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31 Abstract

Constraining the systematic evolution of iodine solubility in borosilicate glasses is required
 for the formulation of adequate glass matrices able to immobilize ¹²⁹I representing a major
 troublesome radioisotopes produced by nuclear anthropic activities.

35 We investigated experimentally the change in iodine solubility in a large series of borosilicate

36 glasses synthesized under high-pressure conditions (1.5 GPa) and at 1350°C. The nature of

are network modifying cation (Na, K, Rb, Ca, Ba and Sr) and the concentration of B_2O_3 (~<10

mol.% and $\sim>10$ mol.\%) have been tested. The XPS measurements showed that iodine

39 speciation in glasses is mostly represented by iodide (I^{-}) for a range of iodine solubility from

40 0.3 to 3.1 mol.% as determined by SEM EDS and LA-ICP-MS analyses.

The iodine solubility is enhanced in glasses with lower B₂O₃ content and with a higher
concentration in network modifying cation. Regardless of the cation nature: alkali or alkalineearth; increasing the cation size appears to induce a decrease in iodine solubility.

44 We used the optical basicity (Λ_{Glass}) and iono-covalent parameter (ICP_{Glass}) to express the large variety of investigated glass compositions; both relating to the electron donor capability 45 of the glass. We show that iodine solubility is positively correlated to Λ_{Glass} and accordingly 46 47 negatively correlated to ICP_{Glass}. It implies that more iodine will be dissolved in glass compositions having a stronger electron donating capability. Evidence of the relationship 48 between iodine solubility and oxygen network is shown by the iodine solubility positive trend 49 with equilibrium constant of the oxygen speciation. Future work should take these parameters 50 into consideration for modeling iodine solubility in borosilicate glasses providing additional 51 information are collected such as the boron, aluminum and silicon speciation in glasses. 52

53 Keywords: iodine solubility, optical basicity, high-pressure, nuclear waste

54

In the many radioactive elements produced by anthropic nuclear sources, iodine (I) is one 56 important volatile element representing a serious problem in the effort for the immobilization 57 of radioactive wastes [1–5]. One particular isotope (¹²⁹I) requires a special attention because 58 of 1) its long half-life (>15 Ma) and 2) its high mobility and volatility in environment [3, 6, 59 7]. Currently, several academic studies aim at developing durable conditioning matrices for 60 this radioisotope but no ideal industrial solution has emerged for immobilizing it in a 61 permanent and safe manner [8–17]. Although alternative surrogates have been recently 62 suggested with phosphate glasses [18, 19], the immobilization of radioactive elements is often 63 achieved in aluminoborosilicate glasses synthesized at ambient pressure, high-temperature 64 and representing a good compromise that 1) will contain high concentration in radioactive 65 elements to reduce the disposal space; 2) will be stable through time; 3) will not be damaged 66 by radiation and heating; 4) will present high chemical durability [20–24]. However, owing to 67 the high iodine volatility this protocol cannot retain efficiently ¹²⁹I radioisotopes that will 68 escape from the melt to the atmosphere. Previous works [25–27] showed that the iodine 69 solubility does not exceed 0.7 mol.% I in that case. 70

Recent investigations [28–30] demonstrate that the use of high-pressure synthesizing protocol 71 of aluminoborosilicate glasses can circumvent this lack of iodine dissolution. For instance, 72 Jolivet et al.[30] reached iodine solubility of 1.3 and 2.5 mol.% I in International Simple 73 Glass (ISG, [31]) and typical Low Activity Waste glass (LAW, [32]) synthesized at 1.5 GPa, 74 respectively. More recently, Morizet et al. [33] showed that the iodine solubility could be 75 further increased by using highly oxidizing conditions promoting the formation of iodate 76 species (I^{5+}) within the glass structure. Regardless, the strong increase in the iodine solubility 77 is ascribed to the increase in thermodynamic activity of the fluidic iodine in equilibrium with 78 the melt phase upon pressure [30, 34, 35]. Although, this represents a major breakthrough in 79

the race for immobilizing efficiently iodine radioisotopes, we still lack a clear fundamental
understanding on how iodine behave as a function of glass composition. At given intensive
conditions, the systematic evolution of iodine solubility as a function of glass composition is
currently poorly known.

Up to now, subsequent experimental investigations showed that iodine is sensitive to 1) the 84 presence of alkali cations in the glass [25-27, 36] and 2) the presence of boron (B₂O₃, [28-85 30]). For simplified aluminoborosilicate glass compositions, McKeown et al. [27] and more 86 recently Morizet et al. [37] demonstrate that iodine dissolved as I⁻ is surrounded preferentially 87 by Na⁺ cations for charge compensation, however, it appears that Ca²⁺ can also play this role 88 but to a lower extent. The formulation of a reliable nuclear waste glass matrix extends well-89 beyond the case of Na and Ca. For example, the SON68 glass composition used in France for 90 immobilizing High Activity nuclear waste is composed of more than 25 different oxides [38]. 91 The role of each element in glasses is fairly apprehended: either network former, or charge 92 compensating cation for network species with excess negative charges (e.g. AlO₄⁻), or 93 network modifying cations. The latter category regroups number of element ranging from 94 alkalis (Na⁺, K⁺, Li⁺, Rb⁺), alkaline-earth (Ca²⁺, Mg²⁺, Ba²⁺, Sr²⁺), rare-earth elements (La³⁺, 95 Yb^{3+}), Bi^{3+} and others. These are supposed to be the elements that are mobilized for charge 96 97 compensating the I⁻ species as the charge compensating cation is tightly associated with the network species having excess negative charges and there is no exchange between oxygen and 98 iodine atoms in network units [37]. As mentioned earlier the effect of Na⁺ and Ca²⁺ on iodine 99 solubility is fairly understood; however, for the other elements we have virtually no 100 information. 101

As a result, there is a need for additional experimental investigations aiming at determining systematically the change in iodine solubility as a function of glass composition in order to propose the most adequate aluminoborosilicate glass formulation that can serve as a matrix

for the immobilization of ¹²⁹I radioisotopes. In the present work, we have investigated the 105 106 change in iodine solubility as a function of glass composition involving different alkalis or alkaline-earth elements. Syntheses were done under high-pressure conditions with a I2 fluid 107 phase as a source of iodine; and, as expected, iodine speciation is represented by iodide 108 species (I⁻). The results are interpreted in terms of electrochemical parameters (optical basicity 109 and iono-covalent parameter) that traduce the glass composition. We propose a discussion and 110 111 some recommendations for future work to model iodine solubility and formulate an adequate aluminoborosilicate glass matrix for the immobilization of ¹²⁹I. 112

