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1 **Local environment of iodine dissolved as iodate in high-pressure aluminoborosilicate**
2 **glasses: A I K-edge X-ray Absorption Spectroscopic study**

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31

32 **Abstract**

33 The use of high-pressure synthesis conditions to produce I-bearing aluminoborosilicate
34 represent a promising issue for the immobilization of ^{129}I radioisotope. Furthermore, iodine
35 appears to be more solubilized in glasses under its iodate (I^{5+}) form rather than its iodide (I^-)
36 form. Currently, the local atomic environment for iodine is poorly constrained for I^- and
37 virtually unknown for I^{5+} or I^{7+} . We used I K-edge X-ray Absorption Spectroscopy conducted
38 at 20 K for determining the local atomic environment of iodine dissolved as I^- , I^{5+} , I^{7+} in a
39 series of aluminoborosilicate glasses. We determined that I^- is surrounded by either Na^+ or
40 Ca^{2+} in agreement with previous works. The signal collected from EXAFS reveals that I^{5+} is
41 surrounded invariably by three oxygen atoms forming a IO_3^- cluster charge compensated by
42 Na^+ and/or Ca^{2+} . The I-O distance in iodate dissolved in glass is comparable to the I-O
43 distance in crystalline compounds at $\sim 1.8 \text{ \AA}$. The distance to the second nearest neighbor (Na^+
44 or Ca^{2+}) is also constant at $\sim 3.2 \text{ \AA}$. This derived distance is identical to the distance between I^-
45 and Na^+ or Ca^{2+} in the case of iodide local environment. For one sample containing iodate and
46 periodate, the distinction between the local environment of I^{5+} and I^{7+} could not be made
47 suggesting that both environments have comparable EXAFS signal.

48

49 I. INTRODUCTION

50 Nowadays, the nuclear energy is a part of energetic mix along with fossil fuels and renewable
51 sources for energy consumption of industrialized countries^{1 2 3}. However, on the contrary to
52 fossil fuels, nuclear energy does not contribute to increase the greenhouse effect³; and on the
53 contrary to renewable energy source (i.e. wind and solar) nuclear energy is continuous and not
54 dependent on seasonality⁴. Although nuclear energy has several benefits, it actually produces
55 radioactive wastes that need to be handled in a durable and safe manner⁵. From the many
56 radioactive isotopes produced by nuclear plant activities, ¹²⁹I represents a major
57 troublesome element, as it is highly mobile in the environment, has a long half-life (15.7 My)
58 and can be assimilated by the human organism^{6 7 8 9 10 11 12 13}. Furthermore, ¹²⁹I does not
59 actually benefit from a fully adequate specific matrix to immobilize this radiotoxic isotope in
60 a permanent manner in natural geological repository site.

61 Many efforts have been conducted in the last decade to propose specific matrices for the ¹²⁹I
62 immobilization such as glass (e.g. phosphate-based, silver-based, borosilicate-based)^{14 15 16 17},
63 crystalline phases^{18 19 20} or glass ceramics^{21 22 23}. Borosilicate glasses are of interest as it has a
64 good chemical and mechanical durability^{24 25 26 27}. However, because borosilicate glasses are
65 made at relatively high-temperature^{24 28 29} and iodine volatilizes at such high temperature,
66 borosilicate glasses cannot dissolve large amount of iodine when adopting this protocol. Riley
67 et al.¹⁶ reported an iodine solubility up to 0.7 mol.% in Low Activity Waste (LAW) glass
68 composition made at near ambient pressure (i.e. sealed-capsule). To bypass this low iodine
69 dissolution level in borosilicate glass matrix, recent works^{30 31 32 33} employed high-pressure
70 conditions to increase drastically the iodine solubility in borosilicate glasses. For instance,
71 recent work by Morizet et al.³³ measured iodine solubility up to ~6 mol.% in low-silica, high-
72 boron, Ca- and Na-bearing glasses synthesized at 1.5 GPa. Jolivet et al.³² measured up to 2.5
73 mol.% in LAW glasses synthesized at 1.5 GPa; representing four times the iodine solubility

74 measured at ambient pressure for comparable glass compositions^{16 17 34}. This recent advance
75 constitutes a potential solution for the future immobilization of ¹²⁹I; however, it requires
76 assessing the durability of these I-bearing glasses synthesized under high-pressure conditions.
77 To do so, a microscopic level of information is required to scrutinize the iodine speciation and
78 its local environment at atomic scale when dissolved in the glass structure.

79 Recent studies demonstrated that such information can be accessed via X-ray Absorption
80 Spectroscopy (XAS) and X-ray Photoelectron Spectroscopy (XPS)^{16 17 30 33 34 35 36}. In
81 particular, XPS measurements clearly identify when iodine is dissolved as iodide (I⁻) or iodate
82 (I⁵⁺) in borosilicate glasses^{33 36 37}. On the other hand, XAS studies have provided valuable
83 information on the iodine atomic local environment as dissolved under its iodide form in
84 borosilicate glasses^{17 35 36}. Furthermore, XAS has been applied to characterize the iodine local
85 environment in a wide variety of samples: from inorganic crystalline compounds^{18 38 39 40 41 42}
86 ⁴³ to organic^{44 45}. For glasses, it was demonstrated that I⁻ anions dissolved in glasses were
87 charge compensated by the available network modifying cations such as Na⁺ or Ca²⁺. The
88 derived coordination number obtained from XAS spectrum modelling suggests that around
89 four Na⁺ contribute to charge balance I⁻, while around two Ca²⁺ contribute to charge balance I⁻
90 in glasses, regardless of their synthesis conditions: ambient or high-pressure^{17 36}.

91 Concomitantly, to address the glass chemical durability, the effect of iodine dissolution on the
92 glass structure has been recently discussed and suggests that iodine dissolution as I⁻ and
93 forming Na-I clusters is likely to induce an increase in the degree of polymerization^{34 36}.

94 However, this is not clearly demonstrated and more advanced investigations (i.e. ¹⁷O NMR)
95 are required. For instance, Jolivet et al.³² showed that the relative proportion of BO₄ ($N_4 =$
96 $[BO_4] / [BO_4 + BO_3]$) could increase or decrease depending on the glass bulk composition.

97 All the recent works focused on the atomic local environment of iodide (I⁻) surrounded by
98 either Na⁺ or Ca²⁺ to form Na-I and Ca-I clusters, respectively. Interestingly, it has been

99 inferred that iodide species correspond to one of the most stable inorganic form found in the
100 environment; however, iodate could also be found noticeably^{46 47}. So far, there has been no
101 investigation on the atomic local environment for iodate species dissolved in glasses.
102 Serendipitously, Morizet et al.³³ showed that the level of iodine solubility achieved in case of
103 the iodate form is four times higher than in case of iodide; therefore representing a serious
104 option for the immobilization of ¹²⁹I. Most iodine waste solid sorbents could be concerned by
105 this approach (see Riley et al.¹⁴ and reference therein). They also showed that increasing the
106 oxidizing conditions could also promote the formation of periodate species (I⁷⁺); although it
107 was suggested that this fully oxidized species was not stable under X-ray excitation. Hence,
108 the local atomic environment for iodate (and periodate) needs investigations in order to
109 evaluate and compare the chemical durability of those I-bearing glass matrices in the case
110 iodide (I⁻) and iodate (I⁵⁺) for future immobilization of ¹²⁹I-bearing nuclear wastes in natural
111 repository geological site.

112 In the present work, we used I K-edge XAS to characterize and to compare at the atomic scale
113 the local environment of iodine atoms dissolved in glasses in presence of iodide, iodate and
114 periodate species. We studied the I-bearing glasses studied by Morizet et al.³³ and synthesized
115 under high-pressure conditions (at identical pressure conditions) and for which I speciation
116 has been fully determined using XPS measurements. For the first time, the atomic distances
117 and coordination number to first and second next nearest neighbors have been determined for
118 iodate species dissolved in aluminoborosilicate glasses. A discussion on the I-bearing glass
119 chemical durability based on the I speciation and atomic environment is also proposed.

