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1 **Kr environment in feldspathic glass and melt: a high pressure, high**
2 **temperature X-ray absorption study**

3
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26 **Abstract**

27

28 Noble gases are used to trace the evolution of the Earth's atmosphere and magmatic
29 processes. However little is known about their solubility mechanisms in silicate melts or
30 glasses, whereas it could be fundamental to interpret these data. We report here the first *in situ*
31 X-ray absorption spectroscopy data at the Kr K-edge on a feldspathic Kr-bearing glass and
32 melt (0.5 wt % Kr) up to 2.7 GPa and 1086°C. Kr fitting of the EXAFS signal shows that Kr
33 is surrounded by oxygen atoms. Two Kr-O distances are identified: 2.49 ± 0.1 Å and 3.32 ± 0.1
34 Å. Results can be interpreted as two Kr populations. Kr surrounded by O atoms at 3.32 ± 0.1 Å
35 suggests a filling of the large cavities available in the silicate network, in agreement with
36 previous studies. On the contrary, Kr surrounded by O atoms at 2.49 ± 0.1 Å, and the observed
37 + 0.6 eV shift of the edge position at high pressure, suggest Kr bonding to O atoms and Kr
38 oxidation inside cages formed by the largest aluminosilicate rings (i.e. ~ 12-membered-rings).
39 Present results show that heavy noble gases incorporation in silicate melts can no longer be
40 considered as a passive filling of the voids.

41

42 **Keywords**

43

44 Krypton, XAS, silicate glass, silicate melt, high pressure

45

46 **1. Introduction**

47

48 Due to their supposed chemical inertia, high volatility, and high dilution, noble gases have
49 been intensively studied by geochemists to understand the formation of the Earth's
50 atmosphere, and to study mantle dynamics. None of Kr stable isotopes ($^{78,80,82,83,84,86}\text{Kr}$) is

51 purely radiogenic, and Pu and U fission yields are very low for Kr. Thus Kr cannot be used to
52 constrain chronology of the atmosphere evolution, and as such has been less studied than He,
53 Ne, Ar, and Xe. However, the small amount of radiogenic Kr makes it suitable to trace air
54 component in fluid inclusions (Böhlke and Irwin, 1992). Earth atmospheric Kr isotope
55 composition, unchanged since at least 3.3 Ga (Avice et al., 2017), falls in-between solar and
56 chondritic compositions (Pepin, 1991). Kr isotopic ratios in CO₂ magmatic well gases that
57 probed the continental lithosphere, showed a significant enrichment in ⁸⁴Kr and ⁸⁶Kr
58 compared to the atmosphere (Holland et al., 2009). The discovery of Kr isotopic fractionation
59 in these well gases, taken as a proxy of deep mantle gases, was interpreted as the signature of
60 a primordial Kr chondritic component (Holland et al., 2009). Nevertheless Holland et al.
61 (2009) argue that early degassing of an accreted primordial chondritic composition, followed
62 by mass fractionation during atmosphere loss, fails to explain the composition of the modern
63 atmosphere. Instead, late accretion of cometary material is assumed to explain Kr isotope
64 signature of the atmosphere. Although very few samples have been analyzed for all Kr
65 isotopes, mantle-derived basalts (MORBs, OIBs) have an atmospheric Kr isotopic
66 composition (Moreira et al., 1998; Trieloff et al., 2000; Graham, 2002). This homogeneous
67 composition could be due to atmospheric Kr recycling at subduction zones (Holland and
68 Ballentine, 2006).

69 To explain highly precise Kr isotopic data, geochemists need an understanding of Kr
70 behavior in silicate melts, including Kr solubility value and mechanism, as well as Kr degree
71 of compatibility.

72 Fractionated fission Kr has also been observed in the Okhlo natural nuclear reactor. In
73 nuclear plants, ⁸⁵Kr is a common fission product. Nuclear waste confinement by vitrification
74 in SiO₂-rich glasses has been used for many years (Ojovan and Lee, 2011). Accumulation of
75 Kr leads to the formation of nanobubbles where pressure may reach 2.6 GPa (Martin et al.,

76 2015) under high temperature generated by irradiation. Understanding of Kr behavior in
77 silicate glasses is thus crucial for long nuclear waste storage.

78 The majority of studies dedicated to noble gases solubility in melts are based on
79 analyses of recovered glassy samples, and did not directly investigate the noble gas structural
80 environment in the silicate network, as noble gases can escape from the silicate structure at
81 ambient conditions. These studies showed that noble gas solubility decreases with increasing
82 radius (from He to Xe) (Caroll and Stolper, 1993, Lux, 1987, Shibata et al., 1998), and that
83 this solubility strongly depends on the chemical composition of the melt. Noble gas solubility
84 was first related to ionic porosity, i.e. the absolute volume of voids (Caroll and Stolper, 1993),
85 whereas Shibata et al. (1998) showed that it was better inversely correlated to the number of
86 non-bridging oxygen per silicon, even if the presence of Al may modify this trend (Bouhifd
87 and Jephcoat, 2006). Based on these findings and noble gas relative chemical inertia, noble
88 gases were supposed to passively fill the voids of the silicate network.

89 *In situ* structural data on the environment of heavy noble gases in silicate melts and
90 glasses are scarce. Wulf et al. (1999) performed an X-ray absorption study at the Kr K-edge in
91 a SiO₂ glass (1.97 wt % Kr). They identified a Kr-O distance of 3.45±0.1 Å, interpreted as
92 corresponding to a local rearrangement of the silicate network into a local clathrasil-type
93 environment around the Kr atom. The supposed chemical inertia of Kr and Xe, the most
94 reactive of the noble gases, has been questioned throughout the past 15 years, with the
95 synthesis of numerous Kr and Xe compounds (see Grochala, 2007 for a review). Bonding of
96 Xe to O in compressed haplogranitic magmas had also been evidenced by *in situ* X-ray
97 diffraction (Leroy et al. 2018).

98 In the present study, we perform *in situ* X-ray absorption spectroscopy (XAS) at the
99 Kr K-edge, to specifically access Kr structural environment in a feldspathic (sanidine) glass.

100 Starting (Na,K)AlSi₃O₈ glass composition was chosen as representative of the
101 chemistry of a major mineral of the continental crust, and proxy of silica-rich melts that can
102 be generated at pressure reaching 2 GPa in orogenic contexts (Jimenez-Munt et al., 2008), and
103 in subduction contexts from melting of hydrous basalt (Prouteau et al., 2001), or silica-rich
104 sediments (Turner et al., 2012). Experiments were conducted at pressures (P) and
105 temperatures (T) up to 2.7 GPa and 1086°C, relevant for both continental crust melting and
106 subduction zone contexts.

107

108 **2. Material and Methods**

109

110 **2.1 Sample: synthesis and characterization**

111

112 The starting glass of Kr/Xe-bearing sanidine was synthesized in a piston cylinder press
113 at 3.5 GPa and 1400°C for 24 hours before quenching. For this purpose, Xe and Kr were
114 loaded as a 1:1 gaseous mix along with sanidine powder in a Pt capsule (Boettcher et al.,
115 1989). Sanidine is a high-temperature feldspar, of atomic composition (K_xNa_{1-x})AlSi₃O₈ with
116 x higher than 0.32 (Bendel and Schmidt, 2008). In our experiments, sanidine powder was
117 obtained by grinding a natural sanidine mineral (K_{0.52}Na_{0.43}Al_{1.05}Si_{2.96}O₈, formula unit
118 retrieved from electron microprobe analysis) from the Sorbonne Université mineralogical
119 collection.