113

- 114 2. Experimental methods
- 115 2.1. Starting materials

Three series of aluminoborosilicate glass compositions were investigated in the present work. 116 We cover a wide range of compositions having a common basis: SiO₂-Al₂O₃-B₂O₃; completed 117 by various elements acting as network modifying or charge balancing cations: Na₂O, K₂O, 118 Rb₂O, CaO, BaO and SrO. The first series consists in several glasses with a single network 119 modifying cation either Na, K or Rb for alkalis or Ca, Ba, Sr for alkaline-earth elements. 120 Within this group series, we prepared two different compositions: one with higher B₂O₃ 121 content (B₂O₃ >10 mol.%) than the other (B₂O₃ <10 mol.%). The glass composition for this 122 series with single network modifying cation is shown in the Table 1 for volatile-free glass 123 124 synthesized at ambient pressure. The second glass series is composed of several Na-rich aluminoborosilicate glasses investigated in Jolivet et al. [39]: BASN3, BASN4, LJ4b (Al-125 free) and LJ8. Two additional compositions have been prepared, Na20Ca15B10Bi0-vf and 126 Na30Ca10B10Bi0-vf, with the purpose of having an Iono-Covalent Parameter [40, 41] close 127 to 1.00 and 0.96, respectively. These compositions have a mixture of CaO and Na₂O for the 128

network modifying or charge balancing cations. The third glass series corresponds to the first
one in which a small amount of Bi₂O₃ (up to 4 mol.%) has been added.

The sample notation is the following: Ca20B20Bi0 that stands for the I-bearing pure Ca 131 132 composition with higher B2O3 content and without Bi2O3; Ca30B10Bi3 stands for the Ibearing pure Ca composition with lower B₂O₃ content and with Bi₂O₃. The numbers in the 133 sample name correspond to the targeted mol.% for each oxide. It should be noted that I-free 134 glass synthesized at ambient pressure are reported in Table 1 and that the extension -vf is 135 added to the sample name for simplicity; on the other hand, the I-bearing glass synthesized 136 under high-pressure conditions are given in Table 2. For glass compositions from Jolivet et al. 137 [39]: BASN3, BASN4, LJ4b (Al-free) and LJ8; we added the extension -vf and -I for I-free 138 and I-bearing glasses in Table 1 and 2, respectively. Although, a potential industrial process is 139 proscribed at pressure conditions of 1.5 GPa, this investigation has multiple objectives in the 140 fundamental understanding of iodine behavior in aluminoborosilicate glass: 1) determine if 141 iodine has higher affinity for one cation or another, 2) determine if the ratio between network 142 143 modifier and network former cations impacts on the iodine solubility and 3) determine the influence of heavy Bi₂O₃ on iodine solubility. 144

The investigated glass compositions were prepared from a mixture of oxides (SiO₂, B₂O₃, Al₂O₃ and CaO) and carbonates (Na₂CO₃, Rb₂CO₃, BaCO₃ and SrCO₃). We used spec pure oxide and carbonate powders that were mixed under ethanol in an agate mortar. Prior to highpressure experiments, the I-free starting material powders were melted at 1200°C in a Pt crucible. After 1h melting, the starting material is quenched to a glass by dropping the Pt crucible in a cold-water bath. Only one melting has been conducted in order to reduce the possible loss of alkali or boron oxides.

We loaded the sample powder into 2.9 mm outer diameter Pt capsule. The iodine was loaded as solid I₂ at the bottom of the capsule prior to add the glass powder. We prepared a mixture with 0.01 g of I₂ and 0.04 g of glass powder that corresponds to ~10 mol.% I in the starting
composition. The Pt capsule is then welded shut using arc-welder at both ends. Our current
knowledge [30] indicates that the amount of loaded I₂ is sufficient to insure oversaturation
and I₂ should be in excess in the fluid phase during the experiments. For the Bi-bearing
sample series, the Bi-free glass powder was mixed with a small amount of Bi₂O₃ to reach 3 to
4 mol.% Bi₂O₃ in the collected I- Bi-bearing glass after the experiment.

160 2.2. High-pressure syntheses

The high-pressure I-bearing glasses were synthesized using end-load type piston-cylinder 161 162 apparatus (LPG Nantes). We used the same pressure and temperature conditions for all the experiments: 1.5 GPa, 1350°C and for run duration of three hours insuring equilibrium to be 163 reached and comparison between the experimental results. The experiments were done using 164 ³/₄ inch talc-Pyrex assemblies and straight walls graphite furnace. Capsules are placed inside 165 Magnorite[©] ceramics preventing from a contact to the graphite furnace. Owing to the small 166 167 capsule diameter, two capsules are placed in the middle of the assembly; hence, both capsules are experiencing the same intensive conditions (e.g. Na30Ca10B10Bi0 along with 168 Na20Ca15B10Bi0). The protocol to reach final pressure and temperature conditions is 169 described in previous works (e.g. [30, 42]): 1) increase in pressure to 1 GPa, 2) increase in 170 temperature to ~550°C for high-pressure assembly relaxation and compaction, 3) increase in 171 pressure to 1.5 GPa, and 4) increase in temperature to 1350°C. During the experiment, the 172 pressure is controlled automatically by a Stigma[©] needle pump; temperature is controlled by 173 a Eurotherm. The latter is accurate to ±1°C that is connected to a type B thermocouple (PtRh₆-174 PtRh₃₀). Due to internal frictions, we applied a 10% correction to the pressure. Experiments 175 176 are stopped by cutting-off the power. The quench rate from 1350°C to room temperature is $\sim 100^{\circ}$ C/s in the first 500°C. The quench is performed isobarically to prevent the formation of 177 bubbles that could distribute throughout the resulting glass. 178

The recovered samples consist in a colored (i.e. pink to brown) glass entirely coated with dark 179 180 coating that appears to be iodine residue. This residue implies that iodine in the fluid phase was distributed throughout the experimental charge and it implies also that iodine was loaded 181 in excess prior to the experiment. We removed the excess iodine by dripping the glass pieces 182 into ethanol and then placing in a drying oven for a few minutes. Microscopic observation did 183 not reveal the presence of unwanted crystalline phases. It should be pointed out that several 184 experiments were replicated (e.g. Rb20B20Bi0-r is a replicate experiment of Rb20B20Bi0; 185 see Table 2) for insuring that measured I content is consistent, fully replicable, and not stained 186 by analytical bias. 187

188 2.3. Scanning Electron Microscopy with Energy Dispersive Spectrometer

We used Scanning Electron Microscopy with Energy Dispersive Spectrometer (SEM EDS) to
characterize the recovered glasses for major element and iodine concentrations. Glass chips
were mounted into epoxy resin plugs and subsequent polishing was done to 1 µm.