120

121 **II. EXPERIMENTAL**

122 **A. Sample dataset**

123 As described in Morizet et al.³³ the samples consist in clear brownish glasses synthesized
124 under high-pressure conditions (1.5 GPa) and high-temperature (1400°C) and using different
125 source of iodine (i.e. I₂ and I₂O₅) leading to different iodine dissolution mechanisms. The
126 investigated glass compositions are aluminoborosilicate glasses prepared in the B₂O₃-SiO₂-
127 Al₂O₃-CaO-Na₂O system. The description for glass synthesis is reported in the subsequent
128 work³³; however, we provide in Suppl. Mat. the reported glass compositions studied here: ~32
129 mol.% SiO₂, ~30 mol.% B₂O₃, 5 mol.% Al₂O₃ and ~35 mol.% CaO + Na₂O. In the
130 investigated glasses, CaO and Na₂O are exchanged on a mole-to-mole basis, keeping the
131 oxygen concentration constant. For instance, C₃₅N₀ stands for a glass without Na and C₀N₃₅
132 stands for a glass without Ca. The investigated samples were fully characterized and
133 especially the iodine solubility and speciation. X-ray Photoelectron Spectroscopy (XPS)
134 revealed that 1) iodine is mostly dissolved under its iodide form (I⁻) in the CN-1 glass series,
135 2) iodine is mostly dissolved under its iodate form (I⁵⁺) in the CN-2 and CN-3 glass series and
136 3) iodine is also present under its periodate form (I⁷⁺) in CN-3 glass series, however, this
137 latter species appeared not to be stable under the X-ray beam during XPS analyses. Most of
138 the samples reported in Morizet et al.³³ (see Table 1) were analyzed using XAS in conjunction
139 with previously published XPS results to determine the local atomic environment (distance
140 and coordination number to next nearest neighbor that is not reachable with XPS
141 investigation) of the different iodine species dissolved in glasses.

142 In addition, crystalline compounds were also studied in order to conduct the fingerprinting for
143 the interpretation of the XAS spectra for I-bearing glasses. Iodides (NaI and CaI₂), iodate
144 (NaIO₃, CaI₂O₆), periodate (NaIO₄), I₂ and I₂O₅. Unfortunately, calcium periodate (CaI₂O₈)
145 could not be acquired. Iodides are highly hygroscopic; hence, it is suspected that iodide have
146 altered to an hydrated form as also pointed out in previous works¹⁷.

147

148 **B. X-ray Absorption Spectroscopy at the Iodine K-edge**

149 X-ray Absorption Spectroscopy was conducted on the glass and crystalline samples at the I K-
150 edge on SAMBA beamline at SOLEIL synchrotron facility operating with a current of 500
151 mA and 2.75 GeV⁴⁸. We acquired the XAS spectra in both the X-ray Absorption Near-Edge
152 Spectroscopy (XANES) and Extended X-Ray Absorption Fine Structure (EXAFS) regions.
153 XAS acquisitions at the I K-edge (~33169 eV) were preferred instead of the I L₃-edge (~4557
154 eV) as in Morizet et al.³⁶ owing to the possible interferences provoked by the Ca K-edge line
155 at ~4038 eV. The energy calibration was performed using a Sb reference foil with a first
156 derivative absorption edge at 30491 eV. Spectrum acquisition was performed in transmission
157 mode. Acquisitions were made in continuous scan mode from 200 eV below the iodine
158 absorption edge (~33175 eV) up to 820 eV above the iodine absorption with a 0.5 eV energy
159 step. The counting time on each point is 0.1 s. To obtain a suitable signal to noise ratio (S/N),
160 at least 5 scans were acquired, however, at the lowest iodine content (CN-1 glass series) we
161 had to collect more than 10 scans. Even using a cautious protocol, the obtained EXAFS signal
162 for CN-1 samples remains weak in comparison to the EXAFS signal obtained for the glasses
163 with the highest iodine content (CN-2 and CN-3 glass series). For crystalline compounds,
164 only 3 scans were necessary for obtaining a suitable S/N. One scan recording time sums up to
165 204 s.

166 The glass powder was crushed, mixed with graphite powder, and pressed as a 6 mm in
167 diameter pellet. We did not weight the mass of glass embedded in the pellet. The beam size is
168 estimated to be 0.49 x 2.76 mm² that focuses on the sample pellet using two cylindrical mirror
169 with a tilt angle of 1 mrad. The different ionization chambers were filled with Ar at 1000
170 mbar absolute pressure. Considering that some iodine species lack stability under an X-ray
171 beam (i.e. I⁷⁺), each spectrum was recorded at 20 K under liquid helium cryostatic conditions.

172

173 C. X-ray Absorption Spectroscopy spectral treatment

174 The normalization and data treatment were performed using Athena software package⁴⁹.
175 EXAFS signals were simulated using Artemis software package⁴⁹. We employed the
176 fingerprinting method for discussing the change in the XANES spectra in between the glass
177 series. The EXAFS spectra were fitted using the scattering equation and standard crystalline
178 structure obtained from the Crystallography Open Database (COD, see Vaitkus et al.⁵⁰ and
179 references therein). Prior to the simulation of the EXAFS spectra for I-bearing glasses we
180 determined the scattering amplitude (S_0^2) and the correction for the edge position (ΔE_0)^{36 51}.
181 We used the spectra obtained on crystalline NaIO₃ and the corresponding NaIO₃ structure
182 from the COD and with a space group *Pbnm*. We derived an $S_0^2 = 0.909$ and $\Delta E_0 = 6.90$ eV.
183 The glass EXAFS spectra were fitted using several single scattering paths in agreement with
184 the observation made from XPS results. For instance, in the CN-2 and CN-3 glass series, the
185 first neighbor to iodine atoms are mostly oxygen in agreement with the iodate local
186 environment determined by XPS. Hence, we used the single scattering path between I and O
187 from either NaIO₃ or CaI₂O₆ structures. However, iodide species have also been identified and
188 in that case the first nearest neighbor to iodine atoms (as I⁻) is either Ca²⁺ or Na⁺ forming Ca-I
189 and Na-I local environment, respectively. For iodide the distance to first neighbor is on the
190 order of 3 Å as shown in previous works^{17 36}. This distance is comparable to the distance to
191 second nearest neighbor for iodate structure ($r_{\text{Na-I}} = 3.52$ Å in NaIO₃). Hence, a single
192 scattering for Na and Ca is added for simulating either the first nearest neighbor in the case of
193 iodide or the second nearest neighbor in the case of iodate local environments for CN-2 and
194 CN-3 glass series. Periodate species were identified in the case of C₃₅N₀-33 implying that the
195 first nearest neighbor to iodine atoms is oxygen and the second nearest neighbor is calcium
196 and the single scattering paths were chosen accordingly. The simulation of the CN-1 glass
197 series EXAFS spectra was more complicated owing to the short EXAFS signal in k-space in

198 addition to the lower I content measured in these glasses. However, previous investigations
199 showed that in the case of iodide, the first nearest neighbor in local environment to iodine
200 atoms is either Ca^{2+} or $\text{Na}^{+17\ 36}$. As a result, we used I to Na and I to Ca paths for the
201 simulation of iodide local environments in CN-1 glasses. We show that the sole use of those
202 paths is not sufficient for fully reproducing the EXAFS spectra and single scattering path I to
203 O is required. It is in favor of the possible presence of iodate species (not identified by XPS)
204 that could result from sample oxidation through time. Furthermore, the scattering path from I
205 to I for I_2 species was required for a reliable simulation of the EXAFS signal for $\text{C}_{35}\text{N}_0-1$. The
206 use of single scattering path from I to I for I_2 species is justified by the identified presence of
207 I^0 species by XPS measurements (see Table 1). However, we did not use systematically the
208 scattering path for I_2 species, even though it was identified via XPS measurements in Morizet
209 et al.³³, as the addition of the I_2 single scattering path to the simulation did not significantly
210 improve the result of the fit.

211 Simulations were conducted with the following protocol to obtain 1) the coordination number
212 ($\text{CN}_{\text{I-X}}$), 2) the distance to the atom counterpart ($r_{\text{I-X}}$) and 3) the Debye-Waller factor ($\sigma_{\text{I-X}}$).
213 The coordination number initialization was set as follow: the $\text{CN}_{\text{I-O}}$, $\text{CN}_{\text{I-Na}}$, $\text{CN}_{\text{I-Ca}}$ and $\text{CN}_{\text{I-I}}$
214 are 3, 4, 2 and 1, respectively. The coordination number for Na and Ca is consistent with the
215 results reported in previous XAS investigations^{17 36}. We applied a $\text{CN}_{\text{I-O}} = 3$ in agreement
216 with the local environment for iodate species, nonetheless we apply the same $\text{CN}_{\text{I-O}}$ for C_{35}N_0-
217 33 in which periodate species have been identified and would therefore require a $\text{CN}_{\text{I-O}} = 4$. In
218 detail, we will show and discuss the fact that the distinction between IO_3^- and IO_4^- is
219 impossible using the EXAFS signal. The Debye-Waller factor was initially set to 0.003 for
220 each path. The distance to first neighbor was set at the standard distance of each
221 crystallographic structure: $r_{\text{I-O}} = 1.79 \text{ \AA}$ from NaIO_3 , $r_{\text{I-Na}} = 3.27 \text{ \AA}$ from NaI , $r_{\text{I-Ca}} = 3.12 \text{ \AA}$
222 from CaI_2 and $r_{\text{I-I}} = 3.54 \text{ \AA}$ from I_2 . The first parameter to be optimized is the distance

223 between iodine atoms and the nearest neighbor (r_{I-X}) for the whole set of scattering paths, then
224 followed by the optimization of the coordination number between iodine atoms and the
225 nearest neighbor (CN_{I-X}) for the whole set of scattering paths. These optimizations are
226 repeated three times, and then the Debye-Waller factors (σ_{I-X}) are optimized. In the final
227 round, the three parameters are successively optimized. In the case that the optimization is not
228 entirely successful, the optimization of the three sets of parameters is conducted again to
229 reach an acceptable fit (i.e. based on r^2 value). We should point out that the proposed
230 simulations are one possible solution amongst others.