120 Starting glass and recovered sample were mounted in epoxy, polished and C-coated.
121 They were observed by Scanning Electron Microscope (SEM) with a Zeiss Supra 55
122 (equipped with a field emission gun). Detection of Xe and Kr was optimized with an
123 acceleration voltage of 20 keV and a working distance of 6.6 mm in backscatter mode.

124 Electron microprobe analyses (EMPA) were done on a CAMECA SX5, at CAMPARIS centre
125 at Sorbonne Université. Operating conditions were 15 kV accelerating voltage, 10 nA beam
126 current, and a focused beam for point analysis. We use the method from Montana et al. (1993)
127 for Kr, which was calibrated by measuring the counts on neighboring elements (i.e. Rb). Xe
128 was calibrated using a known standard analyzed by Particle-Induced X-ray Emission (data
129 published in Leroy et al., 2018).

130 The synthesized starting glass is chemically homogeneous (based on SEM and EMP
131 analyses) with presence of Kr/Xe gas bubbles indicating that saturation was reached. Contents
132 of 2.2 wt % Xe (0.36 at %) and 0.5 wt % Kr (0.13 at %) were measured by electron
133 microprobe analyses from an average of seven points of analysis in areas free of micrometric
134 gas bubbles. Average composition in wt % of the starting glass is given in Table 1. Recovered
135 sample was quenched from 1040°C and 2.7 GPa, where it reequilibrated as partial melt and
136 feldspar crystals (Figure 1), following cooling from fully molten state (1415°C and 3 GPa)
137 which was reached with the initial purpose to collect XAS data at the Xe-edge. Kr and Xe are
138 only observed in the glass, with striking alignments of Kr/Xe gas nanobubbles (Figure 1).
139 Average analyses of the recovered sample are given in Table 1, although degassing upon
140 quenching prevents Xe and Kr contents to be determined by EMP analysis.

141

142 **2.2 Experimental set-up**

143

144 *In-situ* X-ray absorption spectroscopy (XAS) was performed on beamline BM23 at the
145 ESRF, dedicated to general purpose XAS (Mathon et al., 2015). High pressure and
146 temperature conditions up to 2.7 GPa and 1086°C (Table 2) were generated in a Paris
147 Edinburgh Press (Besson et al., 1992). We used a cell assembly developed by Kono et al.
148 (2014) and adapted from Yamada et al. (2011). More details on the cell-assembly and

149 experimental set-up can be found in Rosa et al. (2016). The sample (0.75 mm diameter and
150 1.5 mm height) was encapsulated in a synthetic nanopolycrystalline diamond (NPD) cylinder
151 capped with Pt-Rh caps. The use of NPD prevents glitches from a single or polycrystalline
152 diamond capsule, which deteriorate the XAS signal. Temperature was determined using
153 calibration from Kono et al. (2014), and pressure using unit cell volume of hBN from the cell
154 assembly (based on X-ray diffraction measurements) and equation of state from Le Godec et
155 al. (2000). Error bars are $\pm 50^\circ\text{C}$ for temperature and ± 0.2 GPa for pressure.

156

157 **2.3 XRD and XAS measurements**

158

159 Angle-resolved X-ray diffraction data were recorded on a MAR165 CCD at 15 keV.
160 Image plates were integrated using Fit 2D software (Hammersley, 1997). Cell parameters of
161 hBN were determined using POWDER CELL software (Kraus and Nolze, 1996).
162 XAS transmission measurements were performed first at the Kr K-edge (14326 eV) up to 2.7
163 GPa, upon increase of temperature up to 1086°C, and upon decrease of temperature down to
164 505°C, before quenching to room temperature (Table 2). Xe K-edge spectra were recorded
165 following measurement at the Kr K-edge upon increasing temperature up to 1415°C and 3
166 GPa, and upon cooling to 1040°C at 2.7 GPa followed by quenching. Xe K-edge spectra are
167 however not of sufficient quality to allow fitting, given the very small absorption jump (0.09
168 compared to 0.25 at the Kr K-edge), and are thus not shown here. Energy calibration of the
169 edge position was made by frequent analyses of Kr gaseous standards. The beam size on the
170 sample was 300 x 80 μm^2 . Transmitted X-ray intensity was recorded by ionization chambers
171 filled with gaseous Ar-He mixed gas. Signal was collected from 14244 eV to 14971 eV at the
172 Kr K-edge (451 points analysis). Counting times, number of scans, and P/T conditions are

173 given in Table 2. Energy steps were adapted as a function of the edge position, each scan
174 takes about 1 hour.

175

176 **2.4 Processing of XAS data**

177

178 The edge of the standard was fixed to 14326 eV, and the edge of each sample was
179 recalibrated using the averaged edge value of two gaseous Kr standards taken before and after
180 the sample measurement. For Kr standard, no significant shift of the Kr K-edge was noted
181 (0.4 eV at the largest). After correction of edge position, data were cut at 14800 eV for better
182 normalization.

183 Data processing was performed using ATHENA and ARTEMIS packages, based on the
184 IFEFFIT programs (Ravel and Newville, 2005). Each scan was corrected with a pre-edge and
185 a post-edge baseline. Position of the edge was determined by the position of the first
186 derivative of the absorption. The intensity of the jump at the edge was then normalized to one.
187 After merging of the scans collected at a given P/T condition, data were corrected using a
188 background function. We used an automated background subtraction method (AUTOBKG)
189 developed by Newville (Newville, 2001) and implemented in the ATHENA software. This
190 correction minimizes the features below the first atom-atom distance in the R-space. R_{bkg} was
191 fixed to 1.2 Å.

192 To fit the data at the Kr K-edge, we used a k-range of $\sim 2.2\text{-}6.5 \text{ \AA}^{-1}$ (Table 3), due to low
193 signal to noise ratio at higher k values. A small k-range ensures that all the different
194 contributions to the Fourier transform are not artifacts but really arise from neighboring
195 atoms. Real part of backward Fourier transform was exported to ARTEMIS software to be
196 fitted using R-range $\sim 1.1\text{-}3.8 \text{ \AA}$ (Table 3). Fitting made on real part of backward Fourier
197 transform ensures that all XANES and noise contributions are removed from the EXAFS

198 signal. Fit parameters include: amplitude reduction factor (S_0), average distances of the
199 neighboring atom to the central Kr atom, Debye Waller factor (σ^2), and difference of edge
200 position compared to standard value (ΔE_0). ΔE_0 values remain smaller than 7 eV, attesting
201 consistency of the fits. It was necessary to add a third order anharmonic cumulant expansion
202 fitting parameter (C3) for high pressure or high temperature measurements (Stern et al, 1991;
203 Farges et al., 1994). C3 is a measure of the asymmetry of the signal disorder, which arises in
204 glasses from configurational disorder associated to thermal vibration at high pressure and/or
205 high temperature conditions. The absolute value of C3 remains smaller than 0.009 \AA^3 , similar
206 to values found by Cochain et al. (2015) on silicate glasses and melts at high pressure and
207 temperature conditions. As no Kr standard was analyzed in the course of the experiment
208 besides Kr gas, it is not possible to determine coordination numbers (CN). We therefore fixed
209 S_0 at a common value of 0.79, and fixed the value of CN. In total, seven parameters must be
210 fitted (first interatomic distance, σ^2 and C3 for the two contributions and ΔE_0) whereas N , the
211 number of variables to fit, cannot exceed (Teo, 1986):

212

$$213 \quad N = \frac{2\Delta R\Delta k}{\pi} \quad (1)$$

214

215 In our case $\Delta k \approx 4.3 \text{ \AA}^{-1}$ and $\Delta R \approx 2.8 \text{ \AA}$. Therefore maximum number of parameters N ,
216 which can be fitted is ~ 7.7 , indicating that we can theoretically fit our data as exposed above.

