Speciation data on CaO-SiO$_2$ and CaO-Al$_2$O$_3$-SiO$_2$ systems at the glass transition temperature.

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Predicting physical and thermodynamic properties of silicate liquids is a key objective to understand magmatic processes. To achieve this, structural data on the Al incorporation and the structural role of alkaline earths on the silicate framework, are required. We present new speciation data in the systems CaO-SiO$_2$ (CS) and CaO-Al$_2$O$_3$-SiO$_2$ (CAS) at the glass transition (Tg). Glasses of various compositions (NBO/T up to 2.7, Al/Si up to 0.8) were melted in a vertical furnace and drop quenched in water with a typical quench rate of ∼500K / s. DTA calorimetric experiments were conducted to measure Tg. Raman scattering and 3Q ^{27}Al- ^{29}Si-MAS NMR were used to study the silicate glass speciation.

Tg data for both systems ranges between 1010 and 1130K. CS data are consistent with previous studies, but systematic deviations of Tg are noticed for the CAS system compared to recent conductivity studies.

Q species coexist and equilibrate according to the reaction $2Q^n = Q^{n-1} + Q^{n+1}$ (n = 1,2,3). For the CS system, significantly different unit abundances are distinguished compared to previous studies: Q^4 (15%) is present in more polymerised and Q^0 (7%) in depolymerised glass. Raman scattering coefficients for the different Q^n species were derived and remain constant in the range of NBO/T.

At constant silica content, addition of Al increases the stability of the Q^4 unit, suggesting that Ca^{2+} is acting as charge balancing cation. Using speciation, the entropy of mixing (S$_{mix}$) was derived. A positive trend was found between Tg and 1/S$_{mix}$ but inversely correlated with NBO/T.