231

232 **III. RESULTS AND DISCUSSION**

233 **A. I K-edge XANES**

234 We show the XANES spectra obtained at the I K-edge for crystalline compounds in Figure 1.
235 The spectra are shown in increasing order of oxidation state from reduced (-1 for NaI and
236 CaI_2) to intermediate oxidation state (0 for I_2 , +5 for I_2O_5 , $NaIO_3$ and CaI_2O_6) to high
237 oxidation state (+7 for $NaIO_4$). We observe that reduced crystalline compounds (NaI , CaI_2
238 and I_2) are relatively featureless in comparison to oxidized crystalline standards (I_2O_5 and
239 $NaIO_3$), which have an obvious post-edge structure. The XANES spectra observed for NaI ,
240 CaI_2 and I_2 are consistent with previous works^{17 30 35 52}. Strangely, oxidized standards do not
241 show the same spectrum line shape. For instance, $NaIO_3$ and I_2O_5 exhibit a strong peak
242 located at 33178 eV whereas it is not visible for $NaIO_4$ and CaI_2O_6 . This peak is also reported
243 in previous studies for oxidized iodate compounds^{17 35 39}. Although to our knowledge XANES
244 spectra for $NaIO_4$ have never been published, we believe that $NaIO_4$ and CaI_2O_6 have
245 probably quickly destabilized prior to the XAS acquisition. Using the edge first derivative did
246 not show a systematic change as a function of the redox state of the crystalline standard.

247 Nonetheless, the distinction between reduced and oxidized iodine local environment can be
248 made.

249 The XANES spectra obtained for the three series of glasses are shown in Figure 2: Figure 2A
250 for CN-1, Figure 2B and C for CN-2 and 3, respectively. The iodine speciation expressed as
251 the molar fraction of I^{5+} is also reported. When comparing XANES spectra with those of the
252 reference compounds, samples of the CN-1 series contain predominantly I^- and samples of the
253 CN-2 and CN-3 series contain mainly IO_3^- . The spectra for CN-2 and CN-3 glass series
254 exhibit a strong feature at ~ 33178 eV that is also observed for crystalline $NaIO_3$ and I_2O_5 (see
255 Figure 1). The featureless aspect of the CN-1 glass series spectra is consistent with the spectra
256 recorded for NaI and CaI_2 . We do not observe any difference in between the spectrum
257 obtained for $C_{35}N_0-2$ and the spectrum obtained for $C_{35}N_0-33$. It is rather surprising
258 considering that the $C_{35}N_0-33$ glass contains periodate species (I^{7+}) suspected to be
259 surrounded by four oxygen atoms to form IO_4^- units. We expected a slight change in the
260 spectrum line shape with the appearance of I^{7+} species. In between the glass compositions we
261 do not observe any change in the main line, edge position or post-edge peak positions
262 suggesting that the iodine local environment is similar for the glass compositions explored
263 here. The position of the main line for CN-2 and CN-3 glass series ranges from 33178.3 to
264 33179.3 eV. The position of the edge ranges from 33173.6 to 33177.6 eV but does not exhibit
265 systematic change as function of the glass XNa or I content. To a first level of knowledge, the
266 I K-edge XANES spectra can be used to determine the iodine oxidation state in glasses, for
267 instance using linear combination analyses with spectra of model compounds^{36 53}; however,
268 this approach appears relatively inaccurate in determining the iodine speciation dissolved in
269 glasses using model spectra from crystalline compounds (see Morizet et al.³⁶).

270

271 **B. I K-edge EXAFS**

272 The EXAFS amplitude of the pseudo Radial Distribution Function (RDF) for crystalline
273 standards is shown in Figure 3. This amplitude was obtained from the Fourier transforms of
274 the oscillatory k^2 -weighted. Again, we categorize the spectra with increasing oxidation state
275 from reduced compounds (NaI and CaI_2) to oxidized ones (NaIO_3 , CaI_2O_6 and NaIO_4). The
276 most intense peak on the RDF spectra represents the signature of the first neighbor to iodine.
277 The indicated values correspond to the apparent peak maximum and not to the actual distance
278 between I atom and its nearest neighbor owing to the mathematical form of the Fourier
279 transform. The actual distance between I atom and its first neighbor is obtained by addition of
280 $\sim 0.5 \text{ \AA}$. Nonetheless, we observe that the distance to the iodine first neighbor is shorter in the
281 case of iodate and periodate than in iodide. This is consistent with the standard crystalline
282 structure with $r_{\text{I-O}} \approx 1.8 \text{ \AA}$ in iodates and periodates, with $r_{\text{I-Na or Ca}} \approx 3.2 \text{ \AA}$ in iodides. We also
283 observe a strong signal above 4 \AA in NaI spectrum which could correspond to a potential
284 hydration of the crystalline powder as inferred earlier and asserted in previous works¹⁷.

285 The k -space data for investigated glasses are shown in Figure 4 and categorized as a function
286 composition: Figure 4A for C_{35} , Figure 4C for C_{20} and Figure 4E for C_0 glass compositions.
287 The oscillatory spectra represent the $k^2\chi(k)$ data treated by Fourier transform of the EXAFS
288 signal up to $\sim 800 \text{ eV}$ above the edge position leading to a wavenumber extending up to 14 \AA^{-1}
289 in the k -space. It should be emphasized that an identical treatment was applied to all spectra
290 for adequate comparison.

291 The first striking observation in Figure 4 is that the S/N is far better for glasses from the CN-2
292 and CN-3 series than for the CN-1 series. Currently, we do not have a clear explanation for
293 that and we only have hypotheses. In Figure 4A, the S/N of the spectra is changing for almost
294 an identical I content suggesting that the total I in mol.% is not responsible for the lower S/N
295 in the CN-1 glass series. Although, we did not weigh the sample mass powder introduced to
296 the pellet, we suspect that the lower S/N is ascribed to a lower quantity of CN-1 glass

297 powders introduced in the pellet. Nevertheless, in order to be comparable we considered a
298 constant k range for all the samples from 3 to 12 \AA^{-1} to obtain the RDF spectra.

299 The second observation is that the k -space signal observed for CN-2 and CN-3 glasses
300 appears almost identical. For these glass series, the k space signal is also comparable in
301 between the glass compositions. These two features are anticipated owing to the comparable
302 identified iodine speciation measured in those glasses. On the contrary, the k space signal is
303 different (i.e. shifted phase in comparison to CN-2 and CN-3) for glasses obtained in the CN-
304 1 series. Again, this aspect is due to the change in iodine speciation. The glass corresponding
305 RDF is provided in Figure 4B, D and F for the same glass compositions and with the iodine
306 reported as the molar fraction of iodate species (XI^{5+}). The glasses with iodate identified as
307 the main iodine species (CN-2 and CN-3) exhibit a strong signal at short distance in the RDF
308 ($\sim 1.3 \text{ \AA}$) whereas the glasses with iodide identified as the main iodine species (CN-1) seem to
309 have their first neighbor signal at longer distance at $\sim 2.6 \text{ \AA}$. For this later glass series, we also
310 observe the presence of additional peaks at lower distance (especially visible for $\text{C}_0\text{N}_{35-11}$)
311 which could be ascribed to the presence of iodine species with a local environment close to
312 the one observed for iodate environments. The presence of more oxidized iodine local
313 environments (i.e. iodate) in $\text{C}_0\text{N}_{35-11}$ glass have not been shown from the XPS
314 measurements in Morizet et al.³³. One possible explanation for the presence of oxidized
315 species could be a possible slight alteration of the iodine speciation through time of $\text{C}_0\text{N}_{35-11}$
316 samples. Another hypothesis is that the XPS measurements from Morizet et al.³³ failed to
317 identify the presence of iodate species in $\text{C}_0\text{N}_{35-11}$ sample within the bulk of the glass.

318 The fitting of the EXAFS data is shown in Figure 5 for four different glass compositions:
319 C_{35}N_0 , C_{30}N_5 , $\text{C}_{20}\text{N}_{15}$ and C_0N_{35} . The RDF has been fitted following the protocol described in
320 the experimental section and the entire set of fit can be found in the Suppl. Mat. We show the
321 fit of the RDF of the magnitude along with the fit of the imaginary part of the RDF. The

322 derived distances (r_{I-X}), coordination number (CN_{I-X}) and Debye-Waller factor (σ_{I-X}) are also
323 reported and the whole set of derived parameters are given in Table 1. The reported error bars
324 on the distances and coordination numbers are obtained from Artemis software package⁴⁹. As
325 can be seen in Figure 5 the RDF region fitted is dependent on the glass series. For instance,
326 the CN-2 and CN-3 glasses were fitted between 1 and 3 Å; whereas the fitted RDF region is
327 extending up to 3.5 Å for the CN-1 glasses. Clearly, it can be seen that the fit quality obtained
328 for the CN-2 and CN-3 glasses is far better than for the CN-1 glass. This is explained by the
329 fact that the EXAFS signal quality in k-space shown in Figure 4 has an excellent S/N in CN-2
330 and CN-3 in comparison to CN-1.

