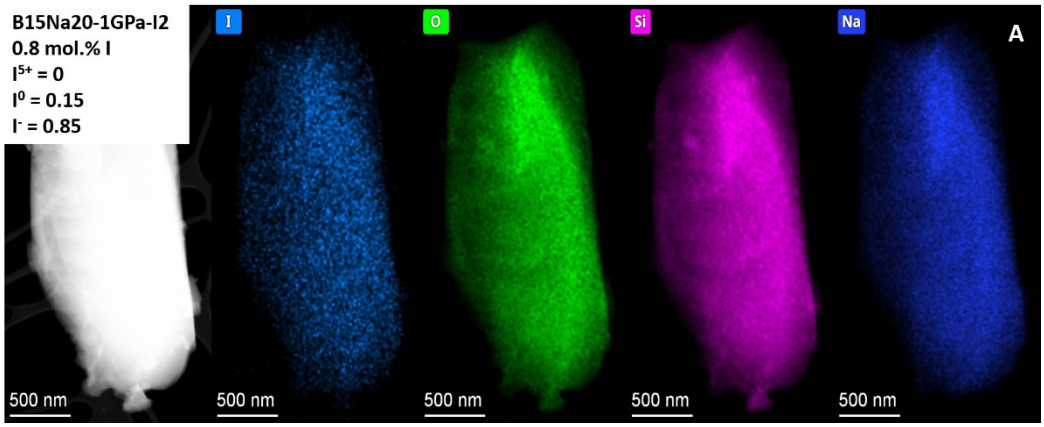
SUPPLEMENTARY MATERIAL: IODINE DISSOLUTION MECHANISMS IN HIGH-PRESSURE BOROSILICATE NUCLEAR WASTE GLASSES AND ITS RELATIONSHIP TO OXYGEN SPECIATION

Scanning/Transmission Electron Microscopy (S/TEM) acquisition in I-bearing glasses

In order to investigate the presence of nanoparticles or nm-size bubbles filled with I_2 fluid in the glasses, we also conducted Scanning/Transmission Electron Microscopy (S/TEM) at 80 kV on a Cs probe corrected Themis Z G3 (Thermo Fisher Scientific) using the High Angle Annular Dark Field (HAADF) detector (with 33-197° collection angle range) and the 4-SDD detectors (Super-X system) for EDS analysis. Samples were previously prepared by dispersing the grinded powder in ethanol and depositing a drop of this solution on a holey-carbon-coated copper grid.



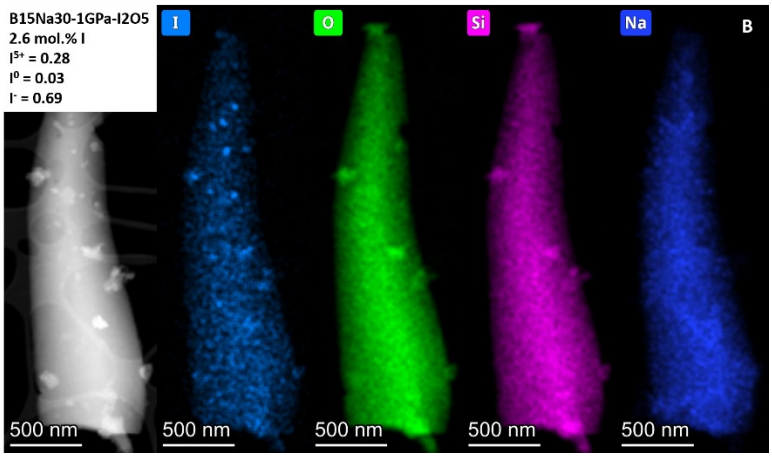


Figure S1: S/TEM element imaging for B15Na20-1GPa-I2 (A) and for B15Na30-1GPa-I2O5 (B). For both samples, the element distribution is homogeneous at the µm scale. We suspect the presence of nm-scale quenching crystal in B15Na30-1GPa-I2O5.

The elemental maps (I, O, Si and Na) are shown in Figure S1 for B15Na20-1GPa-I2 (A) and for B15Na30-1GPa-I2O5 (B). From the shown images, we observe that the obtained I-bearing glasses are homogeneous with respect to element distribution at µm scale. Clearly, we do not observe the presence of nm-scale bubble filled with solid I_2. This suggests that the presence of I^0 determined from XPS I 3d spectra corresponds to iodine dissolved within the glass structure as I^0 and probably under I_2 cluster form.

