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30

31 **Abstract**

32 There is a major environmental concern in finding a sustainable solution to immobilize the
33 ^{129}I , a by-product of nuclear industry. The use of aluminoborosilicate glasses represents a
34 good compromise. However, this solution does not appear adequate for ^{129}I owing to its
35 volatility at high-temperature during the vitrification process. In the present work, we use a
36 high-pressure (1.5 GPa) apparatus to synthesize I-rich aluminoborosilicate glasses.

37 We show that the use of high-pressure conditions enhances the I solubility in glasses by
38 several orders of magnitude as compared to 1 bar synthesis: I solubility up to 5.7 mol.%. We
39 observed that I is more solubilized in Na-rich as compared to Ca-rich glass. Investigation of
40 the I speciation using XPS also reveals that I solubility in glasses is much higher as I
41 dissolves as I^{5+} in comparison to I^- .

42 Our work shows that using high-pressure appears to be a reliable solution for dissolving a
43 large quantity of I within the structure of aluminoborosilicate glasses for the conditioning of
44 nuclear waste. We also demonstrate that oxidized I waste form should be employed to greatly
45 increase I solubility in nuclear waste glasses. Therefore, it represents a potential pathway for
46 solving the immobilization of ^{129}I produced by anthropic nuclear activity.

47 Keywords: nuclear waste, ^{129}I radioisotope immobilization, intensive conditions, densified
48 glass

49

50 **1. Introduction**

51 The radioisotope ^{129}I is a by-product of nuclear reactors and is considered as an intermediate
52 activity nuclear waste owing to its radiotoxicity, its long half-life (15.7 My) and its high
53 mobility in the environment.¹⁻¹⁴ For these reasons, the disposal in geological repository of ^{129}I

54 requires a chemically stable and durable matrix. There has been a great deal of effort in
55 formulating matrixes able to accommodate a large quantity of iodine (I) in their structure;¹⁵⁻²²
56 which are stable through time and under natural environmental conditions (i.e. ground water
57 circulation). In the list of potential matrixes, the use of borosilicate glasses is a general
58 adopted solution for nuclear waste immobilization;²³⁻²⁹ however, it cannot be applied to
59 immobilize I. The standard process to synthesize borosilicate glasses involves melting at high-
60 temperature and ambient pressure. Owing to its high volatility, the borosilicate glass matrix
61 does not retain I sufficiently during the high-temperature process and I escapes in the
62 atmosphere as I₂ gas. Previous studies reported an iodine solubility up to 0.7 mol.% in
63 aluminoborosilicate glasses synthesized at or near ambient pressure.³⁰⁻³³ More recently, there
64 have been several experimental studies conducted under high-pressure conditions and
65 investigating I solubility in glasses with different applications: either Earth sciences^{34,35} or
66 nuclear sciences.³⁶ Under high-pressure conditions, the I solubility is enhanced in
67 aluminoborosilicate glasses. For instance, Jolivet et al.^{36,37} studied the I solubility in the
68 International Simple Glass (ISG)³⁸ and typical Low Activity Waste glass (LAW)^{32,33}
69 synthesized in the pressure range 0.5-2.0 GPa and temperature above 1300°C. They reached a
70 I solubility up to 2.5 mol.% in the typical LAW glass; thus demonstrating that the use of
71 pressure represents a potential adequate solution for immobilizing large quantities of ¹²⁹I in
72 aluminoborosilicate glass matrixes, therefore reducing the volume of nuclear wastes at
73 geological disposal.

74 Nonetheless, we have a limited knowledge of the solubility I behavior in aluminoborosilicate
75 glasses because of the lack of available experimental data. The most recent experimental
76 investigations showed that boron content and alkali content play an important role on I
77 solubility: increasing the boron and alkali and alkaline-earth contents induce an increase in I
78 solubility.^{36,39,40} However, the effect that other cations in the glass composition induces on I

79 solubility is unknown in detail. By analogy, in the case of CO₂, it has been demonstrated that
80 CO₂ solubility in silicate glasses is affected by the nature of the charge compensating
81 cation.^{41,42} Whether I adopts a comparable behavior in aluminoborosilicate glasses is still
82 unknown. Furthermore, the effect of mixed alkaline or alkaline-earth elements on I solubility
83 (i.e. dissolution mechanism) is currently not deciphered. This aspect is crucial to determine
84 because the mixed alkaline or alkaline-earth effect (MAE) is known to affect the glass
85 properties in a complex non-linear behavior.⁴³⁻⁴⁹

86 Iodine has the particularity to present several redox states: -1 (I⁻, iodide), +5 (I⁵⁺ as IO₃⁻, in
87 iodate) and +7 (I⁷⁺ as IO₄⁻, in periodate). Up to now, previous works only studied the I
88 solubility in aluminoborosilicate glasses when I is thought to be dissolved under its reduced
89 form: I⁻ species. Hence, the effect oxidation conditions induce on I solubility in
90 aluminoborosilicate glasses are unknown. This gap in our understanding of I behavior needs
91 to be fulfilled considering that redox conditions are known to dramatically influence the
92 volatile solubility. For example, sulfur (S) is a volatile element implied in magmatic systems,
93 which exhibits several oxidation states: S²⁻ (sulfide) to S⁶⁺ (sulfate).^{50,51} Experimental data
94 and thermodynamic models showed that S solubility was more important in silicate glasses
95 when S dissolved as S⁶⁺ (i.e. SO₄²⁻) species.⁵²⁻⁵⁴

96 In the present work, we followed an experimental approach to investigate the change in I
97 solubility in aluminoborosilicate glasses synthesized under intensive conditions: 1.5 GPa and
98 1400°C. We focused on glass compositions having various XNa (Na/(Na+Ca)) values to
99 determine if the nature of the charge compensating cation plays a role on I solubility.

100 Moreover, we investigated the influence of I redox state (I⁻, I⁵⁺ and I⁷⁺ redox state) on the I
101 solubility. We used spectroscopic methods to determine the iodine speciation in the
102 synthesized glasses. Based on these results, we proposed an I dissolution mechanism as a
103 function of the observed I speciation in glasses. A discussion on the future direction to

104 formulate a borosilicate glass matrix that is specific for a sustainable immobilization of ^{129}I
105 radioisotopes is also proposed.

106 **2. Materials and methods**

107 **2.1. Starting materials and high-pressure synthesis**

108 The investigated aluminoborosilicate glass compositions are reported in Table 1. The starting
109 materials were prepared in the system $\text{SiO}_2\text{-B}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-CaO-Na}_2\text{O}$ from a mixture of spec
110 pure oxides (SiO_2 , Al_2O_3 , B_2O_3 and CaO) and carbonates (Na_2CO_3). In order to determine the
111 effect of varying network modifying cations on I solubility, we prepared the CN starting
112 compositions with varying XNa ($\text{Na}/\text{Na}+\text{Ca}$) values: C₃₅, XNa = 0; C₃₀, XNa = 0.25; C₂₀,
113 XNa = 0.6; C₁₀, XNa = 0.8; C₀, XNa = 1. It should be pointed out that in the synthesized
114 compositions the exchange between Ca and Na is made based on the oxygen quantity (i.e. x
115 mole CaO is replaced by x mole Na_2O). Hence, the number of mole for Na is twice as much
116 as the Ca mole in the exchange. From the electric charge point of view, the exchange between
117 CaO and Na_2O keeps the positive charges unchanged. Starting powders were carefully
118 grinded in an agate mortar under dry conditions. The adopted methodology involved a two-
119 step synthesis: 1) synthesis of the base glass without iodine at ambient pressure and 2) high-
120 pressure synthesis with iodine using the initial base glass. We prepared the ambient pressure
121 glasses (CN-0 series) by melting and quenching in a platinum crucible the starting powders at
122 1200°C in a box furnace under fully oxidizing conditions for two hours and quenching in cold
123 water. The composition of the recovered clear glasses was determined prior to high-pressure
124 experiments (see Table 1).

125 We used the recovered glass powders made at ambient pressure for the high-pressure
126 experiments. Therefore, at a given composition, a comparison between samples of the
127 different series is possible. Any strong departure from the CN-0 glass composition for high-
128 pressure synthesized glass would indicate a possible heterogeneity or partial crystallization.

129 We synthesized three series of high-pressure I-bearing glasses. The CN-1 glass series is
130 loaded with I₂ as the source of I during the experiments. The CN-2 glass series is loaded with
131 I₂O₅ as the source of I during the experiments. The CN-3 glass series is loaded with I₂O₅ +
132 PtO₂ providing an additional source of O₂ during the experiment. The objective is to
133 determine the impact of different I sources and various oxygen concentrations on the I
134 solubility, speciation, and I dissolution mechanism in aluminoborosilicate glasses. The most
135 prominent difference between the I starting source is the oxygen concentration that is higher
136 in the CN-2 and even higher in CN-3 experimental series in which PtO₂ has been added.
137 During the high-pressure and high-temperature experiments, I₂O₅ dissociates at ~350°C into
138 I₂ and O₂; and in a similar manner, PtO₂ decomposes at 450°C into Pt and O₂.

139 We used welded shut 5.4 mm outer diameter Pt capsules for the high-pressure high-
140 temperature experiments. We loaded the I source (and PtO₂) at the bottom of the capsule and
141 the glass powder added on top of it. As shown in Table 1, we loaded approximately the same
142 amount of I in every experiment: ~13 mol.% I as I₂ or I₂O₅ calculated from the number of
143 mole of added iodine divided by the total number of mole of oxides in the glass. This amount
144 of I is supposed to be above the saturation,³⁶ consequently, during the experiments, there is a
145 coexistence between a melt phase and an excess I-rich fluid phase. Considering that the initial
146 amount of I is constant from one experiment to another, the measured I content in the
147 recovered glass corresponds to the actual I solubility (i.e. the maximum I dissolved in the
148 glass matrix at a given composition and given intensive conditions). The amount of added O₂
149 is reported in Table 1 and is calculated considering the complete dissociation of I₂O₅ and
150 PtO₂. For the CN-2 experiments, the calculated O₂ is ~16 mol.%; for the CN-3 experiments,
151 the calculated O₂ is higher with ~20 mol.% O₂ added coming from the dissociation of both
152 I₂O₅ and PtO₂.

