing) shows that  
49 Xe degassing is strongly *P-T* dependent and can be retained in the melt at deep crust conditions,,  
50 while I is totally washed out from the silicate melt by the aqueous phase. Xenon and I degassing  
51 processes are based on different mechanisms, which implies that the atmospheric isotopic signature  
52 of Xe cannot be inherited from a process involving volcanic water degassing. Instead, <sup>129</sup>Xe  
53 depletion may originate from a separation of both elements at depth, by deep fluids, a proposition  
54 that agrees with a deep storage of Xe in minerals.

55

56 **Keywords** iodine, xenon, silicate melt, solubility, speciation, volcanic degassing

57

58      **1. Introduction**

59

60 Iodine (I) and xenon (Xe) are highly volatile elements, differing only by one proton, but **due to**  
61 **their difference in electron configuration**, I is a very reactive halogen element while Xe is a noble  
62 gas. They share a very low abundance compared to chondrites in the Bulk Silicate Earth (BSE) and  
63 low temperatures of condensation (see Marty, 2012). Both I and Xe are potentially “missing” in  
64 the BSE compared to solar abundances. Iodine and Xe elements are neighbours in the periodic  
65 table, and are linked by the radioactive decay of the today extinct  $^{129}\text{I}$  to  $^{129}\text{Xe}$  (half life 16.1 million  
66 years).

67 Yet unsolved issues are: (1) why is the Earth’s atmosphere depleted in elemental Xe and  $^{129}\text{Xe}$ ?  
68 (2) how are I and Xe recycled back to the mantle at subduction zones? (3) whether or not I and Xe  
69 are stored in the deep Earth, and if so, by which processes and to what extent?

70

71

72 Iodine is the heaviest stable halogen element, having the largest ionic radius, and for this reason it  
73 is much less frequently incorporated in minerals than chlorine (Cl) and bromine (Br) (McDonough  
74 and Sun, 1995), whereas they shares many other characteristics. Iodine is mostly found at the ppb  
75 level in magmatic rocks and volcanic glasses (Muramatsu and Wedepohl, 1998; Schilling et al.,  
76 1980; Déruelle et al., 1992; Kendrick et al., 2012). It is more concentrated in sediments than in any  
77 other geologic materials (Muramatsu and Wedepohl, 1998). Being hydrophilic and biophilic, it is  
78 enriched in marine organic matter and associated fluids (Fehn 2012).  $^{129}\text{I}$  is used to trace crustal

79 and volcanic fluids in subduction contexts (Fehn, 2012), where serpentinites are efficient traps for  
80 subducted I (John et al., 2011; Kendrick et al., 2012). Experimental studies have demonstrated that  
81 heavy halogens Br and I may significantly degas from hydrous silicic magmas (Bureau et al., 2000;  
82 2010; 2016). The uncertainty on I outgassing fluxes is due to the lack of constraints on: (1) the real  
83 I content of magmas; (2) the storage capacity of magmas with respect to I, and more specifically I  
84 solubility in melts relevant for subduction-related volcanism; (3) the real abundance of I in the bulk  
85 silicate Earth, (4) how much of subducted I is deeply recycled. Mass balance calculations based on  
86 the I content of MORBs (Mid Ocean Ridge Basalts) have been used to predict the total amount of  
87 I in the bulk silicate Earth (McDonough and Sun, 1995), resulting in a strong depletion of the BSE  
88 compared to solar compositions (i.e. CI chondrites). Two scenarios are proposed: (1) I loss by a  
89 strong degassing event of the magma ocean during the Hadean eon (Bureau et al., 2016); (2) I  
90 storage in the core (Armytage et al., 2013) or in a hidden deep mantle reservoir(s). Alternatively,  
91 there could be no I depletion as indicated by new measurements of halogen contents in chondrites  
92 (Clay et al. 2018).

93 As most noble gases, Xe is a tracer of Earth's dynamics. Xenon isotopes are important markers of  
94 planetary processes, and the I-Pu-Xe system is used to date the formation of the atmosphere (Ozima  
95 and Podosek, 1999, Pepin 2006, Avice and Marty 2014). About 90% of Earth's primordial Xe is  
96 missing from the atmosphere of the Earth (Anders and Owen 1977, Ozima and Podosek, 1999),  
97 this is the "missing Xe" issue. Xenon is depleted by one order of magnitude relative to other volatile  
98 elements (water, carbon, neon, argon and krypton) when normalized to the chondritic composition,  
99 and atmospheric Xe is enriched in heavy isotopes by 3–4%  $\text{amu}^{-1}$  (unified atomic mass unit)  
100 relative to chondritic and solar compositions, this is the "Xe paradox" (Krummenacher et al. 1962).  
101 The Earth is also depleted in radiogenic Xe isotopes, i.e. I-derived  $^{129}\text{Xe}$  and Pu- and U-derived

102 fissionogenic isotopes (Tolstikhin et al., 2014). Recent measurements on deep fluids and fluid  
103 inclusions trapped in Archean crustal minerals show that Xe isotopic fractionation was still  
104 occurring throughout the Archean era (Pujol et al. 2011, Avice et al. 2017). Modelling Xe degassing  
105 and re-gassing over geological times reveals that Xe recycling has been significant after 2.5-2.8 Ga  
106 (Holland and Ballentine 2006, Avice et al., 2017; Parai and Mukhopadhyay, 2018).

107 Xe escape from the atmosphere could explain this evolution (Pepin, 2006; Hebrard and Marty 2014,  
108 Zahnle et al., 2019). That requires either some degree of storage of Xe at depth (Pepin 2006) or the  
109 photoionization of Xe (Hebrard and Marty 2014, Zahnle 2019) providing conditions: the presence  
110 of an atmospheric organic haze and strongly nonlinear photoionization process to compensate for  
111 the weak UV flux in the Archean (Hebrard and Marty 2014), or an unlikely large amount of H<sub>2</sub>O  
112 reduction by FeO during the Archean to provide sufficient H<sup>+</sup> escape flux or yet unexplained Xe  
113 escape bursts (Zahnle et al. 2019).

114 Alternatively, the missing Xe could be stored at depth, in the deep crust or mantle either in high *P*  
115 melts (Leroy et al., 2016) and/or minerals as shown for quartz (Sanloup et al., 2005, Creppisson et  
116 al. 2019) and olivine (i.e. Sanloup et al., 2011; Creppisson et al., 2018), or in the core (Lee and  
117 Steinle-Neumann, 2006, Zhu et al. 2014).

118 In the case of Mars' atmosphere, in which Xe is also depleted both in bulk element content and in  
119 light isotopes, it was proposed that I separated from Xe through a process involving water  
120 (Musselwhite and Drake, 1991) as on a chemical point of view I is hydrophilic whereas Xe is  
121 hydrophobic. Liquid water, supposed to be present at that time, would have trapped I (including  
122 <sup>129</sup>I later transformed in <sup>129</sup>Xe) while Xe was lost to space. This is the model proposed to explain  
123 that for Mars  $(^{129}\text{Xe}/^{132}\text{Xe})_{\text{Mars'atmosphere}} > (^{129}\text{Xe}/^{132}\text{Xe})_{\text{Marsmantle}}$  whereas this is the opposite for

124 the Earth:  $(^{129}\text{Xe}/^{132}\text{Xe})_{\text{Earth's atmosphere}} < (^{129}\text{Xe}/^{132}\text{Xe})_{\text{MORB}}$ . Iodine and Xe should exhibit different  
125 behaviours during an early major water degassing event that may have occurred during the Hadean  
126 magma ocean era.  $^{129}\text{I}$  became extinct about 100 million years after the formation of the solar  
127 system. If I was degassed from the magma ocean and lost from the atmosphere together with water  
128 (Bureau et al., 2016), but not Xe, such a process would have affected the atmosphere only, and  
129 may have contributed to the isotopic atmospheric depletion in  $^{129}\text{Xe}$  observed today. *If Xe was lost  
130 together with I, magma degassing is not the process to explain its atmospheric isotopic depletion.*

131  
132  
133 We test the *effect* of an early water degassing process of the magma ocean *on a potential separation  
134 of I from Xe*. For this purpose, we developed a multi-diagnostic experimental approach to measure  
135 the solubility of both Xe and I in melts using large volume presses, and monitor Xe and I  
136 partitioning between hydrous melts and aqueous fluids in situ at high pressure ( $P$ ) and temperatures  
137 ( $T$ ) during decompression (i.e. degassing of an ascending magma) combining diamond anvil cells  
138 experiments with synchrotron x-ray fluorescence XRF and, with Raman micro-spectroscopy  
139 devoted to measure I speciation in high  $P$  melts/fluids. We propose that Xe and I could be stored  
140 at depth, possibly in deep magma or melt layers and their crystallisation products.

141

## 142 **2. Methods**

143

### 144 *1. Synthesis of the starting materials*



145 Iodine and Xe bearing glasses are synthesized to obtain starting materials for diamond anvil cells  
146 experiments, and determine solubilities in high P silicate melts.

