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IODINE LOCAL ENVIRONMENT IN HIGH PRESSURE BOROSILICATE GLASSES: AN X-RAY PHOTOELECTRON SPECTROSCOPY AND X-RAY ABSORPTION SPECTROSCOPY INVESTIGATION

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Abstract

The ^{129}I radioactive isotope is a by-product of nuclear plants activity. Owing to its strong volatility, there is currently no ideal protocol to immobilize ^{129}I in nuclear waste borosilicate glasses. Recently, we have proposed the use of high-pressure syntheses to dissolve iodine in various glass compositions; however, I speciation and dissolution mechanism could not be determined.

We have adopted an approach combining X-ray Photoelectron Spectroscopy (XPS) and X-ray Absorption Spectroscopy (XAS) methods to determine I speciation and molecular environment in glasses containing from 0.5 to 2.5 mol.% I. The XPS spectra reveal that I is mostly dissolved as iodide (>85% I^-) with a small proportion of elemental iodine (<15% I^0) and the absence of iodate species (I^{5+}). For borosilicate glasses, the XAS results and subsequent spectrum simulations suggested that Na and Ca are involved in the I^- vicinity with averaged derived coordination number (CN) of 3.6 and 2.0 and bond length to the nearest neighbour (r_{X-I}) 2.98 and 2.85 Å, respectively. These results suggest that the coexistence of both I^- and I^{5+} species is not requested for electric neutrality but instead, we explain the I speciation by the possible interplay with oxygen species from the borosilicate matrix. In addition, the results imply that the borosilicate network is affected by the I dissolution.

1. Introduction

Among the many radioactive elements produced by anthropic nuclear activities, iodine (I) is one important element representing a serious glitch in the effort for immobilizing radioactive waste. One particular isotope (^{129}I) requires a special attention because of 1) its long half-life (>15 Ma) and 2) its high mobility and volatility in environment. In particular, the high I concentrations in surface water and atmosphere in industrial countries [1,2] is a health issue considering that I can easily integrate the food chain and fix into living organisms [3,4]. Therefore, there is a need for a solution able to immobilize durably this isotope collected from nuclear waste.

In a recent review, *Riley et al.* [5] provide an exhaustive view of the different methods used to immobilize radioactive I in solid matrices. Either crystalline materials (e.g. [4,6-8]) or nuclear waste glasses (e.g. [9-11]) could be used, however, it appears that there is currently no ideal solution allowing the immobilization of radioactive I in a permanent and safe manner. For instance, classical melting devices operating at ambient pressure do not allow the I retention in significant concentrations in vitrified matrix [12]. At best, under ambient pressure conditions a concentration <0.7 mol.% I can be retained in borosilicate glasses as shown in previous works [9-11]. *Riley et al.* [10] reached almost 0.5 mol.% I in borosilicate glasses using sealed ampoules (i.e. inside pressure above ambient pressure).

One potential solution to circumvent the strong I volatility during glass melting is to consider the I conditioning in borosilicate glass matrix under extreme conditions: high-pressure. Recent investigations [13-15] suggest that I solubility dramatically increases as the confinement pressure increases. For instance, *Jolivet et al.* [15] reached I solubility up to 2.5 mol.% in nuclear waste glass compositions held at 1.5 GPa pressure. *Cicconi et al.* [14] dissolved ~4 mol.% I in B_2O_3-rich glass compositions held at pressure of 150 MPa; however,

77 their investigated compositions (~60 wt.% B_2O_3) were less relevant for the I immobilization
78 in nuclear waste matrices. A comparable behaviour was also observed as a function of
79 pressure for I in boron-free silicate glasses compositions with applications to Earth Sciences
80 [16,17]. *Leroy et al.* [17] showed that I solubility can reach up to 1.5 mol.% in Si-poor H_2O-
81 rich silicate glasses synthesised at 3.5 GPa.

82 One critical aspect is to clarify the I dissolution mechanism into the glass structure. Previous
83 works [10] proposed a generic equation for I dissolution in borosilicate glasses:

84 $$3I_2^{fl} + 3Na_2O^m \rightarrow 5NaI^m + NaIO_3^m \qquad \text{Eq. 1}$$

85 In this reaction, a diiodine molecule (I_2) from the fluid phase interacts with the Na^+ cations to
86 form iodide (NaI) and iodate ($NaIO_3$) within the glass. In the proposed mechanism, Na is a
87 charge compensating cation to the BO_4 units within the structure [18-20]. Hence, removing
88 network modifying Na^+ is likely to induce the interconversion of BO_4 to BO_3 units in order to
89 compensate the excess negative charges. However, the question remains debated, especially
90 as this mechanism is greatly function of the bulk chemical composition [18] and possibly
91 influenced by the intensive conditions for I-bearing glass synthesis. There is the coexistence
92 of different I oxidation states in Eq. 1: -1 in NaI and +5 in $NaIO_3$. In other words, the
93 structural analysis of I-bearing glass samples should reveal the presence of both I^- and I^{5+}
94 species in order to satisfy the electrical charge neutrality.

95 Eq. 1 has been established based on XAS results [10] and to some extent, Raman
96 spectroscopic results [13]. The XAS (both X-ray Absorption Near-Edge Structure, XANES;
97 and Extended X-ray Absorption Fine Structure, EXAFS) is of particular interest as it probes
98 the local environment for a given element. It has been successfully applied for the
99 investigation of I local environment in various materials at both the K- and L-edges:
100 crystalline [4,21-23]; organic [24-26]; solution [27] and glass [9-11,14,28-30].