153 The high-pressure experiments have been carried out in end-loaded piston-cylinder apparatus
154 (LPG Nantes). We used $\frac{3}{4}$ inch talc-Pyrex assembly with the Pt capsule placed inside the
155 graphite furnace and surrounded by MgO-based ceramics for preventing contact between the
156 capsule and the graphite furnace. It should be emphasized that oxygen fugacity conditions
157 were not controlled during the experiments but are intrinsically fixed by the high-pressure
158 talc-Pyrex assembly itself and are relatively oxidizing. We achieved the experimental
159 conditions (1.5 GPa and 1400°C) using the protocol described in previous works.⁵⁵ We
160 applied a pressure of 1 GPa followed by heating to 500°C and left for 5 min for high-pressure
161 assembly relaxation. We then increased the pressure up to 1.5 GPa. We added a 10%
162 correction on the pressure owing to the friction in the talc-Pyrex assembly.⁵⁶ At 1.5 GPa, the
163 pressure is controlled automatically by a Stigma© needle pump preventing the pressure
164 variation during the experiment. The temperature was increased automatically up to 1400°C
165 at a rate of 50°C/min. During the experiment, the temperature was controlled by a B-type
166 (PtRh₆-PtRh₃₀) thermocouple located at the top of the capsule and accurate to $\pm 1^\circ\text{C}$. The run
167 duration was set to 4h for all the experiments to be reproducible. We stopped the experiment
168 by cutting-off the power and quench rate is estimated at $\sim 100^\circ\text{C}/\text{sec}$. in the first 500°C. We
169 performed an isobaric quench to avoid the presence of bubbles in the obtained glass. The
170 recovered capsule was weighed for eliminating any possible leakage and I loss during the
171 experiment. The collected sample consists in a glass tainted in brown and covered at the
172 surroundings and along the experimental charge by a dark residue corresponding to the I
173 excess present during the experiments. Under high-pressure and high-temperature conditions,
174 I is in the fluid state but in a solid state at ambient conditions. The I residue is present across
175 the whole length of the sample suggesting that under run conditions I is distributed throughout
176 the melt. This residue was totally removed by washing in ethanol. Optical examination did not
177 reveal the presence of crystalline phases in the glass; however, for one particular sample

178 (C₀N₃₅-2) we suspect the presence of NaI nanocrystals, however, these crystals are not
179 observed during Scanning Electron Microscopy Energy Dispersive Spectroscopy analysis. A
180 dark residue was present at the bottom of the capsule for CN-3 experiments, corresponding to
181 the Pt coming from the dissociation of PtO₂.

182 **2.2. Scanning Electron Microscopy Energy Dispersive Spectroscopy**

183 The major element and iodine concentrations were obtained with a JEOL JSM 5800LV
184 Scanning Electron Microscope, equipped with a SDD SAMx dispersive spectrometer (SEM
185 EDS, IMN Jean Rouxel Nantes). The analytical conditions were 15 kV for voltage and 0.5 nA
186 for current. The current beam was regularly controlled during all analytical campaigns to
187 ensure a reproducible electron flow. We mounted the CN glass chips in epoxy plugs and each
188 plug includes an ISG glass chip considered as a standard glass to our SEM
189 measurements.^{36,38,57} The ISG standard glass was analyzed prior and after the CN glass chips
190 analyses to check for possible instrumental drift. The acquisitions were conducted on a 20 μm
191 spot size to avoid alkali (Na) loss under the electron beam. We performed 10 scans of 1 min.
192 for each sample as a peak threshold criterion to reduce the minimum acceptable concentration
193 for identification. We used internal standards for the elements quantification: LaB₆ for B₂O₃,
194 corundum for Al₂O₃, wollastonite for SiO₂ and CaO, NaCl for Na₂O, and RbI for I. In most of
195 the case, the B₂O₃ is lower than the expected B₂O₃ (~30 mol.%, see Table 1). With all
196 precautions during SEM EDS analyses, we obtain an uncertainty on element (including
197 iodine) measurements that is typically ±0.2 mol.%.

198 **2.3. Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry**

199 Glass I content was also determined using a Laser Ablation-Inductively Coupled Plasma-
200 Mass Spectrometry (LA-ICP-MS, LPG Nantes) for providing more robust results on the I
201 solubility. The spectrometer is an ArF excimer laser (193 nm, Analyte G2, Photon Machines)

202 that is coupled to a quadrupole ICP-MS (Varian Bruker 820-MS). The ablations were
203 performed in a HelEx II 2-Volume Cell with He as carrier gas. We used a laser energy density
204 of 4.54 J.cm^{-2} and with a repetition rate of 10 Hz. All the analyses were performed in a spot
205 mode with circular spots size of $110 \mu\text{m}$ in diameter. At least five acquisitions were collected
206 on each I-bearing glass sample. Acquisition time was set to 30 s. with points collected every
207 ~ 0.25 s. (total number of point per analysis = ~ 120), preceded and followed by a 30 s. blank
208 acquisition. The washout time of the ablation cell was approximately 50 s., due to the long
209 remanence of iodine in the system. With this analytical setup, the pit size is estimated to ~ 20
210 μm in depth.

211 The data were calibrated against several glass samples. The recorded isotopes were ^{127}I and
212 ^{27}Al and this latter one was used as an internal standard. We calibrated the I content with two
213 high-pressure ISG glasses doped with I (1.29 and 1.34 mol.% I) and with known Al_2O_3
214 content of 4.08 and 4.02 mol.%, respectively. Both I and Al_2O_3 contents have been quantified
215 using Electron Probe Micro-Analyses (EPMA, ISTO Orléans). The good agreement between
216 EPMA and LA-ICP-MS collected data are provided in Suppl. Mat. and indicates that LA-ICP-
217 MS is a reliable technique for the quantification of our elemental concentrations in I-bearing
218 borosilicate glasses.

219 **2.4. X-ray Photoelectron Spectroscopy**

220 We used X-Ray Photoelectron Spectroscopy (XPS) to determine the I speciation in our high-
221 pressure borosilicate glasses. Several crystalline standards (NaI , NaIO_3 and CaI_2O_6) were also
222 analyzed for fingerprinting the I speciation in glasses.

223 We acquired the XPS spectra on Kratos Axis Ultra and Nova spectrometers (IMN Jean
224 Rouxel) equipped with a monochromatic Al $K\alpha$ radiation operating at 1486.6 eV and 300 W.
225 The glass chips ($\sim 3 \times 3 \text{ mm}^2$) showing a surface from the bulk of the experimental charge were

226 loaded into the sample chamber and at high vacuum ($<8 \cdot 10^{-8}$ mbar). The beam size on the
227 sample was $300 \times 700 \mu\text{m}^2$. We acquired the spectra with different pass energy: at 160 eV for
228 the wide spectrum with a step of 0.5 eV and at 20 eV for high-resolution XPS spectra on
229 elements with a step of 0.1 eV. We referenced the spectra against the adventitious C 1s
230 transition at 284.8 eV.^{58,59} We used cycling acquisitions (10 to 15 cycles) to determine if the
231 sample spectra are changing under the X-ray beam. In the case that no change is observed
232 between the cycles, the final spectrum is obtained by averaging the sum of spectra obtained.
233 Currently, this was the case for CN-1 and CN-2 glass series. On the contrary, for CN-3 glass
234 series we observed that after the first cycle the I XPS spectrum was strongly affected by the
235 X-ray beam energy. We also performed XPS acquisitions on several glass chips for a given
236 sample charge to assert the homogeneity of the I speciation.

237 For I species, the high resolution XPS spectra were acquired at the I 3d ~ 620 eV core level.
238 The spectral window was set between 608 and 643 eV to be sufficiently large for background
239 subtraction. The obtained I 3d XPS spectra were treated with CasaXPS© software. We used a
240 Tougaard function for background subtraction.⁶⁰ The I 3d spectra were fitted with asymmetric
241 Gaussian-Lorentzian lines and only the I 3d_{5/2} peak was considered. The I 3d_{5/2} peak exhibits
242 higher intensity than the one for the I 3d_{3/2}.⁶¹

243 **3. Results**

244 **3.1. I content and distribution in glasses from LA-ICP-MS and SEM EDS**

245 Figure 1 shows the I content determined by LA-ICP-MS as a function of the I content
246 obtained by SEM EDS. From the general viewpoint, we observe that both I contents obtained
247 with LA-ICP-MS and SEM EDS provide comparable and consistent results. However, it
248 appears that LA-ICP-MS results are systematically higher than SEM EDS for the samples
249 with the highest I content. As mentioned earlier, the error bar on the I content determined by
250 SEM EDS is on the order of ± 0.2 mol.%. The error bars on the I content determined by LA-

251 ICP-MS determined from the standard deviation of replicated measurements and is within the
252 point except for C₀N₃₅-2 (± 0.6 mol.%).

253 For the remaining of the manuscript, we will preferentially refer to the I content determined
254 by LA-ICP-MS. First, the error on the I content is much smaller from LA-ICP-MS than from
255 SEM EDS. Second, the LA-ICP-MS analyzed glass volume ($\sim 110 \times 20 \mu\text{m}^3$) is much more
256 important than for SEM EDS ($\sim 20 \times 1 \mu\text{m}^3$), therefore, we consider that the reported LA-ICP-
257 MS I content is more representative of the I bulk content. Although, a slight deviation from
258 the true I content in glasses is still possible using LA-ICP-MS results considering that the
259 calibration curve is obtained with two standard glasses with 1.29 and 1.34 mol.% I that is
260 lower than the I content measured in CN glasses (up to 5.7 mol.%). However, the possible
261 deviation will be lower than the one associated with SEM EDS measurements for which RbI
262 (50 mol.% I) is used as a standard.