Whereas the presence of quench crystals has been identified in B15Na30 glasses, in Figure S1B, there is no clear evidence of large enriched iodine crystalline phases at the investigated scale. This implies that the quench crystals are not highly represented in our quenched samples.

Oxides	B15Na20-1GPa-I2		B15Na30-1GPa-I2O5	
	SEM EDS	S/TEM	SEM EDS	S/TEM
SiO_2 (mol.%)	62.6(2)	65.1(100)	58.1(6)	58.6(31)
B_2O_3	14.2(1)	14.2(1)	14.1(1)	14.1(1)
Al_2O_3	6.0(1)	5.7(11)	6.2(1)	5.5(5)
Na_2O	18.4(3)	14.3(27)	26.0(7)	20.3(9)
I	0.8(2)	0.8(1)	2.6(2)	1.5(3)

Table S1: Major element concentrations obtained by SEM EDS and S/TEM for B15Na20-1GPa-I2 and for B15Na30-1GPa-I2O5. The error bars are determined from replicated measurements for both methods. The I content derived by both analytical methods is roughly consistent.

The glass compositions have been obtained from the sample analyses in Figure S1. The results are given in Table S1 and compared to the results obtained from SEM EDS measurements. It should be pointed out that the error obtained on B15Na20-1GPa-I2 is based

on a single measurement whereas the error obtained on B15Na30-1GPa-I2O5 is based on four replicated measures. Although the error bars derived from the S/TEM are likely to be larger than SEM EDS ones, the measured mol.% oxides are consistent. The Na_2O is systematically lower for S/TEM measurements than for SEM EDS. The derived iodine content in B15Na30-1GPa-I2O5 is lower by S/TEM than SEM EDS. This could be due to possible heterogeneity within this sample.

O 1s XPS fitting for B15Na20-1GPa-I2O5

As mentioned in the manuscript, we have observed a very peculiar behavior for B15Na20-1GPa-I2O5. The O 1s XPS spectrum obtained for this sample is shown in Figure S2. If the spectrum simulation appears consistent with the general trend shown in Figure 4, the O 1s spectrum for B15Na20-1GPa-I2O5 departs from this trend. Clearly, there is a need for an additional peak to reproduce the entire spectrum. This peak is located at ~533 eV. It is not clear to which type of oxygen species this peak is attributed to. Malfait[1] suggested that at high binding energy, the peak could correspond to hydrated related species. Surprisingly, this sample is the only one to not show the presence of iodate species (I^{5+}). It could be possible that the I_2O_5 dissociation into I_2 and O_2 led to the incorporation of both I_2 as I^- or I^0 and O_2 without the recombination into IO_3^- clusters. The question remains to be clarified.

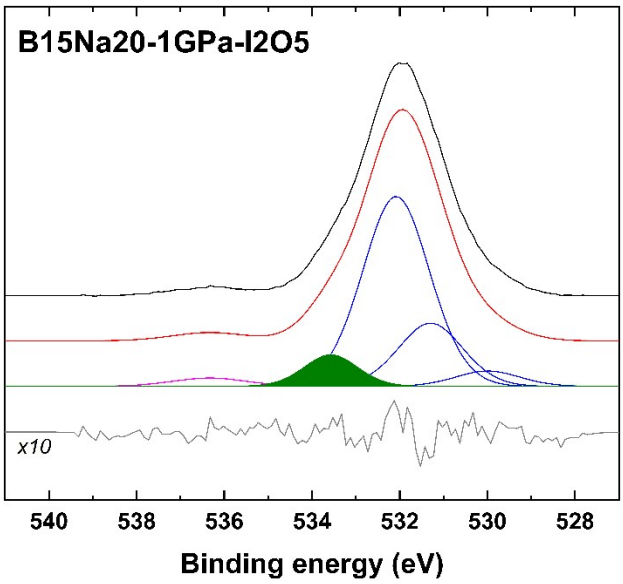


Figure S2: Typical simulations for B15Na20-1GPa-I2O5 glass. The simulation for B15Na20-1GPa-I2O5 requires an additional peak located at >533 eV and possibly attributed to hydrated oxygen species.

Reference:

[1] W. J. Malfait, *Can. J. Chem.*, 2015, **93**, 578-580.