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► **To cite this version:**

Marion Louvel, Anita Cadoux, Richard A Brooker, Olivier Proux, Jean-Louis F Hazemann. New insights on Br speciation in volcanic glasses and structural controls on halogen degassing. *The American Mineralogist*, 2020, 105 (6), pp.795-802. 10.2138/am-2020-7273 . hal-02993148

HAL Id: hal-02993148

<https://cnrs.hal.science/hal-02993148>

Submitted on 6 Nov 2020

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1 **New insights on Br speciation in volcanic glasses and structural controls on**
2 **halogens degassing**

3

4 ***Revision 1***

5

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17

18 **ABSTRACT**

19

20 The volcanic degassing of halogen, and especially of the heavier Br and I, received
21 increased attention over the last 20 years due to their significant effect on atmospheric
22 chemistry, notably the depletion of stratospheric ozone. While the effect of melt composition
23 on halogen diffusion, solubility or fluid-melt partitioning in crustal magma chambers has been
24 thoroughly studied, structural controls on halogen incorporation in silicate melts remain

25 poorly known, with only few studies available in simplified borosilicate or haplogranite
26 compositions.

27 Here, we demonstrate that high-resolution X-ray absorption spectroscopy (HERFD-
28 XAS) with a crystal analyser spectrometer (CAS) is well-suited for the study of Br speciation
29 in natural volcanic glasses which can contain lower Br concentrations than their laboratory
30 analogs. Especially, HERFD-XAS results in sharper and better-resolved XANES and EXAFS
31 features than previously reported and enables detection limits for EXAFS analysis down to
32 100 ppm when previous studies required Br concentrations above the 1000 ppm level.
33 XANES and EXAFS analysis suggest important structural differences between synthetic
34 haplogranite, where Br is surrounded by Na and next-nearest oxygen neighbors and natural
35 volcanic glasses of basaltic to rhyodacitic compositions, where Br is incorporated in at least
36 three distinct sites, surrounded by Na, K or Ca. Similar environments, involving both alkali
37 and alkaline earth metals have already been reported for Cl in Ca-bearing aluminosilicate and
38 our study thus underlines that the association of Br with divalent cations (Ca^{2+}) has been
39 underestimated in the past due to the use of simplified laboratory analogs. Overall, similarities
40 in Cl and Br structural environments over a large array of compositions (46-67 wt% SiO_2)
41 suggest that melt composition alone may not have a significant effect on halogens degassing
42 and further support the coupled degassing of Cl and Br in volcanic systems.

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44 Keywords : halogens, Bromine, magmas, volcanic glasses, speciation, HERFD-XAS

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51 INTRODUCTION

52 Despite their minor concentrations compared to H₂O and CO₂, halogens (F, Cl, Br and
53 I) are critical elements in the evolution of magmatic and volcanic systems, for instance
54 affecting magma rheology and enabling the scavenging and hydrothermal concentration of
55 metals in the crust (Dolejs and Zajacz, 2018; Webster et al., 2018 and references therein).
56 Their release through volcanic degassing has also been demonstrated to affect atmospheric
57 chemistry to different levels, with the rapid transformation of HBr to reactive BrO during
58 explosive eruptions triggering ozone depletion at local (within volcanic plume; Bobrowski et
59 al., 2003; Roberts et al., 2009) to global scales (if the plume reaches the stratosphere; Cadoux
60 et al., 2015; Klobas et al., 2017; Kutterolf et al., 2013). Recent improvements in the analytical
61 characterization and detection limits for F, Cl, Br and I in solid, liquid or gaseous samples
62 (i.e., Cadoux et al., 2017; Lubcke et al., 2014; Roberts et al., 2017; Seo et al., 2011) have also
63 opened new opportunities to use halogen concentrations and elemental ratios (F/Cl, Cl/Br or
64 BrO/SO₂) from volcanic fumaroles, undegassed melt inclusions or degassed lavas as tracers of
65 magma storage conditions, magmatic/hydrothermal activity, or eruption dynamics (Balcone-
66 Boissard et al., 2010; Dinger et al., 2018; Lubcke et al., 2014; Seo and Zajacz, 2016). Yet, the
67 effect of decompression on Br/S fractionation or the role of mineral sinks such as apatites and
68 sodalites in the volcanic cycling of halogens remain poorly constrained and thus limits the
69 interpretation of these samples.

70 The accurate interpretation of the deep information carried in melt inclusions or degassing
71 patterns at different volcanic centres requires the development of comprehensive geochemical
72 models that describe the behaviour of different volatiles during fluid exsolution and especially
73 how they partition from magma (melt + crystals) into bubbles or brines (Burgisser et al.,
74 2015). Accordingly, a large number of studies have already been dedicated to F and Cl.
75 Information on Br and I are much scarcer, mostly due to the analytical challenge associated
76 with their low concentrations in volcanic glasses (generally < 30 ppm Br and < 1 ppm I;

77 Aiuppa et al., 2009; Bureau et al., 2000-2016; Cadoux et al., 2018; Kutterolf et al., 2013,
78 2015). Overall, similarities in the ionic radii of O and F, compare to larger Cl, Br and I, have
79 been suggested to account for the larger solubility of F in silicate melts, and the contrasting
80 preferential partitioning of Cl, Br and I towards fluids (Bureau et al., 2000-2016; Dolejs and
81 Zajacz, 2018; Signorelli and Carroll, 2000, 2002; Webster et al., 2018). In silicate melts, both
82 F, Cl and Br solubilities were also found to be at their minimum in metaluminous composition
83 where the aluminium saturation index ASI ($\text{Al}_2\text{O}_3/(\text{Na}_2\text{O}+\text{K}_2\text{O}+\text{CaO})$) is close to 1. However,
84 while Cl and Br solubilities are higher under peralkaline conditions (alkalis > aluminium), F
85 solubility is higher under peraluminous conditions. Yet, direct constraints on halogens'
86 speciation in melts are extremely scarce, and mostly limited to simplified laboratory analogs,
87 including borosilicates, haplogranite or CaO-MgO-Al₂O₃-SiO₂ glasses (Cicconi et al., 2019;
88 Evans et al., 2008; McKeown et al., 2011, 2015; Schaller et al., 1992; Stebbins and Du,
89 2002). These studies reveal a strong affinity of Cl, Br and I for alkalis and alkaline earths-rich
90 environments, with Cl favouring divalent cations (Ca^{2+} and Mg^{2+}), while Br and I
91 preferentially bond to monovalent alkalis (Na, K). On the contrary, F mostly substitutes for O,
92 forming strong Al-F bonds, and may hence be more efficient in the depolymerisation of
93 aluminosilicate melts (i.e., acting as a network modifier). While these structural controls may
94 lead to the decoupling of halogens from H₂O and from each other, the speciation of halogens
95 in natural volcanic compositions, such as basalt or andesite, remains unknown up to date, and
96 potentially hinders modelling of halogens fractionation upon magma cooling or degassing.