147 We use a natural Island Arc Basalt (IAB, basaltic sample STV301, from St Vincent volcano,  
148 Pichavant et al., 2002), relevant for subduction zones context; a natural Mid Ocean Ridge Basalt  
149 (MORB, BN06-11 from Juan de Fuca Ridge, Prouteau and Scaillet, 2013), and a synthetic  
150 haplogranite (HPG, Bureau and Keppler, 1999), a composition relevant for continental crust melts  
151 (e.g. Schmidt et al., 1997), also used as a proxy for subduction zones magmas (e.g. Bureau et al.,  
152 2003, 2010; 2016).

153 The IAB and MORB powders are obtained by crushing the natural lava samples. The HPG glass  
154 is prepared from a mixture of pure oxides and carbonate powders ( $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Na}_2\text{CO}_3$ ,  $\text{K}_2\text{CO}_3$ ).  
155 The HPG powder is dehydrated and degassed from  $\text{CO}_2$  by a slow ramp heating from room  
156 temperature to  $1200^\circ\text{C}$  during 8 hours, it is melted in an atmospheric furnace for one hour at  
157  $1600^\circ\text{C}$ , quenched in water, crushed and melted again and crushed to a fine homogeneous powder.

158

### 159 *Iodine bearing glasses*

160 To limit iron loss during experiments some platinum (Pt) capsules are doped in iron before the high  
161 *P-T* experiments. The IAB powder is loaded in open Pt capsules and melted in an atmospheric  
162 furnace at the same T and for the same duration as for the high P experiments. Capsules are then  
163 cleaned in hydrofluoric acid before being loaded and sealed. HPG and basalt powders together with  
164 NaI salt (3wt.%) are loaded in Pt capsules without or with distilled water. Pt capsules are welded  
165 and inserted either (1) in a 3.2 cm long (1/2 inch) cell-assembly composed of a graphite heater  
166 surrounded by pyrex and talc sleeves for piston cylinder experiment; or (2) in an internally heated

167 pressure vessel pressurized with an Ar-H<sub>2</sub> gas mixture (ISTO, Orléans). High  $P$ - $T$  conditions of 2-  
168 3.5 GPa and 1400-1600°C are generated using the piston cylinder apparatus for 60 minutes; low  
169  $P$ - $T$  conditions of 0.2-0.4 GPa and 1300°C are generated in the internally heated pressure vessel  
170 for 240 minutes.  $T$  is monitored with a Type C thermocouple. The samples are quenched as glasses  
171 either by turning-off the power supply for the piston cylinder or using a fast quench device for the  
172 internally-heated pressure vessel.

### 173 *Xenon bearing glasses*

174 For glasses not doped in I, hydration is done at 2 GPa and 1400°C using a piston–cylinder apparatus  
175 with a half-inch talc pyrex assembly, a graphite heater, and dried MgO powder packed around the  
176 Pt capsule. Two hydration levels are targeted, 5 wt% and 7 wt%. The glass is sealed with the proper  
177 amount of distilled water in a Pt capsule. Xe doping is done subsequently by gas-loading in another  
178 Pt capsule partially filled with the recovered hydrous HPG glasses, and brought to 3.5 GPa and  
179 1600°C for one hour, followed by rapid  $T$  quenching and decompression at room  $T$ . For I-Xe  
180 bearing glasses the I-glasses are Xe-doped following the same procedure. Experimental conditions  
181 are summarized in **Table 1**.

182

### 183 *2.2 Diamond anvil cells experiments*

184 The degassing process (*i.e.* the separation of a fluid phase from a silicate melt) is monitored *in situ*,  
185 through decompression induced by  $T$  decrease in Bassett-modified externally heated diamond anvil  
186 cells (DAC) equipped with  $P$ -driving membranes (Munsch et al., 2015). The partitioning of Xe and  
187 I between the two phases is measured *in situ* by using synchrotron XRF analysis during  
188 decompression following the same strategy as in previous studies (Bureau et al., 2010; 2016). The

189 DACs are equipped with large culet size (0.8 mm to 1 mm) and 2 mm thick diamonds, and  
190 externally heated by furnaces attached to both anvils.  $T$  is controlled by two K-type thermocouples  
191 touching each diamond anvil, and previously calibrated. The sample chamber is a 300  $\mu\text{m}$  to 500  
192  $\mu\text{m}$  hole drilled in a Re gasket (initial thickness: 250  $\mu\text{m}$ ) compressed between the two diamonds.  
193 Observations are done along the  $P$  axis through the diamond anvils, and the loaded aqueous fluid  
194 is used as  $P$ -medium. Density of the aqueous fluid is calculated by measuring the homogenization  
195  $T$  of a water vapor bubble in liquid water. Knowing the density,  $P$  can be calculated for a given  $T$   
196 from the equation of state of the fluid phase (see Munsch et al., 2015). We obtain a  $P$ -range of 1.21  
197 GPa - >1.68 GPa with a precision of 0.2 GPa for a  $T$ -range of 684°C - >851°C.

198

### 199 *2.3 In situ SXRF*

200 Synchrotron XRF quantitative analysis is performed at the beamline P02.2, Petra III (DESY,  
201 Hamburg). We use a 42.7 keV monochromatic x-ray beam focused down to 4  $\mu\text{m}$  x 6  $\mu\text{m}$ . For each  
202 experiment, the DAC is positioned perpendicularly to the beam, XRF spectra are detected in  
203 transmission geometry with an angle of 8° with the incident beam, with a Silicon Drift x-ray  
204 detector. Iodine and Xe can be detected *in situ* in a DAC as their high  $K\alpha$  and  $K\beta$  Rays (*i.e.* I:  $K\alpha_1$   
205 28.61 keV;  $K\beta_1$  32.99 keV, Xe:  $K\alpha_{\text{Xe}}$  29.78 keV;  $K\beta_{\text{Xe}}$  33.62 keV) are not absorbed by the 2 mm  
206 thick diamond anvils. We use the I-Xe doped HPG glasses as magma analogues (HPGXe-C11,  
207 HPGXeI-04). For the HPG composition, the glass transition occurs at lower  $T$  compared to basaltic  
208 or peridotitic melts, which makes possible a study in resistive heating DAC whose  $T$  are limited to  
209 1000°C in routine mode (max 1100°C). For each experiment, the sample chamber is half-filled  
210 with pieces of glass, and further loaded with pure water. When possible,  $T$  is increased up to total

211 miscibility, and then decreased by steps causing decompression; at each  $T$  step, co-existing aqueous  
212 fluid and silicate melt are analyzed (Bureau et al., 2010; 2016). At the very last stages of  
213 decompression, water bubbles nucleate in the melt and form fluid inclusions until the glass  
214 transition  $T$  is reached, compromising the analysis of the quenched glasses *in situ* in the DAC; the  
215 quenched aqueous fluid is also characterized. XRF analyses are calibrated *in situ* in the DAC at  
216 room conditions using a NIST 610 glass (e.g. Rocholl et al., 1997). For XRF analysis it is not  
217 necessary to use I- and Xe-enriched glasses as standards, because the whole NIST 610 spectrum is  
218 calibrated for multi elemental analysis using glasses containing elements with  $K\alpha$  ray energies  
219 close to that of I and Xe , such as Sb  $K\alpha = 25.2$  keV,  $405 \pm 10$  ppm in NIST610 (Rocholl et al.,  
220 1997).

221

#### 222 *2.4 In situ Raman spectroscopy*

223 Raman spectra are collected *in situ* in a DAC on a Jobin Yvon® HR-460 spectrometer equipped  
224 with an Andor® CCD camera at IMPMC using the 1500 grooves/mm grating mode. Raman signal  
225 is excited using the 514.5 nm wavelength of an  $Ar^+$  laser, delivering 300 mW focused into a  $2 \mu m$   
226 spot by a long-working distance Mitutoyo® x20 objective and collected in back-scattering  
227 geometry. Backscattered Rayleigh light is filtered with a set of holographic Notch filters. Spectral  
228 resolution is about  $2.5 \text{ cm}^{-1}$ . *In situ* measurement collection times are 60 s or 120 s per spectra in  
229 order to get reasonable signal-to-noise ratios. The DAC is loaded with pieces of HPG glass and a  
230 solution of  $H_2O$ -NaI (20 g/l), heated up to total miscibility between the aqueous fluid and silicate  
231 melt, and the first Raman measurements are performed in the supercritical fluid at  $860^\circ C$ .  $T$  is then

232 decreased, and Raman spectra are acquired after 10 min of equilibration in co-existing aqueous  
233 fluid and silicate melt.

234

### 235 *2.5 Analyses of quenched samples*

236 Quenched glasses from large volume press and DAC experiments are recovered, mirror polished  
237 (except for DAC samples) for *ex situ* scanning electron microscopy, electron microprobe and ion  
238 beam analyses. We use a Zeiss Ultra 55 field emission scanning electron microscope (IMPMC)  
239 with a working distance between 3 mm and 7.5 mm, and a voltage of 15 kV to observe crystal-free  
240 glasses texture. Major elements are analyzed using a Cameca SX FIVE electron microprobe at  
241 CAMPARIS facility (Sorbonne Université). Acceleration voltage is set to 15 kV, current to 4 nA  
242 and beam is focused to 15  $\mu\text{m}$  diameter at the surface of the sample. Counting times are 10 s per  
243 element on both peak and background. We use two internal standards (EtC, Bureau et al., 2000 ;  
244 KE12, Bureau and Metrich, 2003). About 10 to 30 analyses are performed for each sample. Major  
245 elements compositions for recovered high P-T samples and starting glasses are listed in **Table 2**.