331 The derived data (r_{I-X} and CN_{I-X} from Table 1) are plotted in Figure 6 as a function of iodine
332 content in mol.%. For clarity, the error on the I content is not reported, however, it has been
333 quantified at ± 0.1 mol.%³³. The change in the r_{I-X} distances is shown in Figure 6A for the
334 whole glass series. Regardless of the glass composition and glass series, the distance between
335 iodine atoms and first nearest oxygen in the iodate configuration is on average constant at r_{I-O}
336 = 1.79 ± 0.01 Å which compares adequately to the r_{I-O} distance observed in crystalline iodates
337 ($r_{I-O} \approx 1.8$ Å). The distinction between iodate and periodate species is not possible on the sole
338 criterion of the first neighbor distance. The distance to either the second nearest neighbor for
339 iodate and periodate or the first nearest neighbor for iodide is also roughly constant for Na
340 and Ca with r_{Na-I} and r_{Ca-I} at $\sim 3.18 \pm 0.06$ and $\sim 3.20 \pm 0.12$, respectively. These distances also
341 compare adequately with the equivalent distance in crystalline compounds at ~ 3.2 Å. Like for
342 the r_{I-O} , from the derived data plotted in Figure 6A we cannot make the distinction between
343 the first and second nearest neighbor configuration in iodate (or periodate) and iodide.

344 Whereas the change in the first neighbor distance can be plotted for the whole set of glass
345 series, we could not plot the change in the coordination number for the CN-1 glasses due to
346 the important scatter in the derived coordination number (see Table 1). For example, the CN_{I-}

347 CN_{Na} ranges from 2.2 ± 0.4 to 4.1 ± 1.3 and $\text{CN}_{\text{I-Ca}}$ ranges from 0.8 ± 0.3 to 1.9 ± 0.2 . Although there
348 is a large dispersion in the derived $\text{CN}_{\text{I-Na}}$ or Ca values, we observe that the $\text{CN}_{\text{I-Na}}$ is
349 systematically higher than the $\text{CN}_{\text{I-Ca}}$, probably because of the lower positive charges on
350 sodium. Comparable results have been found in Morizet et al.³⁶ for glasses of different
351 compositions demonstrating that I requires more charge compensating cations in its
352 surrounding in the case of Na^+ rather than Ca^{2+} . Invariably, the iodine coordination to oxygen
353 in iodate configuration is close to 3 with $\text{CN}_{\text{I-O}} = 3.0 \pm 0.2$ in adequate comparison to the
354 structure of crystalline iodate. However, the distinction between iodate and periodate
355 configuration seems unachievable using EXAFS and the distinction must be combined to
356 another analytical technique such as the XPS method. Surprisingly, we derived a lower
357 coordination between I and the second coordination sphere with Ca and Na in the case of
358 $\text{C}_{35}\text{N}_{0-2}$ and $\text{C}_0\text{N}_{35-2}$. For instance the $\text{CN}_{\text{Na-I}}$ strongly drops from 2.8 to 0.8 between $\text{C}_{20}\text{N}_{15-2}$
359 and $\text{C}_0\text{N}_{35-2}$ (see Table 1). The $\text{CN}_{\text{Ca-I}}$ decrease is less pronounced between $\text{C}_{30}\text{N}_{5-2}$ and
360 $\text{C}_{35}\text{N}_{0-2}$: from 1.9 to 1.2. One possible explanation to this peculiar result is that in the case of
361 both, the Ca and the Na free glass samples, there is no mixed alkali effect⁵⁴ that could induce
362 an aggregation of Na^+ cations forming a Na-rich area. Instead Na^+ are fully dispersed
363 throughout the glass structure. As a result, the solution mechanism for IO_3^- and the average
364 repartition of Na^+ cations does not allow the clustering of several Na^+ surrounding IO_3^- .

365 Whereas XPS is able to investigate the actual iodine speciation from the qualitative and
366 quantitative point of view based on a surface analyses (only a few nm depth), the EXAFS is
367 able to probe in depth the atomic structure and the iodine local environment at the Å scale.
368 Both types of information are required for improving our current knowledge on the iodine
369 dissolution mechanisms into the borosilicate glass matrix with the purpose of building a
370 specific matrix for the immobilization of ^{129}I radioisotopes.

371

372 **C. Structural model for iodine solution in glasses: Insight into the I-bearing glass**
373 **durability**

374 Recently, strong efforts have been made to constrain the iodine solution mechanism in
375 borosilicate glass matrices^{14 17 16 30 31 32 33 34 35 36}. The main objective is to propose a
376 formulation of a specific glass composition in which iodine can be dissolved in large quantity
377 and that is stable. The question of the I-bearing glass chemical durability is currently weakly
378 addressed and only recent work⁵⁵ has focused on the release of iodine from a borosilicate
379 glass matrix through leaching experiments by aqueous solution. This information is essential
380 considering the issue on the ¹²⁹I radioisotopes in the environment and for safety assessment⁴⁶.

381 On the basis of the results obtained from EXAFS simulations, we have constructed a
382 schematic view of the local environment of iodine atoms in the case of pure sodic glass
383 composition (C₀N₃₅) in Figure 7: in iodide configuration (Figure 7A) and iodate configuration
384 (Figure 7B). The common feature in between the two molecular configuration is the distance
385 to the positive charge compensator that is on the order of 3.2 Å (i.e. it applies to all glass
386 compositions whether it is Na⁺ or Ca²⁺). As described earlier, the local environment of iodine
387 for iodate species is the surrounding of 3 oxygen atoms at a distance of 1.8 Å. The same
388 applies to the mixed Ca-Na or pure Ca glass compositions. As discussed above, C₀N₃₅₋₂
389 represents a particular case as a single Na⁺ is requested for the charge compensation of the
390 IO₃⁻ cluster; which we attribute to the absence of mixed alkali effect.

391 Addressing the glass durability is not trivial considering the many involved mechanisms:
392 diffusion rate, ion exchange, structural bond strength and hydration free energy⁵⁶. As recently
393 mentioned by Abdelouas et al.⁵⁷, it is difficult to predict the corrosion for glasses with
394 multicomponent composition, as is our case. Moreover, if recent work by Zhang et al.⁵⁵
395 quantified the release of iodine dissolved as iodide (I⁻) in strongly polymerized borosilicate
396 glasses (i.e. International Simple Glass²⁴), the question of the iodine release remains open in

397 the case of iodine dissolved as iodate (IO_3^-) and for depolymerized borosilicate glass
398 compositions such as the CN glass series. Consequently, specific experiments must be
399 conducted to answer these points.

400 The glass chemical durability is strongly influenced by the concentration of network
401 modifying cation: the glass durability decreases with increasing concentration of network
402 modifying cation⁵⁷. However, the nature of the network modifying cation itself has an impact
403 on the glass durability. For instance, the Na_2O -bearing glass durability is increased in the case
404 Na_2O is accompanied by divalent cations such as CaO ⁵⁷. In the present study, regardless of
405 the alteration conditions (i.e. inherent to environmental conditions), it implies that
406 compositions such as $\text{C}_{10}\text{N}_{25}$ or $\text{C}_{20}\text{N}_{15}$ are likely to have a better resistance to alteration than
407 C_0N_{35} . This is probably ascribed to the mixed alkali or alkaline-earth effect in which Na^+ and
408 Ca^{2+} are mixing together to obtain a more stable glass configuration and both cations are
409 charge compensating the negative charges carried by the Non-Bridging Oxygens (NBOs) of
410 the glass network^{54 58}.

411 The present investigated CN glass composition are strongly enriched with respect to alkali or
412 alkaline-earth (~35 mol.%) and are rather silica-poor (<35 mol.%). Hence, these glass
413 compositions are likely to alter quickly upon leaching experiments and therefore do not
414 represent fully adequate candidates for the ^{129}I immobilization in a durable manner. More
415 suitable glass formulation is required, for instance with less network modifying cation and
416 less B_2O_3 . However, the possible glass corrosion by H^+ forming SiOH molecular groups is
417 questionable. The CN glass composition is depolymerized in nature owing to the high
418 network modifying cation concentration. It implies a high NBOs concentration. As a result,
419 the mechanism to form SiOH groups and involving Si-O-Si bond is probably reduced owing
420 to the strong depolymerization nature of the glass composition.