97 Here, we provide new insights on Br speciation in silicate glasses of increasingly
98 complex compositions (haplogranite, rhyodacite, andesite and basalts). These are, to the best
99 of our knowledge, the first analyses constraining halogens speciation in natural volcanic
100 compositions. X-ray absorption is a widely used technique to characterize the local structure
101 and chemical state (oxidation state, coordination number, bond distances) of elements in
102 aluminosilicate glasses/melts and crystals of geological interest (Calas et al., 1987; Chalmin et

103 al., 2009; Cochain et al., 2015; Farges et al., 2006; Louvel et al., 2013; Wilke, 2018). In the
104 past, **an issue with characterization of Br speciation in silicate glasses/melts has been that**
105 **Br K-edge EXAFS data have weak amplitudes, making it difficult to obtain statistically**
106 **significant structural parameters from EXAFS fitting.** As a consequence, both the study of
107 Cochain et al. (2016) and that of Louvel (2011) show relatively high uncertainties on the
108 coordination number (N) and bond distances ($R_{\text{Br-O}}$) derived from EXAFS fit for granitic
109 glasses and melts. **The weak EXAFS amplitudes are mostly due to large Br-nearest**
110 **neighbour distances and nearest neighbour positional disorder around Br-sites.** One way
111 to overcome this limitation is to use a detection system with a better energy resolution.
112 Especially, ‘site-selective’ crystal analyser spectrometers (Proux et al., 2017) can be used to
113 improve the signal-to-background ratio and reveal spectral features that were invisible to
114 conventional XANES. This high-energy resolution fluorescence detection (HERFD)-XAS has
115 been successfully applied to better detect absorbing atoms (Co, Br, lanthanides) present in
116 different oxidation states or different sites, in metallic oxides, minerals and even high-
117 temperature supercritical fluids (Bordage et al., 2013; Hamalainen et al., 1991; Proux et al.,
118 2017; Vitova et al., 2013). In the present study, HERFD-XAS has been used to investigate Br
119 speciation in natural volcanic glasses. This approach results in **better-resolved** XANES
120 features than previously reported, and ultimately enables us to better understand the structural
121 incorporation of Br in geological melts, even at natural concentration levels (< 300 ppm;
122 Aiuppa et al., 2009).

123

124 **METHODS**

125 **Starting materials and Br quantitative analyses**

126 In order to probe the effect of water, SiO_2 , monovalent alkalis (Na^+ , K^+) or divalent
127 alkaline earth (Ca^{2+} , Mg^{2+} , Fe^{2+}) contents and degree of polymerization, Br speciation was
128 investigated in 7 different glass compositions, including basalt (B600, B3000), andesite (A10,

129 A100), rhyodacite (RD10_Dry, RD500) and haplogranite (Haplo_1wt%) with 10 to 10,000
130 ppm Br (1wt%) and < 0.5 to 6 wt% H₂O. Major element compositions, H₂O and Br contents
131 are reported in Table 1.

132 Haplo_1wt% is a simplified aluminosilicate composition that we use to isolate the structural
133 effects from alkalis (Na, K) from those from alkaline-earth (Ca, Mg). It was synthesized from
134 reagent grade powders of SiO₂, Al₂O₃, Na₂CO₃ and K₂CO₃ that were ground, decarbonized at
135 800 °C and later doped with ~ 1 wt% Br introduced as NaBr powder (SigmaAldrich®). The
136 powder was loaded with a drop of liquid water in a Au₈₀Pd₂₀ capsule and heated to 1200 °C
137 and 1.5 GPa in a piston-cylinder apparatus at ETH Zurich (Louvel, 2011).

138 All other glasses were prepared from natural volcanic products by Cadoux et al. (2017) to be
139 used as standards for Br contents analysis by Secondary Ion Mass Spectrometry (SIMS) and
140 Laser-Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS). The samples
141 consist of basalt, andesite and rhyodacite from Etna and Santorini eruptions that have been
142 crushed, grounded and melted twice at 1400 °C and 1 atm. The powdered material was then
143 loaded in Pt or Au-Pd capsules, together with 2-4 wt% H₂O-NaBr solution containing
144 different Br contents. The Br-doped glasses were finally synthesized at 1200-1250 °C and
145 300-400 MPa in an internally heated pressure vessel (IHPV) at the Institut des Sciences de la
146 Terre d'Orléans (ISTO, France).

147 These glasses were later characterized by electron microprobe (EMP, major elements), and Br
148 contents determined by Instrumental Neutron Activation Analysis (INAA), Rutherford
149 Backscattering Spectroscopy (RBS), X-Ray Fluorescence spectroscopy (SR-XRF), SIMS
150 and/or LA-ICPMS. The different techniques enable Br quantitative analysis down to ~ 1-10
151 ppm with an **accuracy from < 10 to ~ 20 % depending on the method and Br**
152 **concentrations (e.g., < 10% for Br ≥ 10 ppm and > 25% for Br ≤ 5ppm for SR-XRF;**
153 **≤20% for Br > 100ppm by LA-ICPMS; <20% for Br ≤ 1.2 ppm with SIMS)** The details
154 of glass synthesis and Br quantitative analyses can be found in Louvel (2011) and Cadoux et

155 al. (2017). For clarity, only the results of EMP, SIMS, INAA and RBS are reported in Table
156 1.

157

158 **High-Energy Resolution Fluorescence Detected X-ray Absorption Spectroscopy** 159 **(HERFD-XAS)**

160 X-ray absorption is a powerful technique to obtain information about the local
161 structure around **a given absorbing element**. Spectra are generally divided in two parts: the
162 near-edge structure (XANES), from ~100 eV below to 100 eV above the absorption edge (Br
163 K-edge = 13474 eV) and the extended X-ray absorption fine structure (EXAFS). Both parts
164 carry information about the local structure of the absorbing atom, including oxidation state,
165 nature and number of nearest neighbours (oxygen, ligands, metals, etc...), bond length and
166 symmetry. Additionally, pre-edge features located 50 to 30 eV before the absorption edge
167 provide complementary information about site geometry and electronic structure of the
168 absorbing atom (e.g., 1s => 4p transition). **Their position and intensities can also be related**
169 **to different oxidation states of the excited element (e.g., Ti^{4+/5+}; Fe^{2+/3+} - Farges et**
170 **al.,1996; Wilke et al., 2004) or bond distance to the nearest neighbour (i.e, the shorter**
171 **the bond length, the higher the pre-edge peak)**. In conventional XAS, total fluorescence
172 yield is acquired with solid-state detectors (SSD or SDD). The energy bandwidth ΔE of such
173 detectors classically ranges between 120 and 300 eV, depending on the detector quality and
174 shaping time, enabling detection limits in the order of 50 ppm. In comparison, a crystal
175 analyser system (CAS) equipped with spherically bent crystal analysers with a radius of
176 curvature in the 1m range (Fig. 1A) decreases the energy bandwidth to 0.2-2eV. This value
177 being smaller than the core-hole lifetime of the fluorescence line results in improved spectral
178 features (Fig. 1B).

179 HERFD-XAS measurements were conducted at the FAME-UHD French CRG
180 beamline (BM16) of the European Synchrotron Radiation Facility (ESRF; Proux et al., 2017).