246 Particle induced x-ray emission (PIXE), Rutherford backscattering spectrometry (RBS) and Elastic  
247 Recoil Detection Analysis (ERDA) are performed at the nuclear microprobe, CEA Saclay NIMBE  
248 / LEEL. Samples are analyzed by PIXE for I and Xe. The  $3 \times 3 \mu\text{m}^2$  proton beam of 2 MeV, 600 pA  
249 is scanned on large areas ( $250 \times 250 \mu\text{m}^2$  to  $50 \times 50 \mu\text{m}^2$ ) during one to a few hours, corresponding  
250 to deposited charges ranging from 0.6  $\mu\text{C}$  to 2.4  $\mu\text{C}$ . Emitted x-rays are collected using a Silicon-  
251 drift x-ray detector. Simultaneous RBS analysis allows to check the major element compositions  
252 of the glasses, and to map fluid inclusions trapped in the glass. Elemental maps are processed in  
253 order to select the areas of interest (e.g. bubble-free glass areas). Concentrations are obtained as

254 described in Bureau et al. (2010, 2016). Data analysis is calibrated with the NIST 610 Glass,  
255 including the calibration of the PIXE solid angle done on Sb L $\alpha$  line at 3.44 keV (Sb content = 405  
256  $\pm$  10 ppm). The quantification process is cross-checked using the well-known reference glasses  
257 EtC and KE12. To quantify I content of HPG glasses, we use the L $\alpha$  (3.92 KeV) and L $\beta$  rays (4.22  
258 KeV), both rays giving similar concentrations (**Table 2**). To quantify the I content of basaltic  
259 glasses, we use only the L $\beta$  lines due to interferences between the I L $\alpha$  line at 3.94 keV and the  
260 calcium Ca-K $\beta$  line at 3.69 keV (**Figure 1**). To quantify Xe in all glasses, we use the L $\alpha$  line at 4.1  
261 keV.

262 Water contents are obtained by ERDA, a technique based on the detection of protons after their  
263 ejection from the samples through elastic collisions at a grazing angle of 15° induced by a <sup>4</sup>He 4x16  
264  $\mu\text{m}^2$  incident beam of 3 MeV. RBS measurements are performed using an annular detector  
265 positioned at 170° with respect to the incident beam direction in order to monitor the charge  
266 delivered to the sample, necessary to allow hydrogen quantification. Details about the procedure  
267 can be found in Bureau et al (2009).

268

### 269 **3. Results**

270

#### 271 *3.1 I-Xe doped Glasses*

272

273 All glassy samples are chemically homogeneous with respect to major elements, water, and I thus  
274 attesting that chemical equilibrium was reached. For the samples of HPG composition synthesized  
275 at 0.4 GPa, we observe large I-rich bubbles, that are excluded from the maps for PIXE data  
276 processing. The presence of I-rich water bubbles may be due to the fact that at this  $P$  condition,  
277 water solubility in HPG melts is lower than the initial amount of water loaded in the capsule ( $> 5$   
278 wt.% at 0.2 GPa, 800°C, Holtz et al., 1992), water and I degas simultaneously during  
279 decompression (Bureau et al., 2016). Bubbles are not observed in samples of IAB composition as  
280 we use initial water contents ( $< 2$  wt.%) lower than the solubility of water in basalts at high  $P$  (up  
281 to 8 wt% H<sub>2</sub>O at 0.4 GPa, Sisson and Grove 1993). Xe-doped glasses also exhibit large bubbles  
282 due to Xe oversaturation from the gas loading system.

283  
284 Iodine contents range from  $0.46 \pm 0.07$  wt.% I to  $1.33 \pm 0.15$  wt.% I (in the presence of Xe) in both  
285 hydrous HPG, and from  $0.48 \pm 0.07$  wt.% to  $2.97 \pm 0.58$  wt.% I for IAB. At 3.5 GPa (see below),  
286 there is no excess I, added at the level of 2.54 wt.% I (3 wt.% NaI) in the starting material. This  
287 suggests that the solubility at 3.5 GPa may exceed 2.97 wt.%. Solubility expresses the ability of a  
288 solute to dissolve in a solvent; it is given by the maximum concentration of the solute in a solvent  
289 at equilibrium. Therefore we measured I solubility only for experiments performed up to 2 GPa.

290 These concentrations are much higher than the I content measured in basaltic volcanic glasses,  
291 usually a few ppb to a few hundreds of ppb (i.e. Schilling et al., 1980; Déruelle et al., 1992;  
292 Kendrick et al., 2012). We observe a positive trend between I content and  $P$  for the basaltic  
293 composition (**Figure 2A**), similar to that observed for the solubility of chlorine (Webster, 1997)  
294 and bromine (Bureau and Métrich, 2003) in hydrous melts in the absence of aqueous brines and/or

295 hydrosaline fluids (see Webster and Mandeville 2007). For  $P$  up to 2 GPa, I solubility values in  
296 silicate melts are comparable to those of chlorine and bromine (**Figure 2C**). Because the amount  
297 of I dissolved in the basaltic melt at 3.5 GPa (i.e.  $2.97\pm 0.58$  wt.% and  $2.67\pm 0.58$  wt.%) is equal to  
298 the initial amount loaded in the starting sample (about 2.54 wt.%) the melts may not be saturated  
299 with respect to I at these high  $P$ , which means that I solubility is probably higher than 2.97 wt.%  
300 for  $P > 3.5$  GPa. The Fe content of the samples is variable due to Fe loss to the Pt capsules (1.05  
301 wt.% to 8.51 wt.% FeO). Even experiments performed at high  $P$  (2 GPa and 3.5 GPa) and  $T$  (1400-  
302 1600°C) with Fe-doped Pt capsules do not prevent partial Fe loss from the silicate melt (see samples  
303 BA-PC88 and BA-PC89, respectively at 1.75 wt.% and 5.77 wt.% FeO while sample BA-C7  
304 synthesized at 0.2 GPa-1300°C exhibits the right FeO content at 8.51 wt.%). Because the initial  
305 water content is not equivalent for all samples we cannot discuss potential relationship between I  
306 and water contents.

307 The Xe solubility value at 3.5 GPa is much higher for HPG than for basalts: 4 wt.% for HPG falling  
308 down to 0.4 wt.% for IAB and to 0.27 wt.% for MORB (Figure 2B), in agreement with data for  
309 tholeiitic melts (Schmidt and Keppler, 2002).

310 Two experiments are performed for basaltic compositions doped in both Xe and I at 3.5 GPa (**Table**  
311 **2**), i.e. IAB (BA-PC73 1.81 wt.% I, 0.19 wt.% Xe) and MORB (BM-PC73 2.00 wt.% I, 0.33 wt.%  
312 Xe). These concentrations are slightly lower than for experiments performed in the presence of a  
313 single element. **Figure 2A** and **2B** summarize Xe and I concentrations at saturation conditions with  
314 respect to  $P$ . Both Xe and I solubility increase with  $P$  in melts, I solubility is possibly affected by  
315 the composition of silicate melts, which remains to be tested by structural studies, while Xe  
316 solubility is 10-fold higher in HPG than in basalts. However, such high concentrations are not  
317 expected in natural rocks, in the view of their very low terrestrial abundances.



318

319 *3.2. In situ high P-T partition coefficients of iodine and xenon between melts and fluid*

320

321 Xe and I concentrations measured *in situ* at high *P* and *T* in melts and fluids (SXRF), *ex situ* in  
322 glassy phases (PIXE) along with calculated partition coefficients are reported in **Table 3**. *Ex situ*  
323 data illustrate the crucial need of *in situ* data, due to strong Xe and I degassing during  
324 decompression in the aqueous phases that produces Xe-I-rich bubbles (**Figure 3**) and modifies  
325 dramatically the I and Xe concentration in quenched glasses compared to the silicate melts. **If**  
326 **remaining in the glass I content is too low to be detected**. Therefore, in the present case the analysis  
327 of both phases is necessary (silicate melt and aqueous fluid), as illustrated in the SXRF spectra  
328 presented in **Figure 4**. For experiment #02, the quantification of Xe in the supercritical fluid allows  
329 mass balance calculation, at high *P*: 45% melt and 55% aqueous fluid.

330 These partitioning experiments are performed between two phases, they differ from solubility  
331 experiments performed for a single phase. The presence of a water phase in the system strongly  
332 modifies the behaviour of both Xe and I in the silicate melt, the concentrations of these elements  
333 measured in aqueous fluids and in water-saturated silicate melts, in equilibrium with each other,  
334 cannot be compared with the solubility values measured in glasses quenched from high *P-T* liquid  
335 silicates.

