

SUPPLEMENTARY MATERIAL

Change in chlorine solubility as a function of K^*

We show in Figure S1 the change in the measured chlorine content as a function of the K^* and R^* parameters (see Table 1). Both parameters are defined as follow: $K^* = [\text{SiO}_2 + \text{Al}_2\text{O}_3] / [\text{B}_2\text{O}_3]$ and $R^* = [\text{CaO} + \text{Na}_2\text{O} - \text{Al}_2\text{O}_3] / [\text{B}_2\text{O}_3]$. As raised by Du and Stebbins (2005), the initial definition of K and R by Dell et al. (1983) and applied to borosilicate glasses has to be corrected by the Al_2O_3 content in aluminoborosilicate glasses that requires to be charge compensated by either Na_2O or CaO . The current data do not show any clear correlation of the Cl content as a function of R^* . On the contrary, there seems to be a dramatic decrease of the Cl content in glasses with increasing K^* . The increase in K^* is concomitant to an increase in SiO_2 . This increase in SiO_2 will induce an increase in the degree of polymerization (i.e. increase in the concentration of Si-O-Si bonds) that could prevent chlorine from dissolving into the voids of the melt structure under its chloride form. On the other hand, this is probably more complicated than the only aspect of the polymerization degree considering that at low K^* value, we observe a large range of chlorine solubility. As described in the main text, we demonstrate that the nature of charge compensating cation (Ca^{2+} or Na^+) plays also a major role. As a result, we believe that Dell and Bray (1983) model is not adequate for representing the chlorine solubility data that we obtained.

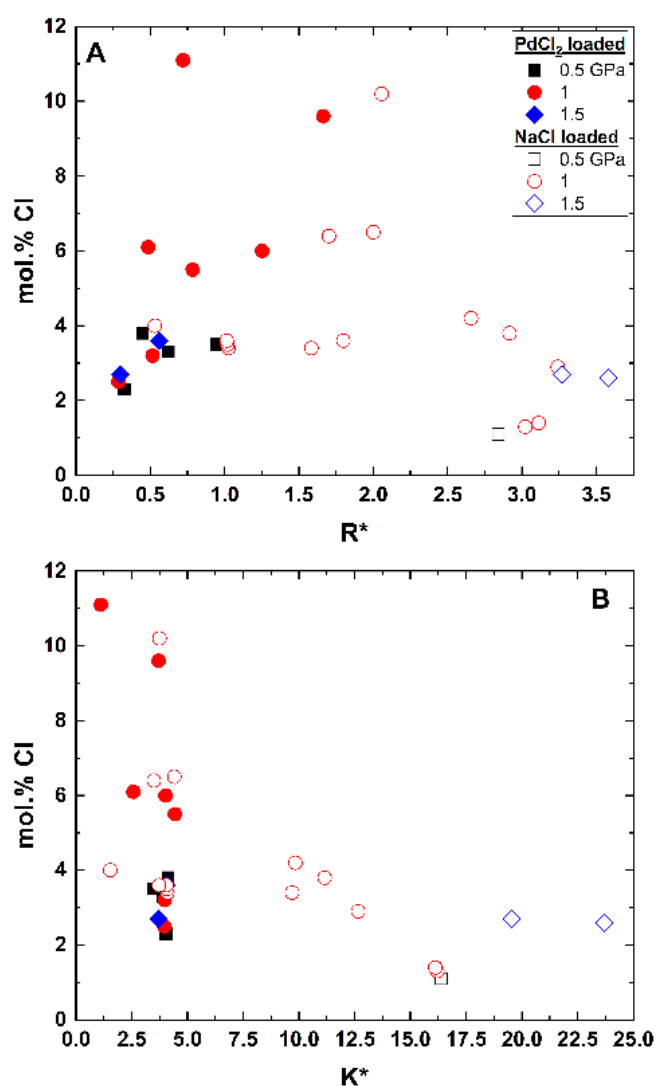


Figure S1: Change in the chlorine content as a function of R* (A) and K* (B) parameters as defined in Du and Stebbins (2005). The data points are categorized as a function of pressure conditions between 0.5 and 1.5 GPa and also as a function of chlorine initial source: NaCl, open symbol; PdCl₂, filled symbol.