181 The beamline optics were tuned to Br K-edge energy (13474 eV) using a double-crystal
182 Si(220) monochromator and Rh-coated mirrors to focus the X-ray beam down to 100 x 300
183 μm (HxV at FWHM). Then, energy selection of the emitted photo-electrons was
184 accomplished using a CAS involving five spherically bent Si(880) crystal analysers aligned
185 with the sample and a Vortex silicon drift detector (SDD2) on intersecting Rowland circles
186 (Fig. 1A and C). These crystals can be considered as secondary monochromators that re-focus
187 the diffracted beams on the fluorescence detector. Note that the current BM16 set-up now
188 includes up to 14 crystals (Si or Ge). The experimental set-up also includes another SDD for
189 total fluorescence yield (SDD 1 on Fig. 1A). The incident energy and beamline optics were
190 calibrated to a Pb foil reference (13035 eV – L3 edge). For the measurements, pristine glass
191 pieces were placed between kapton foils on a motorized sample holder. A helium-filled bag
192 was placed between the sample, the crystal analyser spectrometers (CAS), and the detector
193 (SDD 2) in order to reduce attenuation of the fluorescence signal by air (Fig. 1C). Overall,
194 this set-up enables an energy resolution of ~ 1 eV, smaller than the core-hole lifetime of the
195 fluorescence line (Hamalainen et al., 1991). XAS spectra were collected from 13390 to 13930
196 eV with 0.2 eV steps in the pre-edge/white line region and 2.5 eV steps in the EXAFS region
197 (counting time 10s). When necessary, the incident beam was attenuated by the placement of
198 aluminium foils within the beam path. An average of 10 spectra was collected on each
199 sample.

200

201 EXAFS analysis was conducted using the Athena and Artemis packages (Ravel and
202 Newville, 2005). The XAS spectra were averaged, normalized to the **absorption edge step**
203 and background was removed using the automatic background subtraction routine AUTOBK
204 included in Athena (Newville, 2001). The absorption edge E_0 was set at the maxima of the
205 absorption edge first derivative (13474 eV). **The R_{bkg} parameter, which is a background**

206 **removal parameter that minimizes the contributions to the Fourier transform at**
207 **distances below the atom-atom contact distance, was set to 1.3 Å.**

208 The $\chi(k)$ EXAFS function were Fourier filtered over the 2.5-7 Å⁻¹ range. To take into account
209 the chemical complexity of natural glasses and all the different atomic species that could bond
210 to bromine in the glasses, different correlation models involving 2 to 3 neighbours (O, Na, K
211 or Ca) were tried during the fitting of EXAFS oscillations. For all samples, modelling of the
212 EXAFS oscillations was performed using 4 variables: average coordination number (N),
213 distance to nearest neighbour (R), Debye-Waller factor σ^2 (accounts for structural disorder),
214 and the energy shift ΔE . The amplitude factor S_0^2 was fixed to 1 as previously used for similar
215 studies on Br in high pressure, high temperature fluids and melts (Ferlat et al., 2002; Da Silva-
216 Cadoux et al., 2009; Louvel, 2011). We note that a S_0^2 of 0.82 as used in Cochain et al (2015)
217 does not significantly alter the quality of the EXAFS fit for the reference NaBr powder (Table
218 2). All fits were performed simultaneously with k-weighting of 1, 2 and 3 in order to decrease
219 correlations between N and σ^2 , and R and ΔE (Pokrovski et al., 2009a,b).

220

221

222 **RESULTS AND DISCUSSION**

223 **Pre-edge and XANES features**

224 Figure 2 shows Br K-edge XANES spectra for four glasses: B3000, A100, RD500 and
225 Haplo_1wt%. Note that B600 glass display identical XAS to B3000. Due to low Br
226 concentrations, the spectra for A10 and RD10 are too noisy to be analysed and will not be
227 further discussed. All glasses display a sharp white line that peaks at around 13477 eV,
228 characteristic of Br⁻. The effect of the crystal analyser spectrometer further reveals the
229 presence of pre-edge features that had not been recorded with conventional XAS and result in
230 an overall higher amplitude of both the white line and the first post-edge oscillations.

231 Less polymerized basaltic and andesitic glasses share very similar XAS features (both
232 XANES and EXAFS – **Fig. 2 and 3**), with the first oscillation after the white line peaking
233 around 13494 eV. Slight differences may be recorded in the normalized amplitude of the
234 white line, which is slightly more intense for basaltic composition (both 600 and 3000 ppm).
235 Also, a latent pre-edge shoulder may be seen in the andesitic glass (Fig. 2). Pre-edge features
236 are increasingly defined in the rhyodacite and haplogranite samples. In the rhyodacite, it
237 consists of a large shoulder at 13471 (-3 eV to E_0), preceded by a smaller feature at 13467 (-7
238 eV to E_0). In the haplogranite, only one well-defined feature is located at 13468 eV (-6 eV to
239 E_0). **Pre-edge features at the Br K-edge are attributed to the transition from the 1s core
240 level to an unfilled p state and have previously been reported for compounds where Br is
241 covalently bonded to itself (Br_2), hydrogen (HBr), oxygen or carbon atoms (Burattini et
242 al., 1991; D'Angelo et al., 1993; Evans et al., 2007). Alternatively, the development of
243 such features could also probe different atom-atom interferences (*i.e.*, effect of different
244 network-modifiers) or changes in the symmetry of the local structure, as previously
245 evidenced for Mn-, Fe- or Ti-bearing glasses (Chalmin et al., 2009; Romano et al., 2000).
246 Further modelling of the effect of specific structural variations on the XANES spectra of
247 Br-bearing glasses (for instance using the FDMNES code; Joly, 2001) is unfortunately
248 impossible as molecular dynamic (MD) simulations for Br are lacking.**

249 There is also a significant change in the post-edge oscillations: in the rhyodacite, similar
250 shape as in basaltic and andesitic glasses are reported, only shifted to lower energy by 2eV;
251 the shape is completely different for the haplogranite glass, with a sharper first oscillation
252 located at 13490 eV. Altogether, changes in the pre- and post-edge features of the spectra
253 evidence both a gradual structural change from basaltic to rhyodacite composition, probably
254 induced by increasing polymerization of the glass, and marked differences in the local
255 environment of the haplogranite. The main difference between haplogranite and the other
256 composition lies in the absence of divalent cations (Ca^{2+} , Mg^{2+} , Fe^{2+}) in the former, and it is

257 thus likely that differences between basalt/andesite/rhyodacite and haplogranite arise from the
258 formation of Br-(Ca²⁺/Mg²⁺/Fe²⁺) bonds in the natural volcanic compositions.

259

260 EXAFS

261 Despite the recourse to HERFD-XAS, EXAFS oscillations remain relatively weak **and**
262 **noisy** and do not extend over a much larger k-space range ($< 8 \text{ \AA}^{-1}$ – Fig. 3A) than previously
263 reported in Cochain et al. (2015) and Louvel (2011). **However**, EXAFS analysis is possible
264 for all glasses with Br concentrations down to 100 ppm, significantly smaller than in previous
265 studies. The small amplitude of the EXAFS oscillations **results both from the long Br-**
266 **nearest neighbour distances** and the different contribution of several pair correlations (Br-
267 cation and Br-O), a fact that was also highlighted for Cl K-edge EXAFS in borosilicate
268 glasses (McKeown et al., 2011). The Fourier transforms for basalt, andesite and rhyodacite
269 glasses are characterized by a main contribution at 2.57 Å and a small shoulder at 1.73 Å (Fig.
270 3C - uncorrected positions shifted to about -0.5 Å with respect to the real average bond
271 distance). There are no obvious contribution from second-shell neighbors above 3.5-4 Å. In
272 comparison, the haplogranite glass only display one broad contribution at 2.28 Å. This
273 contribution is similar to that in crystalline NaBr (Fig. 3C), suggesting that Br may be found
274 in haplogranite in a ‘salt-like’ structure surrounded by Na atoms.