336

337 For a *P* range of 1.64 GPa to 1.22 GPa and a *T* range from 860 °C to 650 °C,  $D_{f/m}^{Xe}$  ranges from  
338 0.15 to 2748 (including Xe-I doped experiments), while I partitioning could only be measured at

339 1.5 GPa and 794°C with  $D_{f/m}^I = 0.97$  (**Figure 5**). Partition coefficients increase with decreasing  $P$ ,  
340 implying strong degassing processes for both Xe and I. The comparison with previous results for  
341 I, i.e.  $D_{f/m}^I$  from 1.92 to 41, at  $P$  from 1.8 GPa to 0.1 GPa (Bureau et al., 2016) shows that Xe is  
342 more efficiently lost from the silicate melt during decompression than I. A relationship is observed  
343 between the partitioning of Xe and its melting curve as shown in **Figure 6**, where the melting curve  
344 is presented together with the  $P$ - $T$  conditions for each experiment. For experiment #02, the first  
345 partition coefficient ( $D_{f/m}^{Xe}$  0.15 at 851°C-1.68 GPa) was measured 10°C below total miscibility  
346 conditions (i.e. when the silicate melt and aqueous fluid separate from a single supercritical fluid).  
347 For that experiment only the  $D_{f/m}^{Xe}$  is below unity at 0.15, which implies more Xe dissolved in the  
348 melt than exsolved. It is observed in **Figure 6** that the  $P$ - $T$  conditions of this experiment fall close  
349 to the melting curve of Xe, while those of all other experiments are below this curve, and  
350 correspond to situations where Xe is largely dominant as a fluid phase ( $D_{f/m}^{Xe} \gg 1$ ). It shows that  
351 the exsolution of Xe from the silicate melt during both decompression and decrease of  $T$  is not  
352 promoted by the water phase as is the case for I (highly hydrophilic, Bureau et al., 2016), but is  
353 only determined by the  $P$ - $T$  conditions, in other words by the melting of Xe that is  $P$ - $T$  dependent.  
354 This observation is consistent with previous reports of Xe retention in silicates occurring  
355 systematically above the melting curve of Xe (Sanloup et al. 2005, Sanloup et al. 2011, Crépisson  
356 et al. 2019), a reaction likely driven under  $P$  by the important volume reduction between the  
357 reactants (i.e. silicates and molten Xe with a consequently large molar volume) and the product  
358 (i.e. Xe-doped silicates).

359

360 *3.3. Iodine speciation in hydrous silicate melts*

361  
362 *In situ* Raman measurements are performed in the supercritical fluid enriched with respect to I at  
363 860°C, and in the melt and aqueous fluid in equilibrium close to miscibility at 850°C and 1.5 GPa  
364 (**Figure 7**). We observe a Raman band at about 134 cm<sup>-1</sup> in the aqueous fluid at both room and  
365 high *P-T* conditions, that progressively also appears in the HPG silicate melt albeit with a smaller  
366 intensity close to miscibility conditions, and in the single fluid resulting from total miscibility. We  
367 attribute this band to I species. The 110-174 cm<sup>-1</sup> range is indeed known to correspond to I-I bond  
368 stretching vibration of polyiodides moieties in aqueous solutions, as the Raman band at 180 cm<sup>-1</sup>  
369 for solid I<sub>2</sub> is expected to move towards lower frequencies when di-I interacts with donors to form  
370 complexes (Deplano et al., 1999). We do not observe oxidized I species (IO<sup>3-</sup>) at 779 cm<sup>-1</sup> (Shen  
371 et al., 1937). Spectroscopic data agree well with *in situ* partitioning measurements of Figure 6,  
372 showing a transfer of I to the aqueous fluid ( $D_{f/m}^I > 1$ ) when both *P* and *T* decrease.

373

## 374 **4. Discussion**

375

### 376 *4.1 Iodine and Xenon in silicate melts*

377

378 We measured I solubility in silicate melts from various settings (deep continental crust, subduction  
379 zone). Iodine contents for quenched hydrous glasses are up to 1.33±0.15 wt.% at 3.5 GPa in HPG,  
380 and up to 1.42±0.23 wt.% at 2 GPa for IAB. In all cases we show that I can be significantly  
381 incorporated in the silicate networks, meaning that I may be locally enriched in silicate melts at  
382 depth. This may have consequences on the real I content of the bulk silicate Earth that is believed

383 to be very low, based on measurements performed in basalts recovered at ambient conditions  
384 (McDonough and Sun, 1995).

385 We measured Xe solubility in silicate melts at 3.5 GPa for both HPG (up to 4 wt.% Xe) and basalts  
386 (tholeiites 0.4wt.%, Arc basalts 0.27 wt.% Xe), in agreement with data on tholeiitic melts from  
387 Schmidt and Keppler (2002). All results show that the amount of Xe dissolved in high  $P$  melts at  
388 depth may be significant, provided that  $P$  and  $T$  conditions remain above Xe melting curve. It is  
389 also observed that Xe and Ar have similar solubility values in wt% in silicate melts (this study,  
390 Leroy et al., 2018, Schmidt and Keppler 2002). The high solubility of Xe in HPG melts was shown  
391 to be due to Xe insertion in the melt ring structure (6-membered rings) through the formation of  
392 Xe-O bonds (Leroy et al., 2018), it is suggested that the same process may be at stake for basaltic  
393 melts that have much less 6-membered rings than polymerized silica-rich melts such as HPG, and  
394 a consequently much lower Xe solubility. The incorporation of Xe through  $P$ -induced oxidation  
395 process in the melt differs from the incorporation of I through I-I bonds of polyiodides, and/or  
396 potentially associated to alkali cations.

397 The *in situ* monitoring of Xe and I behaviours in fluids at conditions analogous to magma degassing  
398 show that degassing of I and Xe from silicate melts to the aqueous fluid involve different processes.  
399 I is decoupled from Xe because it systematically degasses with water (forming I<sub>2</sub> moieties in the  
400 aqueous fluid), while Xe only degasses if its retention in the silicate melt is not thermodynamically  
401 favored. Similarly, mantle re-gassing processes at subduction zones could be different for both  
402 elements (see 4.3). We note a slope change in the pressure evolution in  $D_{f/m}^I$  circa 0.5 GPa,  
403 flattening at  $D_{f/m}^I = 4$ ; it might relate to a change of retention mechanism of iodine in the silicate  
404 melt as reported for bromine under pressure (Cochain et al., 2015).

405

406

407 *4.2 Iodine and Xenon in subduction zones*

408

409 Although I is present at the ppb level in igneous rocks, the potential content of I in silicic melts and  
410 natural basaltic melts at high  $P$  can reach a few weight percent, similarly to bromine. This may  
411 have important consequences in subduction zones.

412 About 70% of the I present in the crust is believed to originate from sea water sediments of organic  
413 origin, indicating potentially a significant recycling of I to the mantle. I mobility in subduction  
414 zones is believed to be promoted by the dehydration of serpentinites, because serpentines have the  
415 ability to significantly incorporate I (John et al., 2011).

416 When subducted with marine sediments, part of I is mobilized in fluids and released in brines from  
417 the forearc areas, together with I from old organic-rich marine formations located in the upper plate  
418 of the forearc regions (i.e. Japanese forearc, Tomaru et al.; 2007). Volcanic gases and forearc fluids  
419 from subduction zone volcanoes are enriched in I with respect to other settings, as for example the  
420 Central American volcanic arc (Witt et al., 2008) or in Japan (Tomaru et al.; 2007). The abundance  
421 of I found in the volcanic arc material may therefore be controlled by fluid release from  
422 deserpentinizing slab mantle, a conclusion also supported by the analysis of I in back-arc basin  
423 basalts (Kendrick et al., 2012). The high solubility of I in natural basaltic melts reported here  
424 indicates that most of I released from serpentinites can be incorporated in magmas formed in the  
425 mantle wedge. The first melt produced in the slab at typical  $T$  for sub-arc depths are silica-rich with  
426 high alkali contents such as HPG (e.g. trondhjemites, Prouteau & Scaillet, 2013), possibly enriched

427 in I. Iodine volcanic injection to the atmosphere is potentially having significant consequences on  
428 the stratospheric ozone chemistry (Bureau et al., 2000).

429  
430 While the major part of I present in subducted slabs is reinjected to the atmosphere, another part  
431 may be transported at depth in slabs. This is in agreement with the study of intraplate mantle  
432 xenoliths from various settings, some of them exhibiting I/Cl ratios more than one order of  
433 magnitude higher than the mantle value. It is proposed that I may be transported into the mantle at  
434 least beyond sub-arc depth (Kobayashi et al., 2019). This constrains the amount of subducted I into  
435 the convecting mantle to a few % of the subduction input. A deep storage of I is in agreement with  
436 the presence of I-rich aqueous fluid inclusions in lithospheric diamonds (Burgess et al., 2002), with  
437 the high halogen concentrations of the de-serpentinized harzburgite residues from serpentine  
438 breakdown, that are returned to the deep mantle (John et al., 2011) or in the seawater-derived I  
439 preserved in exhumed mantle wedge peridotite (Sumino et al., 2010). The processes suggested  
440 from our preliminary results may be migration and storage in deep melts.