421 Nevertheless, because iodine dissolution is likely to induce a slight polymerization as
422 suggested in previous works^{33 34 36}; therefore Si-O-Si bonds are formed because of the Na⁺
423 consumed for iodine species charge compensation. In that case, the hydrolysis of Si-O-Si by
424 H⁺ to form SiOH groups is therefore possible. So far, there is only one study that addressed
425 the iodine release from I-bearing aluminoborosilicate glasses from Zhang et al.⁵⁵. Further
426 work is currently required to address the iodine release from aluminoborosilicate glasses
427 under various configurations and with different glass compositions: from iodide to iodate,
428 with various network modifying cations and in glasses with different degrees of
429 polymerization. In addition, alteration under different regime: solution temperature and
430 solution pH, has to be conducted for investigating the stability of iodine species⁷.

431

432 **IV. CONCLUSIONS**

433 In the present work, we have investigated the local atomic environment around iodine
434 dissolved in glasses using XAS. For a series of aluminoborosilicate glasses synthesized under
435 pressure and having different iodine content (up to 6 mol.%) and different iodine speciation
436 (ranging from I⁻ to I⁷⁺) we have determined the distance between iodine atom and its first
437 nearest neighbor and its coordination number.

438 In particular, we provide the first structural data for iodine dissolved in glasses as iodate.

439 Iodate clusters show the expected local structure with 3 neighboring oxygen atoms and at a
440 distance of ~1.8 Å surrounding the I⁵⁺ cation forming IO₃⁻. At longer distance Na⁺ and Ca²⁺
441 are the charge compensating the negative charge of the IO₃⁻ unit with an average of ~3 Na⁺
442 and 1.5 Ca²⁺ cation surrounding the IO₃⁻ cluster.

443

444 **SUPPLEMENTARY MATERIAL**

445 See Supplementary Material for the investigated glass compositions and the fit to I K-edge
446 EXAFS data.

447

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456

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556

557 **FIGURE CAPTION**

558 Figure 1: I K-edge XANES spectra obtained for crystalline standard compounds. The spectra
559 are stacked from the most reduced (i.e. iodide with I⁻ oxidation state) to the more oxidized
560 (periodate with I⁷⁺ oxidation state).

561 Figure 2: I K-edge XANES spectra obtained for the I-bearing CN glasses studied in Morizet
562 et al.³³ The spectra are categorized on the basis of the iodine speciation from XPS
563 measurements: CN-1 with iodide (I⁻) as the main species, Figure 2A; CN-2 with iodate (I⁵⁺) as
564 the main species, Figure 2B; and CN-3 with iodate as the main species but also showing the
565 presence of periodate (I⁷⁺) in C₃₅N₀-33, Figure 2C.

566 Figure 3: Radial Distribution Function (RDF) obtained from k-space signal of the EXAFS
567 spectra for crystalline compounds. The spectra are shown from the most reduced (i.e. iodide

568 with I⁻ oxidation state) to the more oxidized (periodate with I⁷⁺ oxidation state). An indication
569 of the distance between iodine atoms and the first nearest neighbor is represented by the most
570 intense peak in the RDF spectrum.

571 Figure 4: k²-space signal obtained from the EXAFS spectra and the corresponding RDF
572 spectrum for glasses of different compositions: C₃₅N₀ (A and B), C₂₀N₁₅ (C and D), and C₀N₃₅
573 (E and F).

574 Figure 5: Results of the EXAFS fit for several glasses of different compositions and from
575 different series. The absolute amplitude fit ($|\chi(R)|$ in Å⁻³) is shown along with the fit of the
576 imaginary part ($|\chi(R) \text{Img}|$ in Å⁻³). The fitted region is also shown. The derived coordination
577 numbers (CN_{I-X}) and nearest neighbor distance (r_{I-X}) is also reported and also provided in
578 Table 1.

579 Figure 6: Change in the iodine to nearest neighbor (r_{I-X}, Figure 6A) and iodine coordination
580 number (CN_{I-X}, Figure 6B) as a function of iodine content. Data are shown as a function of
581 the glass category: CN-1, CN-2 and CN-3. Due to the large scatter obtained from the fit, the
582 coordination numbers obtained on CN-1 glass series is not shown. The reported error bars
583 (see Table 1) are the ones obtained from the fitting procedure using Artemis EXAFS fitting
584 package⁴⁹. For clarity, the error on the iodine content is not reported and is on the order ±0.1
585 mol.% as provided in Morizet et al.³³

586 Figure 7: Schematic representation of the local environment for iodine dissolution. We
587 propose a representation for Na-rich glass composition with iodide (I⁻) and iodate (IO₃⁻) local
588 environments in Figure 7A and B, respectively.

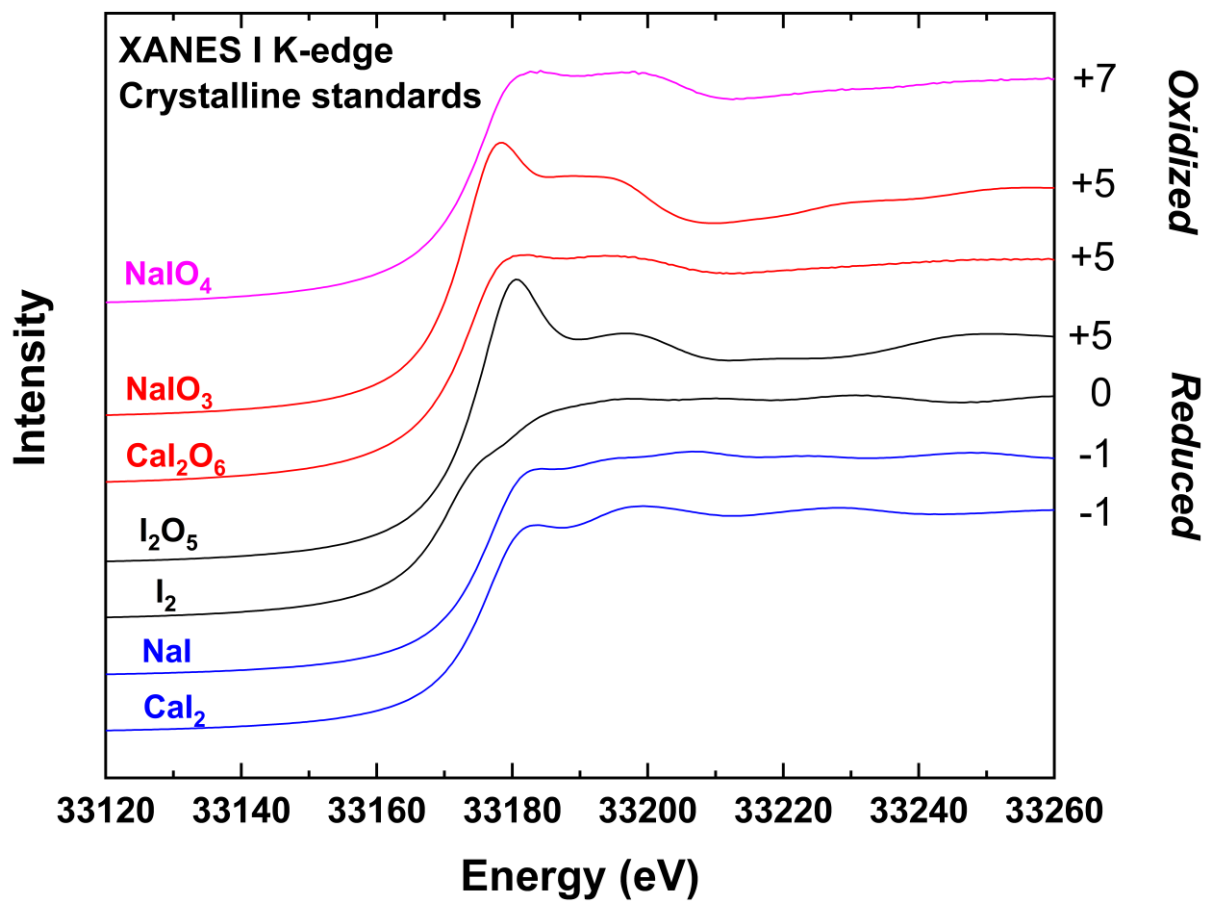
590 Table 1: I K-edge EXAFS fitting results (coordination number CN, distance r and Debye-Waller factor σ) for I-bearing glasses with different I
 591 speciation: I⁻ (CN-1), I⁵⁺ (CN-2 and CN-3) and I⁷⁺ (CN-3).