Measurements were conducted on a JEOL JSM 5800LV SEM (IMN Jean Rouxel), equipped with a SDD SAMx dispersive spectrometer. The analytical conditions were 15 kV for voltage and 0.5 nA for current. We conducted the acquisitions on a 20 µm spot size to avoid alkali (K, Na and Rb) loss under the electron beam. Five scans of 1 min were collected on each sample at different location on the glass chip.

197 We used the following internal standards for quantifying the elements: corundum for Al₂O₃,

198 wollastonite for SiO₂ and CaO, NaCl for Na₂O, BaF₂ for BaO, SrF₂ for SrO, KCl for K₂O,

199 RbI for Rb₂O and I, Bi metal for Bi₂O₃. We did not measure the B₂O₃ present in the

200 borosilicate glasses as it is not reliably quantified using SEM EDS due to the low boron

201 molecular mass. Based on the replicated measurements, we obtain an uncertainty on major

element measurements that is better than 5% in relative to the value and comparable to the

error reported in previous works on the same analytical equipment [30, 39]. For the particular

case of iodine, the typical error bar based on replicated measurement is $\pm 0.2 \text{ mol.\%}$. Data in mol.% are provided in Table 1 for I-free glasses and in Table 2 for I-bearing glasses along with the error that is calculated from the standard deviation of the replicated measurements. The reported error pictures the homogeneity in the element distribution; however, we observed slight heterogeneity in the major element concentrations for Ba30B10Bi0-vf exhibiting larger error bars than for the other glasses.

210 2.4. Laser Ablation Inductively Coupled Plasma Mass Spectrometry

The B2O3 and I contents is determined using a Laser Ablation-Inductively Coupled Plasma-211 212 Mass Spectrometry (LA-ICP-MS, LPG Nantes). The spectrometer is an ArF excimer laser (193 nm, Analyte G2, Photon Machines) that is coupled to a quadrupole ICP-MS (Varian 213 Bruker 820-MS). The ablation is performed in a HelEx II 2-Volume Cell with He as carrier 214 gas. We used a laser energy density of 4.54 J.cm⁻² and with a repetition rate of 10 Hz. We 215 performed the acquisition in a spot mode with a diameter of 110 µm. We performed five 216 217 acquisitions on each I-bearing glass sample in static mode (i.e. point by point) on a glass polished surface from the bulk and embedded into epoxy plug. The acquisition time was set to 218 30 s, preceded and followed by a 30 s blank acquisition. The washout time of the ablation cell 219 was approximately 50 s., due to the long residence time of iodine in the system. We estimated 220 the pit size to $\sim 20 \ \mu m$ in depth that represents a large analyzed sample volume in comparison 221 to SEM EDS analyses. Only the LA-ICP-MS signal obtained slightly below the ablation 222 surface was considered for the quantification of iodine so as to avoid possible alteration in the 223 iodine content that could be generated from sample preparation[43]. 224

225 LA-ICP-MS acquisition for I content is designed to corroborate the I results obtained by SEM

EDS. The data is calibrated against several glass samples. We recorded the ¹²⁷I and ²⁷Al

isotopes and this latter one was used as an internal standard. We calibrated the I content with

two high-pressure ISG glasses [31] doped with I (1.29 and 1.34 mol.% I) and with known

Al₂O₃ content of 4.08 and 4.02 mol.%, respectively. For these two samples, I and Al₂O₃ 229 230 contents have been determined using Electron Probe Micro-Analyses (EPMA, ISTO Orléans) based on 400 points. We used the same protocol to quantify the B2O3 in glasses using LA-231 ICP-MS. For calibrating the B₂O₃ content in our glasses, we used the aluminoborosilicate 232 glasses investigated by Jolivet et al. [39] that have been characterized using multiple 233 techniques (SEM EDS, ¹¹B MAS NMR and ICP Optical Emission Spectrometry) for the 234 quantification of B₂O₃. In particular, we used the LJ3, LJ4 and NH glasses from Jolivet et al. 235 [39] having 34.9, 30.7 and 15.1 mol.% B₂O₃, respectively. The present calibration for I and 236 B₂O₃ could not be used for I-bearing LJ4b glass sample as this glass does not contain Al₂O₃ 237 238 currently used as the internal standard. For this sample, we considered the I content determined by SEM EDS and the B₂O₃ reported in Jolivet et al. [39]. We performed three 239 analytical sessions on distinct glass chips for the Ca-bearing glass samples (Ca20B20Bi0 and 240 Ca30B10Bi0) to check for consistency. 241

242 2.5. X-ray Photoelectron Spectroscopy

243 X-ray Photoelectron Spectroscopy (XPS) measurements were performed on each glass sample to determine the I and the O signatures in our glasses. XPS spectra for crystalline standards 244 were not acquired considering that peak assignment has been previously reported for similar 245 I-bearing glasses[33, 37, 44]. We carried out the XPS analyses on a Kratos Nova spectrometer 246 (IMN Jean Rouxel) using a monochromatic Al Ka radiation operating at 1486.6 eV (15 kV, 247 20 mA). We analyzed glass chips (several mm²) corresponding to a surface fracture from the 248 bulk of the experimental charge. The surfaces were not prepared and the analyses were 249 conducted on raw glass surfaces, hence avoiding possible surface contamination. The glass 250 chips were loaded into the sample chamber under high-vacuum conditions ($<10^{-8}$ mbar). The 251 spot size on the sample is $300x700 \ \mu\text{m}^2$ area of analyses. We recorded survey spectra at a pass 252 energy of 160 eV corresponding to an overall instrument resolution measured on silver Fermi 253

edge of 1.95 eV and a step of 0.5 eV from -5 to 1200 eV. High-resolution spectra of I 3d, O 254 255 1s, and 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 40 eV. We acquired the final 256 257 spectrum with a cycling mode (several scan of the sample) for each element and we did not observe any modification of each individual acquisition that would suggest an alteration of the 258 glass under the X-ray beam. We calibrated the XPS spectra using the adventitious C 1s in the 259 260 binding energy at 284.8 eV. All spectra were treated with CasaXPS© software. We focused on the I 3d_{5/2} peak in the I 3d region, which exhibits the highest intensity as compared to the 261 one for the I 3d_{3/2}. The spectra were fitted with a U2 Tougaard function for the background 262 263 [45]. Subsequent simulations are achieved with a pseudo-Voigt function with a Lorentzian ratio of 50% for the various peaks. The determination of the I species is accurate to within 264 10% of the derived value. 265