217

218 **3.Results and Discussion**

219

220 **3.1. XAS data at the Kr K-edge**

221

222 XAS data were recorded at ambient conditions, at high pressure and high temperature, and
223 after quenching (Table 2). Potassic sanidine (KAlSi_3O_8) is expected to melt around 1500°C at
224 2.6-2.7 GPa (Boettcher et al., 1984). Reports on the KAlSi_3O_8 - $\text{NaAlSi}_3\text{O}_8$ join under
225 anhydrous conditions at 1 atm showed that melting temperature of KAlSi_3O_8 drops by 100°C
226 for our starting composition ($\text{Na}_{0.43}\text{K}_{0.52}\text{Al}_{1.05}\text{Si}_{2.96}\text{O}_8$, atomic formula retrieved from EMPA)
227 (Schairer, 1950). Glass transition temperature (T_g) of felspathic glass at 1 atm was found in-
228 between 907 - 948°C based on viscosity measurements (Petermann et al., 2008; Richet and
229 Bottinga, 1984). Moreover, viscosity is shown to decrease from 0 GPa to 2.5 GPa for both
230 sanidine melt (White and Montana, 1990) and albite melt (Kushiro, 1978). Thus T_g is
231 expected to be even lower than 907 - 948°C at our pressure conditions. Therefore our
232 measurements at 1086°C (and potentially at 920°C) were recorded above T_g and before
233 recrystallization, i.e. on the supercooled liquid, behaving like a melt. Well-defined oscillations
234 are visible in the X-ray absorption signal, and clearly differ from the signature of Kr gas and
235 Kr liquid under pressure (Di Cicco et al., 1996) (Figures 2 and 3).

236 Rapid damping of the EXAFS signal indicates disorder beyond the first shell. We
237 compare in Figure 3 our data with the k^2 -weighted EXAFS function recorded at 27°C on UO_2
238 (8 at % Kr) previously implanted with Kr ions (Martin et al., 2015). Oscillations observed
239 after 4 \AA^{-1} clearly differ from our data sets. The magnitude of the Fourier transform (k -range
240 used is displayed in Table 3) clearly shows two peaks at all measurement conditions (Figure
241 4), indicating that two distances contribute to the signal, with the main distance at $\sim 1.9 \text{ \AA}$,
242 while Martin et al. (2015) reports a main distance at 3.44 \AA . Kr environment in sanidine glass
243 is therefore different from that observed by Martin et al. (2015) in UO_2 , i.e. Kr nanoclusters.
244 There is no noticeable change in the room temperature glass with pressure: data at ambient
245 pressure and after quenching at 1.4 GPa being similar (Figures 2, 3 and 4). The relative
246 intensity of the two peaks however varies with temperature, the magnitude of the Fourier

247 transform (Figure 4) being different at ambient temperature, at 505°C and 706°C, and
248 especially in the melt at 920°C and 1086°C.

249

250 **3.2 Resolving Kr environment in sanidine glass and melt**

251

252 Variations of fitted Kr-O distances over our experimental P/T range are within error
253 (i.e. ± 0.1 Å). We thus evaluate averaged Kr-O distances for the whole P/T range, two Kr-O
254 distances are identified at 2.49 ± 0.1 Å and 3.32 ± 0.1 Å (Table 3, Fig. 5). No other neighboring
255 atom than oxygen could fit the observed XAS signal, although we considered other atomic
256 pairs such as Kr-Kr, Kr-Si, Kr-Na, or Kr-K. Identified distances confirm the absence of Kr
257 neighbors. Indeed Kr-Kr distance in solid cubic Kr is 3.68 Å at 2 GPa and room temperature
258 (Di Cicco et al., 1996). We can interpret these results as two distinct populations of Kr located
259 in two different sites of the silicate network. Results clearly differ from Wulf et al. (1999),
260 who only reported a Kr-O distance at 3.45 Å, as shown in Figure 5.

261 At ambient condition, there is no non-bridging oxygen in sanidine glass (KAlSi_3O_8),
262 and Al coordination number is four for all Al atoms (Thompson et al., 2011). Study of an
263 albite glass ($\text{NaAlSi}_3\text{O}_8$) quenched from the melt at 2.6 GPa showed that less than 3% of Al
264 atoms present a coordination number of five, whereas all remaining Al atoms have a
265 coordination number of 4 (Gaudio et al., 2015). Sanidine glass is thus fully polymerized, with
266 all Na^+/K^+ compensating the charge deficit created by the presence of Al^{3+} in tetrahedral
267 position. Molecular dynamic simulations showed that in soda aluminosilicate glass, for
268 $\text{Na}/\text{Si}=1$, distribution of the aluminosilicate rings at ambient pressure varies from 2 to 13
269 membered-rings, with 6 or 7 membered-rings being the most present ring population (Xiang
270 et al., 2013). Similarly, at ambient pressure, a ring size distribution from 2 to 12-membered
271 rings is predicted for silica glass with 6 to 7 membered-rings being the dominant ring
272 population (Kohara et al. 2011; Guerette et al., 2015). To our knowledge, no pore size

273 distribution data is available for our glass composition. Based on the similarity of ring size
274 distribution between aluminosilicate and silica glass, we assume that size of cages within
275 aluminosilicate rings range from 0.9 Å to 5.9 Å in diameter, like in silica glass (Guerette et
276 al., 2015). This size distribution indicates the presence of 5-5.9 Å-diameter voids, inside the
277 largest (i.e. ~ 12-membered) aluminosilicate rings. The Kr-O distance of 2.49 ± 0.1 Å is
278 therefore compatible with a Kr atom located inside the largest observed rings of the silicate
279 network. This Kr-O distance falls in-between the sum of covalent radii of Kr and O (1.16 Å
280 and 0.66 Å respectively (Cordero et al., 2008)) and the sum of ionic radii of Kr^0 and O^{2-}
281 (respectively 1.78 Å for a coordination number of 6 (Zhang et al. 1995) and 1.4 Å (Shannon,
282 1976)). This result indicates that Kr is interacting closely with the neighboring oxygen atoms,
283 suggesting an oxidation of Kr. Under pressure, the edge position shifts by + 0.6 eV (Figure 6).
284 Shift of the edge can be related to change in the oxidation state as observed for Cu, Co, Fe,
285 Mn (e.g. Klysubun et al., 2015). This observation further supports a change in Kr oxidation
286 due to Kr-O bonding. Kr is in the oxidation state II in most of Kr compounds synthesized,
287 such as KrF_2 , KrF^+ or Kr_2F_3^+ (Grosse et al., 1963, Burbank et al., 1972, Lehmann et al., 2001).
288 Kr oxidation number is expected to increase compared to gaseous Kr, if Kr is surrounded by
289 several O atoms.

