Multi-Spectroscopic Investigations for Comprehensive Structural Analysis of Aluminoborosilicate Glasses: II. Relation between the glass structure and chemical properties

(Supplementary materials)

Hanyu Hu[1] https://orcid.org/0009-0001-4961-3954, Sami Soudani[1,2] https://orcid.org/0009-0001-9301-2566, Jonathan Hamon[1], Nicolas Trcera[3] https://orcid.org/0000-0002-9364-1039, Michael Paris[1] https://orcid.org/0000-0002-8671-0630, and Yann Morizet[1,2] https://orcid.org/0000-0001-9599-245X

1 Nantes Université, CNRS, Institut des Matériaux Jean Rouxel (IMN), 44322 Nantes Cedex, France

2 Nantes Université, Nantes Atlantique Universités, Laboratoire de Planétologie et Géosciences de Nantes (LPG), UMR CNRS 6112, 44322 Nantes Cedex, France

3 Synchrotron SOLEIL, L'Orme des Merisiers, Départementale 128, 91190 Saint-Aubin, France

*Correspondence: Yann Morizet, yann.morizet@univ-nantes.fr

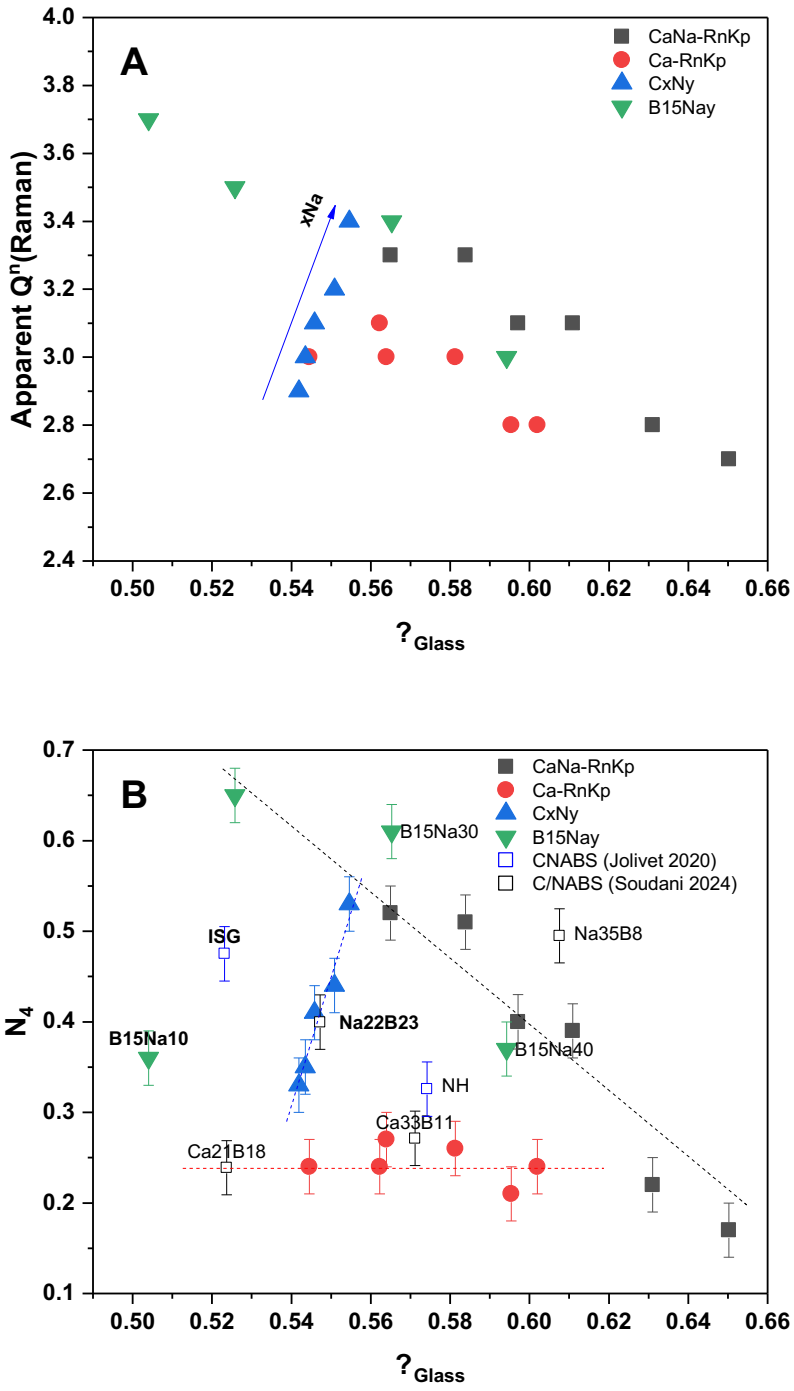

Figure S1. Evolution of apparent Q^n determined by Raman spectra (A) and N_4 value derived from ^{11}B NMR spectra (B) as function of Λ_{glass}. Solid points represent the investigated glasses, and open square correspond to data from the literature. In Figure S1A, the blue arrow indicates the increase of xNa in the CxNy series. In Figure S1B, the black dashed line represents the scenario for depolymerized glasses, where the N_4 value decreases as Λ_{glass} increases. The red dashed line indicates the scenario for Ca-bearing glasses, where the N_4 value remains stable. The bleu dashed line indicates the scenario for CxNy series, where the N_4 value increases as xNa increases. Glasses marked in bold indicate high-polymerized glasses. Error bars for the N_4 value are ±0.03.

1.1. Apparent average Q^n of silicate sites

The structure of silicates in our investigated glass was characterized by Raman spectroscopy. The relationship between Λ_{glass} and the apparent average Q^n is reported in Figure S1A. This figure reveals a strong correlation: Q^n decreases with increasing Λ_{glass} among the CNABS glasses where xNa > 0.5 (e.g., B15Nay and CaNa-RnKp series). The decrease in Q^n is quite pronounced, from 3.7 for B15Na10 (highest SiO_2 content glass) to 2.7 for CaNa-R2K1 (lowest SiO_2 content glass). For CABS glasses, this correlation also exists, though it is not as prominent. In the Ca-RnKp series, as Λ_{glass} increases, Q^n values decrease from 3.1 to 2.8. Furthermore, as the same Λ_{glass} value, the Q^n values for CABS glasses are significantly lower than those for CNABS glasses, with a difference of approximately 0.3. This phenomenon can be also validated by the changes in Q^n in the CxNy series due to the MME. With a decrease in xNa (i.e., as Na is replaced by Ca), the Q^n value decreases markedly, from 3.4 for C0N35 glass to 2.9 for the C35N0 glass.