263 For C₂₀N₁₅-22, we have investigated the I concentration in detail using LA-ICP-MS. I
264 concentration profiles were obtained through the entire Pt capsule length and width (see
265 Figure 2). We acquired several transversal profiles using the laser ablation point mode and 48
266 points were acquired (the entire set of data is provided in Suppl. Mat.). The results are shown
267 in Figure 2 as a contour plot for I. The lines of equal contents have been drawn from linear
268 extrapolation. We observe that the I concentration is almost entirely homogeneous throughout
269 the sample charge. These measurements provide the typical error on the I solubility after high-
270 pressure experiments. For this sample, the I content ranges from 4.5 to 4.8 mol.%. Based on
271 the 48 points, we obtain an average value of 4.6 mol.% I with a standard deviation of 0.1
272 mol.%. This error is taken as representative of the I solubility error for the whole set of
273 samples.

274 **3.2. I solubility in glasses**

275 The measured I solubility in mol.% is reported in Table 1 along with the major element
276 composition measured for each glass. We plotted the I solubility as a function of XNa
277 (Na/Na+Ca in mol.%) in Figure 3. We fitted each I solubility glass series with a polynomial
278 function. For the synthesized high-pressure glasses, the measured I solubility ranges from 0.5
279 to 5.7 mol.%. Three striking features are observed in Figure 3: 1) the highest I solubility is
280 observed for CN-2 glasses loaded with I₂O₅ as the I initial source; 2) the I solubility change is
281 non-linear with respect to the XNa change, regardless of the I source; and 3) the higher loaded
282 O₂ does not lead to the highest I solubility (i.e. lower I solubility in CN-3 than in CN-2
283 glasses).

284 In Figure 3, the higher I solubility in the CN-2 glasses as compared to CN-1 and CN-3 ones is
285 clearly observed for all glass compositions except C₃₅N₀-2. In C₃₀N₅, the difference in I
286 solubility is 1.5 mol.% (0.5 to 2.0 mol.% for C₃₀N₅-1 and C₃₀N₅-2, respectively). Such
287 difference in I solubility is well above any possible error on the I measurement using LA-ICP-
288 MS. For C₂₀N₁₅, the difference in I solubility is even larger: 4.3 mol.%. For the C₃₅N₀ glass
289 composition, the I solubility is comparable regardless of the initial I source or added O₂: 1.2
290 and 1.3 mol.% for C₃₅N₀-1 and C₃₅N₀-2, respectively. The Ca-free C₀N₃₅ glasses exhibit the
291 highest I solubility with 3.9 and 5.7 mol.% for C₀N₃₅-11 and C₀N₃₅-2, respectively. Globally,
292 increasing the XNa in the glass composition induces an increase in I solubility. In fact, Ca-
293 rich glasses are not as favorable for dissolving large quantities of I as Na-rich glasses. Based
294 on X-ray Absorption Spectroscopic results, previous studies also suggested a strong affinity
295 between iodine and sodium.^{31-33,62}

296 For the CN-1 glasses, we observe in Figure 3 a clear parabolic evolution of the I solubility as
297 a function of XNa. The I solubility is decreasing from 1.2 to 0.5 mol.% between C₃₅N₀-1 and
298 C₃₀N₅-1 and C₂₀N₁₅-1, increases to 1.7 mol.% for C₁₀N₂₅-1 and further increases to more than
299 3 mol.% I in C₀N₃₅. The non-linear change in I solubility in the CN-1 glasses as a function of

300 XNa is currently unexplained. We suspect that there is a strong intermixing between Na and
301 Ca cations in the glass structure that could explain the I solubility behavior. It is comparable
302 to the mixed alkali/alkaline-earth effect identified in glasses and inducing non-linear evolution
303 of the glass physical properties.^{48,49,63,64}

304 In CN-2, the I solubility behavior is not the same and does not show a parabolic evolution but
305 a sub-linear trend is observed and shows an increasing I solubility from C₃₅N₀₋₂ at 1.3 mol.%
306 to C₀N₃₅₋₂ at 5.7 mol.%. It should be stressed that both the non-linearity (for instance in CN-1
307 glasses) of I solubility and the impact of the iodine source on the I solubility were not
308 anticipated; demonstrating that I has a complex behavior in aluminoborosilicate matrix. On
309 the contrary to CN-1 glasses, the Ca/Na intermixing does not seem to induce a negative effect
310 on I solubility, which is interpreted as resulting from the increasing oxygen concentration
311 within the glass in CN-2. The increase in oxygen concentration might induce a larger
312 dispersion of positive cation charges for compensation and therefore allowing more space for
313 I to be accommodated. Furthermore, Cormier and Cuello⁶⁵ showed that an increase in cation
314 coordination (due to the increase in oxygen concentration in the case of CN-2 glass series) is
315 accompanied by an increase in bond length; hence, facilitating the I accommodation in the
316 glass. It also implies that the I local environments in CN-2 glass series is not affected by the
317 Ca/Na intermixing and I environments are charge compensated by Ca and Na without
318 distinction.

319 Except for C₃₅N₀, the solubility results for CN-3 glass series appear intermediate between I
320 solubility for CN-1 and CN-2. For C₃₅N₀₋₃₃, the measured I solubility (1.3 mol.%) is on the
321 same order as for C₃₅N₀₋₁ and C₃₅N₀₋₂. It suggests that regardless of the I form the I solubility
322 is not strongly affected in pure calcic glass composition; on the contrary to mixed Na-Ca glass
323 compositions in which the nature of I source plays a major role on I solubility. The
324 intermediate value for I solubility in CN-3 glass series was not expected (i.e. higher I

325 solubility was expected considering the higher O₂ concentration) and is currently not clearly
326 explained and additional experimental work is required for investigating further this aspect.

327 **3.3. I speciation in glasses**

328 **3.3.1. General case**

329 The Figure 4 shows several I 3d_{5/2} XPS spectra obtained for C₃₅N₀ and C₀N₃₅ glass
330 compositions and for the two initial source of iodine: either I₂ (Figure 4A and C) or I₂O₅
331 (Figure 4B and D). The spectra are shown with the same range of energy between 610 and
332 630 eV. The entire set of obtained XPS spectra along with the corresponding simulation is
333 provided in the Suppl. Mat.. The spectra in Figure 4 are also presented with the subsequent
334 deconvolution and the corresponding I speciation.

335 For C₃₅N₀, we observe two different I speciation depending on the initial I source in the
336 starting material. In C₃₅N₀-1 (I₂ loaded, Figure 4A), we observe a peak at ~619 eV and a small
337 shoulder at ~621 eV. In C₃₅N₀-2 (I₂O₅ loaded, Figure 4B), the XPS spectrum exhibits two
338 major contributions: one at ~619 eV and one at ~624.5 eV. The peak at 619 eV can be
339 assigned to I⁻ species,^{61,66,67} the peak at 621 eV can be assigned to I⁰ species,⁶⁸ and the peak at
340 624.5 eV can be assigned to I⁵⁺.^{68,69} In C₃₅N₀-1, when I₂ is loaded in the starting material,
341 iodine is mostly dissolved as I⁻ species (93.9%), and a small proportion of I⁰ is also identified
342 (6.1%). It implies that for a total of 1.2 mol.% I, I⁻ represents 1.13 mol.% and I⁰ represents
343 0.07 mol.% (see Table 1). In C₃₅N₀-2, the deconvolution of the XPS spectrum is more
344 complex as the peak at ~619 eV cannot be decomposed with a single asymmetric line and a
345 small contribution at ~621 eV is requested to reproduce the entire spectrum of the I 3d_{5/2}.
346 Nevertheless, when I₂O₅ is loaded in the starting material, iodine is mostly dissolved as I⁵⁺
347 (58.6%) with a non-negligible contribution of I⁻ (28.8%) and a small contribution of I⁰
348 (12.7%). With a measured I solubility of 1.3 mol.%, I⁵⁺ represents 0.76 mol.%, I⁻ represents
349 0.37 mol.% and I⁰ represents 0.17 mol.%. As shown in Table 1, the other glass samples

350 exhibit the same behavior: when I₂ is loaded, the I speciation in the glass is mostly I⁻ and
351 accompanied by a small quantity of I⁰; when I₂O₅ is loaded, the I speciation in the glass is a
352 mixture of I⁵⁺, I⁰ and I⁻. Combined with the I solubility results, we observe that the maximum
353 I solubility is obtained when I is dissolved mostly as I⁵⁺.

354 The XPS results obtained on the C₀N₃₅-11 glass sample are comparable to the results obtained
355 for C₃₅N₀-1 with I⁻ as the dominant dissolved I species (Figure 4C): 96% I⁻ and 4% I⁵⁺. For
356 this sample, we obtain an I solubility of 3.9 mol.%. The XPS spectrum for C₀N₃₅-2 shows the
357 predominance of I⁵⁺ as the I dissolved species, hence comparable to the results obtained on
358 the other glasses (see Table 1). For C₀N₃₅-2, the I solubility is 5.7 mol.%. For the whole glass
359 compositions, we observe that I solubility is positively correlated to the increase in I⁵⁺.

360 For C₃₅N₀-2 sample, several XPS spectra were recorded on different glass chips collected
361 from the experimental charge with the objective to determine if the I speciation is
362 homogeneous within the experimental charge. Four glass chips from C₃₅N₀-2 were collected
363 along the experimental charge (from top to bottom) and analyzed by XPS for investigating the
364 homogeneity of the I speciation. The results are shown in Figure 5 with an estimated error bar
365 of 10% in relative to the data. The I speciation is slightly heterogeneous: I⁻ ranges from 20 to
366 32%; I⁵⁺ ranges from 58 to 74%; I⁰ is roughly constant from 5 to 9%. We obtain the following
367 average values and standard deviation: I⁻ = 26.1±8.4%, I⁵⁺ = 66.5±8.0, and I⁰ = 7.4±2.9%.

368 Therefore, we suggest that the I speciation in CN-2 glasses is accurate to only ±10% in
369 absolute value. This problem does not apply to CN-1 glass series as I⁵⁺ species are not
370 observed (although 4% I⁵⁺ is determined for C₀N₃₅-11) from XPS measurements (see Table
371 1). We explain the strong difference in I speciation between the CN-1 and CN-2 glasses by
372 the different experimental conditions: I₂ loaded in CN-1 and I₂O₅ loaded in CN-2.