275 A simple approach to derive structural parameters for poorly structured glasses or
276 solutions consist in using a crystalline standard as a structural fingerprint of bond length. For
277 Br, available structural data and XAS spectra are mostly limited to alkali and alkaline earth
278 halides (NaBr, KBr, CaBr₂, FeBr₂) (Cochain et al., 2015). For these compounds, Br-X bond
279 lengths increase in the following order: Fe - 2.63 < Mg - 2.70 < Ca - 2.89 < Na - 2.98 < K -
280 3.30 Å (Brackett et al., 1963; Deshpande, 1961; Haberecht et al., 2001; Wyckoff, 1963).
281 Differences between NaBr and KBr HERFD-XAS are effectively evidenced in the EXAFS
282 oscillations and FT (**Fig.3**).

283 To ensure a valid description of the Br surroundings in the different glasses, EXAFS fits were
284 first performed for crystalline NaBr and the haplogranite glass, which have the simplest
285 structures, only involving Na, O, Si and K. ΔE_0 (energy misfit) derived for crystalline NaBr
286 was fixed to fit the haplogranite glass. Consequently, the best fit for the haplogranite glass is
287 obtained considering a ‘salt-like structure’ composed of ~ 6 Na atoms located at 2.87 ± 0.01 Å
288 from the Br atom and ~ 4 oxygen nearest-neighbours at ~ 3.40 Å. The Debye-Waller σ^2 for
289 Br-Na is fitted as 0.038, a similar value to that obtained for crystalline NaBr (Table 2). These
290 structural parameters closely match those from previous measurements conducted on the
291 Haplo_1wt% glass in a hydrothermal diamond anvil cell **at the X05-LA beamline at the**
292 **Swiss Light Source** (Louvel, 2011). The slight differences in the two datasets (e.g., 5.8 ± 0.7
293 versus 5.9 ± 1.8 Na atoms, located at a distance of 2.87 ± 0.01 versus 2.94 ± 0.03 Å) likely arise
294 from the different experimental geometry and the different k-range used in the present study
295 ($2.5\text{-}7$ Å⁻¹ in comparison to $1.5\text{-}6$ Å⁻¹). These differences remain within error, with Br
296 surrounded by ~ 6 Na atoms and oxygens next-nearest neighbours from the tetrahedral
297 network.

298 The same approach was then used for the B3000 basaltic glass, fixing both ΔE_0 and Debye-
299 Waller σ^2 from Br-Na before fitting. The best fit for this composition consequently involves
300 2.2 ± 0.3 Na at an average distance of 2.97 ± 0.02 Å and two other contributions located at 3.31
301 (X₁) and 3.59 (X₂) Å. Based on known crystalline bond distances, the first unknown
302 contribution X₁ may correspond to Br-K bonds (Wyckoff, 1963). The later one does not
303 match any previously reported contributions and could potentially arise from Si or Al from
304 the network, divalent cations in network-modifying positions (Ca²⁺, Mg²⁺ or Fe²⁺) or Br-Br
305 bonding. Halogens-Si and -Al bonding, involving Br or Cl have previously been discarded
306 based on similarities between Al-free and Al-rich glasses (Sandland et al., 2004). Br-Br
307 bonds of 2.5-2.6 Å have been reported for polybromides (Pichierri, 2011). However, the
308 haplogranite glass, which has the highest Br concentration, does not show the X₂ contribution,

309 and it hence seems unlikely that other glasses containing significantly smaller fraction of Br
310 should involve Br-Br bonds. Furthermore, Br-Br gives rise to a pre-edge contribution, which
311 is not present in those glasses (except RD500). On the contrary, Cl has been reported to bond
312 to divalent Ca^{2+} in borosilicate and (an)hydrous aluminosilicate glasses (Baasner et al., 2014a;
313 Evans et al., 2008; Sandland et al., 2004; McKeown et al., 2011). Therefore, we suggest this
314 third-nearest neighbour to be Ca^{2+} . The higher concentrations of Ca^{2+} compared to Mg^{2+} and
315 Fe^{2+} in our glass compositions further support this hypothesis.

316 Similarly to the B3000 glass, adding up to 3 different contributions (Br-Na, Br-K and Br-Ca)
317 improved the quality of fits for B600, A100 and RD500 glasses (Table 2). For all natural
318 glasses, fits involving a single scattering path (ie., Br-Na, Br-K or Br-Ca) or a simple
319 combination of Br-O and Br-Na/Ca/K as in the haplogranite systematically resulted in
320 physically unrealistic parameter values (i.e., extremely large coordination numbers or
321 negative Debye-Waller factors). The B600 best fit mostly mimics that of B3000 glass with an
322 average of 2.5 ± 0.2 Na, 4.7 ± 0.4 X_1/K and 3.7 ± 0.4 X_2/Ca atoms surrounding Br. Fitted Br-
323 Na, Br-K and Br-Ca coordination numbers all increase for the andesite A100 and rhyodacite
324 RD500 glasses. While it is likely that increasing fraction of Na in andesitic and especially
325 rhyodacitic compositions will favour the development of ‘salt-like’ structure similar to that
326 observed in Haplo_1wt%, the increasing number of Br-K and especially Br-Ca seem more
327 unlikely and may underline limitations in our fitting procedure. Yet, the similar EXAFS shape
328 for all natural glasses supports that a local environment involving three different cations as
329 derived for basalt B3000 and B600 should pertain with increasing SiO_2 and decreasing CaO
330 in the glasses. In the future, more detailed characterization of Br speciation in natural glasses
331 may require using ^{81}Br Magic Angle Spinning Nuclear Magnetic Resonance (MAS NMR)
332 (Trill et al., 2002).

333

334 **IMPLICATIONS**

335 **Halogens incorporation in silicate melts**

336 Our XAS analyses for natural basalt, andesite and rhyodacite suggest that Br may be
337 surrounded by three different neighbours in these glasses: the first one is Na⁺ in a salt-like
338 structure and is probably more common in alkali-rich silicic compositions; the two others may
339 be K⁺ and Ca²⁺. Whether these different bonds occur on a localized domain where network
340 modifiers are mixed together or in distinct clusters containing only Na⁺, K⁺ or Ca²⁺ is difficult
341 to assess as our XAS spectra average the structural information over the excited surface
342 (100x300 μm HxV FWHM). However, current knowledge of aluminosilicate glass structure
343 supports that aluminosilicate melts do not show a random organization where the so-called
344 network-modifiers (Na, K, Ca, Mg, Fe) are dispersed within the tetrahedral network, but that
345 network-modifiers segregate into distinct clusters or percolation channels in a depolymerized
346 silicate tetrahedral network (Kargl and Meyer, 2008; Lee and Stebbins, 2003; LeLosq et al.,
347 2017).