Sample ^a	I content (mol.%) ^a	I speciation ^a				Oxygen			Sodium			Calcium			Iodine		
		I ⁻	I ⁰	I ⁵⁺	I ⁷⁺	r_{I-O}	CN _{I-O}	σ_{I-O}	r_{I-Na}	CN _{I-Na}	σ_{I-Na}	r_{I-Ca}	CN _{I-Ca}	σ_{I-Ca}	r_{I-I}	CN _{I-I}	σ_{I-I}
C ₃₅ N ₀ -1	1.2	93.9	6.1	0		1.73(1) ^b	3.5(12)	0.087(11)				3.26(4)	1.9(2)	0.016(2)	2.80(1)	0.3(1)	0.004(2)
C ₂₀ N ₁₅ -1	0.5	94.1	5.9	0		1.79(2)	0.3(1)	0.003(2)	3.28(1)	2.9(4)	0.002(2)	3.24(1)	1.7(2)	0.008(1)			
C ₁₀ N ₂₅ -1	1.7	85.2	14.8	0		1.79(1)	0.4(1)	0.003(3)	3.19(1)	2.2(4)	0.006(3)	3.1(2)	0.8(3)	0.006(4)			
C ₀ N ₃₅ -11	3.9	96.0	0	4.0		1.79(1)	0.6(1)	0.002(2)	3.25(2)	4.1(13)	0.021(7)						
C ₃₅ N ₀ -2	1.3	28.8	12.7	58.6		1.81(0)	2.9(2)	0.002(1)				3.38(6)	1.2(7)	0.005(9)			
C ₃₀ N ₅ -2	2.0	14.5	0	85.5		1.80(0)	3.1(1)	0.002(1)	3.16(4)	3.6(6)	0.006(5)	3.10(4)	1.9(4)	0.006(5)			
C ₂₀ N ₁₅ -2	4.8	9.2	8.2	82.5		1.80(0)	3.3(1)	0.002(1)	3.14(6)	2.8(7)	0.008(4)	3.07(7)	1.5(5)	0.008(4)			
C ₀ N ₃₅ -2	5.7	21.5	1.3	77.2		1.81(0)	2.7(1)	0.002(1)	3.19(6)	0.8(6)	0.003(9)						
C ₃₅ N ₀ -33	1.3	14.5	4.3	51.0	30.3	1.80(0)	3.1(2)	0.002(1)				3.37(6)	0.9(9)	0.005(9)			
C ₂₀ N ₁₅ -3	2.5	28.5	0	71.5		1.80(0)	2.8(1)	0.000(0)	3.08(3)	3.6(6)	0.007(6)	3.16(3)	1.7(8)	0.006(6)			
C ₁₀ N ₂₅ -3	5.0	21.8	0	78.2		1.80(0)	3.2(1)	0.002(1)	3.14(4)	3.7(7)	0.008(3)	3.06(4)	2.0(4)	0.008(3)			

592 ^a The investigated samples were obtained from Morizet et al.³³. The I solubility data and I speciation obtained from XPS measurement are also reported.

593 ^b The figure between brackets corresponds to the standard error on the last digit reported after the fit by Artemis fitting package.

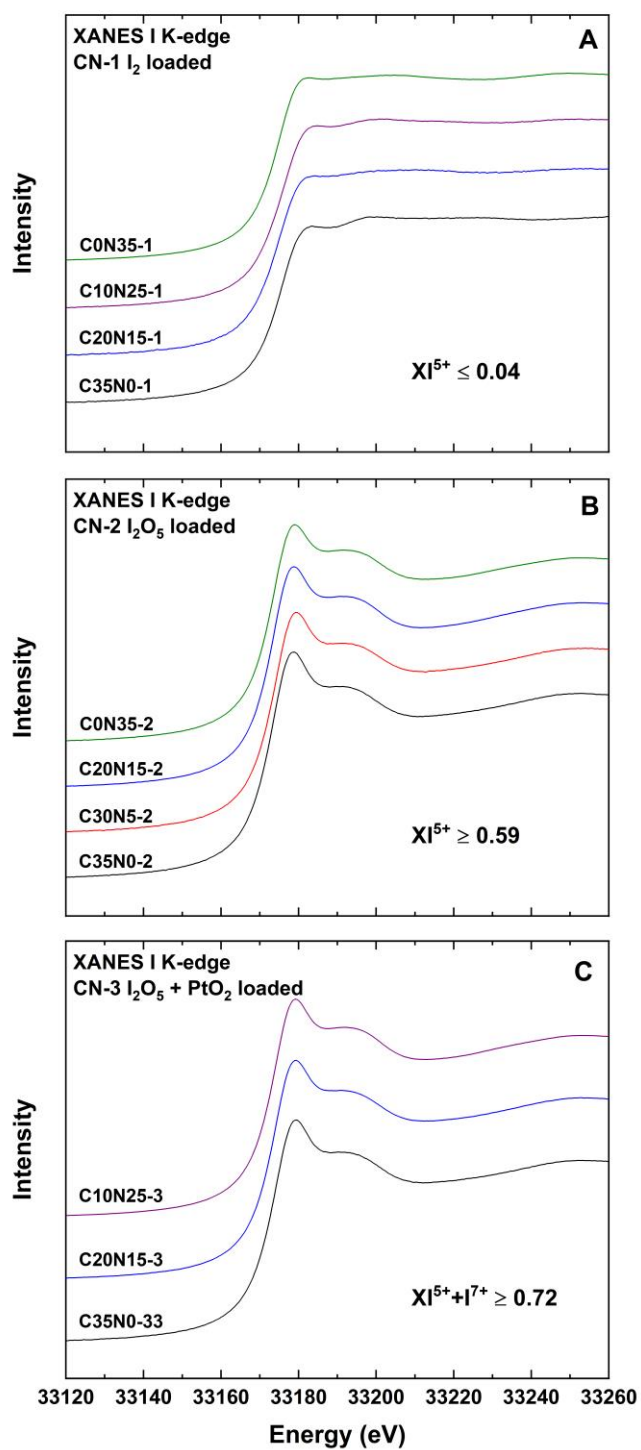
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597 Figure 1

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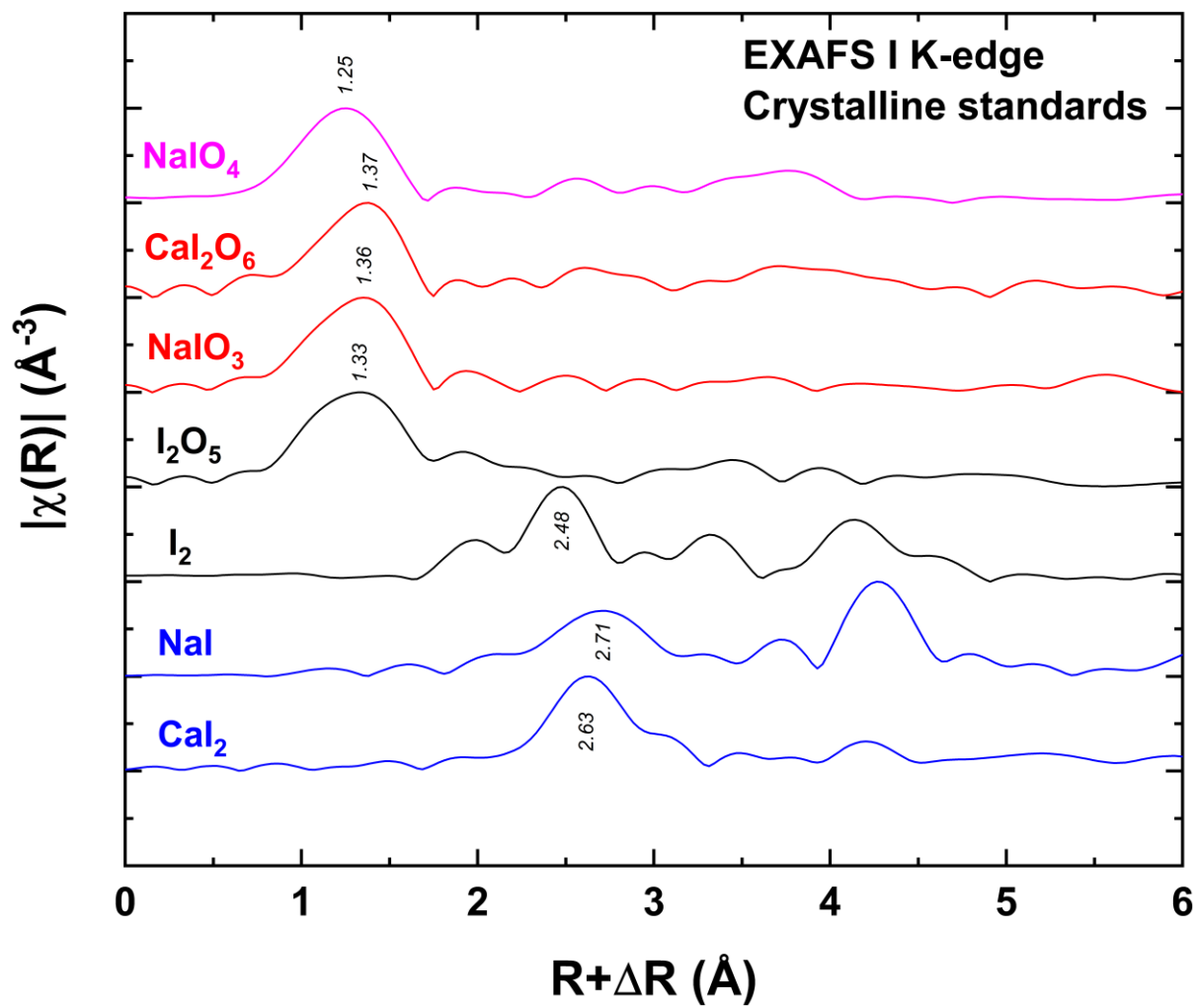