373 **3.3.2. Higher oxidation case: C₃₅N₀-33 glass**

374 The CN-3 glass series represent a peculiar approach aimed to increase the oxidation
375 conditions prevailing during high-pressure experiments. We choose to increase fO_2 conditions
376 by doping the sample with PtO_2 that decomposes into Pt and O_2 at high-temperature. The
377 expected result was an increase in I solubility, however, as shown in Figure 3 we do not
378 observe such an increase: I solubility slightly decreases in CN-3 glasses. During XPS
379 analyses, we have observed that I speciation was highly unstable under X-ray beam. We show
380 in Figure 6 XPS spectra obtained on $C_{35}N_0-33$. Spectra are shown for several successive
381 cycles (Cycle 1, 4 and 9 out of 15) obtained on this glass sample. For the first time, we clearly
382 demonstrate the presence of periodate species with +7 oxidation state with a peak located at
383 ~ 626 eV.^{68,70} The I^{7+} is present along with I^{5+} , I^0 and I^- in this glass sample. This result
384 provides the first evidence for the presence of I^{7+} dissolved in aluminoborosilicate glasses
385 synthesized under high-pressure conditions.

386 The simulation of the XPS spectrum for $C_{35}N_0-33$ suggests that I^{7+} is present in non-
387 negligible quantity. In Cycle 1, I^{7+} species represent almost one third of the I dissolved
388 species. However, it appears that such highly oxidized species is not stable under the X-ray
389 beam during the successive XPS cycles. As shown in Figure 6, I^{7+} decreases significantly in
390 Cycle 4 and becomes negligible in Cycle 9. The change in the I species proportions for this
391 sample are reported in Figure 7 (data are provided in Suppl. Mat.). We clearly see that I^{7+}
392 quickly destabilizes after 4 analysis cycles and after 15 cycles the I^{7+} totally disappears. On
393 the contrary, we see that the proportion of I^{5+} increases conjointly with the decrease in I^{7+} (I^0
394 and I^- remain constant) suggesting that there is a conversion of I^{7+} to I^{5+} resulting from the
395 energy of the X-ray beam. We do not observe any increase in the I^0 and I^- . Although, the
396 statistic is not ideal (i.e. proportions obtained on each cycle), we suggest that the I speciation
397 measured at the first cycle represents the true I speciation prevailing in the $C_{35}N_0-33$ glass and
398 derived proportions after Cycle 1 are reported in Table 1. For the $C_{20}N_{15}-3$ and $C_{10}N_{25}-3$, the

399 periodate species is not observed (see Table 1); however, we cannot exclude its presence
400 during the experiment under high-temperature and high-pressure conditions.

401 Above the fact that periodate species appear highly unstable during analytical characterization
402 by XPS, our results also imply that iodate species are probably the most stable oxidized iodine
403 species (see Figure 7). Therefore, a protocol that focuses on increasing further the oxidation
404 conditions might not be efficient in 1) dissolving more iodine and 2) dissolving iodine in its
405 most stable form.

406 4. Discussion

407 4.1. Iodine speciation and dissolution mechanisms: the influence of the redox state

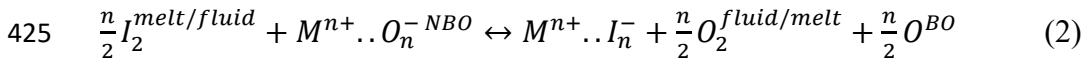
408 In Figure 3, we show that the I loaded form has a dramatic impact on the I solubility and we
409 demonstrate that the change in I solubility is related to the change in I speciation as measured
410 by XPS (see Figure 4). As I^{5+} increases into the glass, there is an increase in I solubility. We
411 have plotted in Figure 8 the change in I solubility as a function of the Overall I Redox State
412 (ORS) calculated from the I speciation in Table 1 with the following equation:

$$413 \quad -1 \times XI^{-} + 5 \times XI^{5+} + 7 \times XI^{7+} = \textit{Overall I redox state (ORS)} \quad (1)$$

414 In Figure 8, we can observe that there is a positive correlation between I solubility and ORS.
415 This positive correlation is clear for most of the glass compositions. For $C_{20}N_{15}$ the trend is
416 less clear whether the increase is linear or not. For $C_{35}N_0$ glass composition, I solubility does
417 not vary with increasing ORS.

418 The present work represents the first evidence showing that, at constant glass composition and
419 constant intensive conditions, the I solubility depends on the I speciation. At high-pressure
420 and high-temperature, I_2 is under supercritical conditions, which implies that the
421 thermodynamic activity of the I_2^{fluid} equals the thermodynamic activity of the I_2^{melt} . Within the
422 melt iodine atoms ionizes in the surroundings of sodium or calcium to form $Na..I$ or $Ca..I$

423 linkages. In the case iodide is only present (i.e. CN-1), we propose the following general
424 chemical reaction for iodide dissolution mechanism:

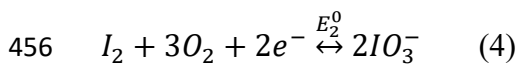
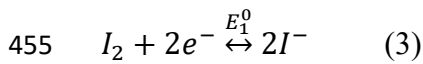


426 In Eq. 2, M^{n+} is a charge compensating cation for I^- species either Na^+ or Ca^{2+} forming $Na..I$
427 and $Ca..I$ species.^{36,62} In Eq. 2 the I dissolution is accompanied by a rearrangement of the
428 glass network: a Non-Bridging Oxygen (NBO) is transformed into a Bridging Oxygen (BO)
429 implying that I dissolution has a polymerizing effect on the glass structure. However, it is
430 probably a little more complicated than currently mentioned, as the oxygens involved in Eq. 2
431 might indeed be NBOs from the boron or silicate units. For instance, Jolivet et al.³⁶ showed
432 that the proportion of BO_4 units (i.e. N4) in the glass is affected by the I dissolution. BO_4
433 concentration can increase or decrease depending on the glass chemical composition. In Eq. 2,
434 accompanying the polymerization of the network is the production of $1/2O_2$ that is released in
435 the fluid phase. By analogy to the I dissolution as IO_3^- that is enhanced in the case an excess
436 O_2 is present (i.e. CN-2 and CN-3), the release of O_2 in the fluid should induce the dissolution
437 of a limited proportion of IO_3^- . Clearly, it is not the case as the I speciation is mostly I^- (only
438 C_0N_{35-11} exhibits the presence of IO_3^- , see Table 1).

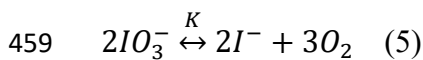
439 Under intensive conditions, the oxygen activity is expressed by the oxygen fugacity (fO_2).
440 During the high-pressure experiments, using talc-Pyrex assemblies, the fO_2 has been
441 estimated to be close to QFM+1 in relative to the solid oxygen buffer Quartz-Fayalite-
442 Magnetite.^{71,72} These conditions are relatively oxidizing. For instance, in C- and S-bearing
443 high-pressure systems, the oxidized CO_2 and SO_2 (or SO_3) are the dominant species in both
444 the fluid phase and the melt phase.^{55,73} However, in the I-bearing system currently studied, I_2
445 is the dominant species in the fluid phase and Eq. 2 is also controlled by I fugacity (fI_2). To
446 our knowledge, there is currently no available Equation-Of-State for I_2 in the fluid phase

447 under temperature and pressure conditions preventing from calculating the I₂ thermodynamic
448 activity in the fluid phase under intensive conditions.

449 In the case of CN-2 glass series, we observe the coexistence between I⁻ and I⁵⁺ species, which
450 means that another oxidation/reduction mechanism has to be proposed for constraining the
451 *f*O₂ conditions. The fact that I⁵⁺ is observed in the glass implies necessarily that there is an
452 increase in the *f*O₂ (*f*O₂ > QFM+1). We used the following chemical reactions for explaining
453 the oxidation/reduction mechanisms and the coexistence of both I⁻ and I⁵⁺ species in the CN-2
454 glasses:



457 The standard potentials for these two reactions are E⁰₁ = +0.54 V and E⁰₂ = +1.8 V. It follows
458 the global equilibrium reaction:



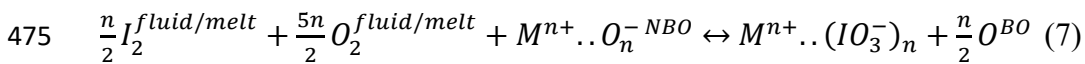
460 With:

$$461 \quad K = \frac{[I^-]^2 \times f_{O_2}^3}{[IO_3^-]^2} \quad (6)$$

462 We combined the Nernst and the Gibbs-Duhem equations to determine the K value at
463 1400°C: 2.56x10⁻⁸. Using the I⁻ and IO₃⁻ concentrations determined for CN-2 glasses in Table
464 1, we were able to estimate the *f*O₂ conditions prevailing during the oxidized experiments
465 with I₂O₅. We obtain a *f*O₂ on the order QFM+3 (the detailed calculation is provided in Suppl.
466 Mat.), which is consistent with the higher oxidizing conditions imposed by the dissociation of
467 I₂O₅ into I₂ and O₂ during the experiment. The QFM+3 only represents an estimate of the *f*O₂

468 condition; a more convenient approach would require the use of solid oxygen buffers during
469 the experiments.