266

267 3. Results

268 3.1.Iodine speciation from XPS

For an adequate comparison, the samples have to exert the same or similar iodine speciation.
Iodine exhibits several redox degree ranging from -1 to +7. During the high-pressure
experiments, no constraints were placed on the redox conditions and the talc-Pyrex assembly
fixes the *f*O₂ intrinsically. It has been previously estimated that talc-Pyrex assembly imposes *f*O₂ conditions relatively oxidizing at +1 log unit above the solid buffer QFM (QFM+1,
Quartz-Fayalite-Magnetite, [46]). Even though the redox conditions are relatively oxidizing,
we have previously shown that under those conditions iodine is mostly dissolved under its

reduced iodide form: $I^{-}[30, 33]$.

The XPS results in the I 3d region is shown in Figure 1. For clarity, we show the spectra 277 278 obtained on the glasses with alkali and high B₂O₃ (Figure 1A) and with alkaline-earth and low B₂O₃ (Figure 1B) cations; the entire set of spectra is available in the Suppl. Mat.. In addition, 279 the XPS spectra in the O 1s region (~532 eV) for the whole set of glasses were acquired. For 280 clarity, the O 1s XPS are only provided in the Suppl. Mat.. The O 1s located at ~532 eV and 281 is approximately symmetric. For the O 1s spectra, the peak maximum position has been 282 determined as a function of glass composition. In Figure 1, we choose to represent only the I 283 3d_{5/2} region that represents the most intense iodine peak. The peak located at 619 eV 284 corresponds to the signature of iodide (I^{-}) species as identified in previous works [33, 37, 44, 285 47, 48]. For several samples (see Suppl. Mat.), we have observed a slight asymmetry on the 286 high-energy side (~621 eV) that could correspond to the presence of I^0 species [49]. 287 Currently, I⁰ has also been identified in previous studies for glasses [37, 44] and could 288 289 correspond to micrometric bubbles of solid I2 or effectively dissolved I2 species within the glass. This aspect is not clarified yet. For K20B20Bi0, we observed an additional peak located 290 at ~624 eV that we assigned to the presence of a slight amount of iodate species (1^{5+} , [33]). It 291 is also observed for several additional samples: Na30B10Bi0, K30B10Bi0, BASN4-I, 292 Na30Ca10B10Bi0 and Na20Ca15B10Bi0; and does not exceed 10% in relative to the iodine 293 species. Nevertheless, the existence of the most oxidized iodine species is systematically 294 observed in the most iodine rich samples. For instance, for K30B10Bi0 in which 1.9 mol.% I 295 is measured by LA-ICP-MS, the proportion of I⁵⁺ is 9.9% whereas in Rb20B20Bi0 in which 296 0.3 mol.% I is measured, the I^{5+} is absent. However, the proportion of I^{5+} is low enough for 297 samples to be compared to each other and in the present work; iodine is mostly dissolved as I⁻ 298 species. The derived XI⁻ is reported along to the spectra and is determined from the spectrum 299 simulation (values are provided in Table 1). As mentioned, this result is consistent with 300

previous work [33, 37] that suggested the following dissolution mechanism for iodine in
aluminoborosilicate glasses:

303
$$\frac{n}{2}I_2^{melt/fluid} + M^{n+}...O_n^{-NBO} \leftrightarrow M^{n+}...I_n^{-} + \frac{n}{2}O_2^{fluid/melt} + \frac{n}{2}O^{BO}$$
 Eq. 1

In Eq. 1, the Mⁿ⁺, O^{NBO} and O^{BO} stand for a charge compensating cation (e.g. alkali or
alkaline-earth cations), a Non-Bridging Oxygen and a Bridging Oxygen from the glass
structure, respectively. Interestingly, the chemical reaction implies that there is, at some point,
an interaction between I₂ molecules in the fluid phase and the oxygen atoms of the melt.
Moreover, the Eq. 1 also suggests that there is a transfer of negative charge from the oxygen
to the iodine to form iodide species. The Eq. 1 points to the fact iodine dissolution is
accompanied by an increase in the degree of polymerization as inferred in recent work [36].

311

312 3.2.Effect of network modifying cations on iodine solubility

The iodine solubility data obtained by LA-ICP-MS and SEM EDS are provided in Table 1. 313 Both acquisitions compare adequately suggesting that acquired iodine solubility data are 314 robust. As mentioned earlier, the error (in bracket) represents the homogeneity of the iodine 315 distribution within the sample (i.e. standard deviation obtained on multiple analyses).. For 316 SEM EDS measurements, the analytical error is on the order of ± 0.2 mol.% similar to the 317 error reported in Jolivet et al. [30]. The analytical error associated with LA-ICP-MS is 318 suspected to be lower ($\pm 0.1 \text{ mol.}\%$) and more representative of the glass iodine content. The 319 320 volume analyzed by LA-ICP-MS spot is larger (spot of 110 µm in diameter by 20 µm in depth) than the surface analyzed by SEM EDS (~20 μ m²). For the remaining of the 321 manuscript, we will preferentially consider the data obtained by LA-ICP-MS unless those are 322 not available. 323

The change in iodine solubility as a function of the network modifying cation is represented in 324 Figure 2, for glass compositions with B₂O₃>10 mol.% and with B₂O₃<10 mol.%. In Figure 2, 325 the glass compositions have been categorized in term of increasing cation charge (alkali 326 before alkaline-earth) and increasing cation size (Na⁺ \rightarrow K⁺ \rightarrow Rb⁺ and Ca²⁺ \rightarrow Sr²⁺ \rightarrow Ba²⁺). 327 At B₂O₃<10 mol.%, we observe that iodine solubility seems to be higher in alkali-bearing 328 glasses than in alkaline-earth bearing glasses. In detail, the iodine solubility is higher for Na-329 bearing glass than for Ca- and Sr-bearing glasses. We observe that iodine solubility for K- Ca-330 and Sr-bearing glasses are roughly the same. Previous investigations [27, 30, 33] suggested 331 that iodine dissolved as I⁻ species has a better affinity towards alkali atoms rather than 332 alkaline-earth atoms. Our results are consistent with that statement at least for Na-bearing 333 glass in comparison to alkaline-earth ones. However, at $B_2O_3>10$ mol.%, the evolution of the 334 iodine solubility depending on the network modifying cation nature is much more complex. 335 There is a clear decrease in the iodine solubility with increasing cation size within each 336 category: alkali, I solubility decreases from Na to Rb; alkaline-earth, I solubility decreases 337 from Ca to Ba. We observe a non-monotonic change in iodine solubility with a jump in iodine 338 solubility between Rb and Ca glass compositions. Unexpectedly, the iodine solubility appears 339 higher in alkaline-earth bearing glasses than in alkali-bearing glasses at B₂O₃ concentration 340 above 10 mol.%. 341