290 The Kr-O distance of 3.32 ± 0.1 Å cannot correspond to the presence of Kr atoms inside
291 aluminosilicate rings, as the size distribution is limited to 5.9 Å in diameter. This larger Kr-O
292 distance is similar to the 3.45 ± 0.1 Å distance reported in SiO_2 glass at ambient pressure and 5
293 K (Wulf et al., 1999), and close to predictions from first principle molecular dynamics. Zhang
294 et al. (2009) indeed found $\text{Kr-O} = 3.5$ Å in liquid silica, with Kr coordination number varying
295 from 10 to 15 depending on pressure. Similar result was found by Guillot and Sator (2012)
296 using molecular dynamics with $\text{Kr-O} = 3.45$ Å in silica melt and 3.31 Å in rhyolite melt. This
297 large distance can be explained by the formation of large cavities in the melt where noble

298 gases are accommodated, in agreement with a passive filling of the void space, or with a
299 clathrasil-like environment (Wulf et al., 1999). Contribution of Kr fluid to this longer distance
300 cannot be ruled out if the few Kr bubbles observed on starting and quenched samples are not
301 fully homogenized with the melt at high pressure and temperature.

302 Disappearance of the larger Kr-O distance at higher temperatures (Figure 4), indicates
303 that smaller Kr-O distance is more favorable, possibly with the increase of Kr reactivity.
304 Moreover, the Debye Waller factor associated with the smallest Kr-O distance (σ^2), is twice
305 larger at room temperature than at high temperature (Table 3), suggesting that ordering of the
306 smaller Kr-O environment is higher. Measurements at high pressures and temperatures are all
307 above Kr melting point, whereas measurement after quenching at 1.4 GPa is below Kr
308 melting point (Ferreira and Lobo, 2008). Kr reactivity therefore seems enhanced above Kr
309 melting curve, suggesting that it is pressure-induced, i.e. it favors smaller volume, as observed
310 for Xe incorporation in olivine (Sanloup et al., 2011). Besides, the larger Kr-O distance
311 vanishes in the melt, i.e. at 920°C and 1086°C (Figure 4), indicating structural changes
312 between the melt and the glass. A complementary explanation could be a contribution of Kr
313 fluid to the longer Kr-O distance, which would diminish with temperature due to the increase
314 of Kr solubility in the melt.

315 Current knowledge of glass and silicate melt structures therefore supports the
316 hypothesis of two Kr populations, with one population of Kr, oxidized and possibly located in
317 the largest aluminosilicate rings, and one population filling the large cavities available in the
318 silicate network.

319

320 **4. Conclusion**

321

322 The present work provides evidence for the reactivity of Kr with silicate that adds up to the
323 previously reported evidences of Kr reactivity (Grochala, 2007). Kr oxidizes in feldspathic
324 glass and melt at high P/T conditions as shown by creation of short Kr-O bonds (2.49 ± 0.1 Å)
325 and shift of the edge position. Kr behavior in compressed magmas thus appears to be
326 intermediate between that of an inert noble gas (He, Ne, Ar) and that of the heavier Xe.
327 Indeed Xe is shown to fully oxidize in compressed haplogranitic melts with Xe in the most
328 abundant 6-membered rings containing 12 nearest O, Xe-O distance of 2.05 ± 0.05 Å is
329 similar to distance reported for covalent Xe-O bond in crystalline silicates (Probert, 2010;
330 Kalinowski et al., 2014; Crépisson et al., 2018). Both results question the supposed passive
331 filling of the void spaces by heavy noble gases (Carroll and Stolper, 1993; Shibata et al.,
332 1998), and the assumption that all noble gases can be considered as zero-charge cation (e.g.
333 Brooker et al., 2003).

334 Creation of short Kr-O bonds in sanidine melt at depth, supports the role of Kr recycling at
335 subduction zones, proposed by Holland and Ballentine (2006), as Kr will efficiently dissolve
336 in the melt. Hydrated melts will now need to be studied to test the influence of water, which is
337 thought to dramatically increase noble gases solubility (Nuccio and Paonita, 2000).

338 The Earth's atmosphere is depleted in heavy Kr isotopes compared to chondrites (Holland et
339 al., 2009). Observation of short Kr-O bonds in silicate melt, implying Kr reactivity, suggests
340 potential isotopic fractionation during partial-melting and melt percolation, as shown for
341 instance for Cu (Huang et al., 2017), and / or during fluid / melt interactions either upon fluid
342 injection at depth in subduction zones or degassing during magma ascent. This phenomenon
343 could have contributed to enrichment of well gases from the continental lithosphere in heavy
344 Kr isotopes, while most of the samples from the Earth's mantle (OIBs and MORBs) have an
345 atmospheric Kr isotopic composition due to intense recycling.

346

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348

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372 **References:**

- 373 Avice G., Marty B., and Burgess R. 2017. The origin and degassing history of the Earth's
374 atmosphere revealed by Archean xenon. *Nature communications*, 8, 15455.
- 375 Bendel V. and Schmidt B.C. 2008. Raman spectroscopic characterisation of disordered alkali
376 feldspars along the join $\text{KAlSi}_3\text{O}_8\text{--NaAlSi}_3\text{O}_8$: application to natural sanidine and
377 anorthoclase. *European Journal of Mineralogy*, 20, 1055–1065.
- 378 Besson J.M., Hamel G., Grima T., Nelmes R.J., Loveday J.S., Hull S., and Häusermann D.
379 1992. A large volume pressure cell for high temperature. *High Pressure Research*, 8, 625-630.
- 380 Boettcher A., Guo Q., Bohlen S., and Hanson B. 1984. Melting in feldspars-bearing systems
381 to high pressures and the structures of aluminosilicate liquids. *Geology*, 12, 202-204.
- 382 Boettcher S.L., Guo Q., and Montana A. 1989. A simple device for loading gases in high-
383 pressure experiments. *American Mineralogist*, 74, 1383-1384.
- 384 Böhlke J.K. and Irwin J.J. 1992. Brine history indicated by argon, krypton, chlorine, bromine,
385 and iodine analyses of fluid inclusions from the Mississippi Valley type lead-fluorite-barite
386 deposits at Hansonburg, New Mexico. *Earth and Planetary Science Letters*, 110, 51-66.
- 387 Bouhifd A. and Jephcoat A.P. 2006. Aluminium control of Argon solubility in silicate melts
388 under pressure. *Nature*, 439, 961-964.
- 389 Brooker R.A., Du Z., Blundy J.D., Kelley S.P., Allan N.L., Wood B.J., Chamorro E.M.,
390 Wartho J.A., Purton J.A. 2003. The 'zero charge' partitioning behaviour of noble gases during
391 mantle melting. *Nature*. 423, 6941, 738-741.
- 392 Burbank R.D., Falconer W.E., and Sunder W.A. 1972. Crystal Structure of Krypton
393 Difluoride at -80°C . *Science*, 178, 1285-1286.

394 Carroll M.R. and Stolper E.M. 1993. Noble gas solubilities in silicate melts and glasses: New
395 experimental results for argon and the relationship between solubility and ionic porosity.
396 *Geochimica et Cosmochimica Acta*, 57, 5039-5051.

397 Cochain B., Sanloup C., De Grouchy C., Crépisson C., Bureau H., Leroy C., Kantor I., and
398 Irifune T. 2015. Bromine speciation in hydrous silicate melts at high pressure. *Chemical*
399 *Geology*, 404, 18-26.

400 Cordero B., Gomez V., Cremades E., Alvarez S. 2008. Covalent radii revisited. *Dalton*
401 *Transactions*, 2832-2838.

402 Crépisson C., Blanchard M., Balan E., and Sanloup C. 2017. New constraints on Xe
403 incorporation mechanisms in olivine from First-principles calculation, *Geochimica et*
404 *Cosmochimica Acta*.