To the specific case of borosilicate glasses, the study of *McKeown et al.* [11] is a landmark work. In a series of various borosilicate glasses typical of nuclear waste application, they determined the local environment of dissolved I (up to 0.66 mol.%) using K-edge XAS measurements at 33,169 eV. They applied the fingerprinting method (with crystalline standards) to investigate the I K-edge XANES spectra and modelled the I K-edge EXAFS spectra. Their results demonstrate that I dissolves in borosilicate glasses as I^- with a next nearest neighbour at a distance of ~3.04 Å. They suggest that the next nearest charge compensating cation is Na^+ and based on the EXAFS treatment that the coordination number for I^- is ~4. These results apply to borosilicate glasses synthesised at ambient pressure. The effect of pressure is known to induce bond length and coordination changes (e.g. [31-34]); therefore, the results obtained by *McKeown et al.* [11] may not apply to the case of borosilicate glasses synthesised under high-pressure conditions.

In the present work, we have investigated the I local environment using L_3-edge XAS (both XANES and EXAFS). We have studied a series of borosilicate glasses synthesised under high-pressure conditions (0.5-1.5 GPa) and reported in the work of *Jolivet et al.* [15]. In addition, one sample having Na-free composition was also investigated for determining the local environment around iodine atoms in the case of Ca surrounding. The range of I content in the studied glasses is 0.5 to 2.5 mol.%. The I local environment was determined using fingerprinting method for the XANES part and modelling of the EXAFS part using standard crystalline structure. Based on these results and previous literature data, we propose a discussion on the I dissolution mechanisms in borosilicate glasses synthesised under pressure conditions.

2. Analytical methods

2.1 Starting samples

125 Several types of glass composition were used for this work. The samples as well as the
126 synthesis method are fully described in *Jolivet et al.* [15]. The investigated compositions are
127 two aluminoborosilicate glasses, International Simple Glass (ISG, [35]) and a Low Activity
128 Waste (LAW) glass called NH, and one boron-free aluminosilicate glass, TY. The
129 aluminoborosilicate glass compositions are in the system SiO_2-Al_2O_3-B_2O_3-CaO-Na_2O; the
130 ISG composition contains additional ZrO_2 (~1.7 mol.%). The TY aluminosilicate glass
131 composition is in the system SiO_2-Al_2O_3-CaO-Na_2O. Except for ISG (issued from an
132 industrial batch), the NH and TY compositions were prepared from a mixture of oxides (SiO_2,
133 B_2O_3, Al_2O_3, CaO) and sodium carbonate (Na_2CO_3). The powder mixtures were carefully
134 ground into an agate mortar and were melted twice in a Pt crucible at 1150°C for 1 h for NH
135 and at 1500°C for 20 h for TY (see [15] for details). Because the compositions studied by
136 *Jolivet et al.* [15] are both Na- and Ca-bearing glasses, discriminating the I local environment
137 between either Ca or Na is rendered difficult. Whereas the local charge compensation for I^- by
138 Na^+ cation is currently well admitted, the potential role for Ca^{2+} is currently not recognized.
139 Therefore, we also investigated one glass composition C35 that is a Na-free Ca-rich glass.
140 This investigated glass has the following composition: 31.8 SiO_2, 29.2 B_2O_3, 4.9 Al_2O_3, 32.5
141 mol.% CaO; as provided by the analyses from Scanning Electron Microscopy coupled with
142 Energy Dispersive X-ray Spectroscopy (SEM EDS).

143 We conducted the high-pressure experiments in a piston cylinder apparatus at temperatures
144 between 1300 and 1500°C and for pressures between 0.5 and 1.5 GPa using the pressurizing
145 protocol described in *Jolivet et al.* [15]. The volatile-free glass powder were mixed with a
146 known amount of solid I_2. The mixture was loaded in a Pt capsule that was then sealed by arc-
147 welding. The run duration was ~4h and the sample was quenched to room temperature by
148 cutting off the power. The recovered samples consisted in clear glass covered with a dark
149 residue suggesting an I excess during the experiments. The I excess was removed by cleaning

in ethanol the glass samples. All the synthesised glasses was characterized by SEM EDS and the I content ranges from 0.5 to 2.5 mol.% as reported in *Jolivet et al.* [15]. The I content measured in C35 is 1.6 mol.%. The details of the sample composition are reported in *Jolivet et al.* [15] and are given in *Supplementary Material* and the I content measured for each glass is given in *Table 1*.

2.2 X-ray Photoelectron Spectroscopy

X-ray Photoelectron Spectroscopy was performed for several samples (see *Table 1*) to determine the I speciation in our glasses with the aim to provide constraints for the EXAFS simulations. Several crystalline standards (NaI, $NaIO_3$ and CaI_2O_6) were also analysed, serving as a fingerprint for I speciation in the glasses. We could not acquire XPS spectra for solid crystalline I_2 and CaI_2 owing to the sublimation of I_2 under high vacuum conditions and the poor stability of CaI_2.

We carried out the XPS analyses with two spectrometers: a Kratos Nova and a Kratos Axis Ultra using a monochromatic Al Kα radiation operating at 1486.6 eV (15 kV, 20 mA) with a charge neutralizer. The glass chips (~3x3 mm^2) showing a surface fracture from the bulk of the experimental charge were loaded into the sample chamber and at high vacuum (<10^{-8} mbar). The sample surface was not prepared and the analysis was conducted on a raw glass surface, hence avoiding possible surface contamination. The spot size on the sample is 300x700 μm^2 area of analyses. We recorded survey spectra at a pass energy of 160 eV corresponding to an overall instrument resolution measured on silver Fermi edge of 1.95 eV and a step of 0.5 eV from -5 to 1200 eV. High resolution spectra of Na 1s, I 3d, O 1s, Ca 2p, C 1s core levels were recorded with an instrument resolution measured on silver Fermi of 0.49 eV and a step of 0.1 eV at a pass energy of 20 eV. The calibrations were performed on the adventitious C 1s in the binding energy at 284.8 eV [36,37]. All spectra were treated with