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601 Figure 2

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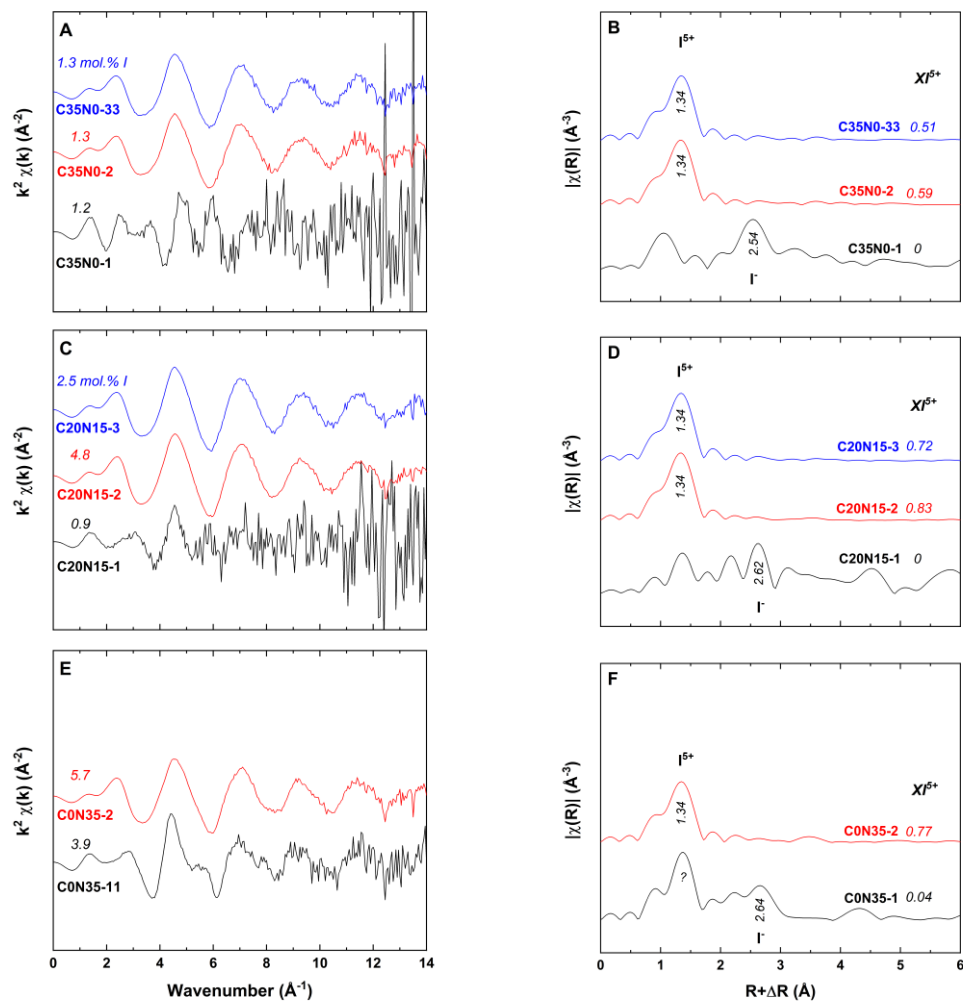
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605 Figure 3

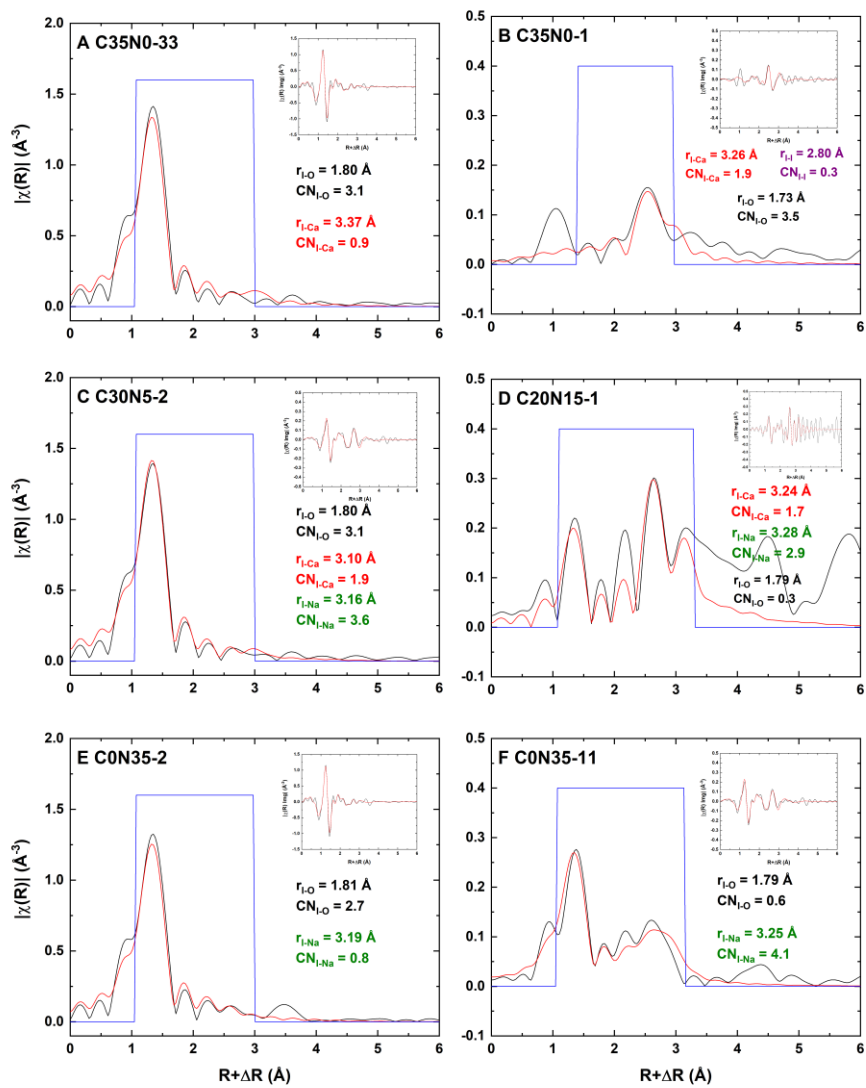
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609 Figure 4

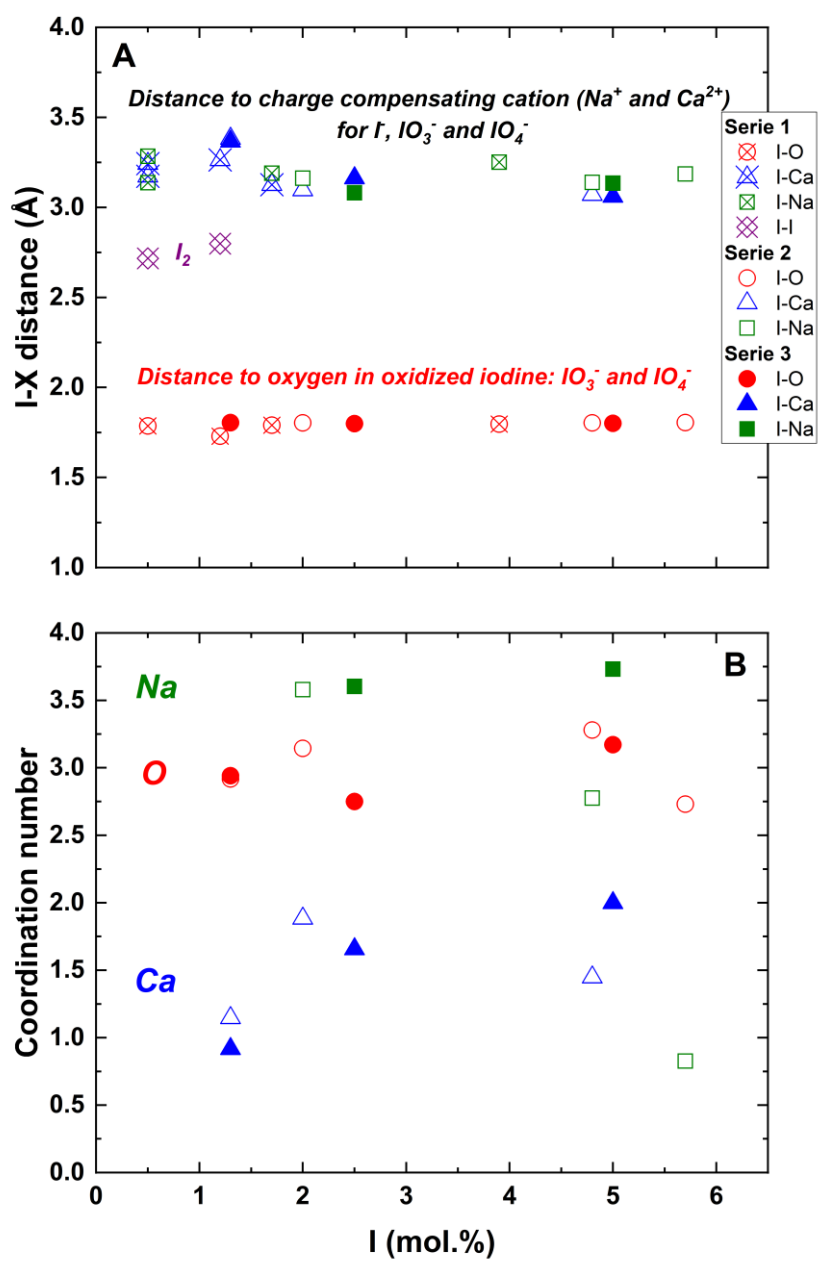
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613 Figure 5