441 We show the appearance of polyiodides moieties in hydrous silicate melt and supercritical fluid at  
442 850°C and >1.5 GPa pressure. In a recent study of bromine in high  $P$  hydrous melts of HPG  
443 composition, Cochain and co-workers (2015) show that significant amounts of Br (up to 2.2 wt.%)  
444 can be retained in silicate melts at 3.4 GPa in the presence of water (up to 4.4 wt.%). They observe  
445 a change of Br coordination shell from a  $\text{Br}[\text{Na}_x(\text{H}_2\text{O})_y]$  complex at low  $P$  to an alkali structure  
446 at high  $P$  (at least from 2 GPa on although it remains to be investigated at lower  $P$ ), whereby Br is  
447 surrounded by two oxygens at 1.9 Å and a mean of 6.6 Na atoms at 3.7 Å. A similar process may  
448 occur for I at high  $P$ , allowing a storage at depth in hydrous high  $P$  melts.

449 Xenon is also believed to be significantly recycled in the mantle (e.g. Holland and Ballentine 2006;  
450 Parai and Mukhopadhyay, 2018). Different processes are involved for I and Xe “ingassing” of the

451 mantle. During slab dehydration, a significant part of I would be efficiently washed out from the  
452 slab by aqueous fluids, and degassed back to the surface, while Xe is also recycled through aqueous  
453 fluids (**Figure 6**) but then it would remain in the mantle where it is expected to be stored in deep  
454 silicate melts/minerals. The recent examination of noble gases (including Xe) and halogens in  
455 serpentinites and secondary peridotites illustrates the key role played by serpentinites and other  
456 equivalent metamorphosed minerals where all these elements are progressively less abundant  
457 during dehydration processes and then recycled in the mantle (Kendrick et al., 2018). For Xe and  
458 possibly I, en route to the deep Earth, successive incorporations in mineral lattices and silicate  
459 melts may occur such as at the boundary between the transition zone and the lower mantle during  
460 dehydration melting process (Schmandt et al., 2014).

461

462

#### 463 *4.3. The depletion in light xenon of the Modern Earth's atmosphere and the missing xenon*

464

465 The monitoring in real time of I and Xe partitioning during conditions analogous to magma ascent  
466 reveals two distinct behaviours. I is efficiently washed out of the silicate melt by water ( $D_{f/m}^I \gg 1$   
467 see Bureau et al., 2016). Xenon is lost from the silicate melts much more significantly ( $D_{f/m}^{Xe}$  up  
468 to 2748) but only below its melting curve. Water can therefore not be involved in the depletion in  
469 light Xe of the Modern Earth's atmosphere, except *in the eventuality of deep hydrous fluids*  
470 *trapping I, implying a deep storage of  $^{129}\text{Xe}$ , daughter isotope of  $^{129}\text{I}$ , that would cause an increased*  
471 *( $^{129}\text{Xe}/^{132}\text{Xe}$ ) ratio in mantle partial melts (MORB).* If the Early Earth was wet, both elements  
472 should have been totally degassed from the upper magma ocean, and potentially from the whole

473 magma ocean through effective mixing by convection. Fractional crystallization processes are  
474 proposed to account for the missing Xe, Xe can be stored in olivine up to 0.4 wt.% (Crepisson et  
475 al., 2018) through Si substitution in the olivine lattice and consequent oxidation of Xe, such as  
476 observed in high  $P$  melts (Leroy et al., 2018). Fractional crystallization of the magma ocean may  
477 have separated I from Xe by keeping Xe in minerals at depth while I (including  $^{129}\text{I}$ ) is concentrated  
478 in the melt and later lost to space.

479 In the current day Earth both I and Xe, can be stored in supercritical fluids if the  $T$  is high enough.  
480 Xe can be efficiently stored in deep crustal melts (i.e. very high Xe solubility in haplogranitic  
481 melts) and in the mantle, and/or in melt layers, such as at the lithosphere asthenosphere boundary  
482 (Crépisson et al., 2014), at 350 km depth (Tauzin et al., 2010), at the top of the transition zone at  
483 410 km depth or below the TZ at 660 km depth (Schmandt et al. 2014), at the core mantle boundary  
484 CMB (Labrosse et al., 2007). This would contribute to the “missing Xe” and would imply a  
485 significant storage of I at depth, questioning in turn our knowledge of the abundance of I in the  
486 bulk silicate Earth.

487

488

## 489 **Conclusions**

490

491 We have studied Xe and I behaviour at magmatic conditions, from room conditions up to 3.5 GPa  
492 and 1600°C, and under hydrous conditions for two magmatic systems, haplogranite (magma  
493 analogue for silicic melts) and basalts (MORB and IAB). We show that both elements reach high  
494 solubilities at high  $P$ , albeit with a strong composition dependence for Xe only. This strongly



495 contrasts with the low abundances of these elements in mantle products. Results illustrate that  
496 despite the proximity of Xe and I in the periodic table, their respective behaviour in silicate melts  
497 involve different mechanisms. I is incorporated as polyiodides (I-I bonds) while Xe is oxidized at  
498 depth (Xe-O bonds, Leroy et al., 2018). The *in situ* monitoring of shallow water degassing process  
499 reveals that both elements totally degas during decompression, but while water enhances the  
500 degassing of I, it has not effect on the degassing of Xe. Instead Xe degassing is strongly T-  
501 dependent with a partition coefficient one order of magnitude higher than for I at low  $T$ , but lower  
502 than unity below the Xe melting curve. Water can therefore not be involved in the depletion in light  
503 Xe of the Modern Earth's atmosphere, except for deep aqueous fluids [in the eventuality of a deep](#)  
504 [storage, at conditions below the Xe melting curve. Storage of Xe in deep melt layers melts layers,](#)  
505 [such as at the lithosphere-asthenosphere boundary, or deeper, may account for the missing Xe,](#)  
506 [possibly associated to fractional crystallization processes as](#) Xe incorporation in olivine can be  
507 significant (up to 0.4 wt.%, Crepisson et al., 2018).

508 Iodine is not expected to enter the lattice of nominally anhydrous phases, it is concentrated in  
509 silicate melts, causing the separation of  $^{129}\text{I}$  (later  $^{129}\text{Xe}$ ) from Xe. Deep silicate melts may favour  
510 the storage of I (and Xe) in the bulk silicate Earth, either upon early Earth's differentiation or upon  
511 modern recycling at subduction zones. The high capability of magmas to incorporate I at depth and  
512 to degas I during ascent in subduction zones is also a potential significant source of I for the  
513 atmosphere, an output that still lacks quantification today.

514

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530

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**Table 1: Experimental conditions**

Sample	P (GPa) ( $\pm 0.05$ GPa)	T ( $^{\circ}$ C) ( $\pm 50^{\circ}$ C)	Duration (min)	Starting materials	Description
HPGI-03	0.4	1300	240	HPG + NaI + H <sub>2</sub> O	internally heated pressure vessel
HPGI-05	0.4	1300	240	HPG + NaI + H <sub>2</sub> O	internally heated pressure vessel
HPGXe-02	3.5	1400	60	HPG + Xe + H <sub>2</sub> O	Piston cylinder
HPGXe-C11	3.5	1600	60	HPG + Xe + H <sub>2</sub> O	Piston cylinder
HPGXe-C17	3.5	1400	240	HPG + Xe + H <sub>2</sub> O	Piston cylinder
HPGXe-C6	3.5	1400	240	HPG + Xe + H <sub>2</sub> O	Piston cylinder
HPGXeI-04	3.5	1600	240	HPG + Xe + NaI + H <sub>2</sub> O	Piston cylinder
BA-C7	0.2	1300	240	STV301 + NaI + H <sub>2</sub> O	internally heated pressure vessel
BA-PC82	3.5	1600	60	STV301 + NaI + H <sub>2</sub> O	Piston cylinder
BA-PC83	3.5	1600	60	STV301 + NaI + H <sub>2</sub> O	Piston cylinder
BA-PC87	2	1400	60	STV301 + NaI + H <sub>2</sub> O	Piston cylinder
BA-PC88	2	1400	60	STV301 + NaI	Piston cylinder - Fe-doped Pt capsule
BA-PC89	2	1400	60	STV301 + NaI	Piston cylinder - Fe-doped Pt capsule
BA-PC71	3.5	1600	60	STV301 + Xe + H <sub>2</sub> O	Piston cylinder
BM-PC71	3.5	1600	60	MORB + Xe + H <sub>2</sub> O	Piston cylinder
BA-PC73	3.5	1600	60	STV301+ NaI + Xe + H <sub>2</sub> O	Piston cylinder
BM-PC73	3.5	1600	60	MORB + NaI + Xe + H <sub>2</sub> O	Piston cylinder

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690 Sample names: HPG stands for Haplogranite composition, BA for Basalt of Arc (IAB) composition, BM  
691 for Basalt of MORB composition