CasaXPS© software. All spectra were fitted with a U2 Tougaard function [38] for the background and with a pseudo-Voigt function with a Lorentzian ratio of 50% for the various peaks. Although, the associated error on the different components provided by the CasaXPS© fitting package is relatively low owing to the good quality of the XPS spectra, we believe that the simulations are accurate to within 10% of the derived value. Only the I $3d_{5/2}$ peak in the I 3d region with the highest intensity was fitted as compared to the one for the I $3d_{3/2}$. The obtained peak position did not show dependency on I content or glass composition. Therefore, determining the exact nature of the charge-compensating cation (i.e. Na^{+} or Ca^{2+}) surroundings I atoms could not be possible. We obtained several acquisitions for each element. We did not find any modification of each individual acquisition suggesting that the glass is stable under the X-ray beam.

2.3 X-ray Absorption Spectroscopy

We collected the I L_3-edge XAS spectra on LUCIA beamline at SOLEIL synchrotron operating with a current of 450/500 mA and an energy of 2.75 GeV [39]. The energy of the incoming photons was selected by using double crystal monochromator Si(111). The XAS spectra on the glass were collected in fluorescence mode with a silicon drift diode detector. To avoid the self-absorption effect, the geometry of the beamline was set to a low angle between the sample surface and the detector (2°). The energy calibration of the incoming photons was achieved on titanium foil by selecting the first inflexion point of the spectrum at 4966 eV. We used in our experiment an unfocused beam with a size of 4x2 mm^2 for maximizing the count rate. The glass powder samples were stuck on a copper plate using carbon tape and acquisition were conducted under vacuum conditions. Prior to acquisition, the region of interest for the X-ray fluorescence lines had to be optimised to avoid interferences arising from the proximity between Ca K-edge fluorescence line (~3691 eV) and the I L_3-edge fluorescence line (~3926 eV). The optimisation of the fluorescence region was

conducted such as that the higher tail of the Ca fluorescence line did not contribute to the I signal. However, we suspect that removing the contribution of the Ca fluorescence line appears to be incomplete, especially for C35 in which Ca is 20 times more concentrated than I.

The XAS spectra were collected at the L_3-edge of I in the range 4510-4850 eV. For each point, the counting time was 10 s. We collected at least three spectra on each sample in order to obtain an average spectrum with a good signal to noise ratio. The recorded scans are identical and the presented spectra correspond to an average of the different scans. A slight colouring of the glass powder is observed after XAS acquisition. Several acquisitions were also made on crystalline standards for comparison and fingerprinting of the XAS glass spectra: NaI, CaI_2, I_2, $NaIO_3$, CaI_2O_6. In these crystalline compounds, the I oxidation state varies from -1 in iodides to +5 in iodates. As a result, the XAS signal (XANES and EXAFS) can be used for constraining the I oxidation state in the borosilicate glasses. Because crystalline iodides (NaI and CaI_2) are highly sensitive to H_2O adsorption, the crystalline sample powders were stored in a sealed glove box and quickly loaded into the vacuum chamber for XAS analysis. We did not observe any visible sign of phase transformation under X-ray beam; moreover, repetitive scans on the crystalline powders were almost identical.

Both XANES and EXAFS spectra were simulated to determine the I speciation in glasses and the first coordination sphere around I atoms. The XAS spectra were reduced by using the DEMETER package [40,41]. The normalisation and the merge of the XAS spectra as well as the background removal were carried out with the Athena software [40,41]. In addition, the self-absorption effect was checked using the Fluo software implemented in Athena [40,41]. The first coordination sphere to I atoms was obtained from the simulation of the EXAFS signal by using the single scattering signals determined with known crystalline structure. We used k^2-weighted signal function in the k-space and the simulation of the EXAFS region was

done using the Artemis software [41]. A description of the EXAFS fitting protocol is provided later in the Discussion section.

We simulated the ISG, NH, TY and C35 XANES spectra following the method described by *Schlegel et al.* [25] using a linear combination of the crystalline compound spectra. Linear fitting combinations were performed in the range 4540-4590 eV with the implemented tool in Athena software. It should be emphasised that the choice of crystalline structure for EXAFS or XANES spectrum simulations is based on the results obtained by the XPS, which provides the I speciation in the investigated glasses.

3. Results

3.1 Iodine speciation by XPS

We determined the I oxidation state using the XPS technique. The XPS spectra for crystalline compounds and glasses are shown in *Fig. 1*. We chose to represent only the $3d_{5/2}$ from the I doublet peak for clarity and because it is the most intense peak compared to the $3d_{3/2}$ [42-44]. For crystalline powders, there is an obvious distinction in the XPS spectra between the I oxidation states and therefore I local environment. For NaI in which I is present as -1 oxidation state, there is a peak located at ~619 eV; for $NaIO_3$ and CaI_2O_6 in which I is present as +5 oxidation state, there is a peak located at ~624 eV. For I-bearing glasses studied here, we observe in all the cases a single prominent peak located at ~619 eV (ranging from 619.0 to 619.4 eV obtained from the simulated spectra) and the absence of a peak at ~624 eV. The presence of the peak at 619 eV suggests that I is dissolved in the glass mostly as I^- species. A keener scrutiny reveals a peak at 624.4 eV for NH23-2 implying a small proportion of I^{5+} species within the glass. For several samples, we also observe a slight asymmetry on the high-energy side of the 619 eV peak. We interpret this asymmetry as the possible presence of I_2 species [45]. This suggests the possible presence of I dissolved in glasses as I_2 species.

Furthermore, most of the investigated samples were clear glass indicating the absence of I_2-filled bubbles. Brownish bubbles were only identified in TY glass samples and were interpreted as bubbles filled with residual I_2.