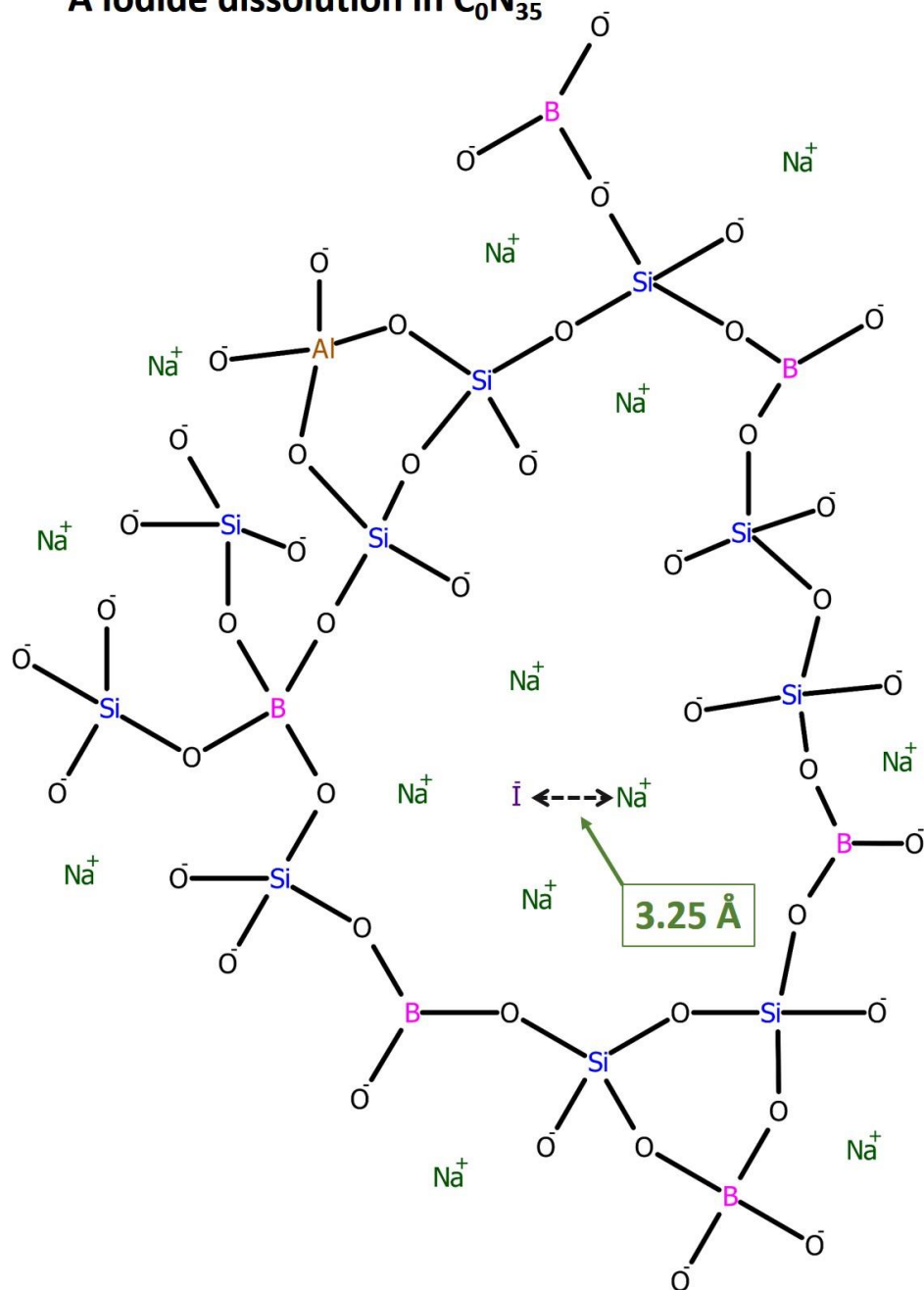
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617 Figure 6

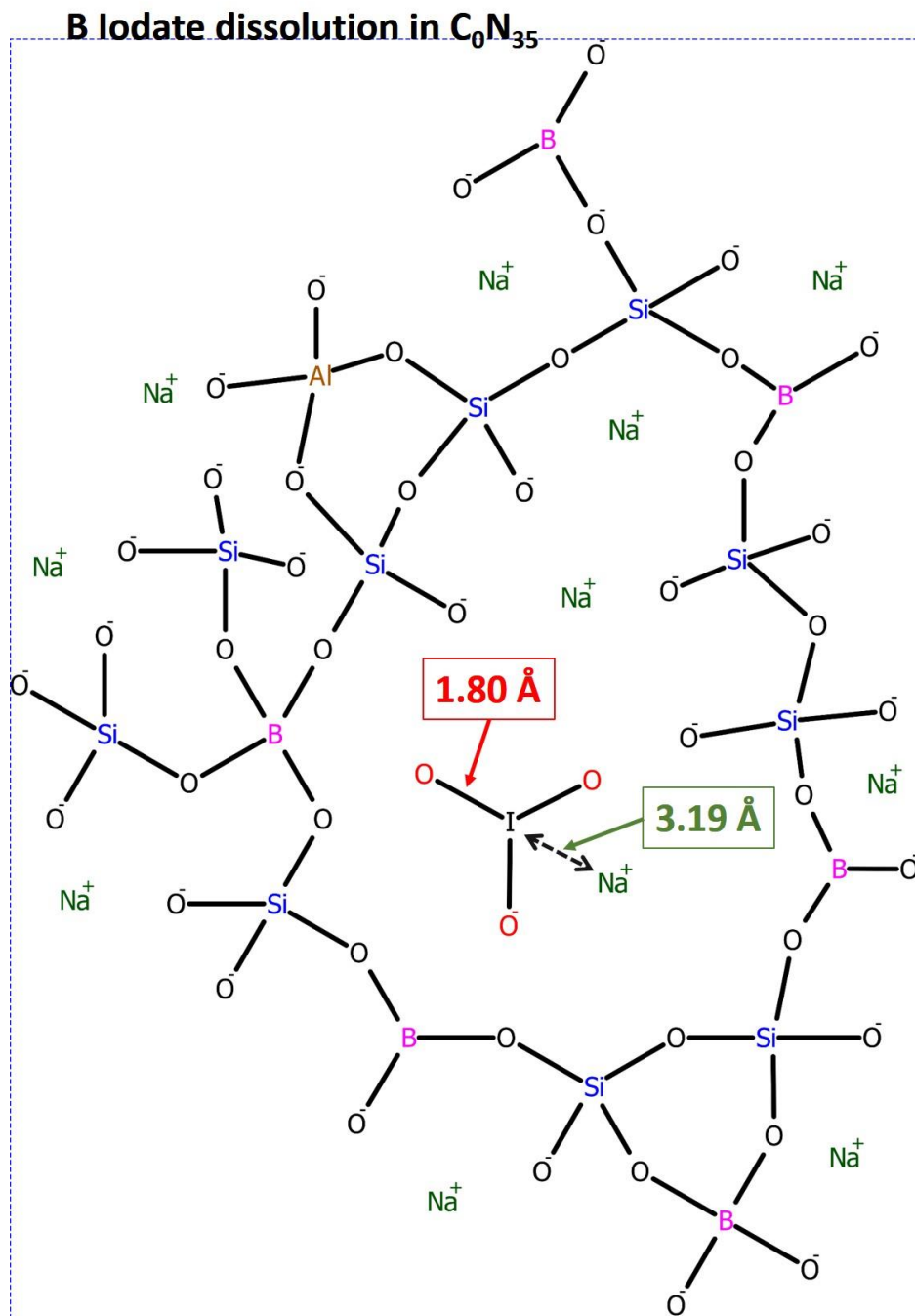
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A Iodide dissolution in C_0N_{35} 

620

621 Figure 7A

622



624

625 Figure 7B

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