470 With regards to the actual I dissolution mechanisms within the glass structure, the global
471 equation proposed by Riley et al.³² involves the coexistence of I⁻ and I⁵⁺ species to the
472 proportions of 5:1; however, it cannot apply to our study as the proportion of I⁵⁺ in CN-2
473 glasses is well above this ratio (see Table 1). We propose the following equation (Eq. 7)
474 describing the dissolution of I⁵⁺ species:

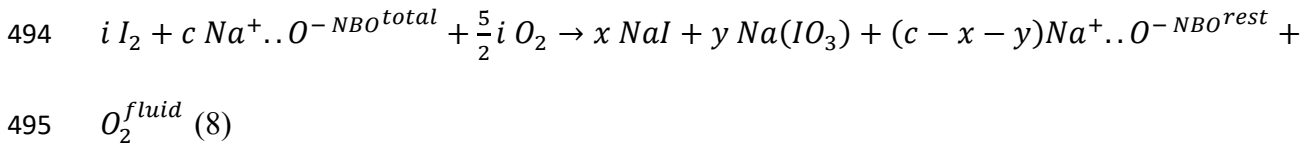


476 In Eq. 7, O₂ from the fluid phase (from the dissociation of I₂O₅) and oxygen from the melt (O⁻
477 ^{NBO}) are used to form iodate species (IO₃⁻) with surrounding charge compensating cation Mⁿ⁺
478 either Na⁺ or Ca²⁺ forming Na⁺(IO₃⁻) or Ca²⁺(IO₃⁻)₂ units dissolved in the glass. Eq. 7 also
479 implies that the dissolution of I as IO₃⁻ is favored by an increase in *f*O₂ during the experiment.
480 This implication is only true to a certain extent considering that we do not observe an increase
481 in the proportion of the IO₃⁻ proportion in the CN-3 glass series. In a similar way to Eq. 2, the
482 I dissolution as IO₃⁻ induces a rearrangement of the glass network by consumption of NBOs
483 that change to BOs as a result of the charge compensation by the cation, either Na⁺ or Ca²⁺.

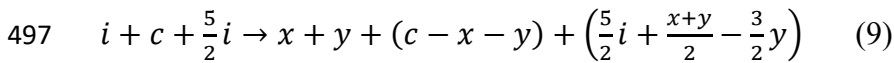
484 **4.2. Consistency between measured I speciation and dissolution mechanisms**

485 Although I dissolved as I⁻ in glasses equilibrated with pure I₂ is consistent with previous
486 works,³⁶ it is surprising not to observe IO₃⁻ coexisting with I⁻ considering that O₂ is produced
487 during I dissolution (see Eq. 2). Similarly, the mixed IO₃⁻/I⁻ speciation in glasses equilibrated
488 with pure I₂O₅ is questioning, as the quantity of oxygen brought by the dissociation of I₂O₅
489 should be enough to promote the I dissolution as IO₃⁻ only (see Eq. 7). We have done the
490 mass balance on oxygen consumed and produced during I dissolution as I⁻ and IO₃⁻ as
491 observed in the CN-2 and CN-3 glass series. For the sake of clarity, we have considered that

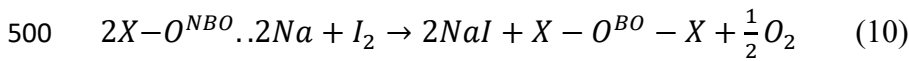
492 sodium is the charge balancing cation (i.e. considering calcium as balance element gives the
 493 same results).



496 With the following number of mole:



498 In Eq. 9, the $\frac{x+y}{2}$ on the right-hand side for O_2^{fluid} corresponds to the number of mole produced
 499 by the transformation of O^{NBO} to O^{BO} for example with the following equation:



501 In which X stands for a network former cation such as Si or B. The $x + y$ is also equal to the
 502 dissolved iodine number of mole, $2i$. In Eq. 9, the $\frac{5}{2} i$ quantity corresponds to the number of
 503 mole coming from the I_2O_5 dissociation, and the $-\frac{3}{2} y$ quantity corresponds to the
 504 consumption of O_2^{fluid} to form iodate. Therefore, the net proportion of O_2 produced in the
 505 fluid on the right-hand side of Eq. 9 is $\left(\frac{7}{2} i - \frac{3y}{2} \right)$. The I dissolution implies necessarily that
 506 $\left(\frac{7}{2} i - \frac{3y}{2} \right)$ is either equal to 0 or positive. It follows that $3y \leq 7i$. Therefore, we can extract
 507 the proportion of iodate formed $\frac{y}{2i} \leq \frac{7}{6}$. Assuming this mass balance on the oxygen, it implies
 508 that the upper limit for IO_3^- concentration is 100% in the case I_2O_5 is added to the system. The
 509 same calculation can be conducted for the I_2 loaded during the experiment. In such case, the
 510 $\frac{5}{2} i$ is removed from the calculation and the upper limit to the proportion of iodate becomes
 511 $\frac{y}{2i} \leq \frac{1}{3}$, which corresponds to 33% of IO_3^- formed.

512 As shown in Table 1, under no circumstances those upper limits are achieved: there is no IO_3^-
513 in the CN-1 glass series and IO_3^- reaches a maximum of 85% in $\text{C}_{30}\text{N}_5-2$. Consequently, the
514 oxygen availability appears not to be the limiting factor for the formation of IO_3^- species and
515 other controlling parameters (e.g. thermodynamic) are involved in the equilibrated speciation
516 that we actually measure.

517 **4.3. Exploring leads for future ^{129}I immobilization in aluminoborosilicate glasses**

518 ^{129}I radioisotope represents a serious environmental problem that requires specific matrixes
519 for immobilization. One goal to our approach is to provide highlights for guiding future
520 research in the elaboration of matrixes for the geological disposal of ^{129}I . However, we are
521 perfectly aware that the synthesized glasses in the present work are essentially designed to
522 obtain the fundamental understanding of the role of Ca and Na on the iodine dissolution in
523 glasses. For instance, the investigated pressure (1.5 GPa) is high in comparison to an
524 industrial process using Hot-Isostatic Press^{19,39,40} and the chemical durability of the presently
525 investigated glass compositions remains to be asserted.⁷⁴ Considering the lack of experimental
526 data on I solubility, it appears presumptuous to build a reliable model that can be used for
527 predicting I solubility for a wide range of aluminoborosilicate glass compositions.
528 Nonetheless, we can provide a series of preconisation for a future permanent immobilization
529 of ^{129}I radioisotopes.

530 In Figures 3 and 8, we show that C_0N_{35} glass composition represents the best candidate to
531 dissolve efficiently ^{129}I nuclear waste providing that high oxidation state is imposed during
532 the experiments and I is dissolved in the glass as iodates species. It should be emphasized that
533 the iodate species are the most advantageous form of I with respect to environment as its
534 mobility in clays is lower than the iodide species.^{75,76} We suggest that the increase in I
535 solubility with increasing I oxidation state is resulting from the availability of oxygen atoms
536 within the melt to form IO_3^- units. Interestingly, increasing strongly the oxygen concentration

537 tends to promote the formation of periodate; however, as shown in Figure 7, this species lacks
538 stability within the glass under the XPS beam. This lower stability is likely due to the higher
539 oxygen coordination environment around I^{7+} .⁷⁷ Although the periodate stability under natural
540 environmental conditions should be investigated, we suggest that exceedingly high oxidative
541 conditions should be avoided to prevent the formation of periodate species. Meanwhile,
542 sufficiently high oxidation conditions should be maintained to maximize the I solubility. Solid
543 sorbents such as crystalline $NaIO_3$ could be used to ensure high I load and high oxidation
544 conditions during the vitrification process. Moreover, this methodology would increase the Na
545 content in the matrix composition and consequently increasing I solubility due to the higher I
546 affinity for Na-rich glass compositions.

547 Further experimental work has to be conducted in order to decipher the I solubility change in
548 aluminoborosilicate glasses considering the large range of chemical compositions for nuclear
549 waste glasses.^{25,78} For instance, the rationale for I solubility as a function of the nature of the
550 charge compensating cations is not clearly determined. In the present work, we clearly show
551 that I dissolution is favored in Na-rich compositions as compared to Ca-rich compositions.
552 Both cations are close in size but with different charges and different roles within the glass
553 structure. Na^+ is known to act as a charge compensating cation to BO_4 units and AlO_4 units;⁷⁹⁻
554 ⁸³ whereas Ca^{2+} acts as a network modifying cation inducing the depolymerization of the glass
555 network.⁸⁴⁻⁸⁵ As a result, Na^+ is located in the surroundings of weakly charged oxygen atoms
556 (i.e. bridging oxygen, BO), whereas Ca^{2+} is surrounded by highly charged oxygen atoms (i.e.
557 non-bridging oxygen, NBO). However, the nature of oxygen atoms surrounding Na^+ and Ca^{2+}
558 is mitigated considering the mixed alkali effect.⁴⁵ Na^+ has more affinity with I^- or IO_3^- species
559 than Ca^{2+} , which can be explained by the weaker nature of the $Na-O^{BO}$ bonds in the structure
560 compared to $Ca-O^{NBO}$ bonds. In the case of pure Ca glass composition, Ca^{2+} adopt both roles:
561 charge compensating and network modifying; and I dissolution in that case is still possible (I

562 solubility different from 0) but to a limited extent. As a result, it could be pertinent to
563 investigate the change in I solubility as a function of the size and charge of the non-network
564 forming cations (i.e. Li^+ , K^+ , Rb^+ , Sr^{2+} , Ba^{2+}).

565 **5. Conclusions**

566 Better understanding of the I behavior in borosilicate glasses is a prerequisite for the
567 formulation of future matrixes able to immobilize ^{129}I in geological repositories. In the present
568 work, we have investigated the change in I solubility in a series of borosilicate glass 1) held
569 under high-pressure conditions (1.5 GPa), 2) with varying Ca/Na ratios, and 3) with different
570 sources of I and oxygen to study the effect of redox conditions.

571 We have demonstrated that I solubility is strongly enhanced when the iodine source is I_2O_5
572 instead of I_2 . Under highly oxidizing conditions, XPS measurements revealed that iodine is
573 essentially dissolved as I^{5+} species. Increasing further the oxidizing conditions is
574 counterproductive as it implies the presence of the unstable I^{7+} species and does not lead to an
575 increase in I solubility.

576 Regardless of the I speciation, we have shown that there is a non-linear behavior of I
577 solubility as a function of XNa value. Globally, we show I solubility is favored in Na-rich
578 glass compositions, in agreement with previous experimental investigations.

579

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588

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726

727 **Figure caption**

728 Figure 1: I concentration measured by LA-ICP-MS as a function of I concentration measured
729 by SEM EDS. The 1:1 line is reported. The provided error is calculated from the standard
730 deviation of the replicated measurements: at least 5 spots by LA-ICP-MS, 10 scans by SEM
731 EDS.