348 We believe the proposed structure involving three distinct neighbours (**Fig. 4**) should pertain
349 in high-temperature volcanic/magmatic melts. Whether measurements on quenched glasses
350 probe a more ordered speciation than that of their high P-T liquid counterparts has been a
351 matter of debate for years. However, an increasing number of *in-situ* high-temperature
352 spectroscopic analyses supports that structural changes associated to fast quench below the
353 glass transition remain relatively small when dealing with ‘low’ pressure conditions (< 2-3
354 GPa) (Drewitt et al., 2013; Le Losq et al., 2017; Malfait et al., 2018). For instance, *in-situ* X-
355 ray scattering analyses of Fe local environment by Drewitt et al. (2013) mostly report a small
356 shortening of bond distances from liquid to glassy basalts at ambient pressure (±0.05 Å). For
357 Br, previous *in-situ* XAS by Cochain et al. (2015) suggested significant re-ordering associated
358 with melting, resulting in an increase of Br-Na bond length from 2.98 (as in NaBr) to 3.55-
359 3.75 Å at pressure above 2 GPa. We however note that the Br K-edge EXAFS reported by
360 Cochain et al. (2015) for granitic glass (2.3 wt% Ca) share more similarity with our basaltic,

361 andesitic and rhyodacitic glasses than with Ca-free haplogranite, with the fitted Br-X bond
362 length of 3.55-3.75 Å similar to the one we here attribute to Br-Ca. Thus, the importance of
363 multi-site incorporation and potential Ca-complexation may have been underestimated in this
364 study.

365 Overall, we argue Br shows no particular affinity for Na over other network-modifier
366 cations and may actually occur in three different sites, involving either Na⁺, K⁺ or Ca²⁺ (**Fig.**
367 **4**). Similar environment was previously suggested for Cl in boro- and aluminosilicate glasses
368 (Baasner et al., 2014a; McKeown et al., 2011). More surprisingly, F-Ca sites have also been
369 found to be dominant in peralkaline aluminosilicate glasses, even with Ca being the least
370 common cation (Baasner et al., 2014b). However, Iodine appears to favour a **site-selective**
371 configuration, bonding to Na⁺ even in the presence of large Ca amounts (up to 12 mol%)
372 (Cicconi et al., 2019; McKeown et al., 2015). McKeown et al. (2011, 2015) attributed Cl and I
373 different local environments to their different ionic radius (1.81 Å for Cl in comparison to 2.2
374 Å for I), which results in Cl having a larger charge density and hence greater affinity for
375 higher charged cations. Br's ionic radius (1.96 Å) is closer to that of Cl, which could support
376 its complexation with divalent Ca²⁺.

377

378 **Potential influence on halogens degassing**

379 The efficiency of halogens degassing, and their potential fractionation from one
380 another, depends on a complex interplay between P-T conditions, magma composition and
381 eruption dynamics and kinetics (i.e., do halogens actually have time to diffuse and degas upon
382 magma ascension?) (Balcone-Boissard et al., 2009). If occurring under equilibrium
383 conditions, the efficiency of halogens degassing will solely depend on their fluid-melt
384 partitioning; however, degassing may also occur out of equilibrium, and the final composition
385 of the volcanic gas may then depend on diffusion rates rather than partition coefficients.

386 Experimental fluid-melt partition coefficients underline the preferential partitioning of Cl, Br
387 and I in aqueous fluids or gas (Bureau et al., 2000, 2016; Cadoux et al., 2018; Webster et al.,
388 2018 and references therein). Nevertheless, comparison between melt inclusions and residual
389 volcanic glasses suggest that at least a tenth of the pre-eruptive Cl and Br contents may be
390 retained in the erupted lava (Dolejs and Zajacz, 2018 and references therein). In natural
391 systems, chemical controls on halogen degassing may especially be difficult to distinguish
392 from the effects of eruption dynamics. Indeed, while fluid-melt partition coefficients increase
393 slightly with SiO₂ contents under typical volcanic conditions (900-1100 C and 100-200
394 MPa)(Cadoux et al., 2018; Dolejs and Zajacz, 2018; Webster et al., 2018 and references
395 therein), comparison between the residual halogen contents from plinian clasts and lava
396 domes suggest that fast decompression during explosive eruptions prevents equilibrium
397 between the different volatiles species and consequently precludes degassing of halogens with
398 H₂O (Balcone-Boissard et al., 2010). The similarities we report in the incorporation
399 mechanisms of Br (and Cl) in basaltic, andesitic, and to a lesser extent, rhyodacitic melts
400 suggest that the effect of melt composition and structure on Cl and Br initial solubility and
401 degassing from hydrous calc-alkaline melts may be relatively small and mostly linked to the
402 larger availability of interstitial alkali and alkaline-earth rich domains in less polymerized
403 basaltic and andesitic compositions. In the case of fast explosive degassing, large amount of
404 Cl and Br may also be retained in alkali and alkaline earth-rich domains depleted in water, as
405 suggested by the similar speciation reported in anhydrous versus hydrous sodium disilicate
406 and haplogranite glasses (Louvel, 2011).

407 Similarities in the local environment of Br in basaltic to rhyodacite compositions also point to
408 Br (and by extension Cl) having comparable diffusion rates in hydrated and (Na, K, Ca)-
409 bearing melts. Balcone-Boissard et al. (2009) reported that alkali content affects Cl diffusivity
410 so that Cl diffuse faster in K-bearing phonolitic melts. They attributed this different behaviour
411 to stronger Cl-Na interactions that would slow down Cl diffusion and potentially prevent Cl

412 degassing upon fast eruption. However their experiments did not consider the effect of Ca
413 (Ca-free glass) and the reported differences may not hold to natural composition including
414 several wt% CaO. Experiments on Ca-rich basaltic compositions by Alletti et al. (2009) show
415 no significant differences in the diffusivity of F, Cl and Br under anhydrous and hydrous
416 conditions ($D = 3-4 \cdot 10^{11} \text{ m}^2\text{s}^{-1}$ at 1250 °C and 1 GPa), suggesting limited effect of ionic radius
417 and preferential complexation on halogen diffusion for this composition. Coupled degassing
418 of Cl and Br should also be expected, regardless of their initial contents in the melt. This is
419 further supported by the relatively constant Cl/Br reported in both volcanic gas and residual
420 volcanic glasses from various tectonic settings (e.g., Hawaii, Nyiragongo, Etna, Stromboli,
421 Reunion, Masaya or Montserrat; Balcone-Boissard et al., 2010; Cadoux et al., 2018;
422 Villemant et al., 2008).

423 Larger controls on F, Cl, Br and I degassing efficiency may arise from the crystallization of
424 phases such as apatite, hauyne or nosean, which act as sinks for the halogens and retain them
425 in the magma. McKeown et al. (2015) demonstrated that I-Na environment in borosilicate
426 glasses mimics that of NaI-sodalite. Such an environment could act as precursor to the
427 crystallization of halogens-rich minerals and significantly hinder I degassing. While hauyne,
428 nosean and apatite have all been suggested to crystallize in phonolite at Cl concentrations
429 close to or below melt saturation (Baudoin and Parat, 2015) and are common late-stage phases
430 of volcanic activity that crystallize below 1000 °C and 300 MPa, the heterogeneous
431 distribution of Br (and Cl) within the melt structure could favour their transport in the
432 ascending melts and ultimately lead to a more efficient degassing than for I.