**Table 2: Major elements (EMPA), iodine and xenon (PIXE), and water (ERDA) compositions.**

Starting materials and samples wt. %	SiO <sub>2</sub>	TiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	FeO	MnO	MgO	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	I L $\alpha$	I L $\beta$	Xe L $\alpha$	H <sub>2</sub> O	Total
HPG (1)	73.65		11.77					4.66	4.26				5.02	99.36
IAB (2)	47.01	1.07	15.28	8.79	0.16	12.5	10.95	2.23	0.47					98.47
N-MORB (3)	49.97	2.27	13.68	12.69	0.22	6.83	10.56	2.69	0.27					99.54
HPGI-03	75.17 (0.54)		12.10 (0.22)					4.11 (0.11)	4.04 (0.14)	0.47 (0.09)	0.47 (0.07)		4.04 (0.61)	99.92
HPGI-05	74.43 (0.55)		11.91 (0.31)					4.10 (0.18)	3.93 (0.19)	0.46 (0.06)	0.45 (0.07)		5.48 (0.82)	100.3
HPGXe-02	71.33 (0.66)		11.99 (0.22)					4.61 (0.07)	4.13 (0.17)			4.00 (0.80)	5.06 (0.75)	100.8
HPGXe-C11	72.03 (0.67)		11.86 (0.27)					4.44 (0.12)	4.06 (0.12)			3.54 (0.50)	4.66 (0.70)	100.3
HPGXe-C17	69.91 (0.63)		11.67 (0.13)					4.23 (0.11)	3.95 (0.13)			1.89 (0.38)	7.75 (1.1)	99.36
HPGXe-C6	69.57 (0.44)		11.41 (0.20)					4.26 (0.13)	3.89 (0.24)			3.72 (0.53)	7.74 (1.02)	100.6
HPGXeI-04	71.48 (0.50)		11.75 (0.20)					4.35 (0.15)	3.81 (0.13)	1.33 (0.15)		3.64 (0.52)	4.37 (0.65)	100.7
BA - C7	45.72 (0.43)	1.12 (0.04)	14.91 (0.18)	8.51 (0.30)	0.17 (0.05)	11.85 (0.12)	10.65 (0.16)	2.60 (0.08)	0.32 (0.04)		0.48 (0.07)		3.97 (0.60)	100.3
BA-PC82	46.91 (0.51)	1.37 (0.07)	15.16 (0.27)	0.95 (0.09)	0.16 (0.05)	11.58 (0.15)	10.58 (0.18)	2.98 (0.08)	0.50 (0.03)		2.97 (0.58)		3.82 (0.57)	96.98
BA-PC83	47.86 (0.45)	1.47 (0.09)	15.63 (0.28)	1.20 (0.07)	0.15 (0.07)	11.79 (0.15)	10.82 (0.22)	2.87 (0.08)	0.49 (0.04)		2.67 (0.58)		1.64 (0.25)	96.59
BA-PC87	49.83 (0.55)	1.36 (0.10)	16.34 (0.23)	1.05 (0.06)	0.12 (0.05)	12.40 (0.12)	11.42 (0.28)	2.82 (0.08)	0.40 (0.03)		1.42 (0.23)		2.33 (0.35)	99.49
BA-PC88**,**	50.83 (0.49)	1.29 (0.11)	16.54 (0.17)	1.75 (0.08)	0.15 (0.07)	12.89 (0.12)	11.43 (0.17)	2.66 (0.08)	0.45 (0.03)		0.66 (0.13)		0.66 (0.10)	99.31
BA-PC89*	48.51 (0.45)	1.25 (0.07)	16.04 (0.20)	5.77 (0.16)	0.17 (0.05)	12.23 (0.12)	11.09 (0.25)	2.88 (0.10)	0.36 (0.03)		1.02 (0.17)		0.13 (0.02)	99.45
BA-PC71	51.41 (0.67)	1.20 (0.06)	16.91 (0.27)	0.29 (0.09)	0.15 (0.04)	13.34 (0.12)	12.07 (0.17)	2.48 (0.06)	0.57 (0.05)			0.27 (0.10)	1.26 (0.20)	99.96
BM-PC71	55.74 (0.67)	2.65 (0.07)	14.78 (0.28)	1.02 (0.26)	0.22 (0.04)	7.47 (0.13)	11.98 (0.23)	2.93 (0.10)	0.33 (0.05)			0.40 (0.21)	1.89 (0.28)	99.41
BA-PC73	50.04 (0.48)	1.41 (0.04)	16.35 (0.28)	0.15 (0.08)	0.09 (0.07)	12.32 (0.13)	11.65 (0.19)	2.79 (0.09)	0.48 (0.04)		1.81 (0.19)	0.19 (0.16)	1.48 (0.42)	98.75
BM-PC73	54.77 (0.35)	2.81 (0.06)	14.43 (0.19)	0.34 (0.10)	0.17 (0.06)	7.36 (0.08)	12.07 (0.12)	3.35 (0.12)	0.27 (0.05)		2.00 (0.21)	0.33 (0.19)	1.46 (0.41)	99.36

(1) Bureau and Keppler, 1999; (2) STV301, Pichant et al., 2002; (3) BN06-11, Prouteau and Scaillet 2013. \* Fe-doped Pt capsules, \*\*water leak during the run. Sample names: HPG stands for Haplogranite composition, BA for Basalt of Arc (IAB) composition, BM for Basalt of MORB composition

**Table 3:** Concentrations and partition coefficients calculated from data collected in situ at pressures and temperatures

Exp.	Starting glass	T °C	P GPa	X <sub>e</sub> <sup>fluid</sup> wt. %	X <sub>e</sub> <sup>melt or glass</sup> wt. %	D <sup>X<sub>e</sub></sup> <sub>f/m</sub>	I <sub>fluid</sub> wt. %	I <sub>melt or glass</sub> wt. %	D <sup>I</sup> <sub>f/m</sub>
#01	HPGXe-C11	761	1.44	3.78	0.0148	255			
		692	1.31	3.88	0.0111	348			
		684	1.21	3.93	0.0014	2748			
		RT	RP	4.33					
		RT**	RP**		0.0283*			< DL	
		RT**	RP**		0.0345*			< DL	
#02	HPGXe-C11	>851 <sup>S</sup>	>1.68	2.915					
		851 <sup>CS</sup>	1.68	3.74	0.5645	0.15			
		791	1.50	5.16	0.1778	6.63			
		741	1.40	4.74	0.0252	188			
		692	1.31	4.011	0.0191	210			
		RT	RP	4.97					
		RT**	RP**		< DL				
		RT**	RP**		< DL				
#03	HPGXeI-04	794	1.51	4.6	0.053	86.4	1.72	1.77	0.97
		789	1.50		0.039			1.256	
		RT**	RP**		0.9682*			0.2547*	
		RT**	RP**		0.9953*			0.3153*	

Exp. Experiment. <sup>S</sup>supercritical fluid, in agreement with complete miscibility data for HPG-water after Bureau and Keppler (1999); <sup>CS</sup> close to supercritical \*quench bubbles included, \*\*from PIXE; Analytical uncertainties are 10% for SXRF, 5% for PIXE analysis. DL detection limit. Uncertainty on pressure is 0.2 GPa. Temperatures are corrected from the calibration performed at room pressure from chemicals of known melting points.

## Figures Captions

**Figure 1:** PIXE spectrum for A-HPGI-03 sample, B-BA-PC82 sample. x-rays are labelled. The dark line represents the experimental spectrum, dotted and dashed lines correspond to the theoretical fits for potassium K, calcium Ca and iodine I x-rays (see legends).

**Figure 2:** Xe wt.% (A) and I wt.% (B) concentrations measured in haplogranite (HPG) and basaltic glasses versus Pressure (GPa). These concentrations reflect the solubility data, except for I at 3.5 GPa, because the total amount of I in the starting compositions corresponds to the concentrations measured after the experiment. The concentration for Xe are in good agreement with the solubility measured in tholeiites (Schmidt and Keppler, 2002). Dark squares: HPG enriched in Xe, open squares: HPG enriched in both Xe and I, open circles: basalts enriched in Xe, dark circle: Basalts enriched in both Xe and I, diamonds: data from Schmidt and Keppler (2002). (C) Halogen element (I, Br, Cl) solubility in wt.% versus pressure in GPa for HPG melt and I solubility in IAB melts for comparison at low pressures (P max 0.4 GPa). Data for I (HPG: dark squares, IAB: open square) are from this study, data for Br (HPG: dark triangle) are from Bureau and Métrich (2003), data for Cl (HPG black circles) are from Webster (1997). Uncertainties are within the size of the symbols. All halogens exhibit similar ranges of solubility values in both melt compositions.

**Figure 3:** SEM images of the three quenched samples recovered from HP-HT DAC experiments. A. Sample chamber of exp #01, the arrow indicates the area zoomed in fig. 5.B ; B. Zoom on the large glassy globules showing the high density of Xe-I-rich bubbles that contaminate the glass analysis; C High density of Xe-I-rich bubbles in the glass that strongly contaminate the analysis. D. exp #02, small glassy globule, without bubbles.

**Figure 4:** In situ SRXF spectra of Xe content in DAC, in supercritical fluid (green) at  $T > 851^\circ\text{C}$ , aqueous fluid (red) and silicate melt (black) at 1.68 GPa and  $851^\circ\text{C}$  for experiment #02. The  $K\alpha$  and  $K\beta$  rays of Xe are observed at 29.78 keV and 33.62 keV respectively, measurements are performed in the supercritical fluid, then in the aqueous fluid and silicate melt at equilibrium at  $860^\circ\text{C}$  and 1 GPa. Xe is immediately lost from the silicate melt to the aqueous fluid formed upon cooling the supercritical fluid.