In the literature, there are few confirmations of Q^n for complex glasses, whether using Raman spectroscopy or ^{29}Si NMR spectroscopy; relevant information is sparse. Therefore, no comparison with literature data was conducted.

1.2. Coordination state of borate species

The structure of boron in the glass can be characterized by ^{11}B NMR, where derived N_4 value represents the proportion of 4-fold coordinated borate species relative to the total borate species ($N_4 = [^{[4]}B]/([^{[3]}B]+[^{[4]}B])$). The relationship between Λ_{glass} and N_4 is shown in Figure S1B.

The Figure S1B reveals that there is no direct correlation between Λ_{glass} and N_4 because the data points are scattered throughout the graph. However, several scenarios can be observed. For depolymerized glasses (R' > 1), including the B15Nay series (except B15Na10 glass), the CaNa-RnKp series, and N35B8 glass (R' = 2.6) [1], as Λ_{glass} increases from 0.52 to 065, N_4 decreases significantly from 0.65 to 0.17. This negative correlation is almost linear. For CABS glasses, regardless of whether the R value is greater than 1, such as in C21B18 (R' = 0.8), C33B11 (R' = 1.9) [1], and the Ca-RnKp series (R' = 1.5 – 2.5), the N_4 value does not change with Λ_{glass} and remains around 0.25. Therefore, the N_4 values in the CABS system are generally lower than those in the CNABS system, except for CaNa-R2K1 and CaNa-R3K2 glasses (N_4 = 0.17). This observation can also be supported by the MME in the CxNy series, where the N_4 value decreases significantly as Na in the glass is replaced by Ca. Finally, there are some unassigned data points scattered across the graph, marked in bold, such as B15Na10 (R = '0.5), ISG (R' = 0.9) [2], and Na22B23 (R = 0.9) [1]. These glasses share a common characteristic of having an R' value less than 1, indicating that they are highly polymerized glasses according to the model of Dell [3]. In these glasses, the N_4 value is expected to depend on the R' value. However, the presence of Al_2O_3 in the glass, which competes with B_2O_3 for the consummation of compensators (e.g. Na or Ca), may cause deviations from the Dell model in CNABS glass system, highlighting the complexity of the relationship between N_4 and glass composition in aluminoborosilicate glasses.

References

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