

Investigation of aluminosilicate glasses by coupling experiments and simulations:

Part I- Structures

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Supplementary Information

I NMR spectra for ²⁷Al for the glasses in series 2

Figure SI1 presents the ²⁷Al MAS NMR spectra for the glasses in series 2. Whatever the composition considered, the Al atoms remain in a tetra coordinated environment.

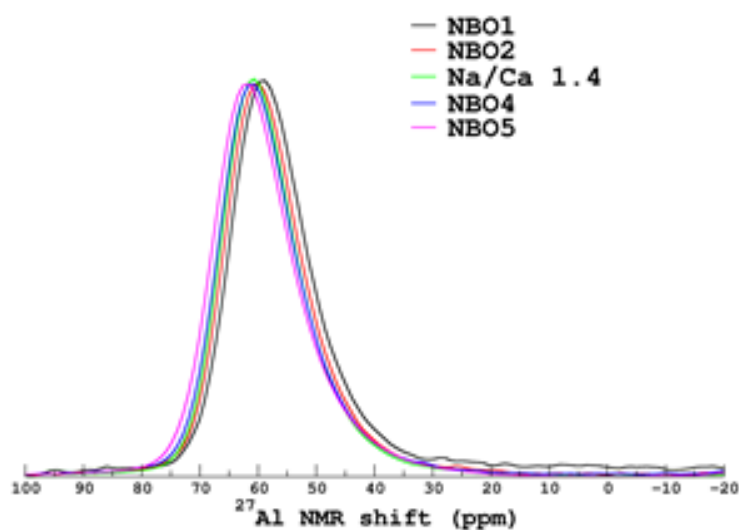


Figure SI1: ²⁷Al MAS NMR spectra for the glasses in series 2.

II ²⁷Al NMR parameters

²⁷Al MAS NMR spectra were fitted using distribution of NMR parameters as described in Ref. (Angeli et al., 2007). The variations of the NMR parameters extracted from the ²⁷Al MAS NMR spectra are displayed in Figure SI2. The bars represent standard deviation values of the NMR parameter distributions.

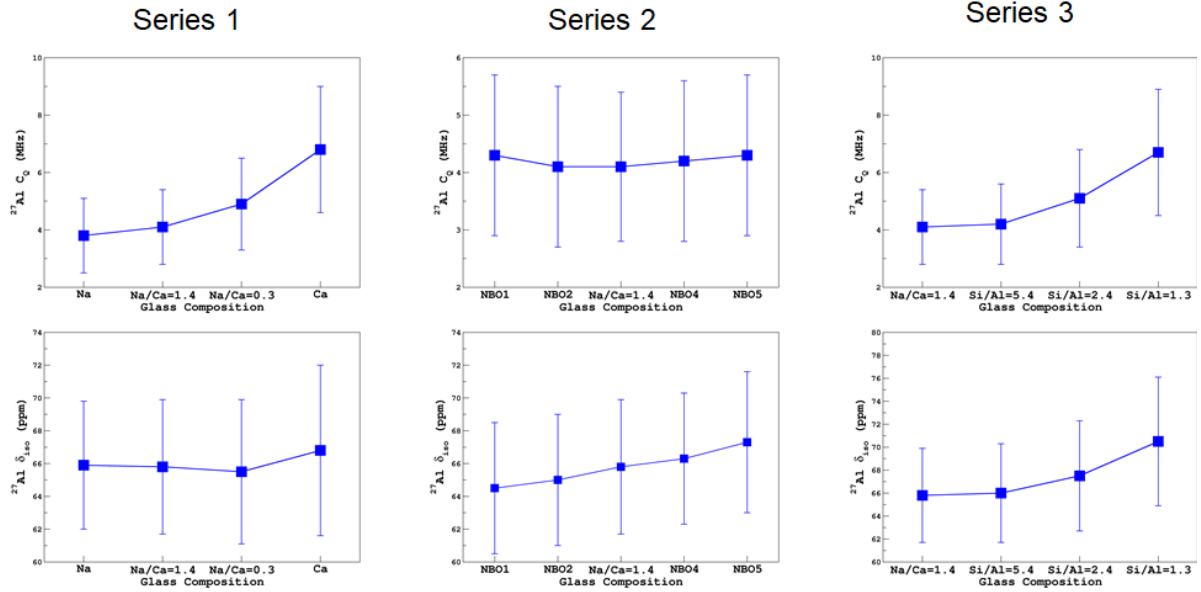


Figure S12: ^{27}Al Mean quadrupolar coupling constant (C_Q , top row) and isotropic chemical shift (δ_{iso} , bottom row) extracted from the MAS NMR spectra for the glasses in the three series. Bars represent the standard deviation value distribution.