405 Di Cicco A., Filipponi A., Itié J-P., and Polian A. 1996. High-pressure EXAFS measurements
406 of solid and liquid Kr. *Physical Review B*, 54, 9086-9098.

407 Farges F., Brown G.E., Calas G., Galois L., and Waychuna G.A. 1994. Structural
408 transformation in Ni-bearing $\text{Na}_2\text{Si}_2\text{O}_5$ glass and melt. *Geophysical Research Letters*, 21,
409 1931-1934.

410 Ferreira A.G.M., and Lobo L.Q. 2008. The fusion curves of xenon, krypton, and argon. *The*
411 *Journal of Chemical Thermodynamics*, 40, 618–624.

412 Gaudio S.J., Leshner C.E., Maekawa H., and Sen S. 2015. Linking high-pressure structure and
413 density of albite liquid near the glass transition. *Geochimica et Cosmochimica Acta*, 157, 28–
414 38.

415 Graham D.W. 2002. Noble gas isotope geochemistry of Mid-Ocean Ridge Basalt and Ocean
416 Island Basalts: characterization of mantle source reservoirs. in *Noble gases in Geochemistry*
417 *and Cosmochemistry*, *Reviews in Mineralogy and Geochemistry*, 247-318.

418 Grochala W. 2007. Atypical compounds of gases, which have been called ‘noble’. *Chemical*
419 *Society Reviews*, 36, 1632-1655.

420 Grosse, A.V., Kirshenbaum, A.D., Streng, A.G, and Streng L.V. 1963. Krypton Tetrafluoride:
421 Preparation and Some Properties. *Science*, 139, 1047-1048.

422 Guerette M., Ackerson M.R., Thomas J., Yuan F., Watson E.B., Walker D., and Huang L.
423 2015. Structure and Properties of Silica Glass Densified in Cold Compression and Hot
424 Compression. *Nature Scientific Reports*, 5.

425 Guillot B., and Sator N. 2012. Noble gases in high-pressure silicate liquids: A computer
426 simulation study. *Geochimica et Cosmochimica Acta*, 80, 51-69.

427 Hammersley A. 1997. FIT2D: An Introduction and Overview. Technical Report
428 No.ESRF97HA02, ESRF.

429 Holland G., and Ballentine C. 2006. Seawater subduction controls the heavy noble gas
430 composition of the mantle. *Nature*, 441, 186-191.

431 Holland G., Cassidy M., and Ballentine C.J.. 2009. Meteorite Kr in Earth’s Mantle Suggests a
432 Late Accretionary Source for the Atmosphere. *Science*, 326, 1522-1525.

433 Huang J., Huang F., Wang Z., Zhang X., Yu H. 2017. Copper isotope fractionation during
434 partial melting and melt percolation in the upper mantle: Evidence from massif peridotites in
435 Ivrea-Verbano Zone, Italian Alps. *Geochimica et Cosmochimica Acta*, 211, 48-63.

436 Jiménez-Munt I., Fernandez M., Vergés J., and Platt J.P. 2008. Lithosphere structure
437 underneath the Tibetan Plateau inferred from elevation, gravity, and geoid anomalies. *Earth*
438 *and Planetary Science Letters*, 267, 276-289.

439 Kalinowski J., Rasanen M., Gerber R.B. 2014. Chemically-bound xenon in fibrous silica.
440 *Physical Chemistry Chemical Physics*, 16, 11658–11661.

441 Klysubun W., Hauzenberger C.A., Ravel B., Klysubun P., Huang Y., Wongtepa W., and
442 Sombunchoo P. 2014. Understanding the blue color in antique mosaic mirrored glass from the
443 Temple of the Emerald Buddha, Thailand. *X-ray spectrometry*, 44, 116-123.

444 Kohara S., Akola J., Morita H. , Suzuya K., Weber J.K.R., Wilding M.C., and Benmore C.J.
445 2011. Relationship between topological order and glass forming ability in densely packed
446 enstatite and forsterite composition glasses. *PNAS*, 108, 14780-14785.

447 Kono Y., Park C., Kenney-Benson C., Shen G., and Wang Y. 2014. Toward comprehensive
448 studies of liquids at high pressures and high temperatures: Combined structure, elastic wave
449 velocity, and viscosity measurements in the Paris–Edinburgh cell. *Physics of the Earth and*
450 *Planetary Interiors*, 228, 269-280.

451 Kraus W. and Nolze G. 1996. POWDER CELL - a program for the representation and
452 manipulation of crystal structures and calculation of the resulting X-ray powder patterns.
453 *Journal of Applied Crystallography*, 29, 301-303.

454 Kushiro I. 1978. Viscosity and structural changes of albite ($\text{NaAlSi}_3\text{O}_8$) melt at high
455 pressures. *Earth and Planetary Science Letters*, 41, 87-90.

456 Le Godec Y., Solozhenko V.L., Mezouar M., Besson J-M., and Syfosse G. 2000. In situ X-ray
457 diffraction studies of formation of cubic and hexagonal graphite-like boron nitride by the
458 reaction of elemental boron with supercritical hydrazine. *Science and Technology of High*
459 *Pressure*. Universities Press, Hyderabad, India, 2, 1031-1034.

460 Lehmann J.F., Dixon D.A., and Schrobilgen G. 2001. X-ray Crystal Structures of alpha-KrF₂,
461 [KrF][MF₆] (M=As, Sb, Bi), Kr₂F₃][SbF₆].KrF₂, [Kr₂F₃]₂[SbF₆]₂.KrF₂, and
462 Kr₂F₃][AsF₆].[KrF][AsF₆]; Synthesis and Characterization of [Kr₂F₃][PF₆].nKrF₂; and
463 Theoretical Studies of KrF₂, KrF⁺, Kr₂F₃⁺, and the [KrF][MF₆](M = P, As, Sb, Bi) Ion
464 Pairs. *Inorganic Chemistry*, 40, 3002-3017.

465 Leroy C. Sanloup C., Bureau H., Schmidt B.C., Konopkova Z., Raepsaet C. 2018. Bonding of
466 xenon to oxygen in magmas at depth. *Earth and Planetary Science Letters*, accepted.

467 Lux G. 1987. The behavior of noble gases in silicate liquids: Solution, diffusion, bubbles and
468 surface effects, with applications to natural samples. *Geochimica et Cosmochimica Acta*, 31,
469 1549-1560.

470 Martin P.M., Vathonne E., Carlot G., Delorme R., Sabathier C., Freyss M., Garcia P.,
471 Bertolus M., Glatzel P., and Proux O. 2015. Behavior of fission gases in nuclear fuel: XAS
472 characterization of Kr in UO₂. *Journal of Nuclear Materials*, 466, 379-392.

473 Mathon O., Beteva A., Borrel J., Bugnazet D., Gatla S., Hino R., Kantor I., Mairs T., Munoz
474 M., Pasternak S., Perrina F., and Pascarelli S. 2015. The time-resolved and extreme
475 conditions XAS (TEXAS) facility at the European Synchrotron Radiation Facility: the
476 general-purpose EXAFS bending-magnet beamline BM23. *Journal of synchrotron radiation*,
477 22, 1548-1554.

478 Meshik A.P., Kehm K., Hohenberg C.M. 2000. Anomalous xenon in zone 13 Okelobondo.
479 *Geochimica et Cosmochimica Acta*, 64, 9, 1651-1661.