732 Figure 2: I concentration determined by LA-ICP-MS for C₂₀N₁₅-22 glass sample. The I
733 content was measured along and across the Pt capsule to determine the homogeneity with
734 respect to I content. 48 spots were acquired through the entire experimental charge. The
735 average I concentration is 4.6 mol.% and the standard deviation is ±0.1 mol.%.

736 Figure 3: Change in I solubility as a function of XNa = Na/(Na+Ca) for the investigated
737 glasses. The I solubility for the three experimental series is represented: CN-I₂ (CN-1), CN-
738 I₂O₅ (CN-2) and CN-I₂O₅+PtO₂ (CN-3). I solubility can reach up to 5.7 mol.% and is
739 maximised for CN-2 glass series in which I is dissolved as I⁵⁺.

740 Figure 4: XPS spectra obtained for C₃₅N₀ and C₀N₃₅ glasses showing I dissolved mainly as I⁻
741 (CN-1) or I⁵⁺ (CN-2). The spectrum simulations are also reported along with the quantified
742 species. We show that I dissolves as several species in the glasses: I⁻ (~610 eV) and I⁰ (~621
743 eV) for the less oxidized ones (CN-1); I⁵⁺ (~624 eV), I⁻ and I⁰ for the most oxidized ones
744 (CN-2).

745 Figure 5: Distribution of I speciation as measured by XPS on four glass chips for C₃₅N₀₋₂
746 glass. The I speciation appears relatively homogeneous in C₃₅N₀₋₂ glass (±10%).

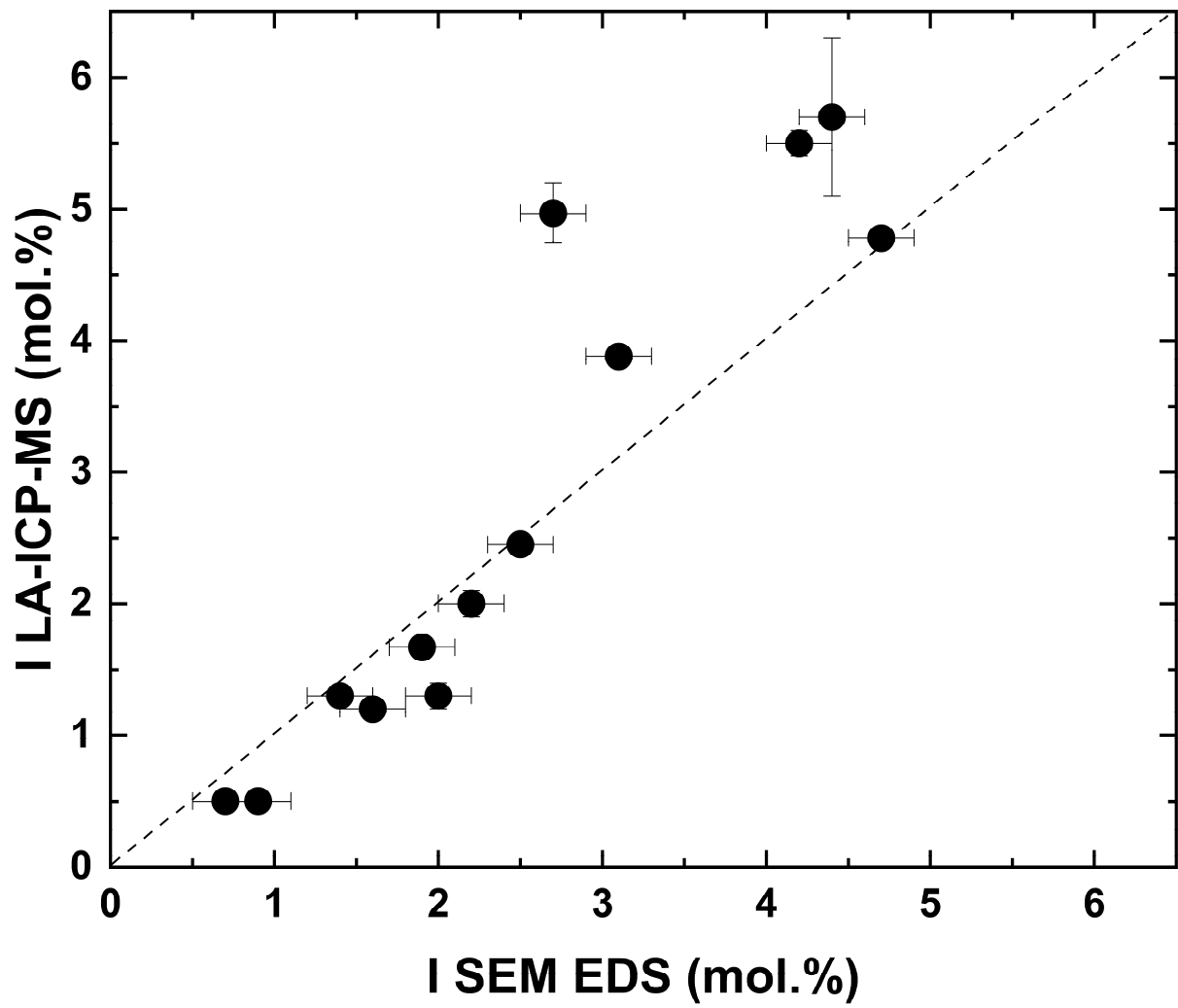
747 Figure 6: XPS spectra obtained on C₃₅N₀₋₃₃ showing the presence of I⁷⁺ species (~626 eV)
748 along with I⁵⁺, I⁻ and I⁰ species dissolved in the glass. Spectra are shown for several cycles of
749 acquisitions. There is a gradual decrease in the I⁷⁺ concentration from 30.3 to 3.8% between
750 Cycles 1 and 9, respectively; demonstrating the weak stability of I⁷⁺ within the glass under the
751 X-ray beam. The entire set of data is provided in the Suppl. Mat..

752 Figure 7: Change in the I species concentrations (I⁷⁺, I⁵⁺, I⁻, I⁰) as a function of the XPS cycle
753 for C₃₅N₀₋₃₃. Periodate I⁷⁺ is gradually converted to iodate I⁵⁺; and I⁷⁺ concentration is close
754 to 0 after 10 XPS cycles.

755 Figure 8: I solubility as a function of the I Overall Redox State (ORS). The ORS is calculated
756 from Eq. 1 and using the I speciation obtained from XPS spectrum simulations. An estimate
757 of the fO_2 conditions is provided: QFM+1 in CN-1 series and QFM+3 in CN-2 series. The I
758 solubility is positively correlated to the increase in oxidizing conditions for Na-bearing glass
759 compositions (i.e. from $C_{30}N_5$ to C_0N_{35}) but seems unaffected for Ca-bearing glass (i.e.
760 $C_{35}N_0$).

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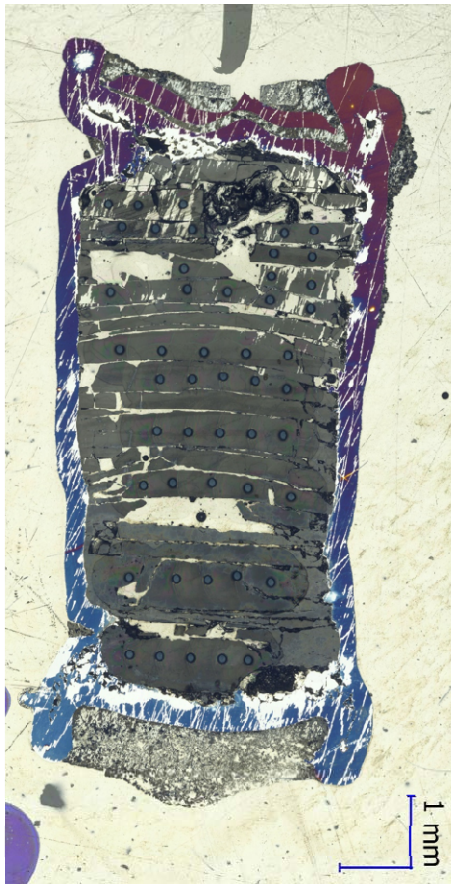


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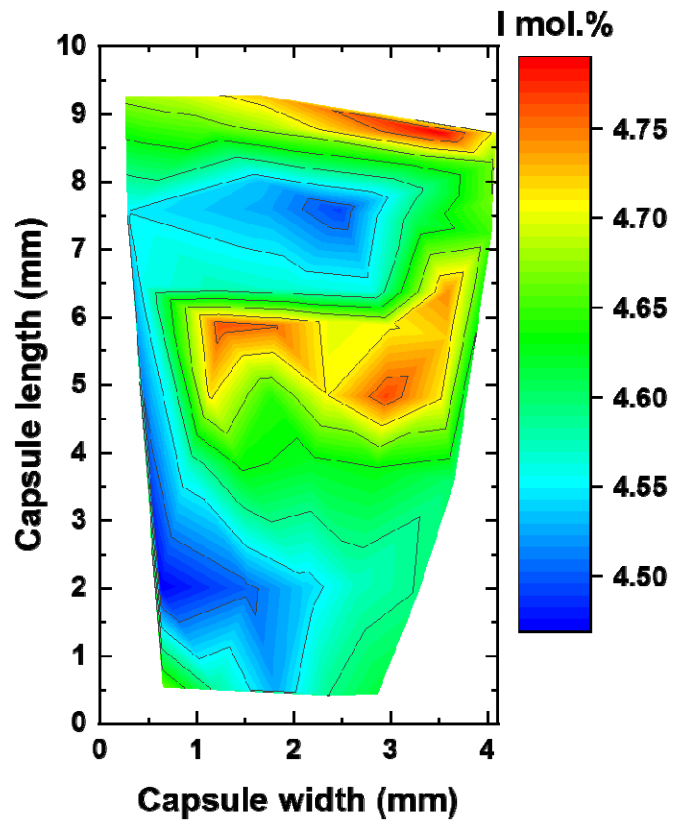
764 Figure 1