**Figure 5:** Pressure versus partition coefficient,  $D^{f/m}$ , for HPG starting glasses enriched in I and Xe. I data: this study in the presence of Xe (grey square), from Bureau et al., 2016 (open squares); Xe

data: this study (dark circles grey circle in the presence of I). The cross represents the uncertainties. The inset represents all the data, including high  $D_{f/m}$ . The diagram shows a stronger affinity of Xe for the fluid phase compared to I with respect to pressure (i.e. magma ascent), except at high P where the opposite is observed, and the consequent decoupling of both elements. Grey symbols represent partition coefficient of I (square) and Xe (circle) when both elements are present in the system. They show that the presence of Xe has no influence on I partitioning and reciprocally. The slope change in the pressure evolution in  $D_I^{f/m}$  at 0.5 GPa, might relate to a change of retention mechanism of iodine in the silicate melt (see text).

**Figure 6:** Pressure versus temperature conditions of the three series of partitioning experiments (Table 3): #01 (open squares), #02 (open triangles), #03 (open circles Xe and I present), performed with starting glasses HPGXe-C11, HPGXeI-04 (see Table 1). Labels are the partition coefficients measured for Xe ( $D_{Xe}^{f/m}$ ). The grey curve is the melting curve of Xe after Belonoshko et al. (2006). The dashed curve is the P-T regime of crustal xenoliths after Rodriguez-Vargas et al. (2005). The P-T regime of the oceanic slab is out of the scale of the diagram. Results show a good agreement between the  $P$  and  $T$  conditions of one experiment performed  $10^\circ\text{C}$  below total miscibility (02,  $851^\circ\text{C}$ , 1.68 GPa) where most of the Xe is still in the silicate melt ( $D_{Xe}^{f/m}=0.15$ ). All the other experiments are located below the Xe melting curve, when most of the Xe, if not all, is transferred to the fluid phase. It suggests that Xe is recycled in the mantle in aqueous fluids where it can be incorporated in silicate melts.

**Figure 7:** In situ Raman spectroscopy in the DAC in the supercritical fluid ( $860^\circ\text{C}$ , 1.6 GPa), and in the aqueous fluid and silicate melt ( $850^\circ\text{C}$ , 1.5 GPa). This experiment was performed with a I-free HPG glass and I-enriched aqueous fluid ( $\text{H}_2\text{O-NaI}$  20 g/l) as starting materials following the protocol defined in Bureau et al. (2016). We observe a band at around  $134\text{ cm}^{-1}$  corresponding to I-I bond stretching vibrations (Deplano et al., 1999).

Figure 1

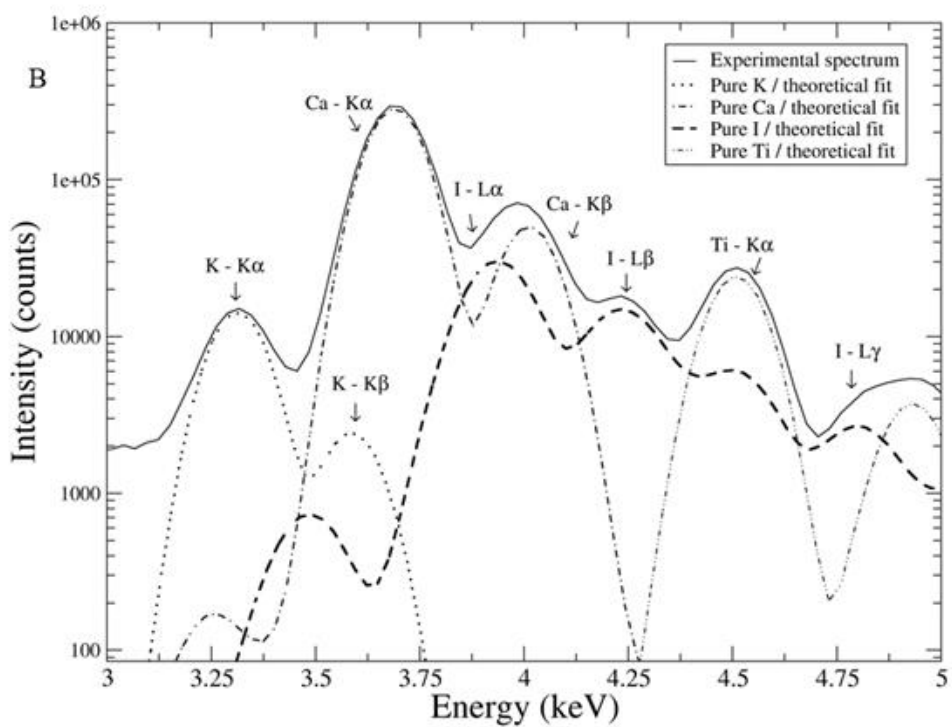
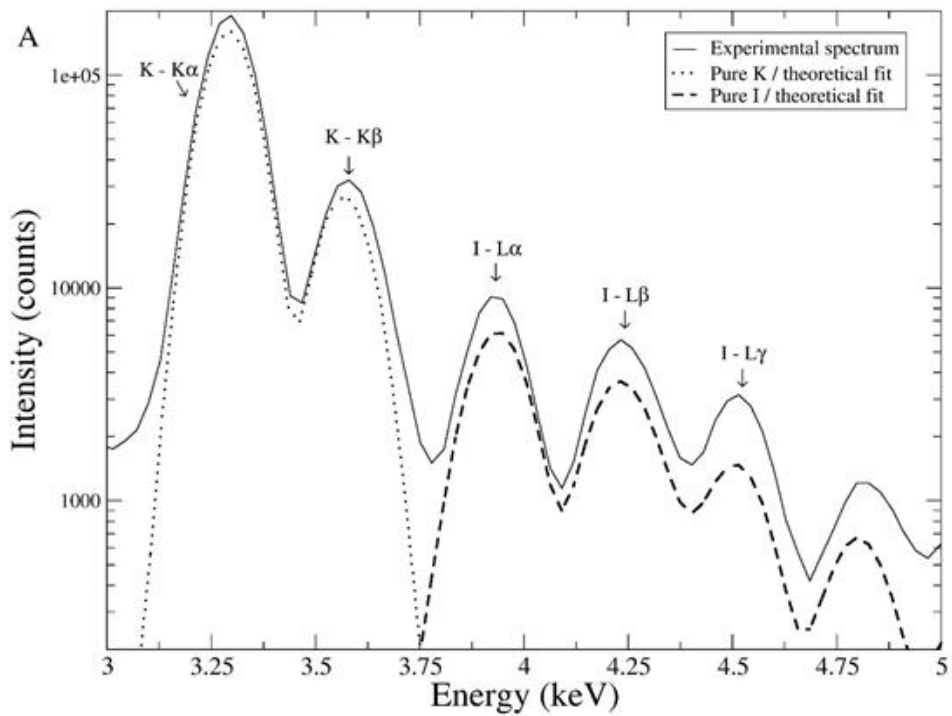