Subsequent simulation of the I $3d_{5/2}$ peak reveals that I_2 is present as a dissolved species in glass. In NH23-2 glass, we have identified the presence of I^{5+} at a total I fraction of 3.0%. The results of the simulations are shown in *Table 1* with the I speciation and the XPS spectrum simulations are provided in *Supplementary Material 1*. In all investigated glasses, the quantitative simulation of the peak reveals that I is present on average as 95.6% I^- and 4.1% I_0, presumably I_2. The determination of the I speciation will be used for constraining the simulations conducted on both the L_3-edge XANES and EXAFS.

Scrutinizing the I local environment with XPS simulations appears complicated, as the I $3d_{5/2}$ peak position does not change as a function of glass composition. For instance, for C35 (i.e. Na-free) for which the surrounding cation for I^- is Ca^{2+} exhibits a peak maximum at 619.2 eV comparable to the peak position observed for the other glasses that are Na- and Ca-bearing compositions.

3.2 I L_3-edge XANES

L_3-edge XANES spectra for crystalline and I-bearing glasses are shown in *Fig. 2*. We provide the entire set of spectra in *Supplementary Material 2*. In *Fig. 2*, all spectra exhibit a main absorption edge located at ~4563 eV. There is no pre-edge peak observed. The crystalline I_2 spectrum is relatively featureless whereas the spectrum for other salts shows a distinguishable edge peak at ~4563 eV, roughly symmetric except for NaI in which the edge peak seems to be a composition of several components. For iodates ($NaIO_3$ and CaI_2O_6), there is a strong shoulder with a maximum at ~4574 eV. This peak is not clearly visible for NaI, however, we observe a peak at ~4570 eV and a broad feature extending up to ~4590 eV in the EXAFS

region. For the iodates, there is a strong broad asymmetric peak with a maximum at ~4592 eV and corresponding to the beginning of the EXAFS region.

We followed the description provided by *Schlegel et al.* [25] for a tentative of assignment. The peaks at ~4563 and ~4574 eV are attributed to the transition to 5d levels. The broad features observed are assigned to 2p to d transitions [14]. We did not attempt to determine the I oxidation state for crystalline compounds [46,47] as there is no apparent change in the edge position, and also because the line broadening is important at the L edge for heavy elements such as I. Instead, we use the crystalline spectra to decipher the I local environment in the studied glasses.

The I L_3-edge XANES spectra are reported for six glass samples. It should be emphasised that within a glass series (ISG, NH or TY) we did not observe any significant difference in between the spectra (see *Supplementary Material 2*) suggesting that I has comparable local environment for all samples of a given series. As observed in *Fig. 2*, the C35 XANES spectrum contrast to the spectra for NH and ISG, therefore indicating that the I local environment in C35 is not the same as the one in ISG and NH glasses. This observation appears in contrast to the XPS results showing that I is dissolved as I^-, regardless of the glass composition. However, the XPS method only provides first level of information (i.e. I oxidation state) and does not scrutinize the next nearest neighbour to the I atoms.

The XANES spectra for ISG and NH look alike to the spectrum of NaI and to a lower extent to CaI_2. This suggests that ISG and NH spectra are possibly a combination of both NaI and CaI_2 XANES spectra. There is a well-marked peak at ~4563 eV as well as a broad peak with a maximum at ~4574 eV and a broad shoulder at ~4585 eV. Together, these features could witness the presence of Ca- and/or Na-iodates or a mixture between iodates and Ca- and/or Na-iodides; however, the XPS results obtained on those samples do not indicate the presence

296 of IO_3^- molecular species in the glass structure. We did not observe the presence of
297 unaccounted crystalline phase in the bulk of the glass as shown by the X-ray diagram obtained
298 [15]. Therefore, the XANES signal recorded corresponds to the I local environment in the
299 glass. The XANES spectrum for C35 that is Na-free glass composition has common features
300 with the XANES spectrum for CaI_2, however, as observed in *Fig. 2*, it appears unlikely that the
301 C35 spectrum will be reproduced with only the spectrum from CaI_2. This observation
302 emphasises the difficulty to reproduce XANES spectrum for glasses with the sole use of
303 XANES spectrum from crystalline compounds.

304 Nonetheless, in *Fig. 3* we propose an attempt of XANES simulations using the method of
305 linear combination described by *Schlegel et al.* [25] to reproduce the XANES spectrum for the
306 glasses. We strongly emphasise that this approach represents only an attempt and is by no
307 mean an absolute result. The reason being that we simulate a XANES spectrum for a glass
308 using XANES spectra obtained on crystalline compounds: NaI, CaI_2, I_2, $NaIO_3$ and CaI_2O_6,
309 shown in *Fig. 2*. The simulation results are also provided in *Table 1*. The first step of the
310 simulation involved using the entire set of spectra for crystalline compounds without
311 constraints (except for C35 glass that is Na-free glass composition). We tested all the possible
312 combinations to obtain the fit using the Linear Fitting Combination package. The entire set of
313 simulation is provided in *Supplementary Material 2*. The combination results involving
314 negative parameters were discarded. We limited the possible combination to three
315 independent components. From *Fig. 3*, it can be observed that the simulated spectra do not
316 reproduce entirely the measured I-bearing glass spectra. As mentioned, it appears difficult to
317 completely reproduce the XANES glass spectra with the XANES crystalline spectra as it does
318 not take into consideration the variations in bond length or bond angle that is a specificity of
319 disordered glass materials (e.g. [48-52]).