III NMR spectra for ^{23}Na for the glasses in series 2

The NMR spectra for ^{23}Na in the glasses of series 2 are quite close one to another (see Figure S13). NMR parameters were extracted similarly to aluminium-27 (Angeli et al., 2011, 2007) and are plotted in Figure S14.

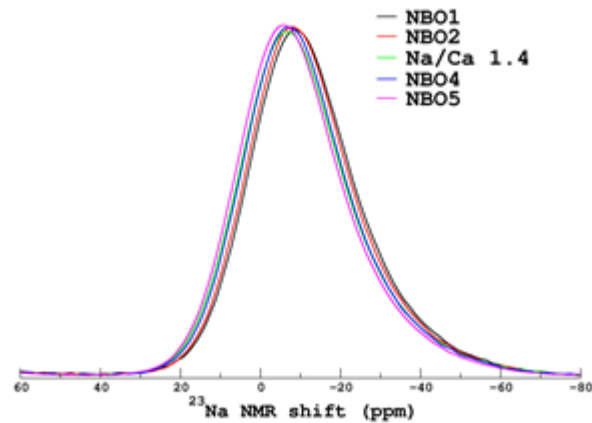


Figure S13: ^{23}Na MAS NMR spectra for the glasses in series 2.

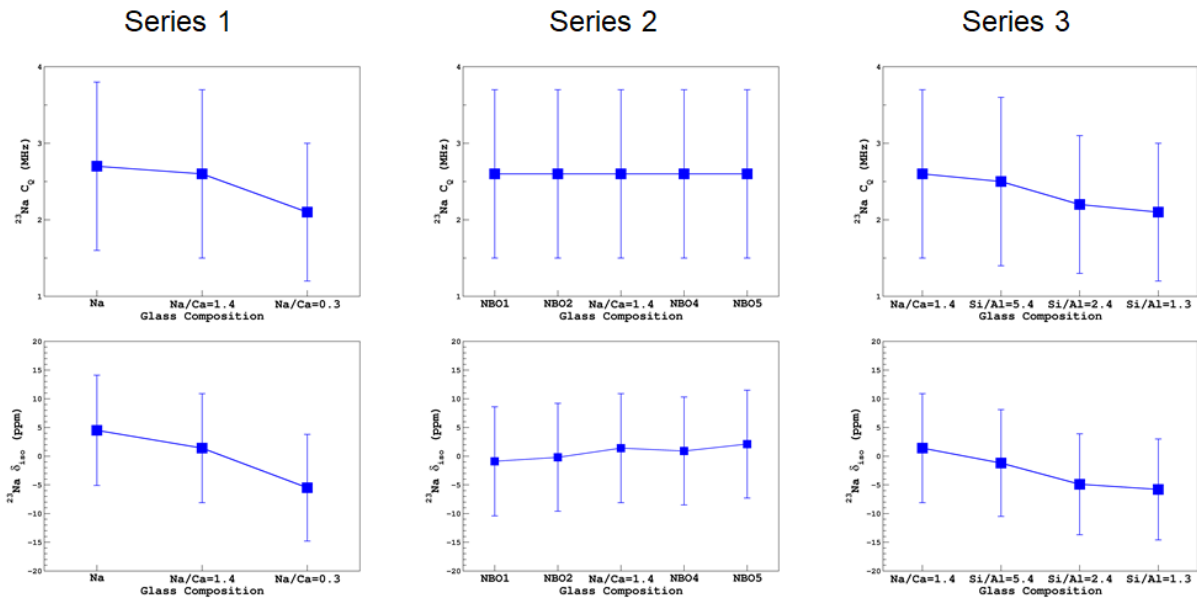


Figure S14: ^{23}Na Mean NMR parameters extracted from the MAS NMR spectra for the glasses in three series. Top row: Quadrupolar coupling constant (C_Q). Bottom row: Isotropic chemical shift (δ_{iso}).