342 4. Discussion

343 4.1. Electrochemical parameters for aluminoborosilicate glass compositions and the344 relationship to oxygen activity

In the present study, the range of investigated glass compositions is relatively large: different boron contents, different network modifying cations, and mixing between network modifying cations; therefore explaining the change in the iodine solubility requires expressing the studied glass compositions with chemically relevant bulk parameters. To do so, we have

focused our approach on the pioneer work by Duffy [50, 51] that defined an oxide glass by its 349 350 optical basicity (Λ). The optical basicity takes its origin into the Lewis acidity concept. The optical basicity also relates to the Jørgensen's nephelauxetic parametrization that corresponds 351 to the electron donation to cations and the resulting degree of charge reduction experienced by 352 these ions [52, 53]. The optical basicity has been applied for describing many properties such 353 as the refractive index, the UV transparency, the redox behavior of glass melts, and the 354 355 viscosity dependence with temperature [54]. In the present work, we have calculated the glass optical basicity (Λ_{Glass}) according to the equation of Duffy [50]: 356

357
$$\Lambda_{Glass} = \sum \frac{X_i}{\gamma_i} = \sum X_i \times \Lambda_i$$
 Eq. 3

In which X_i represents the molar fraction of the oxide i and γ_i corresponds to the basicity 358 moderating parameters of the oxides. For the investigated glasses, we used the γ_i or Λ_i (1/ γ_i) 359 for SiO₂, Al₂O₃, B₂O₃, CaO, SrO, BaO, Na₂O, K₂O, Rb₂O and Bi₂O₃ reported in previous 360 works (e.g. compilation of γ_i values in Rodriguez et al. [55]). The calculated A_{Glass} is reported 361 362 in Table 1 for volatile-free glasses and in Table 2 for I-bearing glasses. It should be pointed out that the calculated Λ_{Glass} represents a theoretical value as the true optical basicity value 363 (Λ_n) can only be obtained via the glass refractive index (n) measurement [56–58]. Because of 364 the small glass sample size, we could not measure the optical refractive index. 365

The second glass bulk parameter considered here has been defined by Portier et al. [40, 41] and corresponds to the Iono-Covalent Parameter (ICP). The ICP is related to the acidic strength and takes into account the ionic-covalent character of a bond. In other words, the ICP takes into account the ionic forces (polarizing power) and the covalent forces (electronegativity). This aspect is particularly designed for glasses having both covalent and ionic characters. Furthermore, providing that iodine is dissolved as I⁻ species it has a ionic character and I⁻ is surrounded by network modifying cation (Na⁺ or Ca²⁺, [37]), it is likely that a relationship between ICP and iodine solubility exists. The ICP_i parameter for each oxide is
calculated with the following equation from Portier et al. [40, 41]:

375
$$ICP_i = log\left(\frac{z_i}{r_i^2}\right) - 0.6\chi_{i(a-r)} + 1.21$$
 Eq. 3

Where z_i/r_i^2 corresponds to the polarizing power of cation i and $\chi_{i(a-r)}$ is the cation electronegativity as defined by Allred and Rochow [59]. The ICP for the glass is then determined as follow:

379
$$ICP_{Glass} = \sum X_i ICP_i$$
 Eq. 4

Where X_i is the molar fraction of the cation in the glass composition. The values for ICP_{Glass}
are provided in Table 1 and Table 2. The calculation of AGlass and ICPGlass are provided in
Suppl. Mat..

The data points are shown in Figure 3 and the ICP_{Glass} is reported as a function of Λ_{Glass} only 383 for the volatile-free glasses obtained at ambient pressure. In the present calculations, several 384 aspects related to structural information are not taken into account in the calculation of Λ_{Glass} . 385 Recent works [53, 60] indicate that the theoretical optical basicity values will be better 386 387 approached if we take into account 1) the distribution of BO₄ and BO₃ within the glass (i.e. N₄ and N₃ values, [20, 39, 61, 62]), 2) the distribution of silicate network Qⁿ species [63–66], and 388 the distribution in the aluminum species (i.e. 4-, 5- and 6-coordinated species, [67–69]. In the 389 390 present work, we do not have access to this information, as it would involve advanced NMR acquisition. Furthermore, our glass samples are prepared under high-pressure conditions and 391 the effect of this intensive parameter on the optical basicity and iono-covalent parameter 392 393 defined by Duffy [50] and Portier et al. [40, 41] is currently not constrained but should exist. For instance, Kuryaeva [70] shows that increasing pressure induces an increase in the glass 394 refractive index. The increase in the refractive index increases the oxide ion polarizability [56, 395

57, 71] and hence changes the optical basicity value [51, 57, 71]. In the Suppl. Mat. we
provide the same figure as Figure 3 but completed with the I-bearing data provided in Table 2.
The reason for which we do not include those points in the actual Figure 3 is because the
effect of pressure and iodine on the ICP_{Glass} and A_{Glass} is currently unknown.