433

434 **ACKNOWLEDGMENTS**

435 M. Louvel acknowledges funding by the Natural Environment Research (NERC) Council via
436 grant NE/M000419/1 awarded to Michael J. Walter from the University of Bristol to support

437 the ESRF experiments. The FAME-UHD project is financially supported by the French
438 "grand emprunt" EquipEx (EcoX, ANR-10-EQPX-27-01), the CEA-CNRS CRG consortium
439 and the INSU CNRS institute. The authors thank an anonymous reviewer and S.A.T. Redfern
440 for handling of the manuscript.

441

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629 **LIST OF TABLE AND FIGURES**

630 **Table 1.** Composition of Br-bearing glasses.

631 **H₂O (wt%) measured by SIMS; **H₂O nominal; ***Br contents measured by Instrumental Neutron*
632 *Activation Analysis INAA or Rutherford backscattering RBS (Haplo_1wt%).*

633 ***RD10_Dry represents the re-melted, i.e., water-free, RD10 standard glass from Cadoux et al. (2017).***

634

635 **Table 2.** Structural parameters derived from the Br K-edge EXAFS analysis of the NaBr powder
636 reference and the different silicate glasses.

637 *N is the Br-X coordination number (where X is the nearest to next-nearest atom, O, Na, K or Ca); R is*
638 *the average bond distance between Br and X in Å; σ^2 is the Debye-Waller factor (in Å²), which*
639 *accounts for structural disorder around the excited atom. $\Delta E0$ is the energy misfit; R-factor and Xred*
640 *are internal parameters describing the goodness of the fit that are used to select the optimal fit. All fits*
641 *were conducted with a S0₂ of 1.*

642 **parameters that were fixed during fitting procedure.*

643

644 **Fig. 1.** (A) Schematic view of the experimental set-up for HERFD-XAS at the BM16 beamline of
645 the ESRF (Grenoble, France). The emitted photons are first selected in energy with the crystal
646 analyzers (CAS) and then collected by a standard SDD detector (SDD 2). (B) Comparison of XAS
647 collected on the rhyodacite RD500 glass sample, using conventional XAS detection (SDD1 –
648 black line) and high-resolution energy (CAS+SDD2 – red line). (C) Photograph of the
649 experimental set-up showing the glass samples, Helium bag and SDD2.

650

651 **Fig. 2. Normalized XANES spectra for basaltic (B3000), andesitic (A100), rhyodacitic**
652 **(RD500) and haplogranitic (Haplo_1wt%) glasses. HERFD-XAS spectra from NaBr and**
653 **KBr crystalline powders, which are used as structural fingerprints, have been uploaded**
654 **from the SShade spectroscopic database**
655 **(<https://www.sshade.eu>)(10.26302/SSHAD/EXPERIMENT_OP_20180115_002;**

656 **10.26302/SSHADE/EXPERIMENT_OP_20180115_003). They were both collected on the**
657 **BM16 beamline at ESRF, using a similar experimental design as described here. The dashed**
658 **line underlines similarities in the white line of silicate glasses and NaBr crystalline powder.**

659

660 **Fig. 3. (A) k^2 -weighted $\chi(k)$ EXAFS oscillations and (B) corresponding Fourier transforms**
661 **(FT) in the $2.5 - 7 \text{ \AA}^{-1}$ range of basaltic (B3000), andesitic (A100), rhyodacitic (RD500) and**
662 **haplogranitic (Haplo_1wt%) glasses. Red dashed lines are least-square fits obtained with**
663 **IFEFFIT. EXAFS and FT from the NaBr and KBr crystalline powders are also reported for**
664 **comparison. Peak positions in the FT (C) are uncorrected from backscattering phase shift,**
665 **with the corrected interatomic bond distances reported in Table 2.**

666

667 **Fig. 4.** Proposed schematic volcanic glass structure. Br is in Na, K or Ca-rich domains within the
668 partially depolymerized silicate tetrahedral network. Note that silicate tetrahedra may include
669 bridging and non-bridging oxygens. Depending on P-T conditions and melt composition, water
670 may be found as OH groups or free water molecules (Xue and Kanzaki, 2004).

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683 **TABLES**

684 **Table 1.**

	B600	B3000	A10	A100	RD10_Dry	RD500	Haplo_1wt %
SiO ₂ (wt%)	46.49	47.01	56.70	55.58	70.10	67.14	75.0
TiO ₂	1.65	1.64	1.06	1.14	0.44	0.39	
Al ₂ O ₃	15.42	15.66	15.3	15.26	14.63	13.82	9.4
FeO _{tot}	9.17	8.99	6.76	6.19	2.80	2.56	
MnO	0.17	0.18	0.22	0.24	0.08	0.13	
MgO	6.00	5.95	2.74	2.60	0.72	0.69	
CaO	9.84	9.90	6.18	6.08	2.30	2.28	
Na ₂ O	3.03	3.22	4.01	4.33	4.17	4.56	7.4
K ₂ O	1.88	1.93	1.55	1.60	3.03	2.91	3.8
P ₂ O ₅	0.72	0.73	0.23	0.25	0.13	0.12	
H ₂ O	2.0**	2.07*	4.98*	4.90*	0.04*	4.75*	3.3**
<i>Br (ppm)</i> ***	<i>634</i>	<i>3240</i>	<i>9.9</i>	<i>90.3</i>	<i>10.0.</i>	<i>496</i>	<i>9600</i>

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702 **Table 2**

Glass	Shell	N	R(Å)	$\sigma^2(\text{Å}^2)$	ΔE_0 (eV)	R-factor	Xred
NaBr	Na	5.83 ±0.35	2.97 ±0.01	0.038 ±0.002	-2.7 ±0.3	0.031	
B600	Na	2.53 ±0.25	2.97 ±0.01	0.038*	-2.7*	0.014	136
	X_1/K	4.67 ±0.37	3.30 ±0.03	0.011*			
	X_2/Ca	3.71 ±0.37	3.57 ±0.01	0.020*			
B3000	Na	2.22 ±0.34	2.97 ±0.02	0.038*	-2.7*	0.013	323
	X_1/K	4.46 ±0.27	3.31 ±0.01	0.011 ±0.002			
	X_2/Ca	3.48 ±0.47	3.59 ±0.02	0.020 ±0.005			
A100	Na	4.17 ±1.55	3.03 ±0.07	0.038*	-2.7*	0.082	242
	X_1/K	5.69 ±1.20	3.31 ±0.05	0.011*			
	X_2/Ca	6.09 ±1.80	3.58 ±0.07	0.020*			
RD500	Na	5.32 ±0.66	2.96 ±0.03	0.038*	-2.7*	0.038	204
	X_1/K	6.12 ±0.65	3.28 ±0.03	0.011*			
	X_2/Ca	6.84 ±0.77	3.55 ±0.04	0.020*			
Haplo_1wt%	Na	5.83 ±0.71	2.87 ±0.01	0.038 ±0.003	-2.7*	0.018	85
	O	3.44 ±0.96	3.39 ±0.03	0.020 ±0.010			