IV NMR spectra for ^{29}Si for the glasses in series 3

The MAS NMR spectra for ^{29}Si in the glasses of series 3 are not very different one to another (see Figure S15).

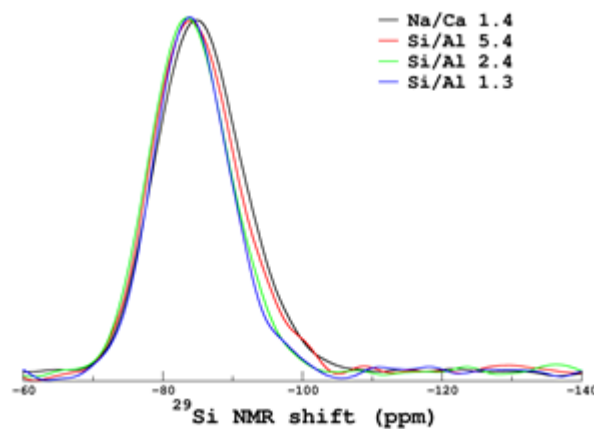


Figure S15: ^{29}Si MAS NMR spectra for the glasses in series 3.

V Oxygen-17 NMR data analysis

The ^{17}O MQMAS NMR spectra were fitted as detailed in (Angeli et al., 2011, 2008). In order to better constraint our deconvolution, the composition were used to provide constraints on %NBO (Na and Ca content and using the fact all aluminum in in AlO_4 units), and relative population in Si-O-Si, Al-O-Si and Al-O-Al : %BO gives the total population and the Al/Si constraints the number of Al-O-Si, and Al-O-Al if present (in the latter case, the MQMAS spectrum determines the fraction of Al-O-Al). Discussion of the ^{17}O NMR parameters are out of the scope and will be discussed elsewhere. Note that effects of the RF

pulse sequence and finite spinning frequency were accounted for to provide quantitative analysis. Note the difficulties in defining the separation between SiO(Na/Ca) (NBO in mixed Ca/Na environment) with SiOCa (NBO in Ca environment) so that a single component – SiO(Ca/Na) – is reported in the main text.

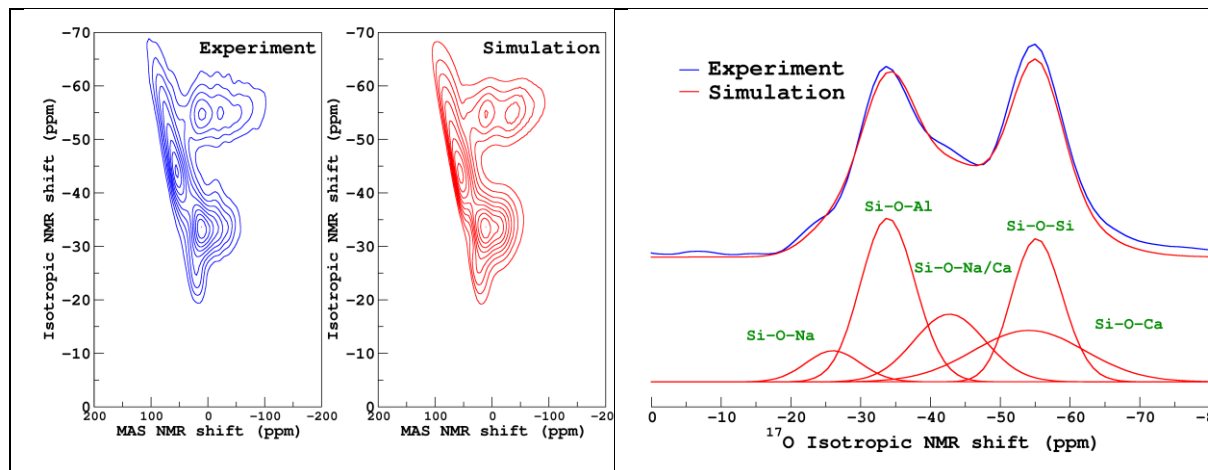


Figure S16. Experimental and simulated ^{17}O MQMAS spectra of Na/Ca 1.4 glass.