Raman spectroscopy

Raman spectra were acquired to investigate the possible presence of H₂O dissolved in glasses.

We used a LabRam HR800 equipped with a solid diode laser operating at 532 nm and set at

100 mW output power. A high resolution ($\sim 0.4 \text{ cm}^{-1}$) was obtained using a 1800 grooves/mm grating. We performed 10 accumulations of 20 s. on each sample. The spectra acquired in the aluminoborosilicate region ($250\text{-}1750 \text{ cm}^{-1}$) and the H_2O region ($2600\text{-}3800 \text{ cm}^{-1}$) are shown in Figure S2. We concentrate our effort on NH22-2 PdCl_2 and pCABS2-Cl PdCl_2 that exhibited an additional unexpected signal in their Cl K-edge EXAFS spectra at low RDF value. This unexpected signal in the EXAFS spectrum is interpreted as either an artefact from the XAS acquisition or to an actual existing chlorine species that is not identified using XPS acquisition.

One potential candidate is the formation of H-Cl molecular group coming from the conjoint dissolution of H_2O and Cl. This species exhibits a short molecular bond with distance at $\sim 1.3 \text{ \AA}$. According to the literature H-Cl has a stretching vibration located at 2886 cm^{-1} (Mayo et al, 2004). There is clearly no evidence for such species in the spectra shown in Figure S2; however, the asymmetric peak at 3500 cm^{-1} indicates the presence of dissolved H_2O . In the absence of relevant calibration for determining H_2O concentrations in borosilicate glasses using Raman spectroscopy, we believe that the concentration of water remains relatively small. Nonetheless, the absence of H-Cl vibration suggests that the short distance signal observed in the EXAFS spectra is probably due to an artefact of the XAS acquisition.

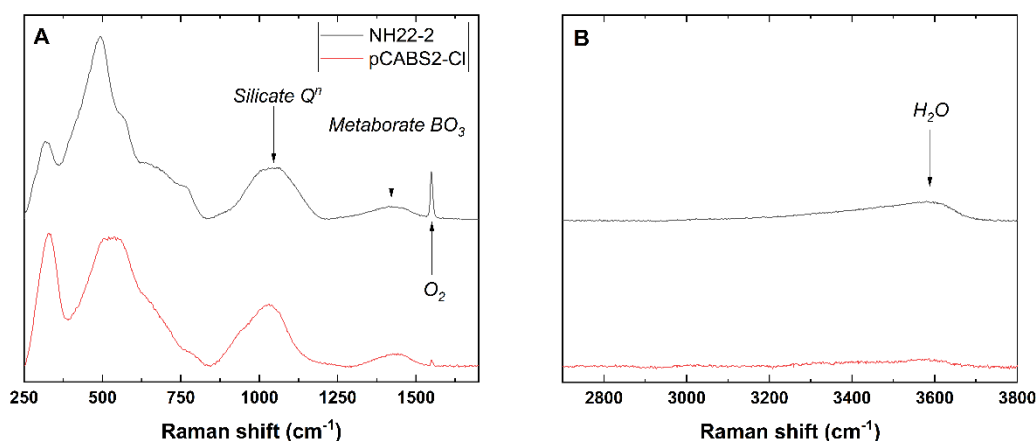


Figure S2: Raman spectra acquired for NH22-2 and pCABS2-Cl glass samples and showing the aluminoborosilicate network vibrations region between 250 and 1750 cm⁻¹ (A) and the water vibration region between 2600 and 3800 cm⁻¹ (B).

Spectral treatment and correction of the Cl K-edge EXAFS spectra

As mentioned earlier, difficulties were encountered in the treatment of the Cl K-edge EXAFS signal for determining the chlorine atoms first coordination sphere. On the basis of the XPS results, we have found that chlorine is dissolved only as chloride species (Cl⁻, see Figure 4) and we did not find evidence for oxidized chlorine species such as chlorate (ClO₃⁻). In chloride species (e.g. NaCl, CaCl₂, PdCl₂), crystallographic data show that the first coordination sphere around chlorine exhibits distances between chlorine and the first nearest neighbour that are at least 2.3 Å for PdCl₂ and reaches bond lengths up to 2.8 Å for CaCl₂. As a result, we should observe a main peak in the RDF at 1.8 to 2.3 Å. This is clearly observed in Figure S3 showing the entire magnitude of the EXAFS signal as a function of the RDF in Å for pCABS2-Cl. There is a main peak that is located at ~2.4 Å and that corresponds to the actual distance between Cl⁻ and a first neighbour namely Na⁺ or Ca²⁺. In addition, there is a lower contribution at ~1.8 Å that we believe could correspond to Cl⁻ species surrounded by