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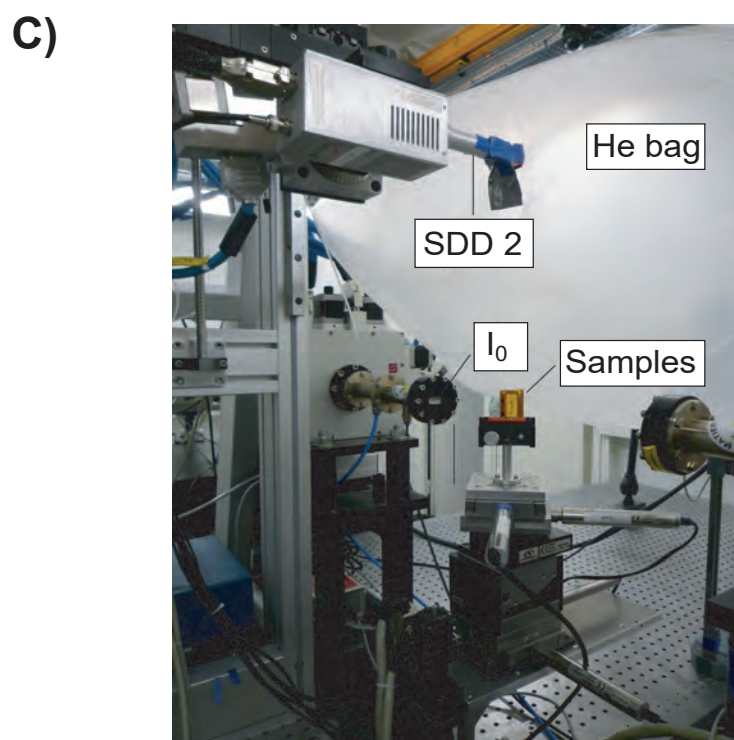
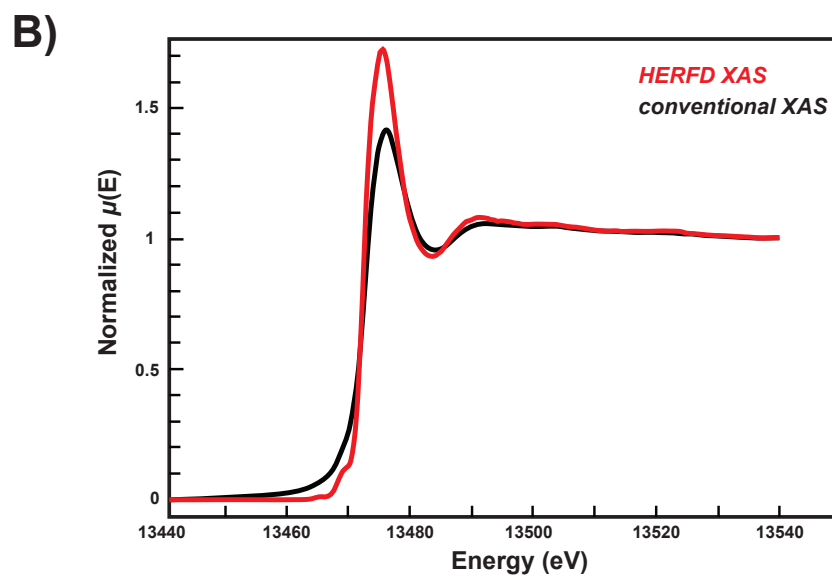
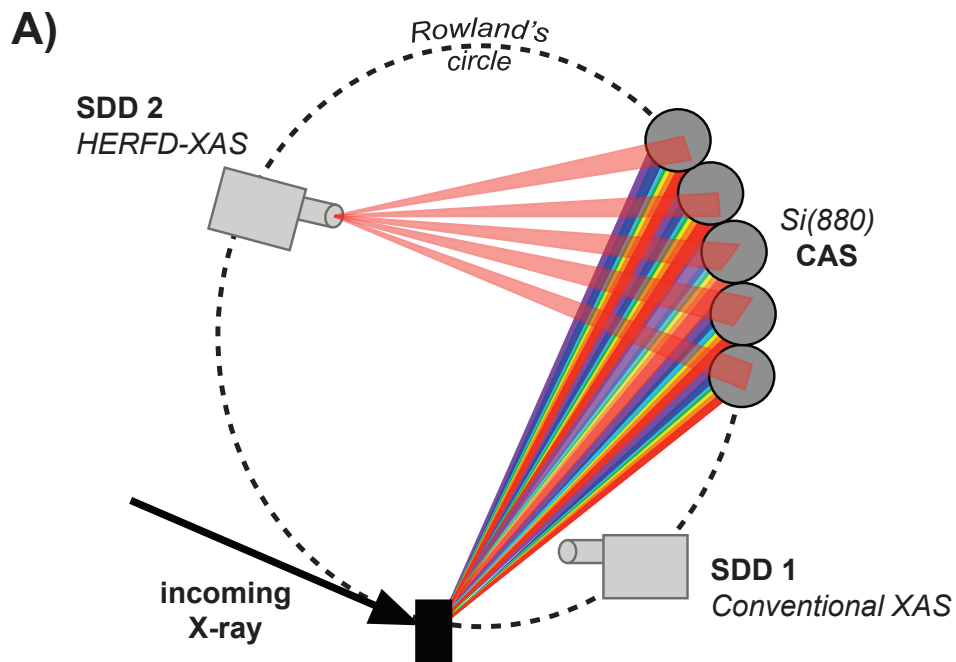


