

## A molecular dynamics study of the glass transition in $\text{CaAl}_2\text{Si}_2\text{O}_8$ : Thermodynamics and tracer diffusion

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### ABSTRACT

Molecular dynamics (MD) simulation provides a unique window into the microscopic processes controlling the properties of amorphous silicates of geochemical importance. Of special interest are changes in structure and dynamics around the glass transition temperature. Seventeen simulations for composition  $\text{CaAl}_2\text{Si}_2\text{O}_8$  in a microcanonical ensemble of 1300 particles (O + Si + Al + Ca) were conducted at temperatures from 1700 to 5000 K at approximately 1 GPa. A pair-wise potential allowing for Coulombic and Born-Mayer interaction was used. Simulation durations were in the range of 50 to 150 ps. Particle trajectories were collected and used to build a picture of the structure and dynamics of equilibrium liquid, supercooled liquid and glassy  $\text{CaAl}_2\text{Si}_2\text{O}_8$  as a function of temperature along the 1 GPa isobar. The computer glass transition was detected at  $T_g \sim 2800$  K by study of thermodynamic properties, speciation equilibria and tracer diffusivity.  $T_g$  is observed as a change in slope of enthalpy ( $H$ ) vs. temperature at  $T = T_g \sim 2800$  K. The configurational isobaric heat capacity of supercooled melt relative to the glass is  $53.3 \text{ J}/(\text{K}\cdot\text{mol})$ , within a factor of two of the experimental value. The “computer” isobaric heat capacity for equilibrium liquid at 3000 K is  $457 \pm 35 \text{ J}/(\text{K}\cdot\text{mol})$  vs. the calorimetric value of  $461 \text{ J}/(\text{K}\cdot\text{mol})$ . In equilibrium liquid, speciation defined by equilibria such as  $^{16}\text{O} + ^{18}\text{O} = 2 \text{ }^{17}\text{O}$  and  $\text{TO}_4 + \text{TO}_6 = 2 \text{ TO}_5$  are temperature-dependent with  $\Delta H$  and  $\Delta S$  approximately equal to  $-39 \text{ kJ/mol}$  and  $19 \text{ J/mol K}$  and  $-10 \text{ kJ/mol}$  and  $12 \text{ J/mol}$ , respectively; these are in good agreement with laboratory values. The computer glass point at 2800 K is identified as the temperature at which speciation equilibria become “frozen”. The static structure factor for O-O confirms the conclusion, based on pair correlation statistics, that the glass transition is not associated with significant changes in the static structure. Dramatic differences in the mobility of all atoms monitored by tracer diffusion are noted as a function of temperature. Self-diffusivity orders at fixed temperature according to  $D_{\text{Ca}} > D_{\text{O}} > D_{\text{Al}} > D_{\text{Si}}$  with  $D_{\text{Ca}} \sim 20\%$  larger than  $D_{\text{O}}$  and  $D_{\text{O}} \sim 2 D_{\text{Si}}$ . Activation energies for diffusion for all atoms lie in the range 170 to 190 kJ/mol. The small range in tracer diffusivity and activation energy ( $E_a$ ) found for different atoms suggests cooperative motion is important. At  $T_g/T \geq 1$  for the nonequilibrium glass,  $E_a$  decreases by  $\sim 40\%$  for all atoms compared to corresponding high-temperature (equilibrium melt) values. The crossover between continuous (hydrodynamic-like) motion and atomic hopping motion shows up clearly in the time-dependence of the mean square displacement as a function of temperature. The qualitative view is that a given particle and its neighbors remain trapped for a finite waiting time before undergoing cooperative thermally activated rearrangement. The waiting time distribution is strongly temperature-dependent and related to the rapid increase in structural relaxation time as temperature approaches  $T_g$ . Shear viscosity computed from relaxation of microscopic density fluctuations, the Eyring relation and the Green-Kubo formalism are 0.04 Pa-s, 0.09 Pa-s, and 0.02 Pa-s, respectively; these values are all somewhat higher than the extrapolated laboratory value of  $\sim 0.005$  Pa-s.