Nevertheless, in Figure 3, we clearly see that there is a negative correlation between ICP_{Glass} 400 and Λ_{Glass} . This relationship is expected and has been shown in previous works [72, 73]: Λ is 401 402 the numerical expression of the average electron donor power of the oxide species and ICP 403 represents the influence of ionic-covalent bonding in an oxide on the acid strength of the cations. Furthermore, Reddy et al. [74] demonstrated that Λ correlates linearly with the 404 405 average electronegativity. Hence, both parameters (ICP_{Glass} and Λ_{Glass}) are correlated to each other; however, the method to calculate each parameter is different. Λ is strongly dependent 406 on the cation polarizing power: in ionic solids (i.e. cations have weak polarizing power), the 407 charges are focused on each ion and the oxygen will be able to give an important partial 408 negative charge to a new cation; in solids with important covalent character in the chemical 409 410 bonds, the negative charge will be shared by the cation and the anion and the oxygen will 411 have a weak electron-donating power. In the present dataset, the extremes of the trend define two different glass behaviours: one more acidic at lower Λ_{Glass} and higher ICP_{Glass}, one more 412 413 basic at higher Λ_{Glass} and lower ICP_{Glass}. The latter case implies higher electronegativity global value and a higher electron donation capacity from the oxygen atoms. From Figure 3, 414 the two investigated parameters can be used to express the bulk chemical properties of the 415 glasses. In the investigated glasses, the alkaline-earth-bearing glasses have the highest ICP_{Glass} 416 417 values and the lowest Λ_{Glass} . On the contrary, the alkali-bearing glasses have the lowest 418 ICP_{Glass} and the highest Λ_{Glass} . For glasses with a mixture of CaO and Na₂O, the ICP_{Glass} and the Λ_{Glass} values are located in the region of the alkali-bearing data point, which could be 419 explained by the higher concentration of Na₂O in comparison to CaO (see Table 1). 420

In the present work the glass optical basicity can only be accessed through calculation; 421 422 however, it has been shown that Λ_{Glass} is negatively correlated to the change in O 1s peak maximum measured by XPS considering that the Λ_{Glass} represents the measure of the valence 423 charge density surrounding the oxygen ion in the network [56, 75, 76]. The change in the 424 Λ_{Glass} for volatile-free glasses as a function of the O 1s peak maximum is shown in Figure 4. 425 The same figure is proposed in the Suppl. Mat. and includes the data for I-bearing glasses. 426 427 The correlation observed in Figure 4 witnesses that the optical basicity relates intimately to the oxygen activity within the glass [77]. It also shows that the positioning of the optical 428 basicity numerical value is correct from one glass composition compared to another even 429 430 though the glass structure is only partially known.

4.2. I solubility prediction using glass optical basicity and iono-covalent parameter 431 The prime objective of this work is to investigate the change of iodine solubility as a function 432 of glass composition that can be expressed by different bulk chemical parameters. We show 433 434 the change in iodine solubility (in mol.% I) as a function of Λ_{Glass} and ICP_{Glass} in Figure 5A and 5B, respectively. In Figure 5, we added the data points from Jolivet et al. [30] acquired at 435 identical pressure (1.5 GPa) and for two different glass compositions: ISG and NH. The 436 recent I solubility data points from Morizet et al. [33] are also added. These data were 437 obtained on Ca- and Na-bearing aluminoborosilicate glasses synthesized at pressure 438 conditions of 1.5 GPa. 439

The data from Jolivet et al. [30] and most of the data from Morizet et al. [33] compare adequately with our data in Figure 5. One data point ($\Lambda_{Glass} = 0.747$ and 3.9 mol.% I) from Morizet et al. [33] seems to be off the general trend. Actually, one possible explanation is the presence of a substantial quantity of I⁵⁺ in this glass sample that has not been accounted for and would explain the high I solubility for instance for their C0N35 at 3.9 mol.% I. Although, there is a significant scatter in the data, which we believe, is resulting from an inadequate

approximation in the Λ_{Glass} and ICP_{Glass} as mentioned earlier; we observe a reasonable 446 correlation between iodine solubility and Λ_{Glass} and ICP_{Glass}. There is a positive correlation of 447 iodine solubility with increasing Λ_{Glass} and a negative correlation with ICP_{Glass}, which is 448 consistent with the observed correlation between Λ_{Glass} and ICP_{Glass} shown in Figure 3. 449 The results shown in Figure 5 suggest that iodine solubility in aluminoborosilicate glasses can 450 be derived providing the optical basicity or the iono-covalent parameter are known, however, 451 a better accuracy is requested in the calculation of these compositional parameters. As 452 mentioned earlier, knowledge on the distribution of boron species (i.e. N₄ and N₃) is required 453 for calculating a more accurate value for Λ_{Glass} . In Figure 5A, the NH23-1 from Jolivet et al. 454 [26] has been fully characterized in Jolivet et al. [26] that report a N₄ value at 0.45 with iodine 455 content at 1.9 mol.%. The iodine speciation for this sample is provided in Morizet et al. [33] 456 and is 100% I⁻. With the current simple calculation for the glass optical basicity: all B₂O₃ is in 457 trigonal boron unit (BO₃) configuration and considering $\gamma_{BO3} = 2.47$ [78]; we obtain a 458 $\Lambda_{\text{Glass}}(\text{NH23-1}) = 0.730$. Taking into account the distribution of B₂O₃ as 55% BO₃ and 45% 459 460 BO₄ (N₄ = 0.45 reported in Jolivet et al. [26]) and γ_{BO4} = 4.17 [60], we calculate a $\Lambda_{\text{Glass}}(\text{NH23-1}) = 0.707$. Such a change represents a variation of ~2% in relative to the value. 461 We report the difference in Λ_{Glass} (NH23-1) in Figure 5A. Unfortunately, it appears impossible 462 463 to apply systematically this Λ_{Glass} variation to all the data points as the change in N₄ value is a complex function of the glass composition and the optical basicity variation in the studied 464 glasses is not necessarily identical to the one calculated for NH23-1. 465 Previous works [26] suggest that N₄ value is likely to influence the iodine solubility. 466 Currently, the model from Lu et al. [79] determines the N₄ for a large range of glass 467 composition; however, this model is not designed to be applied for high-pressure glasses. 468 There is a gap in our understanding of the effect of pressure on the distribution of boron 469 species in glasses. Previous investigations [80-82] demonstrate that increasing pressure 470

provokes an increase in the N₄ value. Nevertheless, Jolivet et al. [26] showed that the change
in N₄ value upon pressure increase is probably dependent on the glass composition.
Furthermore, it is not clear if the iodine dissolution itself have or not an effect on the N₄
value.

In a similar manner, the distribution in the silicate network units (i.e. Q^n species where n represents the number of bridging oxygen) should be determined for calculating an accurate Λ_{Glass} as suggested by Dimitrov et al. [60]. From another viewpoint, the distribution of Q^n species describes the degree of polymerization of the glass, namely, the connectivity between silicate network units. The higher the SiO₂, higher is the degree of polymerization and silicate network units have higher connectivity.