Figure 1

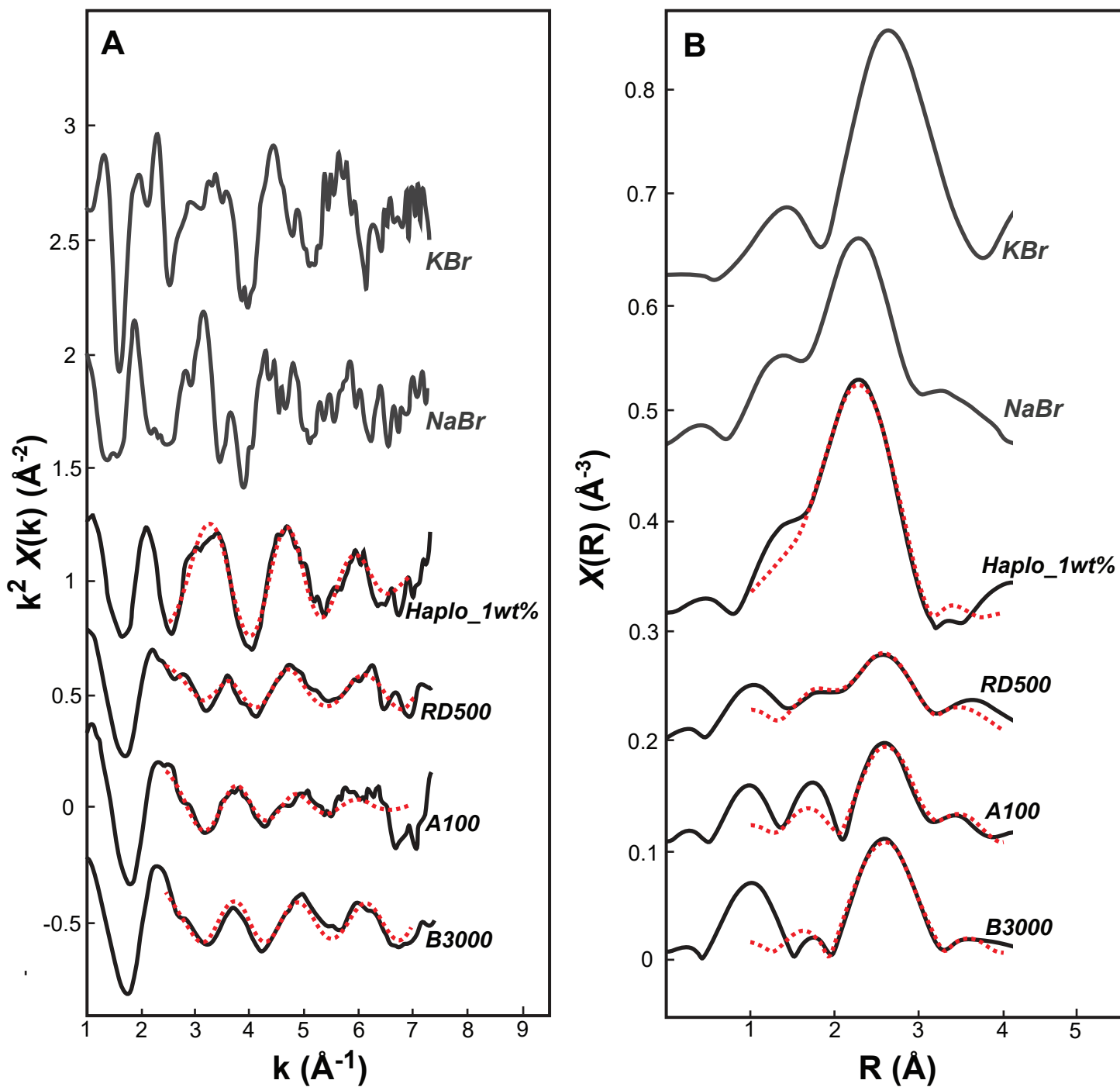
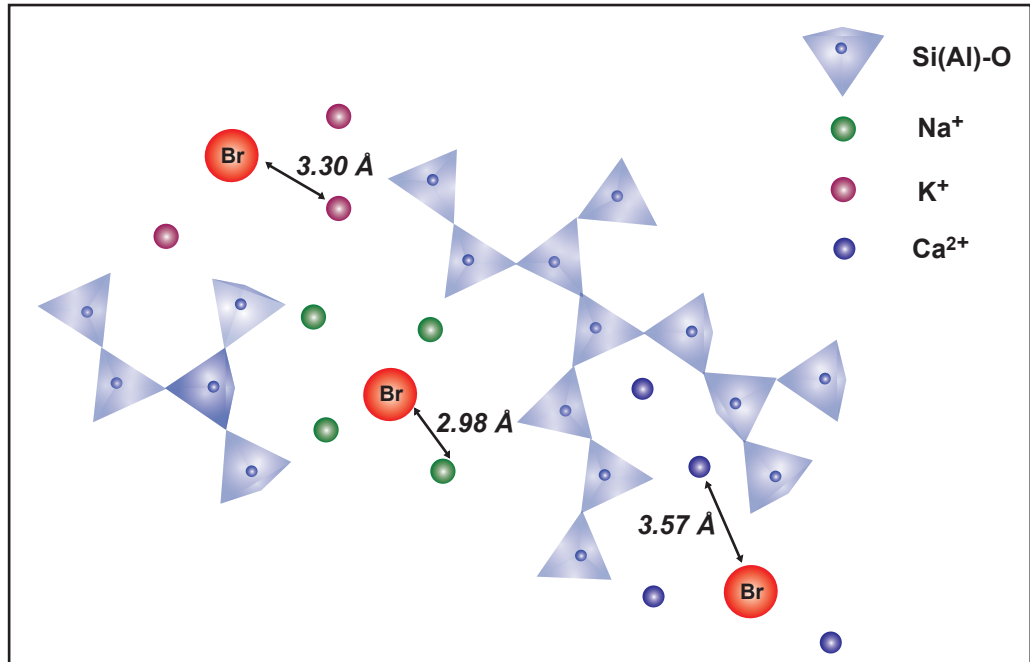


Figure 3

Figure 4



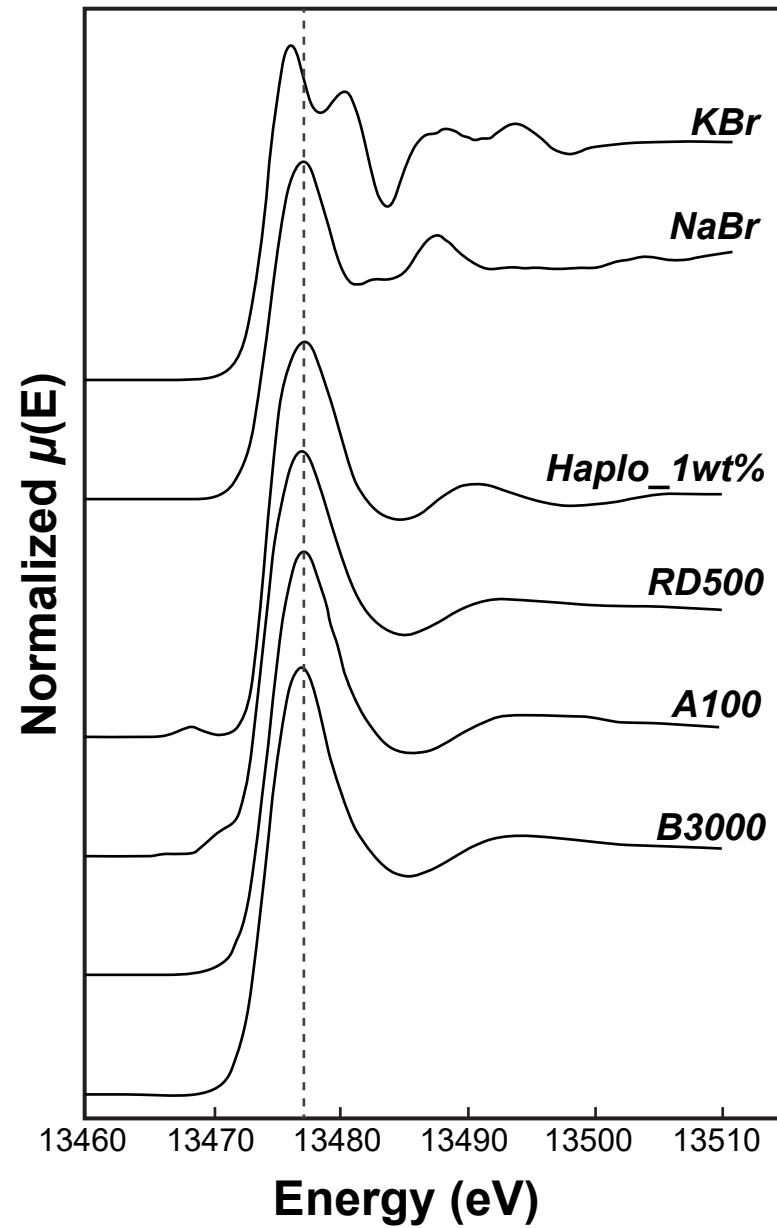


Figure 2