Figure 2

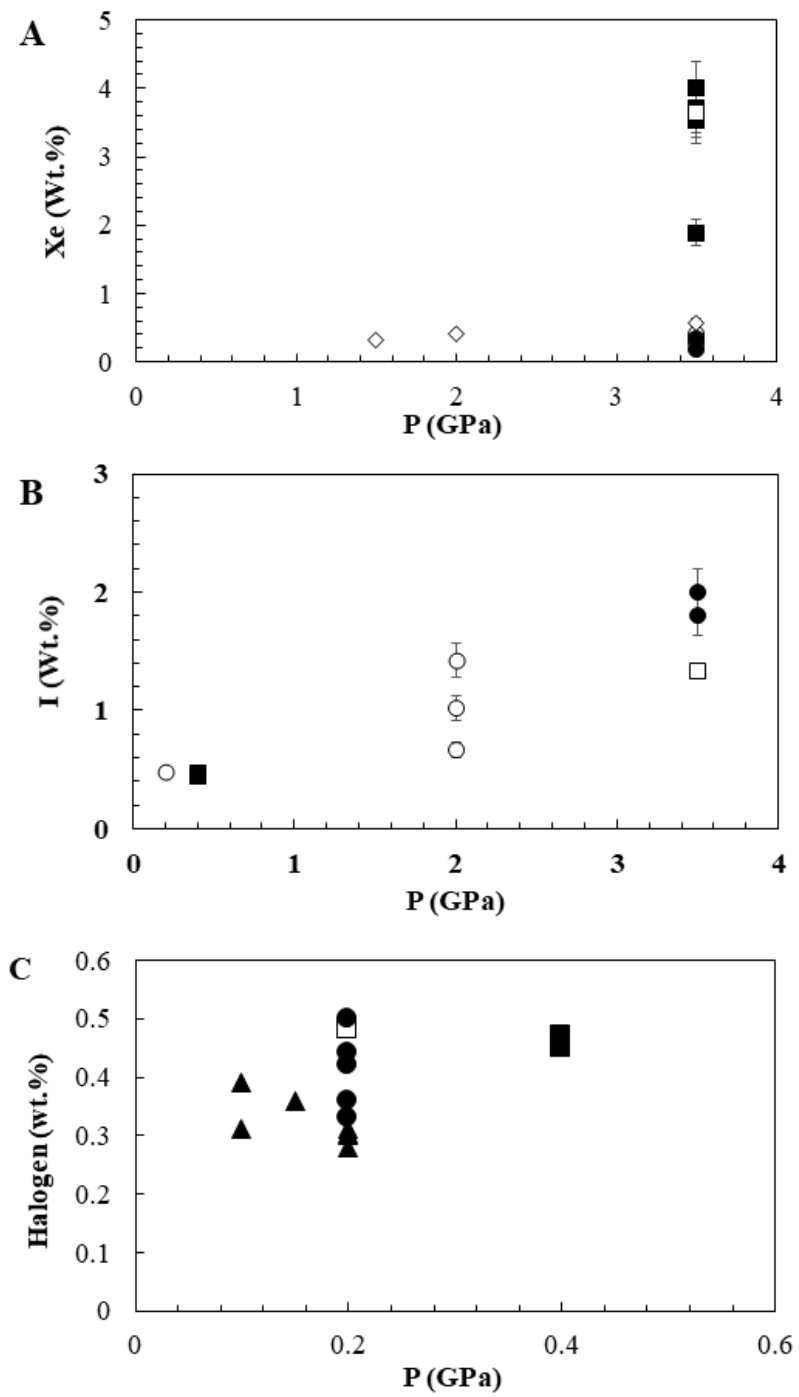


Figure 3

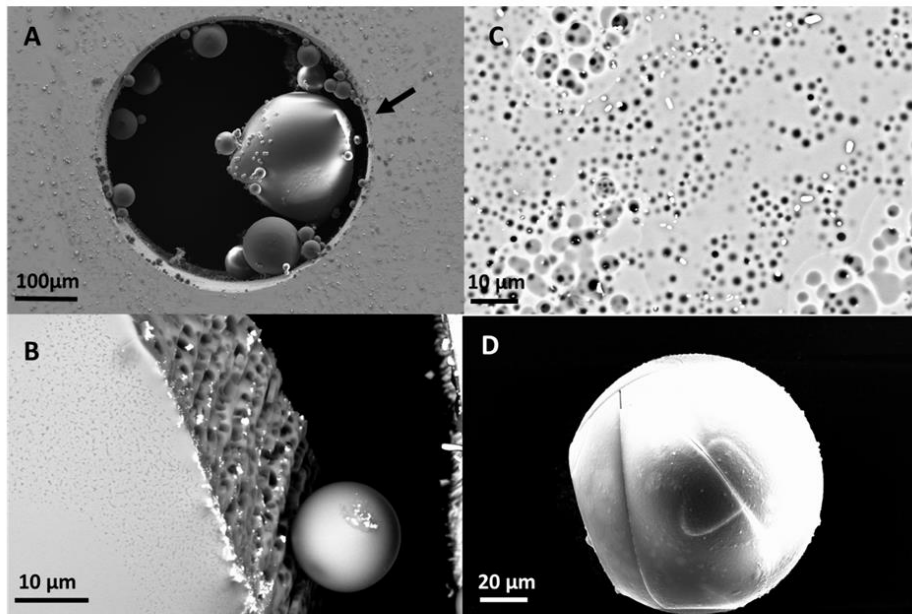


Figure 4

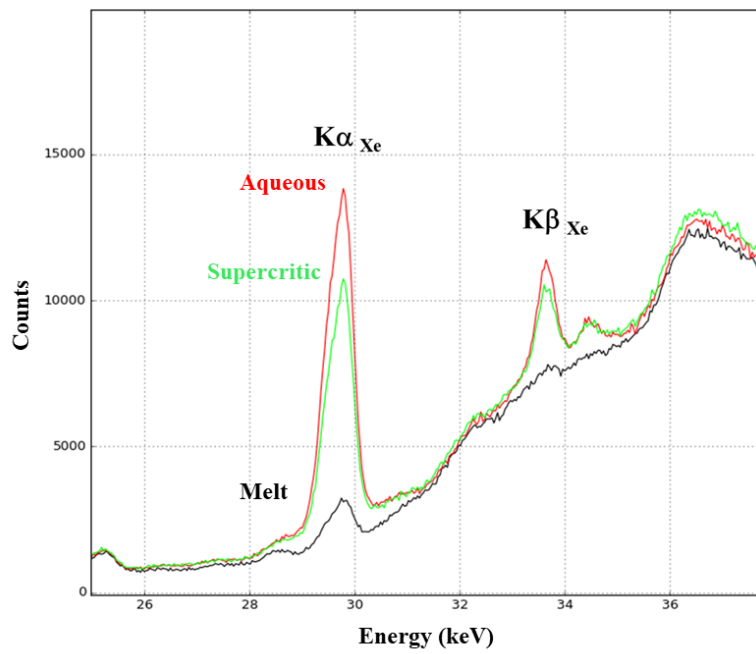




Figure 5

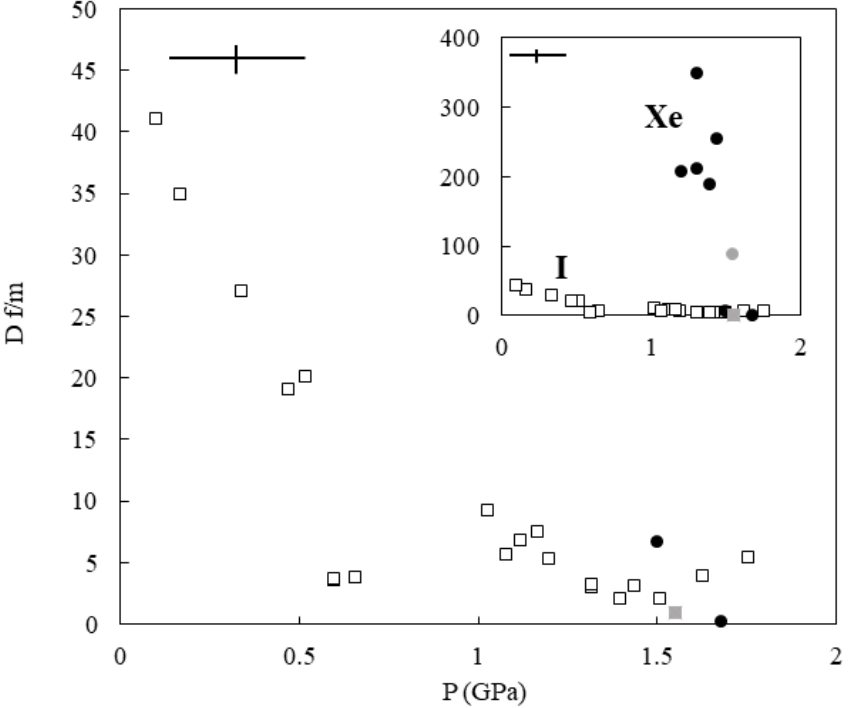


Figure 6

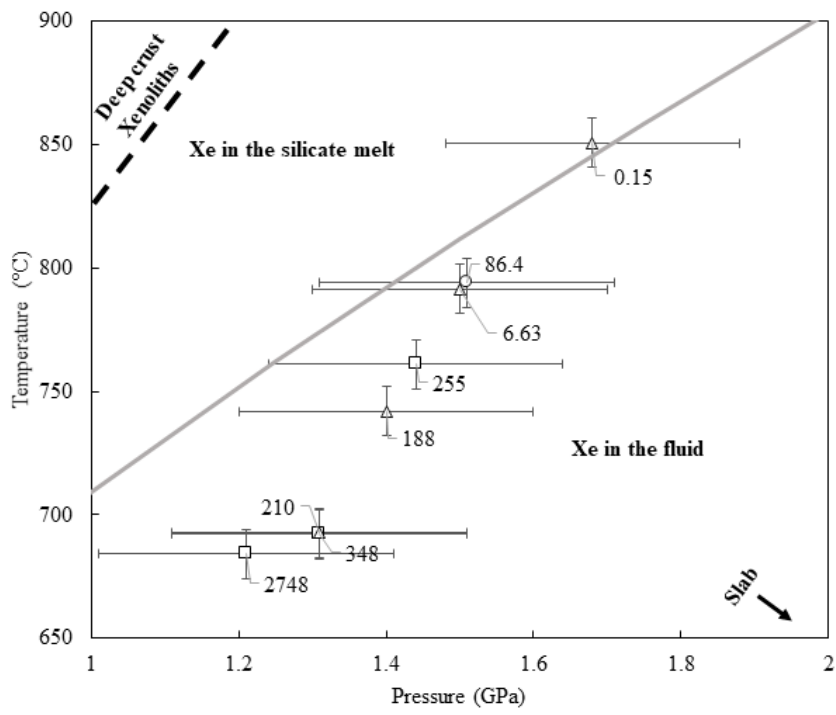


Figure 7