In the present work, the use of bismuth oxide could appear odd, however, we justify the addition of Bi₂O₃ to the studied glass compositions by two aspects: 1) Bi₂O₃ is often used in nuclear waste glasses for its good radiation shielding ability and 2) with its low γ value, Bi₂O₃ could be a good oxide candidate that increases the A_{Glass} and hence we expect an increase in I solubility with the addition of Bi₂O₃. These two aspects are further discussed below.

First of all, bismuth (present as Bi³⁺) is recognized to present good shielding capacity to 486 irradiation [83], hence representing a pertinent oxide to add in the borosilicate glass matrix for 487 the immobilization of nuclear waste. Moreover, recent works demonstrate that bismuth is 488 gaining great interest in glass technology, in particular in optics and photonic (e.g. [84–87]). 489 490 As mentioned earlier, the role of bismuth in glasses is similar to the one of alkali (or alkalineearth) elements. It acts as a network modifying cation inducing a depolymerization of the 491 glass structure and high concentration of NBOs in the surrounding of Bi³⁺ ions. It is 492 recognized that these two aspects have a positive effect on the higher dissolution of iodine[30, 493 33, 36]. In Figure 5A, adding a small quantity of Bi₂O₃ seems to induce an increase in the I 494 solubility for alkali-bearing glasses. For alkaline-earth-bearing glasses, we observe that 495

adding Bi₂O₃ to Ca-bearing glasses has an opposite effect and I solubility is decreasing. This
aspect is currently not explained and needs further investigations.

498 Second of all, in term of optical basicity, Bi₂O₃ has a low moderating parameter ($\gamma_{Bi2O3} =$

499 0.84; [84]) that induces an increase in Λ_{Glass} and an increase in iodine solubility is expected.

500 Hence, the small addition of element having low moderating parameters such as Cs_2O with

501 $\gamma_{Cs2O} = 0.60$ [51] would be beneficial for dissolving higher concentration of iodine in glasses.

502 This aspect remains to be confirmed. For instance, the Rb-bearing glass composition

503 (Rb20B20Bi0-vf) for which Rb₂O has a low moderating parameter ($\gamma_{Rb2O} = 0.67$, [53]), on the

504 contrary, does not exhibit a high iodine concentration: 0.3 mol.% I in Rb20B20Bi0. Further

505 experimental work is currently required to address in more details the change in iodine

solubility in presence of heavy elements such as bismuth.

507 4.3. Iodine solubility and dissolution mechanism and its relationship to the glass degree of
508 polymerization

It has been shown that a borosilicate melt could be described by a speciation model made of several equilibrium reactions. In particular, several types of oxygen species coexist within the melt with the following equilibrium reaction to describe it [77, 88–90]:

512
$$20^{-NBO} \stackrel{K_{Oxygen}}{\longleftrightarrow} 0^{0BO} + 0^{2-free}$$
 Eq. 5

513 Where O^{- NBO} represents the Non-Bridging Oxygen, O^{0 BO} represents the Bridging Oxygen 514 and O^{2- free} is a free oxygen species that could be linked to available cations such as alkalis, 515 alkaline-earth cations or bismuth. In other words, Eq. 5 represents the degree of 516 polymerization of the melt as seen from the anionic oxygen species viewpoint. From Eq. 5, 517 the equilibrium constant can be written as follow:

518
$$K_{Oxygen} = \frac{a_{OoBO}^{Melt} \times a_{O2-free}^{Melt}}{\left(a_{O-NBO}^{Melt}\right)^2}$$
Eq. 6

519 Where a_i^{Melt} corresponds to the thermodynamic activity of the i species in the melt; that is 520 related to the actual concentration of the i species from standard thermodynamic relationship 521 such $a_i^{j} = X_i^{j}\Gamma_i^{j}$; where X_i^{j} and Γ_i^{j} are the molar fraction and the activity coefficient of the i 522 species, respectively. Since we do not have access to a measure of the actual molar fraction of 523 the different oxygen species, the Koxygen cannot be solved directly; nevertheless, Moretti [77] 524 mentioned that the Koxygen is related to the optical basicity by the following equation:

525
$$K_{Oxygen} = \exp[4.662 \times (\sum X_M^{m+} \gamma_M^{m+} - \sum X_T^{t+} \gamma_T^{t+}) - 1.1445]$$
 Eq. 7

In Eq. 7, the K_{Oxygen} is a function of the molar fraction (X_i) and the optical moderating parameter (γ_i). The K_{Oxygen} is calculated with the difference between the network forming (T^{t+}) and the network modifying cations (M^{m+}). Although Moretti [77] used this approach to silicate melts and glasses, we believe that the same can apply to the present study for aluminoborosilicate glasses.

In the present work, the network forming cations are Si^{4+} , Al^{3+} and B^{3+} whereas the network 531 modifying cations are Na⁺, K⁺, Rb⁺, Ca²⁺, Sr²⁺, Ba²⁺ and Bi³⁺. The calculated values for 532 K_{Oxygen} are provided in Table 2 and we plotted the change in iodine solubility in mol.% as a 533 function of the Koxygen value in Figure 6. For the whole investigated series, there is a clear 534 increase in the mol.% I with the increase in the Koxygen value. Three series (the mixed alkali 535 536 and alkaline-earth, the alkali without Bi₂O₃ and the alkali with Bi₂O₃) have been fitted with an exponential growth function as a guide for the reader. The Koxygen values for the alkaline-earth 537 series did not allow to fit reasonably the data. 538

539 Considering that the K_{Oxygen} is calculated regardless of the iodine content, the observed

540 increase in Figure 6 is related to the distribution of oxygen species concentrations. In the

541 present work we have shown that iodine is dissolved as I^{-} species and from previous works

542 [30, 33] it has been shown that the dissolution mechanism follows the Eq. 1 chemical reaction

in which I⁻ is charge compensated by alkali or alkaline-earth cations. From the results in
Figure 6, we suggest that iodine dissolution could be related to the presence of free oxygen
within the glass structure (and by extension to the presence of network modifying cations).
According to the proposed model, the more free oxygen is present the more iodine can be
dissolved as I⁻. Hence, the iodine dissolution reaction proposed with Eq. 1 could also be
rewritten by considering the presence of free oxygen such as:

549
$$I_2^{fluid} + O^{2-free} ... \frac{2}{m} M^{m+free} \to 2I^- ... \frac{2}{m} M^{m+} + \frac{1}{2} O_2^{fluid}$$
 Eq. 8