The XANES spectrum for TY33 is reproduced with a combination of NaI (~66%), CaI_2 (~14%), and a non-negligible proportion of I_2 (~21%). Considering that TY33 contains 0.5 mol.% I, the proportion of I_2 ~0.1 mol.%. The presence of I_2 appears consistent with the fact that TY glass samples showed a slight brownish colouring (see *Jolivet et al.* [15]). As shown in *Table 1*, the XANES simulation invoked the presence of iodate for several samples showing the highest I content. Except for NH23-2, this result does not appear consistent with the XPS results; however, at low concentration the presence of $NaIO_3$ would not be detected by XPS measurements. For NH and ISG glasses, the XANES spectra are reproduced with a combination of NaI and CaI_2 to more than 90% in proportion. The XANES simulations suggest the presence of I_2 in ISG and TY glasses. The ISG33-2 appears to be a particular case as the simulated amount of I_2 is relatively high (~40%); although this is not consistent with the observed XPS results (see *Table 1*) suggesting that only 3.3% of I is dissolved as I_2. A small contribution of iodate (CaI_2O_6) is suggested in all NH glasses. If we consider NH23-2 with 2.5 mol.% I dissolved, the proposed speciation will correspond to ~2.2 and ~0.3 mol.% of iodide and iodate, respectively. For C35, the XANES spectrum is reproduced with a contribution of 92.9 and 7.1% from CaI_2 and CaI_2O_6, respectively. This result is consistent to a certain extent to the XPS result that suggests I to be dissolved as I^- species, although, the presence of I^{5+} has not been identified.

From the general point of view the results illustrated in *Fig. 3* are consistent with the XPS results given in *Table 1*. The most important discrepancy is observed for ISG33-2 with ~40% I_2 observed by XANES against 3% by XPS. In detail, it appears complicated to extract reliable I species proportions from the simulation of the XANES spectrum owing to the difficulty in simulating adequately the I L_3 XANES spectra for a glass with crystalline compounds; therefore there is a large error associated to the derived proportion from XANES simulation.

Although the associated error to the simulation is probably large and the spectra are not reproduced adequately, it tends to discriminate the different iodide species present in the glass. Invariably, the best linear combination induces the presence of NaI and CaI_2 suggesting that both iodide species are present in the glasses. This aspect is also strengthened by the fact that I can dissolve in the structure of the Na-free Ca-rich C35 glass composition. For instance, we failed to simulate the spectra with one and not the other iodide crystalline spectrum. Nonetheless, in the current work and the subsequent XANES simulations, we propose that both Na^+ and Ca^{2+} are involved into the charge compensation of the I^- species.

3.3 I L_3-edge EXAFS

I L_3-edge EXAFS spectra are shown in *Fig. 4* for several glasses. We classified the spectra as a function of the I content and glass composition: from TY33 with 0.5 mol.% I to NH23-2 with 2.5 mol.% I. The spectrum for C35 is also added as this sample highlights the role of Ca^{2+} cations in the surrounding of I^- species. *Fig. 4A* represents the k^2-weighted data. *Fig. 4B* represents the amplitude of the radial distribution function (RDF) as obtained from the Fourier transforms of the oscillatory k^2-weighted EXAFS signal in the k-space. As a compromise between short and long distance, we chose to use the k^2 oscillatory signal of the $\chi(k)$ function. In the k-space, the signal to noise ratio (S/N) of the oscillatory signal is changing between each sample. It appears that there is an increase in the S/N with increasing I content. For instance, the NH23-2 with 2.5 mol.% I has a good S/N whereas TY33 with 0.5 mol.% the S/N is relatively poor. Owing to the data quality and in order to keep for each sample analysis the same range in the k-space spectra, the region used for the Fourier Transform of the EXAFS spectra is set between 2.5 and 6.7 $Å^{-1}$. This limit at 6.7 $Å^{-1}$ corresponds to the higher point usable for the data with the poor quality.

In *Fig.4B,* the amplitude signal shows an intense peak with a maximum around 2.5 Å. This peak corresponds to the I first neighbour atoms. Surprisingly, the peak maximum is at higher position for C35: 2.82 Å, suggesting a longer distance to first neighbour. In addition, for C35 we observe a prominent peak located close to 1.5 Å that we explain by the possible existence of I^{5+}. This I^{5+} could be due to an evolution of the sample under the high energy of the X-ray beam during XAS acquisition. It appears consistent with the suggested result of the XANES fit but not with the XPS result that has a lower energy flux. In order to minimize the possible artefacts in the signal for this peak in the fitting procedure, we applied a background filter in the R space between 0 and 1.5 Å. The RDF peaks below 2.5 Å do not correspond to any contribution from backscattering shells. In our case, the perturbations from the Ca excitation in the glass (~500 eV below the I L_3-edge) can be considered weak compare to the noise due to the amorphous structure of the glass that decreases the EXAFS signal quickly after the threshold. The peak for TY33 is very weak and strongly overlapped with satellite scattering signal. As inferred earlier, the low S/N in the k-space will affect the definition of the I nearest neighbour in the R-space. Regardless of the glass chemical composition and I content, it appears that the peak maximum, which does not correspond to the actual distance between I atoms and its surrounding, are roughly identical to within <0.1 Å in radial distance. For instance, in borosilicate glasses NH23-1 (1.9 mol.% I) has a peak maximum at 2.42 Å whereas the ISG22-2 (1.2 mol.% I) has a peak maximum at 2.40 Å. The boron-free TY33 has a peak maximum at 2.45 Å comparable to the one observed for borosilicate glasses NH and ISG.

Hence, the distance between I and its surrounding for ISG, NH and TY would change between 2.8 and 3.0 Å; and is possibly higher for C35. The estimated distance for ISG, NH and TY is lower than the distance observed in iodide crystalline compounds: $r_{Na\text{-}I}$ = 3.24 Å [51] and $r_{Ca\text{-}I}$ = 3.12 Å [54]; however consistent with the distance reported in *McKeown et al.*

393 [11] of 3.04 Å in Na-bearing borosilicate glasses synthesised at ambient pressure. This
394 distance was attributed to I atoms surrounded by several Na atoms [10,11]. The estimated
395 distance to the nearest neighbour also seems consistent with the XANES simulation results
396 (*Fig. 3*) suggesting Ca and Na as the nearest neighbour to iodide species.