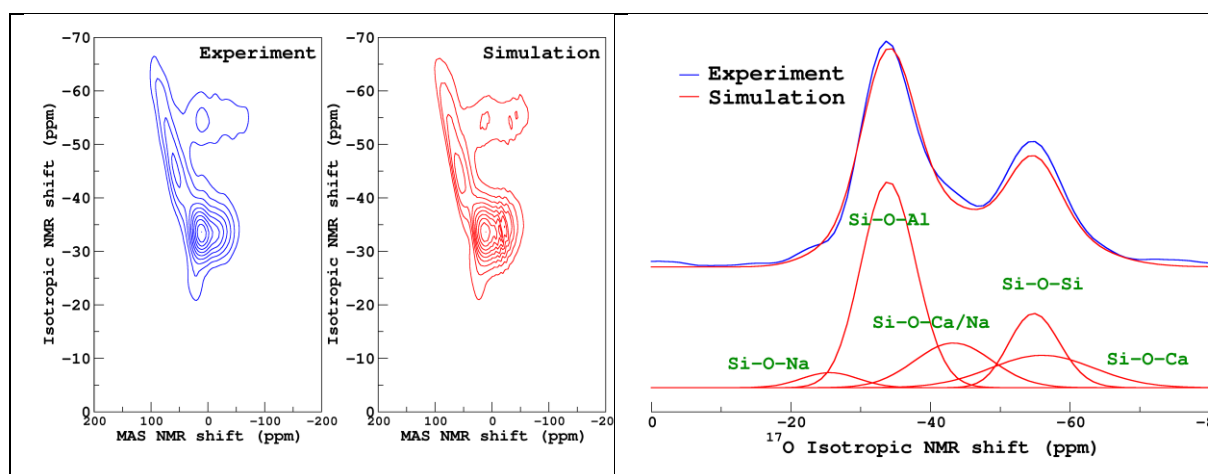


Figure S17. Experimental and simulated ^{17}O MQMAS spectra of Si/Al 5.4 glass.

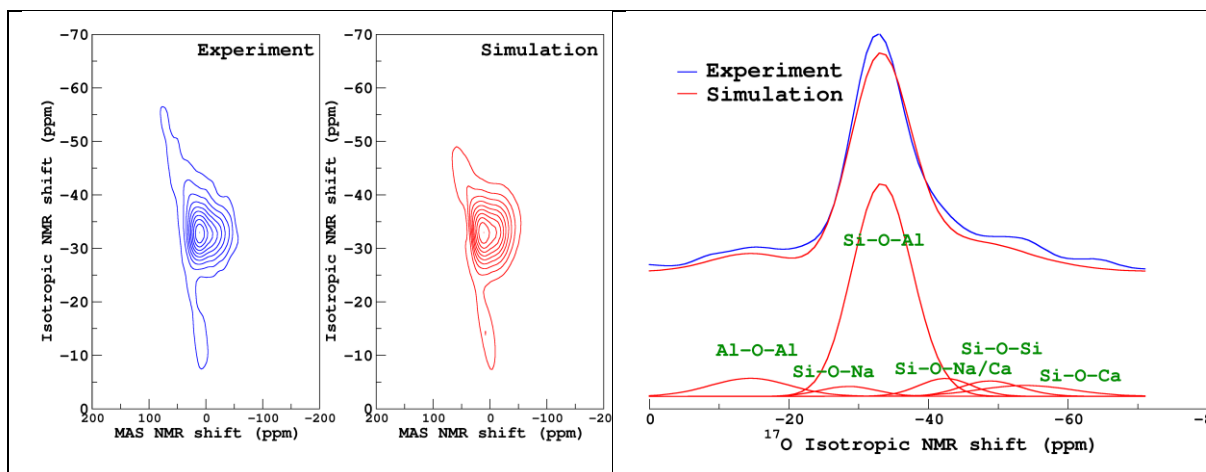


Figure S18. Experimental and simulated ^{17}O MQMAS spectra of Si/Al 2.4 glass.

REFERENCES

- Angeli, F., Gaillard, M., Jollivet, P., Charpentier, T., 2007. Contribution of ^{43}Ca MAS NMR for probing the structural configuration of calcium in glass. *Chem. Phys. Lett.* 440, 324–328. <https://doi.org/10.1016/j.cplett.2007.04.036>
- Angeli, F., Villain, O., Schuller, S., Ispas, S., Charpentier, T., 2011. Insight into sodium silicate glass structural organization by multinuclear NMR combined with first-principles calculations. *Geochim. Cosmochim. Acta* 75, 2453–2469. <https://doi.org/10.1016/j.gca.2011.02.003>