In Eq. 8, the formation of iodide is promoted by the fact that iodine thermodynamic activity in 550 the fluid phase is high owing to the excess iodine loaded during the experiment. Regardless of 551 the glass compositional effect, the iodine solubility is proportional to the iodine fugacity 552 imposed by the experimental pressure and temperature conditions: $[I^-] \propto f_{I_2}^{fluid}$. On the 553 contrary at ambient pressure the iodine fugacity is close to 1 and the iodine solubility is low 554 [25, 27, 36]. At high optical basicity (i.e. high Koxygen value), the high free oxygen 555 concentration facilitates the formation of iodate species (IO₃⁻), which means that free oxygen 556 species are not entirely exsolved in the fluid phase. 557

558 In the mechanism proposed in Eq. 8, there is no apparent change in the degree of

polymerization of the glass, however, because free oxygen is exsolved in the fluid phase upon

iodine dissolution, there should be a re-equilibration in the distribution of NBO and BO

561 concentrations. This contrasts with the recent proposition by Morizet et al. [33] in which the

562 involved oxygen species in the iodine dissolution are NBOs that are transformed into BOs

inducing an increase in the degree of polymerization of the glass. Currently, in the absence of

- strong advanced NMR investigations (i.e. ¹⁷O NMR) we can only propose reasonable
- 565 hypotheses for type of oxygen species involved in the dissolution of iodine. Nevertheless, the

iodine dissolution has necessarily an impact on the glass structure with a change in thedistribution of oxygen species.

568

569 5. Summary

In the present work, we have synthesized a large series of aluminoborosilicate glasses under 570 high-pressure conditions (1.5 GPa) in equilibrium with a iodine fluid phase. With the different 571 572 syntheses, we have tested 1) the effect of various network modifying cation (Na, K, Rb, Ca, Sr and Ba), 2) the effect of boron concentration with either <10 mol.% or >10 mol.% B₂O₃ 573 574 and 3) the effect of the addition of a small quantity of Bi₂O₃ (~4 mol.%). We have shown that there is a complex change in iodine solubility with the nature of glass 575 576 containing cations but also dependent on the B₂O₃ concentration: at high B₂O₃, iodine solubility increases with the following suite of cation: Rb < Ba = K < Na < Ca; at low B₂O₃, 577 iodine solubility increases with the following suite of cation: Ba < Sr < Ca = K < Na. 578 579 Increasing the B₂O₃ concentration in the glass (i.e. decreasing the network modifying cation 580 concentration) does not favor the iodine dissolution and solubility decreases. Apart for Cabearing glasses, the addition of Bi₂O₃ induces an increase in iodine solubility that we ascribe 581 to the structural role of Bi atoms comparable to the network modifying cation. 582

We have shown that iodine solubility is correlated positively with the optical basicity (Λ_{Glass}) and negatively correlated to the Iono-Covalent Parameter (ICP_{Glass}). This is consistent with the fact that Λ_{Glass} reflects the electron donor capacity of oxygen and that there is a transfer of negative charge to dissolve iodine as I⁻ species. As a result, both ICP_{Glass} and Λ_{Glass} could serve as predicting parameters for formulating a glass matrix able to immobilize a large quantity of ¹²⁹I. The most adequate glass composition should exhibit a high optical basicity; however, there is a compromise to find as increasing the glass optical basicity would reducethe glass chemical durability.

591

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864 Figure caption

Figure 1: I 3d XPS spectra obtained on I-bearing glasses for the alkali-bearing glass

compositions with $B_2O_3 > 10 \text{ mol.}\%$ (A): Na20B20Bi0, K20B20Bi0 and Rb20B20Bi0; and

alkaline-earth-bearing glass compositions with $B_2O_3 < 10 \text{ mol.}\%$ (B): Ca30B10Bi0,

868 Sr30B10Bi0 and Ba30B10Bi0. The spectra are shown in the I 3d_{5/2} region for clarity. The

determined iodine speciation is reported next to each spectrum. The entire set of spectra is

available in the Suppl. Mat..

Figure 2: Change in the iodine solubility (in mol.%) as a function of glass composition

expressed by the cation nature (alkali and alkaline-earth) and cation size (Na⁺ \rightarrow K⁺ \rightarrow Rb⁺

and $Ca^{2+} \rightarrow Sr^{2+} \rightarrow Ba^{2+}$). The data points for the two investigated glass series are shown:

874 $B_2O_3 < 10 \text{ mol.}\%$ and $B_2O_3 > 10 \text{ mol.}\%$.

Figure 3: Change in Iono-Covalent Parameter (ICP_{Glass}) as a function of optical basicity

 (Λ_{Glass}) for iodine-free glasses reported in Table 1. The ICP_{Glass} values are calculated

following the description of Portier et al. [40, 41], the Λ_{Glass} is calculated following the

description of Duffy [50]. There is a negative correlation between ICP_{Glass} and Λ_{Glass} that is

related to the overall electronic configuration of the glass composition.

Figure 4: Change in O 1s peak position as determined from the XPS spectra as a function of Λ_{Glass} for iodine-free glasses reported in Table 1. The negative correlation observed is consistent with the nature of the Λ_{Glass} that corresponds to the electron donor capacity of oxygen atoms within the glass. An error of ± 0.1 eV is considered for the peak position and corresponds to the actual analytical error.

Figure 5: Iodine solubility (in mol.%) as a function of Λ_{Glass} (A) and ICP_{Glass} (B). The iodine 885 solubility is positively correlated and negatively correlated to A_{Glass} and ICP_{Glass}, respectively. 886 High Λ_{Glass} values represent a higher basic glass media able to share electrons from oxygen 887 atoms and high ICP_{Glass} values represent a glass media with electronegative charges. These 888 aspects are favoring the iodine dissolution as I⁻ species. I solubility data points from Jolivet et 889 al. [30] and Morizet et al. [33] have also been added. We calculated the Λ_{Glass} for NH23-1 890 from Jolivet et al. [30] using $N_4 = 0$ and $N_4 = 0.45$ so as to show the impact of N₄ value on the 891 892 Λ_{Glass} .

Figure 6: Change in iodine solubility as a function of K_{Oxygen} for the different studied glass series. The K_{Oxygen} has been calculated with the equation of Moretti [77] that relates the K_{Oxygen} to the element moderating parameters (γ_i). The increase in K_{Oxygen} denotes the increase in the free oxygen concentration according to Eq. 6. Several glass series: alkali with and without Bi₂O₃ and mixed alkali – alkaline-earth cation; have been fitted with an exponential function of the form $y = y_0 + A x \exp(x / t)$; however, these trends remain hypothetical.