480 Montana A., Guo Q., Boettcher S., White B.S., and Brearley M. 1993. Xe and Ar in high-
481 pressure silicate liquids. *American Mineralogist*, 78, 1135-1142.

482 Moreira M., Kunz J., and Allègre J.C. 1998. Rare gas systematics in popping rock: Isotopic
483 and elemental compositions in the upper mantle. *Science*, 279, 1178-1181.

484 Newville M. 2001. EXAFS analysis using FEFF and FEFFIT. *Journal of Synchrotron*
485 *Radiation*, 8, 96-100.

486 Nuccio P.M., and Paonita A. 2000. Investigation of the noble gas solubility in H₂O-CO₂
487 bearing silicate liquids at moderate pressure II: the extended ionic porosity (EIP) model. *Earth*
488 *and Planetary Science Letters*, 183, 499-512.

489 Ojovan M.I., and Lee W. E. 2010. Glassy wastefoms for nuclear waste immobilization.
490 Metallurgical and Materials Transactions A, 42, 4, 837-851.

491 Pepin R. 1991. On the origin and early evolution of terrestrial planet atmospheres and
492 meteoritic volatiles. *Icarus*, 92, 2–79.

493 Pertermann, M., Whittington, A.G., Hofmeister, A.M., Spera F.J., Zayak J. 2008. Transport
494 properties of low-sanidine single-crystals, glasses and melts at high temperature.
495 *Contributions to Mineralogy and Petrology*, 155, 689-702.

496 Probert, M.I.J. 2010. An ab initio study of xenon retention in α -quartz. *Journal of Physics of*
497 *Condensed Matter*, 22, 025501.

498 Prouteau, G., Scaillet, B., Pichavant, M., and Maury, R. 2001. Evidence for mantle meta-
499 somatism by hydrous silicic melts derived from subducted oceanic crust. *Nature*, 410, 6825,
500 197–200.

501 Ravel B., and Newville M. 2005. ATHENA, ARTEMIS, HEPHAESTUS: data analysis for X-
502 ray absorption spectroscopy using IFEFFIT. *Journal of Synchrotron Radiation*, 12, 537–541.

503 Richet P, and Bottinga Y. 1984. Glass transitions and thermodynamic properties of
504 amorphous SiO_2 , $\text{NaAlSi}_n\text{O}_{2n+2}$ and KAlSi_3O_8 . *Geochimica et Cosmochimica Acta*, 48, 3,
505 453-470.

506 Rosa A.D., Pohlentz J., de Grouchy C., Cochain B., Kono Y., Pasternak S., Mathon O.,
507 Irifune T., and Wilke M. 2016. *In-situ* characterization of liquid network structures at high
508 pressure and temperature using X-ray Absorption Spectroscopy coupled with the Paris-
509 Edinburgh press. *High Pressure Research*, 36, 332-347.

510 Sanloup C., Schmidt B.C., Gudfinnsson G., Dewaele A., and Mezouar M. 2011. Xenon and
511 Argon: a contrasting behavior in olivine at depth. *Geochimica et Cosmochimica Acta*, 75,
512 6271–6284.

513 Schairer J. F. 1950. The alkali-feldspar join in the system NaAlSiO_4 - KAlSiO_4 - SiO_2 . The

514 Journal of Geology, 58, 512-517.

515 Shannon R.D. 1976. Revised effective ionic radii and systematic studies of interatomic
516 distances in halides and chalcogenides. *Acta Crystallographica*, A32, 751-767.

517 Shibata T., Takahashi E., and Matsuda J.I. 1998. Solubility of neon, argon, krypton, and
518 xenon in binary and ternary silicate systems: A new view on noble gas solubility. *Geochimica
519 et Cosmochimica Acta*, 62, 1241-1253.

520 Stern E.A., Livins P., and Zhang Z. 1991. Thermal vibration and melting from a local
521 perspective. *Physical review B*, 43, 8850-8860.

522 Thompson L.M. and Stebbins J.F. 2011. Non-bridging oxygen and high-coordinated
523 aluminum in metaluminous and peraluminous calcium and potassium aluminosilicate glasses:
524 High-resolution ^{17}O and ^{27}Al MAS NMR results. *American Mineralogist*, 96, 841–853.

525 Trieloff M., Kunz J., Clague D., Harrison D., and Allègre J.C. 2000. The nature of pristine
526 noble gases in mantle plumes. *Science*, 288, 5468, 1036-1038.

527 Turner, S., Caulfield, J., Turner, M., vanKeken, P., Maury, R., Sandiford, M., and Prouteau,
528 G. 2012. Recent contribution of sediments and fluids to the mantle's volatile budget. *Nature
529 Geoscience*, 5, 1, 50–54.

530 White B.S., and Montana A. 1990. The effect of H_2O and CO_2 on the viscosity of sanidine
531 liquid at high pressures. *Journal of Geophysical Research: Solid Earth* *Banner*, 95 (B10),
532 15683-15693

533 Wulf R., Calas G., Ramos A., Büttner H., Roselib K., and Rosenhauer M. 1999. Structural
534 environment of krypton dissolved in vitreous silica. *American Mineralogist*, 84, 1461–1463.

535 Xiang Y., Du J., Smedskjaer M.M., and Mauro J.C. 2013. Structure and properties of sodium
536 aluminosilicate glasses from molecular dynamics simulations. *The Journal of Chemical
537 Physics*, 139.

538 Yamada A., Wang Y., Inoue T., Yang W., Park C., Yu T., and Shen G. 2011. High-pressure
539 x-ray diffraction studies on the structure of liquid silicate using a Paris–Edinburgh type large
540 volume press. *Review of Scientific Instruments*, 82.

541 Zhang Y. and Xu Z.. 1995. Atomic radii of noble gas elements in condensed phases.
542 *American Mineralogist*, 80, 670-675.

543 Zhang L., Van Orman J.A., and Lacks D.J. 2009. Effective radii of noble gas atoms in silicate
544 from first principles molecular simulation. *American Mineralogist*, 94, 600-609.

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561 *Table 1: Average composition of the starting glass (7 data points) and recovered sample (20*
 562 *data points both in the glassy and crystalline parts) in oxide wt %, in brackets: standard*
 563 *deviation.*

	Na₂O	SiO₂	Al₂O₃	K₂O	CaO	Xe	Kr	Total
Starting material	4.80 (0.2)	63.6 (0.40)	19.2 (0.14)	8.70 (0.24)	0.78 (0.05)	2.18 (0.04)	0.52 (0.05)	99.7 (0.47)
Recovered sample	2.9 (0.6)	65 (1)	19.8 (0.6)	11(1)	0.3 (0.2)	[0-1.3]*	[0-0.5]*	100(1)

564 * due to degassing upon quenching Kr and Xe contents cannot be properly evaluated by
 565 EMPA. Ranges of analyzed contents are given as an indication.