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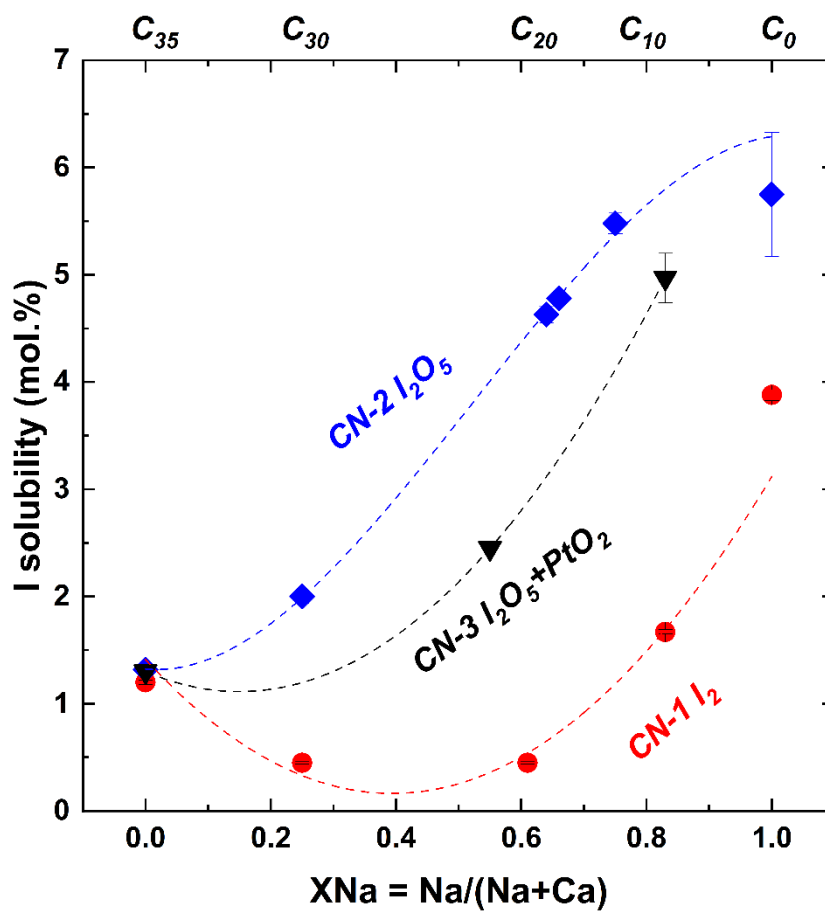
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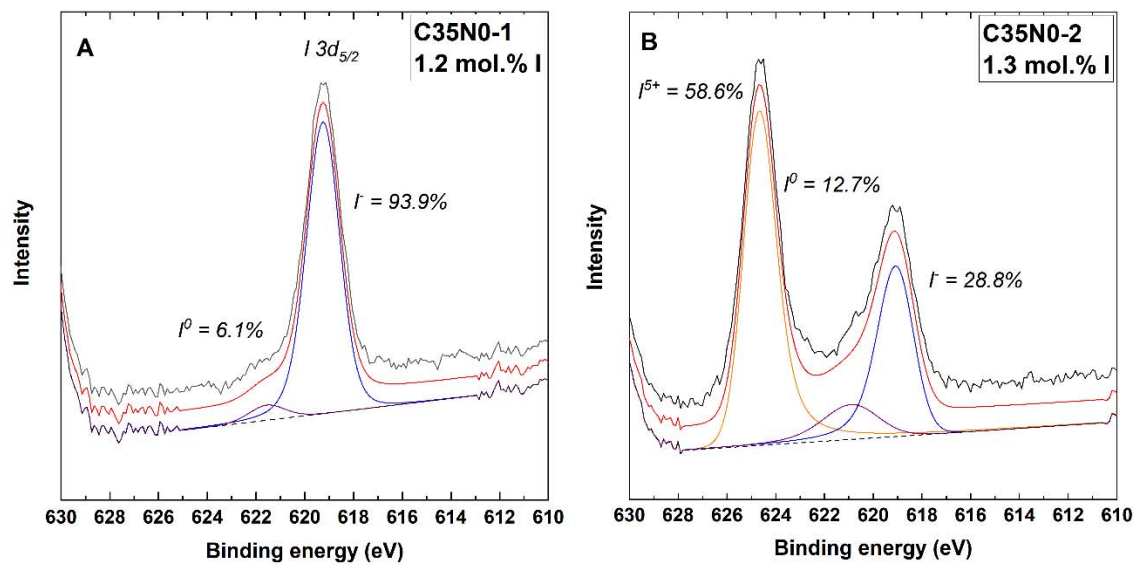
768 Figure 2

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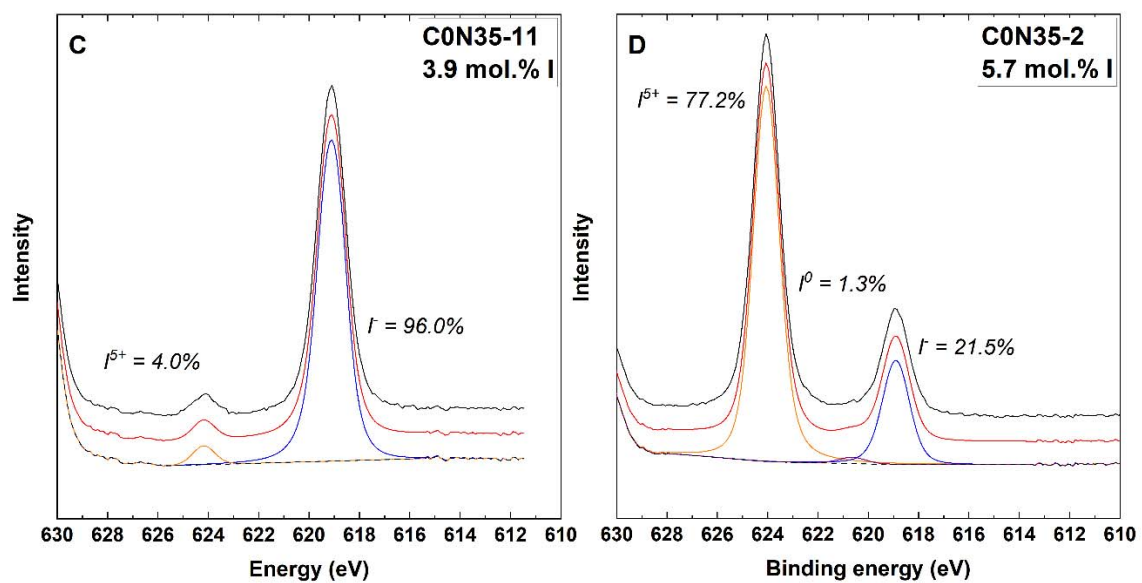
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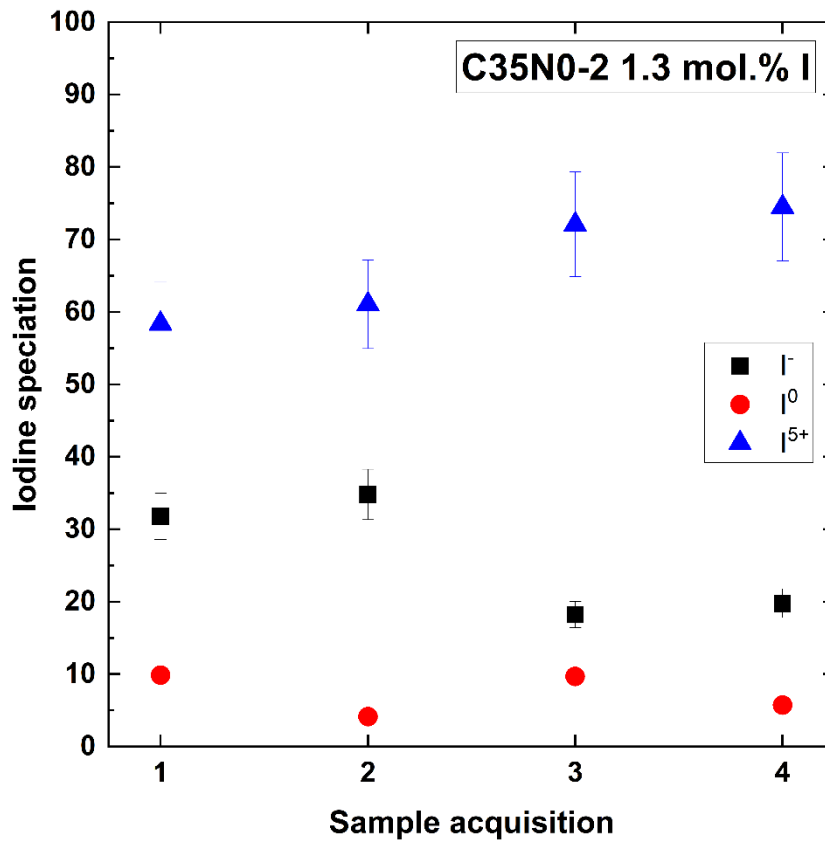


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777 Figure 4

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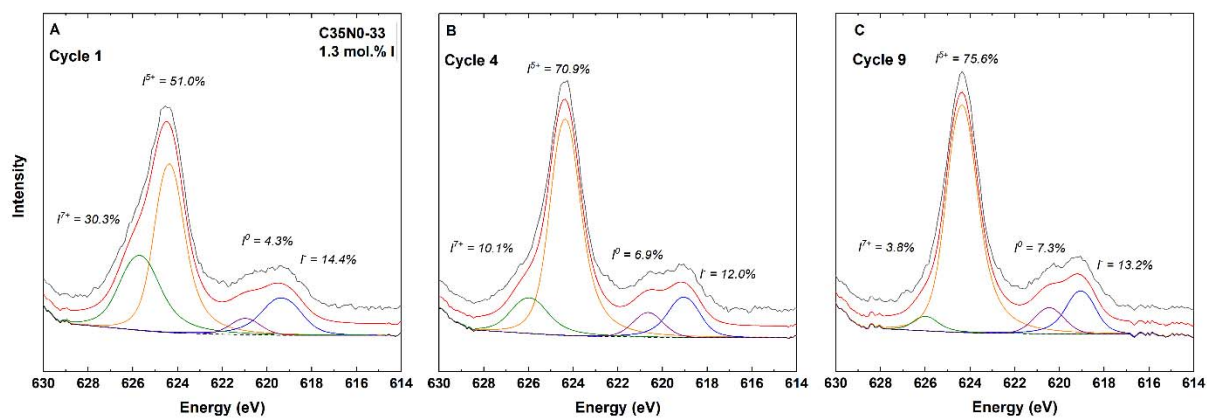


