

CO₂ speciation in Ca- and Na-aluminosilicate glasses as a function of melt polymerization: A multi-nuclear NMR study

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It is generally known that CO₂ dissolves in silicate melts/glasses as molecular CO₂ and CO₃²⁻ species, with the latter dominant for depolymerised compositions and polymerized compositions with high Al/Si ratios. However, how the CO₃²⁻ groups are incorporated in the melt and how it affects the silicate structure were less certain, because of controversial interpretations of vibrational and ¹³C MAS NMR results. Our recent *ab initio* calculations on CO₃²⁻ groups in various environments showed that both vibrational frequencies and ¹³C chemical shift tensor are sensitive to the local environments of carbonates, and the combined *ab initio* calculation and new experimental ¹³C MAS and static NMR data on ¹³CO₂-bearing glasses of diverse silicate compositions indicate that carbonates are present dominantly as free carbonates (carbonates not bonded to any network-formers, e.g. Si, Al) for depolymerized compositions, and as network carbonates (carbonates bonded to two Si/Al via two of its oxygens) for polymerized compositions [1].

Here we further extend our study to systematically investigate the CO₂ speciation change as a function of melt polymerization. A series of ¹³CO₂-bearing glasses (mostly ~ 1 wt%) across the Na₃AlSi₂O₇ - NaAlSi₂O₆ and Ca_{1.5}AlSi₂O₇ - Ca_{0.5}AlSi₂O₆ joins (with a constant Al/Si ratio, but varying nominal NBO/T of 0.67 to 0) were prepared by quenching melts at 1.5 GPa and 1400-1600°C in a QUICKpress piston cylinder apparatus. Multi-nuclear (¹H MAS, ²⁷Al MAS & 3QMAS, ¹³C static and MAS) NMR (@9.4 T) and Raman measurements were performed. The data revealed systematic change in CO₂ speciation from dominantly free carbonates in depolymerized glasses to network carbonates + molecular CO₂ in fully polymerized glasses for both series, consistent with our previous study. The Ca aluminosilicate glasses show broader ¹³C MAS NMR peaks, indicating greater local structural disorder, compared to the Na- counterparts.

[1] Xue & Kanzaki (2013) *Min Mag*, **77** (5) 2533