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582 *Table 2: P/T conditions and state of the sample for each XAS measurement. n.s = number of*
583 *scans, count. time = counting time per point analysis (451 point analysis).*

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Kr K-edge				
P (GPa)	T (°C)	state	n.s	count . time
0	20	glass	7	2s
2.6	920	melt	4	2s
2.7	1086	melt	5	2s
2	706	glass	5	2s
2	505	glass	5	2s
1.4	20	quench	4	2s

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600 *Table 3: Pressure-Temperature conditions and EXAFS-derived structural parameters.*

601 *Conservative error bars are ± 0.05 eV for ΔE_0 , ± 0.1 Å for Kr-O distances and ± 0.05 Å² for*

602 *σ^2 .*

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P (GPa)	T (°C)	k-range (Å⁻¹)	R-range (Å)	ΔE_0 (eV)
0	20	2.2 - 6.5	1.1 - 3.5	3.32
2.6	920	2.3 - 6.5	1.2 - 4.0	6.09
2.7	1086	2.3 - 6.5	1.1 - 3.8	7.00
2	706	2.3 - 6.5	1.1 - 3.5	6.45
2	505	2.3 - 6.5	1.1 - 3.8	5.84
1.4	20	2.2 - 6.5	1.1 - 4.0	3.50
P (GPa)	T (°C)	Kr-O1 (Å)	σ^2_1 (Å²)	C3₁ (Å³)
0	20	2.42	0.025	-
2.6	920	2.45	0.009	0.0021
2.7	1086	2.51	0.014	0.0078
2	706	2.53	0.009	0.0085
2	505	2.53	0.012	0.0076
1.4	20	2.49	0.021	0.0035
P (GPa)	T (°C)	Kr-O2 (Å)	σ^2_2 (Å²)	C3₂ (Å³)
0	20	3.38	0.048	-
2.6	920	3.27	0.040	-0.0090
2.7	1086	3.37	0.042	0.0090

2	706	3.34	0.064	-0.0034
2	505	3.29	0.045	-0.0090
1.4	20	3.30	0.049	-0.0057

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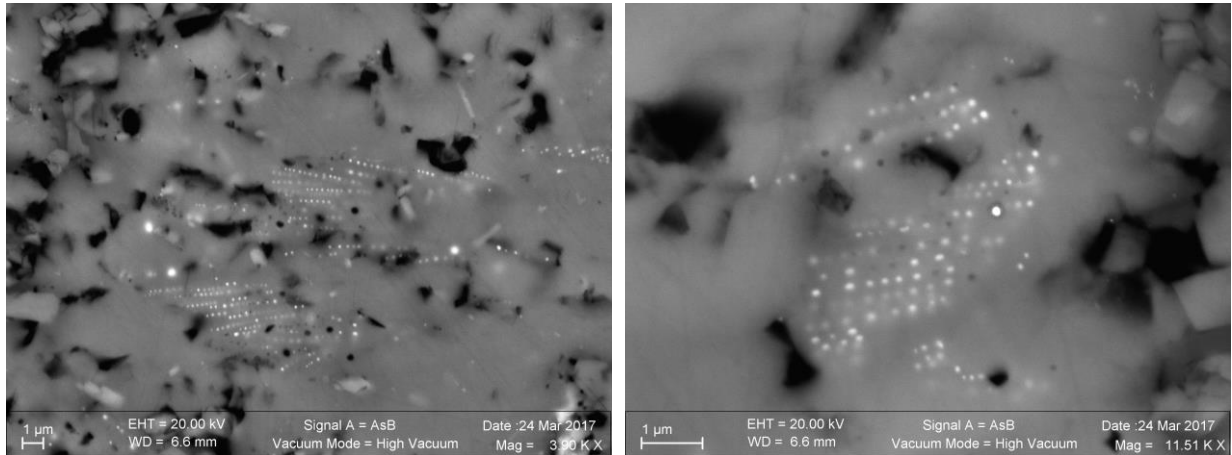
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623 *Figure 1: SEM images in backscatter mode of recovered sample after XAS measurements.*

624 *Feldspars recrystallized upon cooling to 1040°C at 2.7 GPa, coexisting with partial melt*

625 *recovered as a glass upon quenching. Kr/Xe-nanobubbles (bright dots) are visible.*

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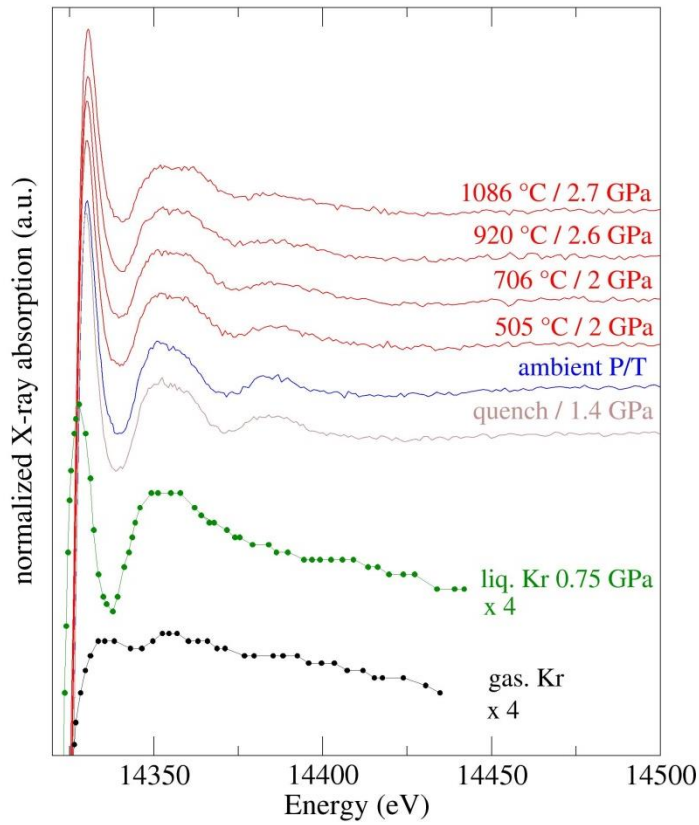
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641 *Figure 2: Normalized X-ray absorption spectra for sanidine glass and supercooled liquid,*
642 *gaseous Kr at ambient conditions, and liquid Kr at 0.75 GPa (Di Cicco et al., 1996).*