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781 Figure 5

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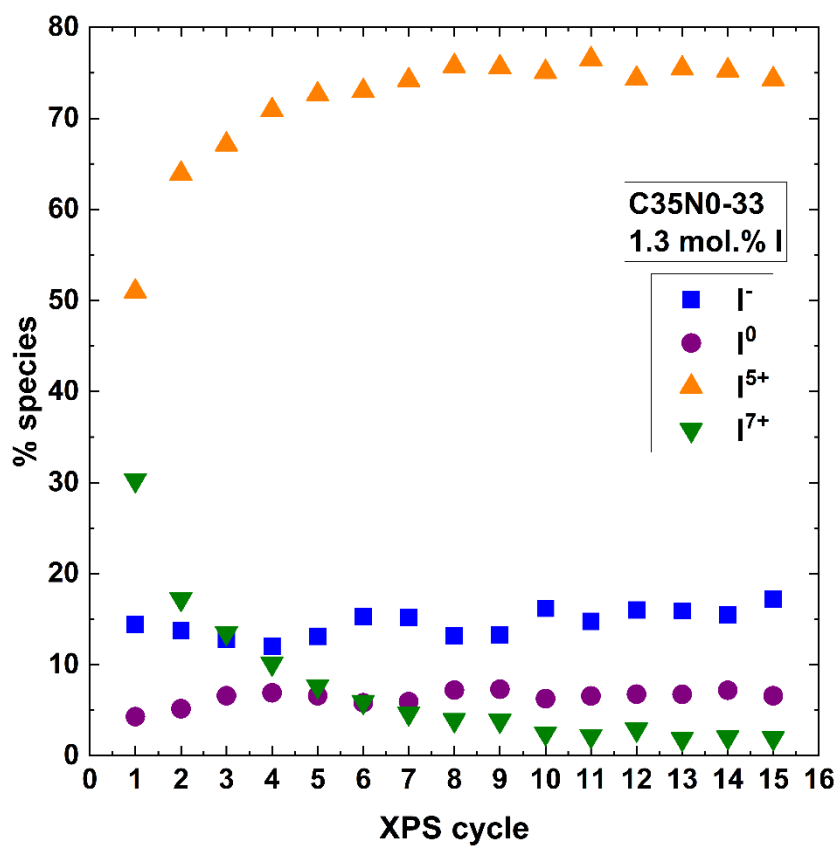


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785 Figure 6

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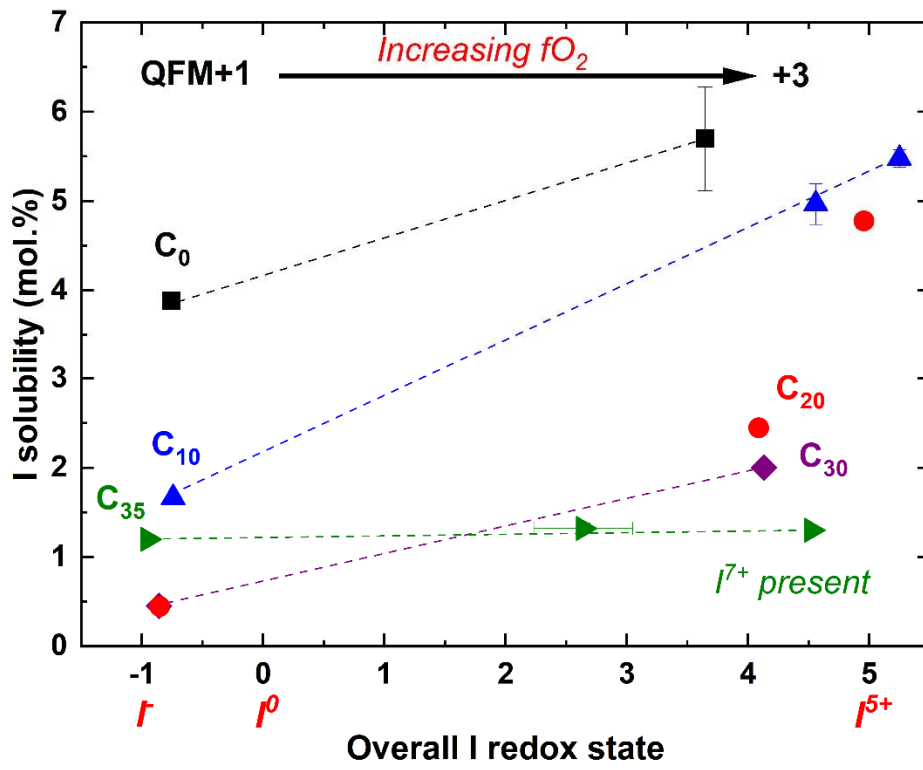


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789 Figure 7

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793 Figure 8

Table 1: Major elements, I solubility and speciation for CN glass series loaded with I₂ (CN-1), I₂O₅ (CN-2) and I₂O₅+PtO₂ (CN-3).

Sample	I loaded (mol.%)	Added O ₂ (mol.%)	Major elements (mol.%) ^a						I speciation ^b					I solubility (mol.%) ^d	
			SiO ₂	B ₂ O ₃	Al ₂ O ₃	CaO	Na ₂ O	XNa	I ⁻	I ⁰	I ⁵⁺	I ⁷⁺	I Overall Redox State (ORS) ^c	I SEM EDS	I LA ICP MS
CN-0 I-free 0.0001 GPa 1200°C															
C ₃₅ N ₀ -0	0	0	32.4	29.1	4.9	33.6	0	0							
C ₃₀ N ₅ -0	0	0	31.7	29.7	5.2	28.4	5.0	0.26							
C ₂₀ N ₁₅ -0	0	0	33.9	29.0	5.0	17.9	14.3	0.62							
C ₁₀ N ₂₅ -0	0	0	32.9	29.6	4.9	8.9	23.6	0.84							
C ₀ N ₃₅ -0	0	0	31.5	30.7	5.3	0	32.5	1							
CN-1 I₂ loaded 1.5 GPa 1400°C 4h															
C ₃₅ N ₀ -1	13.4	0	31.8	29.2	4.9	32.5	0	0	93.9	6.1	0		-0.94	1.6	1.2
C ₃₀ N ₅ -1	13.3	0	32.1	29.9	5.0	27.7	4.7	0.25	86.4	13.6	0		-0.86	0.7	0.5
C ₂₀ N ₁₅ -1	12.9	0	33.5	30.0	4.8	17.4	13.4	0.61	94.1	5.9	0		-0.94	0.9	0.5
C ₁₀ N ₂₅ -1	13.5	0	31.6	31.1	5.1	8.8	21.5	0.83	85.2	14.8	0		-0.85	1.9	1.7
C ₀ N ₃₅ -11	12.4	0	31.5	29.2	5.3	0	31.0	1	96.0	0	4.0		-0.76	3.1	3.9
CN-2 I₂O₅ loaded 1.5 GPa 1400°C 4h															
C ₃₅ N ₀ -2	12.6	15.7	32.0	23.8	5.2	36.9	0	0	28.8	12.7	58.6		2.64	2.0	1.3
C ₃₀ N ₅ -2	13.1	16.4	31.2	27.3	5.2	29.3	4.8	0.25	14.5	0	85.5		4.13	2.2	2.0
C ₂₀ N ₁₅ -2	12.6	15.8	31.6	26.9	5.1	15.3	14.9	0.66	9.2	8.2	82.5		4.03	4.7	4.8
C ₂₀ N ₁₅ -22 ^e	12.1	16.2	32.0	28.6	4.8	16.1	14.1	0.64	nd	nd	nd		nd	4.4	4.6
C ₁₀ N ₂₅ -2	12.9	16.7	31.6	28.4	5.4	11.5	17.5	0.75	9.9	2.4	87.7		4.29	4.2	5.5
C ₀ N ₃₅ -2	13.4	15.1	31.6	29.9	5.3	0	28.9	1	21.5	1.3	77.2		3.65	4.4	5.7
CN-3 I₂O₅ + PtO₂ loaded 1.5 GPa 1400°C 4h															
C ₃₅ N ₀ -33	12.0	18.8	33.0	29.8	5.6	30.3	0	0	14.5	4.3	51.0	30.3	4.53	1.4	1.3
C ₂₀ N ₁₅ -3	13.1	20.4	34.8	29.5	5.8	17.0	10.5	0.55	28.5	0	71.5		3.29	2.5	2.5
C ₁₀ N ₂₅ -3	13.6	21.6	33.0	29.8	5.7	8.3	20.9	0.83	21.8	0	78.2		3.69	2.7	5.0

^aThe major element concentrations are determined by SEM EDS, the ISG (Gin et al. 2013) was used as a chemical reference.

^bThe I speciation is determined from the simulation of the XPS spectra acquired in the I 3d spectral region (610-640 eV). The error on each species concentration is estimated to be better than 10% in relative to the value.

^cThe I Overall Redox State represents an empirical value corresponding to the balance between the different oxidation states (I⁻, I⁰, I⁵⁺) determined through the XPS analysis.

^dThe I content is measured in the bulk glass. The error bar obtained on each value is obtained on the replicated analyses. Typical error on the SEM EDS measurement is ±0.2 mol.% and the typical error on the LA ICP MS measurement is better than 0.1 mol.%.

^eThe C20N15-22 is a solid copy of the C20N15-2, to assess the reproducibility of the method. The I solubility has been measured by LA ICP MS with the acquisition of 48 analytical points.