397 The objective in the treatment of the EXAFS spectra is to obtain an estimate on the
398 parameters for the first coordination sphere around I atoms: the average distance and the
399 coordination number to I atoms to the nearest neighbour. It should be emphasised that the
400 reported spectrum simulations and associated results represent only one possible solution. The
401 I EXAFS simulations were conducted in the radial distance range between ~1.5 and ~3.5 Å
402 (see *Fig. 5*). We could not investigate the signal to longer distance for several reasons: 1) the
403 EXAFS S/N ratio did not allow it as shown in *Fig. 4A* and 2) the proximity of the L_2-edge line
404 (~4850 eV) prevents from acquiring a long EXAFS signal. In order to obtain further
405 information about I second or third neighbours, we would require a longer k-space acquisition
406 than actually acquired. Due to the extremely low signal, we did not attempt to simulate the
407 EXAFS spectra for TY glass samples but only on ISG, NH and C35 glass spectra. To conduct
408 the simulations, we used standard crystalline structures taken from Crystallographic Open
409 Database ([55] and references therein): NaI and CaI_2. These structures were chosen in
410 agreement with the XPS results and XANES simulations that suggest the presence of mostly
411 iodide species dissolved in the glass structure. The presence of I_2 and CaI_2O_6 was not
412 considered in the simulation owing to the low abundances observed by XPS (see *Table 1*). For
413 the particular case of C35, we only used the scattering path from CaI_2 considering that the
414 glass composition is Na-free.

415 Prior to the simulation, the EXAFS spectra were calibrated for the scattering amplitude and
416 corrected for the edge position [56]. We simulated the spectrum obtained on CaI_2 with the
417 CaI_2 crystalline model. We obtained $S_0^2 = 0.984$ and $\Delta E_0 = -7.73$ eV. We took the single

418 scattering paths of each structure as given by the FEFF calculations in Artemis. For NaI, the
419 path Na to I has Coordination Number (CN_{Na-I}) = 6, r_{Na-I} = 3.236 Å; for CaI_2, CN_{Ca-I} = 3, r_{Ca-I}
420 = 3.117 Å. As *McKeown et al.* [11] derived an average CN_{Na-I} in their studied glasses close to
421 4, we choose a CN_{Na-I} = 4 and CN_{Ca-I} = 2 as starting guess prior to the simulations. The
422 simulations are conducted in several steps: 1) the optimization of the distance to the first
423 neighbour (r_{X-I}) is conducted with fixed initial coordination numbers (CN_{X-I}) and Debye-
424 Waller attenuation factor (σ^2); 2) the optimization of the σ^2 is conducted at fixed CN_{X-I} and r_{X-I}; 3) the optimization of the CN_{X-I} is conducted at fixed σ^2 and r_{X-I}. Each category of
426 parameter (r, σ^2 or CN) is optimized for the whole set of scattering paths in the same time. We
427 repeated the procedure several times until obtaining the best possible fit of the radial distance
428 signal. We did not place any restraints on the parameter values to solve the EXAFS equation.

429 **4. Discussion**

430 *4.1 Local environment of iodine in aluminoborosilicate glasses*

431 EXAFS simulations are shown in *Fig. 5* for NH23-2, ISG22-2 and C35. We present for each
432 sample the fit of the RDF total amplitude (*Fig. 5A*) and the imaginary part (*Fig. 5B*). The fitting
433 results (CN_{X-I}, r_{X-I} and σ^2_{X-I}) are given in *Table 1* and *Supplementary Material 2*.

434 The results obtained on the nearest neighbour distance to I are comparable to the previous
435 results from *McKeown et al.* [11]. For the iodide species (Ca-I and Na-I) and in the case of Na
436 and Ca-bearing glasses (NH, ISG and TY), we obtain distances changing from 2.76 to 3.01 Å.
437 On average the distance between I^- and Ca^{2+} is shorter than the distance to Na^+, which can be
438 explained by the higher cationic charge of calcium for an equivalent ionic radius (1.20 and
439 1.24 Å for Na^+ and Ca^{2+}, respectively; [57]). We observe that the derived r_{X-I} are
440 systematically lower than the one reported in *McKeown et al.* [11] (i.e. 3.04 Å). One reason for
441 these lower I to first neighbour distances could be due to the intensive conditions (i.e. high-

pressure) at which our glasses were held considering that high-pressure conditions are known to influence the local environment of cations [31-33]. On the other hand, as suggested, the derived r_{Ca-I} in the case of C35 is larger (3.60 Å) than the one derived for ISG and NH glasses. This aspect is currently unexplained; however, it should be pointed out that the C35 glass composition is significantly different from the ISG and NH glass compositions. It has more B_2O_3 (~30 mol.%) and less SiO_2 (~30 mol.%) as compared to ISG and NH that could therefore greatly influence the glass structure. Furthermore, it is currently well-accepted that the distribution of network modifying cations within the glass structure is strongly affected by the nature of those cations in the so-called mixed alkali or alkaline-earth effect [58-61]. In the case of Na and Ca-mixed silicate glass compositions (for instance similar to ISG, NH and TY), it has been shown that there is a strong intermixing between Ca^{2+} and Na^{+} cations; in other words the oxygen negative charge compensation is preferably accomplished by both cations rather than only one sort of cation. As such, C35 represents a very peculiar glass composition that cannot be readily compared to ISG and NH ones. Nevertheless, it has the advantage to show that it is possible to find local environment of I^{-} species surrounded by Ca^{2+} as a charge compensation cation.