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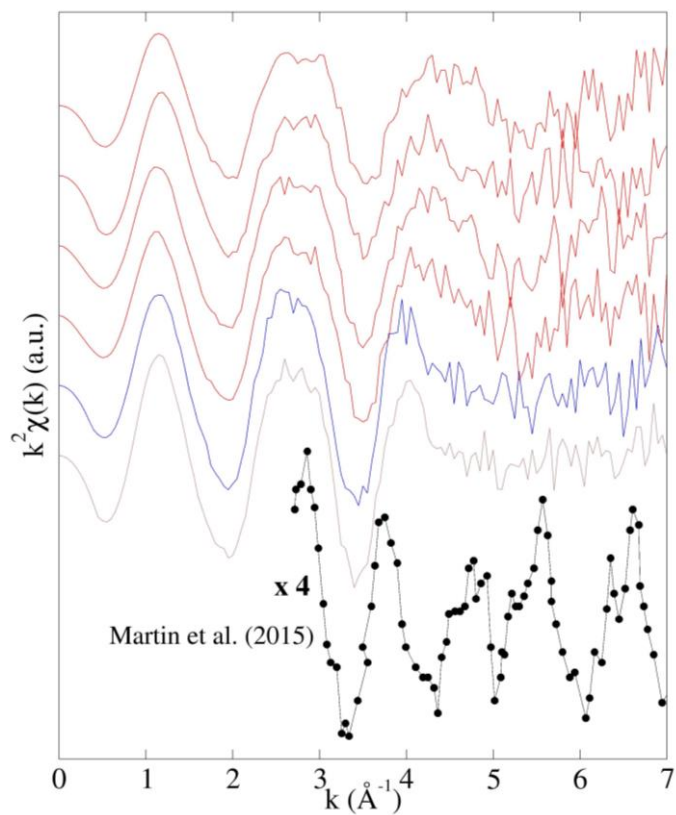
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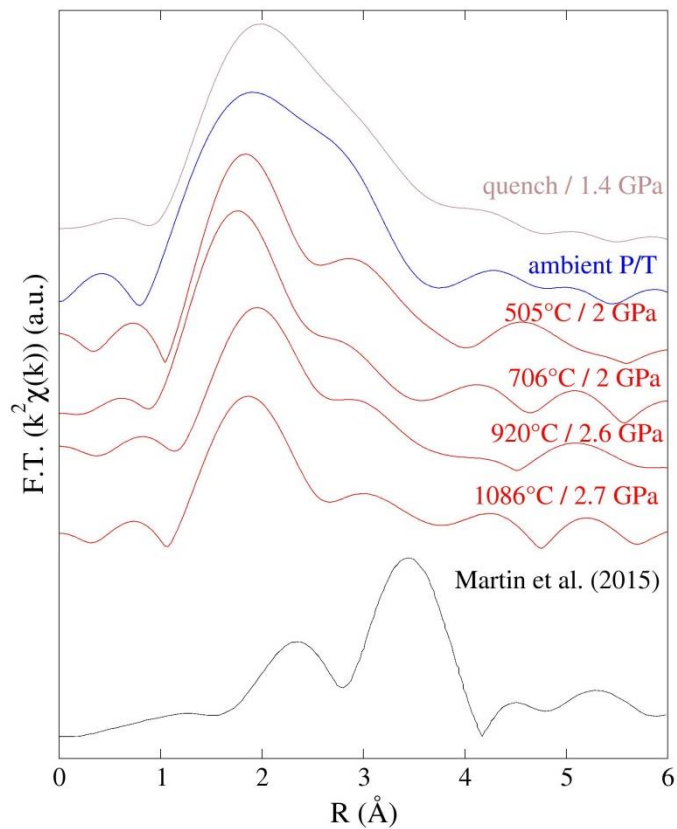
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653 *Figure 3: k^2 -weighted EXAFS function for sanidine glass and supercooled liquid (color*
654 *coding: same as Figure 2), and for UO_2 at room conditions (Martin et al., 2015).*



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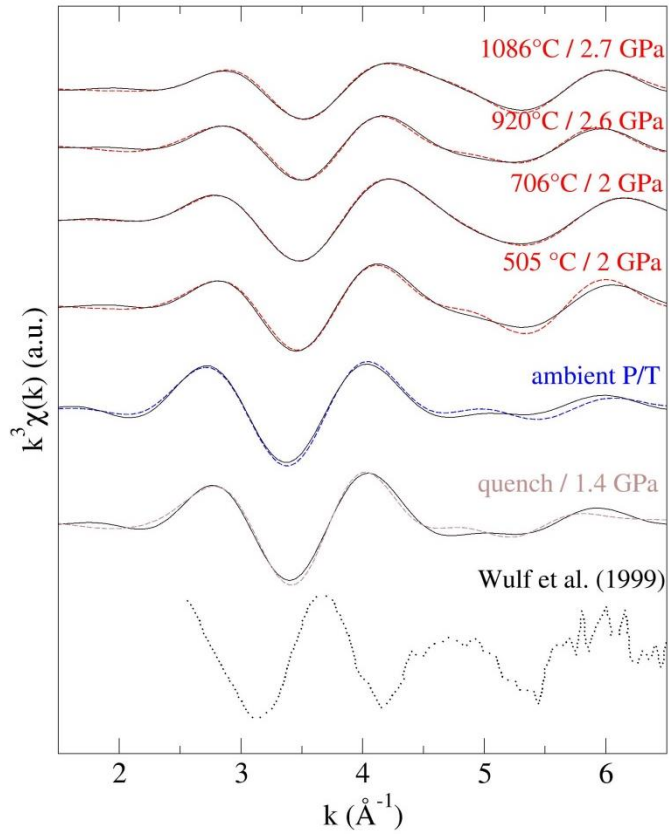
669 *Figure 4: Magnitude of the Fourier transform of the k^2 -weighted Kr EXAFS function without*
670 *phase correction (same samples as Figure 3). The peak observed at ~ 1.9 Å corresponds to*
671 *Kr-O = 2.49 Å, and the peak at ~ 2.9 Å corresponds to Kr-O = 3.32 Å. A general decrease of*
672 *the amplitude is observed with increasing temperature (as noticed by Stern et al., 1991).*
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684 *Figure 5: Real-part of backward Fourier transform (in dashed lines) and fit to the data (plain*
685 *black line) for sanidine glass and supercooled liquid, and Kr-bearing SiO₂ glass (Wulf et al.,*
686 *1999).*

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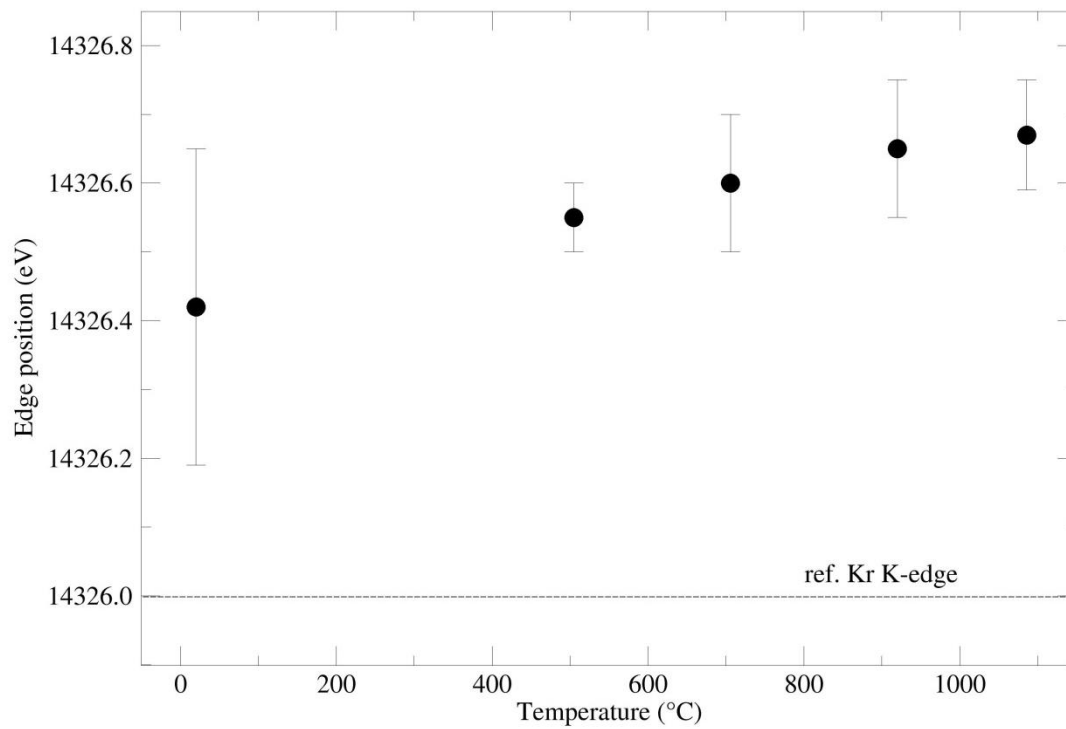
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698 *Figure 6: Shift of the Kr K-edge from 1.4 to 2.7 GPa (cf Table 2) compared to the standard*
699 *reference value (14326 eV).*



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