Pd^{2+} as PdCl_2 was used as the chlorine initial source. In Figure S3, we have reported three spectra treated in three different manner by varying the applied R background value between 1 and 2. The R background corresponds to the energy cut-off between the data and the background. A R background default value is equal to 1. Below this value, the Fourier signal is close to 0.

We observe a strong signal located at $\sim 1.2 \text{ \AA}$ and could correspond to nearest neighbour with a distance on the order of 1.7 \AA . Currently, the only known chlorine species that could exhibit such a low distance is chlorine present as chlorate or H-Cl molecular groups. We demonstrated that this could not be possible as chlorate has not been observed using XPS and H-Cl vibration is not seen in the Raman spectra. Consequently, applying a R background close to 2 is required in order to suppress what we consider as an artefact signal and not the true signal representative of the chlorine coordination sphere. As R is increased the magnitude signal becomes sensibly close to 0.

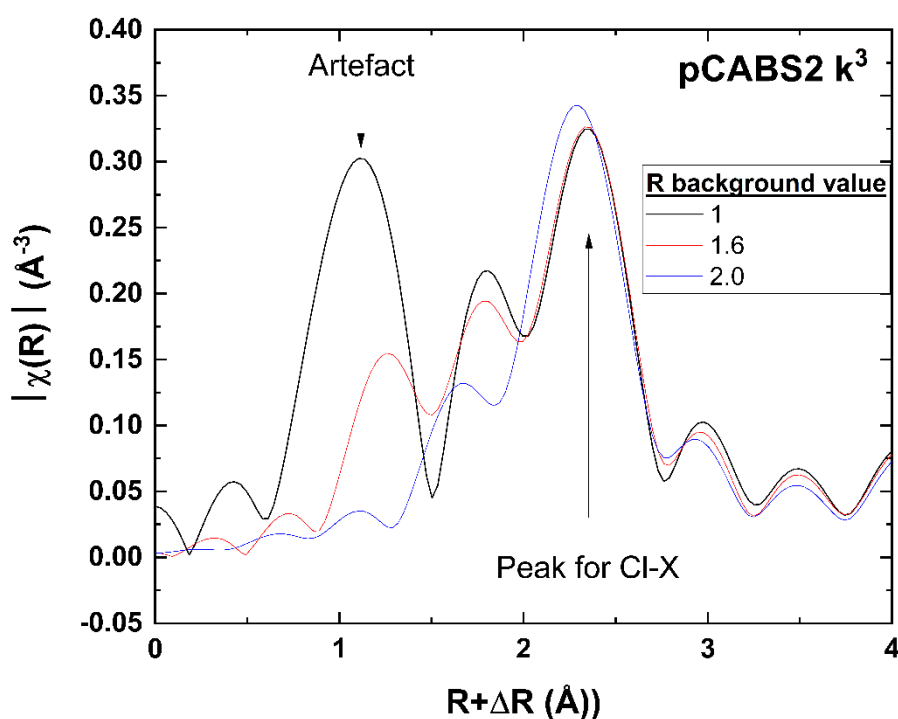


Figure S3: EXAFS magnitude spectrum as a function of Radial Distribution Function for pCABS2-Cl. Three spectra are reported and obtained with three different R background correction: 1 that is the default value, 1.6 and 2.0.

References

- Dell, W.J., Bray, P.J., and Xiao, S.Z. (1983) ^{11}B NMR studies and structural modeling of $\text{Na}_2\text{O-B}_2\text{O}_3\text{-SiO}_2$ glasses of high soda content. *Journal of Non-Crystalline Solids*, 58, 1-16.
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- Mayo, D.W., Miller, F.A., and Hannah, R.W. (2004) Course note on the interpretation of infrared and Raman spectra. John Wiley and Sons, Inc., pp. 600.