We have reported the change in the derived r_{X-I} as a function of I content in *Fig. 6A*. The point representative of C35 glass is not reported considering that this glass composition is not similar to the NH and ISG ones. From *Fig. 6A*, we do not observe a clear pattern as a function of I content, however, it seems that the highest r_{X-I} are observed for the highest I content. For instance, in ISG glasses there is a slight increase in both Ca-I and Na-I bond lengths. We also observe that the r_{X-I} bond distances are systematically higher for NH glass than for ISG glass. It suggests that the I local environment is probably a function of the glass bulk composition. Typically, the difference observed in r_{Ca-I} (>0.1 Å) might be explained by the change in Ca content: 5.7 and 8.0 mol.% CaO in ISG and NH, respectively. This would also be consistent

467 with the higher r_{Ca-I} (3.60 Å, see *Table 1*) observed for C35 having 32.5 mol.% CaO.
468 Although, r_{Na-I} seems less affected (<0.1 Å) for a larger variation in Na_2O content: 12.6 and
469 24.2 mol.% Na_2O in ISG and NH, respectively. Considering the small number of investigated
470 compositions and samples, further work is currently requested to investigate the possible
471 change of r_{X-I} as a function of both I content and glass bulk composition.

472 In a similar manner, we have plotted the change in the CN_{X-I} values derived for iodide as a
473 function of I content in *Fig. 6B*. The normalised CN_{X-I} derived from the fit of the EXAFS
474 signal provided in *Table 1*. For Ca, the CN changes from 1.5 to 2.2. For Na, the CN changes
475 from 2.3 to 4.2. The derived CN_{Na-I} of 2.3±0.2 is anomalously low and is obtained for ISG31
476 glass sample having a low I content (0.8 mol.%) and synthesised at the lowest pressure (0.5
477 GPa). As shown in *Fig. 6B*, we do not observe any correlation between the derived CN and the
478 I content. The CN_{Ca-I} exhibits the lowest variation in coordination number. The average CN_{Na-I}
479 and CN_{Ca-I} (not including the C35 value of 1.5) are 3.6±0.6 and 2.0±0.1, respectively. The
480 higher CN_{Na-I} is consistent with the lower positive charges of Na as compared to Ca to
481 compensate the negative charges of the iodide.

482 The obtained CN values cover the lower end range reported in *McKeown et al.* [11] (*Fig. 7*). We
483 plotted the obtained normalised CN_{X-I} values as a function of the obtained r_{X-I} values for
484 iodide species in *Fig. 7*. We also reported the experimental data points from *McKeown et al.*
485 [11] for comparison. We observe that our I-bearing glasses synthesised under high-pressure
486 conditions have comparable r_{X-I} bond length as the one reported in *McKeown et al.* [11]. The
487 derived CN_{X-I} have a narrower range as compared to the values reported in *McKeown et al.*
488 [11]. The possible reasons for lower CN_{X-I} values could be: 1) the intensive pressure
489 conditions are responsible for the lower derived CN_{X-I}; 2) the higher dissolved I content
490 induces a lower global charge compensation in the surrounding of I^- species.

We applied bond valence theory using the bond valence parameters reported in *Brese and O'Keeffe* [62]. We used the following equation that relates the I valence (v_{X-I}) to the bond length (d_{X-I}):

$$v_{X-I} = exp\left(\frac{R_{X-I}-d_{X-I}}{b}\right) \qquad \text{Eq. 2}$$

Where X is the cation (i.e. Na^+ or Ca^{2+}), r_{X-I} is the bond valence parameter: 2.56 and 2.72 for Na^+ and Ca^{2+}, respectively; b is a constant 0.37. The valence v_{X-I} is related to the CN with the following relation v = z/CN, where z is the cation charge. Using the average CN derived from EXAFS simulation (i.e. 3.6 and 2.0 for Na and Ca); we obtain d_{X-I} of 3.03 and 2.72 Å for Na-I and Ca-I bond length, respectively. These values are in good agreement with the obtained values in *Table 1* from EXAFS. The calculated d_{X-I} value for Ca-I bond appear lower than the one derived from EXAFS (2.85±0.09 Å on average for Ca-I). Bond valence theory calculates a bond length without considering possible surrounding perturbation, however, Na^+ and Ca^{2+} cations do not only share their positive charges to I^- anions but also to oxygen atoms from the silicate and borate networks within the glass [63]. Thus, due to the perturbation brought by surrounding oxygen atoms, the measured distance to I^- by EXAFS is expected to be different from the one calculated with the bond valence theory.

4.2 Iodine dissolution mechanism during a high-pressure experiment under oxidizing conditions

In the present work, we have shown that I is mostly dissolved as iodide species (I^-). This behaviour was expected and is consistent with previous studies on the I dissolution mechanisms in borosilicate glasses [9-11,13] and the chemical reaction for I dissolution represented by Eq. 1 in which an I_2 molecule from the fluid phase interacts with Na atoms in the melt phase to form both NaI and $NaIO_3$ in the melt. Based on the XANES and EXAFS

results, we propose an additional reaction involving the Ca as a possible nearest neighbour for I^- such as:

$$6I_2^{fl} + 6CaO^m \rightarrow 5CaI_2^m + CaI_2O_6^m \qquad \text{Eq. 3}$$

However, these two chemical reactions suffer from the fact that iodates are not observed in our glasses or at extremely low concentrations; lower than the 1/5 ratio in Eq. 1 and 3. In the absence of I^{5+} dissolved as iodate or the absence of cation capable of changing its oxidation state (e.g. Fe changing from Fe^{2+} to Fe^{3+}, [10]), there is an excess of negative charges due to the reduction of I_2^{fl} into I^-. One possible solution is to invoke an exchange between I and oxygen from the melt with oxygen released in the fluid phase during the experiments such as:

$$I_2^{fl} + O^{2-,m} \rightarrow 2I^{-,m} + O_2^{fl} \qquad \text{Eq. 4}$$

Unfortunately, we have no way to test this hypothesis, besides we were not able to measure the O_2^{fl} concentration at the capsule opening after the experiments. The nature of oxygen that can be involved in this reaction is still to be determined [19,64-67]. At first level of knowledge, the obvious candidate is to use Non-Bridging Oxygen (NBO) in the melt structure, however, it could be NBOs from the silicate network or from the borate network [19,65]. *Jolivet et al.* [15] suggested that the I dissolution is accompanied by a change in the distribution of boron species (i.e. BO_3 and BO_4). Based on the Raman spectroscopic results, they also showed that the silicate network appears unaffected by the I dissolution. In that case, we expect an interplay between I atoms and the borate network with an increase in the BO_3 species and decrease in BO_4. If it is currently observed for ISG glass samples, it is the opposite of NH glass samples: BO_4 increases with increasing I content and BO_3 decreases. In any case, further experimental work is currently required using ^{17}O NMR to determine the nature of the oxygen involved in the dissolution mechanisms of iodine as I^- species.

5. Conclusion

In the subsequent work, we have investigated the local environment of I atoms dissolved in glasses of various compositions synthesised under high-pressure conditions. To do so, we used two complementary spectroscopic methods: XPS and I L_3-edge XAS. The studied glasses are from three different compositions fully detailed in *Jolivet et al.* [15]. The range of I investigated is 0.5 to 2.5 mol.%.

With the XPS, we show unambiguously that I is mostly dissolved as iodide (I^-) species. However, we could also observe small proportions of other species such I_2 and CaI_2O_6. Such a speciation is also confirmed with the modelling of the I L_3-edge XANES using simple spectrum linear combination. In addition, it also infers that Na^+ is not the only nearest neighbour of I atoms and we propose that Ca^{2+} cations are also acting as a charge balancing cations to the negative charges on I^-.

The simulation of the EXAFS spectra suggests that on average I^- anions has a bond length of 2.98 to 2.85 Å to the nearest neighbour, either Na^+ or Ca^{2+}. This range of values is consistent with previous investigations. We derived a coordination number to Na of 3.6 and to Ca of 2.0.

The main outcome of those results is that Ca is able, like Na, to dissolve I in its surrounding. This new observation is likely due to the high pressure conditions used for synthesising the I^- bearing borosilicate glasses. Although the question of I-bearing glass matrix is to be determined, we show that solubilizing I in glass matrix at high pressure is a promising protocol to immobilize radioactive ^{129}I in nuclear waste glasses.

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744

745 **Figure caption**

746 Figure 1: XPS spectra in the I $3d_{5/2}$ energy region obtained on I-bearing glasses of ISG and
747 NH compositions from *Jolivet et al.* [15] along with XPS spectra for crystalline compounds:
748 NaI, $NaIO_3$ and CaI_2O_6. The peak at ~619 eV is attributed to I^- species and the peak at ~624
749 eV is attributed to I^{5+} species.

750 Figure 2: I L_3-edge XANES spectra for I-bearing glasses (ISG, NH, TY and C35) and solid
751 crystalline compounds (I_2, NaI, CaI_2, $NaIO_3$ and CaI_2O_6) in the 4540-4600 eV region. The
752 strong feature at 4563 eV corresponds to the white line and is visible on almost all spectra
753 except I_2 that exhibits relatively featureless spectrum. There are two broad peaks located at
754 ~4574 and 4590 eV are assigned to transitions in the 5d levels and 2p to d, respectively.

755 Figure 3: Linear Combination Fitting of the I L_3-edge XANES spectra for I-bearing glasses
756 (A, TY33; B, ISG22-2; C, NH23-2; and D, C35) with spectra from crystalline compounds.
757 The residual from the fit is also shown. The derived proportion of each component is reported
758 and is a combination of NaI, CaI_2, I_2 and to a lower part CaI_2O_6 (see *Table 1*).

759 Figure 4: Typical I L_3-edge EXAFS spectra for investigated glasses and represented in the k-
760 space (A) and R-space (B). Spectra are stacked with increasing I content from TY33 (0.5
761 mol.%) to NH23-2 (2.5 mol.%). In addition, spectrum from C35 (1.6 mol.%) is also reported.
762 The strong peak at ~2.5 Å corresponds to the actual EXAFS signal for the nearest neighbour
763 of the I atoms.

764 Figure 5: Examples of I L_3-edge EXAFS simulation of the RDF for NH23-2 (A), ISG22-2 (B)
765 and C35 (C). The simulation of the imaginary part of the EXAFS signal is also shown. The
766 simulation are conducted in the 1.5 to 3.5 Å region to derive the CN_{X-I} and r_{X-I}. We used
767 single scattering paths from crystalline structure: NaI and CaI_2, in agreement with the

768 observed components from XANES simulations. The EXAFS fitting results are reported in
769 *Table 1*.

770 Figure 6: Change in the derived r_{X-I} in Å (A) and CN_{X-I} (B) from EXAFS simulations as a
771 function of I content in mol.%. The data are reported for Ca-I and Na-I and for ISG and NH
772 glass compositions. The error bars on each point is determined from the EXAFS fitting
773 results.

774 Figure 7: Change in the I CN as a function of r_{X-I} in Å. Data are obtained from EXAFS
775 simulations of the I-bearing studied glasses (ISG and NH) and are compared to the data
776 obtained by *McKeown et al.* [11]. The values for crystalline compounds are also shown.