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Structure, thermodynamic and transport properties of $CaAl_2Si_2O_8$ liquid. Part I: Molecular dynamics simulations

Frank J. Spera [a,*], Dean Nevins [a], Mark Ghiorso [b], Ian Cutler [a]

[a] *Department of Earth Science, University of California-Santa Barbara, Santa Barbara, CA 93106, USA*
[b] *OFM-Research, 7336 24th Ave. NE Seattle, WA 98115, USA*

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Abstract

Molecular dynamics simulations for liquid $CaAl_2Si_2O_8$ have been carried out at 72 state points spanning ranges in density (ρ: 2398–4327 kg/m^3), temperature (T: 3490–6100 K) and pressure (P: 0.84–120 GPa) relevant to geosystems. The atomic scale structure of the melt is determined by analysis of nearest neighbor coordination statistics as a function of T and P. Dramatic structural change occurs as pressure increases especially for $0 < P < 20$ GPa at all temperatures. Changes in structure are encapsulated by examining the coordination of Si, Al, Ca and O around oxygen and *vice versa*. Si and Al change from predominantly fourfold at low-P to dominantly sixfold for $P >\sim 20$ GPa. Pentahedrally coordinated Si and Al in distorted trigonal bipyramids attain abundance maxima corresponding to ~60% of total (Si, Al)O_n at 3–5 GPa and weakly depend on T. The coordination of Ca by oxygen increases from 7 to 10 for $0 < P < 20$ GPa and changes slowly for $P > 20$ GPa at 3500 K. Similar behavior is seen at 6000 K except that the interval of rapid changes occurs at higher pressure. Oxygen with only one nearest Si or Al neighbor (i.e., non-bridging oxygen, NBO) decreases whereas oxygen with two or three nearest neighbors of Si, Al or Ca increases as pressure increases. Changes in melt structure are reflected in the variation of thermodynamic and transport properties of the liquid. Values of the self-diffusivities of Ca, Al, Si and O are fit to a modified Arrhenian expression and compare well to limited laboratory data. Self-diffusivities are best fit using 'low P' and 'high-P' expressions, identical in form but with different parameters, with activation energies and activation volumes in the range 150–200 kJ/mol and +5 to −1 cm^3/mol, respectively. Green–Kubo calculations for liquid shear viscosity are presented and compare well with limited laboratory results. Application of the Eyring model to determine the characteristic size and number of atoms in the activated cluster based on independently computed D and η suggests that the activated cluster decreases from ~8 to ~3 atoms from low to high pressure while its characteristic size shrinks from ~14 Å to ~3 Å providing insight into dynamics of atom mobility and possible cooperative behavior. The equation of state and variation of internal energy with T and V are used in Part II (Ghiorso et al., 2009) to derive a comprehensive thermodynamic description of liquid $CaAl_2Si_2O_8$. This is best accomplished by allowing for EOS expressions broken into high and low pressure intervals consistent with coordination statistics and MD-derived transport properties.

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1. INTRODUCTION

This paper is part of a series in which the structure, thermodynamic and transport properties of molten multicomponent silicates relevant to geochemical and geodynamical problems are investigated at elevated temperatures (2500–5000 K) and pressures (0–135 GPa) by combining Molecular Dynamics (MD) simulations with macroscopic equation of state (EOS) and transport property analysis. So far relatively unpolymerized melts such as Mg_2SiO_4 and $MgSiO_3$ have been studied in some detail in order to construct of equations of state and transport property relations (e.g., Stixrude and Karki, 2005; Wan et al., 2007; de Koker et al., 2008; Martin et al., 2009; Nevins et al., 2009).

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[*] Corresponding author. Tel.: +1 805 893 4880.
E-mail address: spera@geol.ucsb.edu (F.J. Spera).

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Although several natural or archetypical silicate liquids have been investigated by laboratory (e.g., shock wave, see Akins et al., 2004) or computational methods (e.g., Guillot and Sator, 2007a,b; Lacks et al., 2007), a multicomponent silicate liquid thermodynamic and transport property model valid throughout the Earth's mantle remains elusive. Although the conceptual basis for a fully multicomponent thermodynamic treatment is on hand (e.g., see Ghiorso 2004a,b; Ghiorso and Kress, 2004) the lack of EOS information at elevated temperature and pressure for multicomponent liquids has hampered development of models useful for geochemical and geophysical applications. Construction of an EOS requires approximately 75–100 state points more or less evenly distributed over the appropriate *P*–*T* region; a few *P*–*T* points on a few compositions are woefully insufficient. In this study (Part I) and its companion (Part II, Ghiorso et al., 2009) molten $CaAl_2Si_2O_8$ is studied in detail. In Part I (this study) details on the MD simulations, retrieved thermodynamic and transport properties and melt structures are provided and compared with available laboratory information. These results are used in Part II (Ghiorso et al., 2009) to construct a thermodynamic equation of state for liquid $CaAl_2Si_2O_8$ and to compare the EOS predictions with shock wave (Asimow and Ahrens, 2008) and other laboratory thermodynamic data.

Knowledge of the properties of naturally occurring silicate liquids is key for understanding the current and previous dynamical states of the Earth. For example, quantitative information regarding liquid shear viscosity, the self-diffusivity of oxygen, silicon, aluminum, the alkalis, alkaline earths and transition metals and the thermal and ionic conductivity of molten silicates is indispensable for analysis of magma transport phenomena. The thermodynamic properties and structure of molten silicates are also relevant to magma genesis and crystal-liquid equilibria including the thermal properties and trace element systematics of erupted liquids. A number of arguments suggest that the Earth and other terrestrial planets underwent substantial or complete melting during formation by collisional accretion (e.g., Ohtani et al., 1985; Abe, 1997; Debaille et al., 2008). In the case of Earth, subsequent giant Moon-forming impact also deposited large amounts of heat (Canup and Agnor, 2000; Solomatov, 2000; Canup, 2004). The state of the mantle following magma ocean solidification set the initial conditions for growth and evolution of the lithosphere, hydrosphere and the atmosphere and mediated the start of plate tectonics on Earth (Anderson, 2007). On the Moon, the formation of a plagioclase-rich crust by floatation upon the lunar magma ocean was of paramount importance. Many terrestrial (silicate plus metal) exoplanets circling nearby (<1000 lightyear distant) stars await discovery (Valencia et al., 2007) and so the necessity of understanding the properties of molten silicates at extreme conditions on 'super earths' will undoubtedly arise in the future. Arguments have been made for the presence of localized regions of melt along the core–mantle boundary of the Earth today (Garnero et al., 1993; Revenaugh and Sipkin, 1994; Williams and Garnero, 1996; Revenaugh and Meyer, 1997). These few illustrative examples underscore the importance of understanding the properties of multicomponent silicate liquids for application to myriad geochemical and geodynamical problems on Earth and other planets.

In addition to geochemical and geodynamical applications, an understanding of the amorphous state (liquids and glasses), specifically the relationship between liquid structure, the EOS and transport properties, is of interest in its own right. Liquid–liquid phase separation, in which two liquids of distinct composition coexist at a single state point, are quite common in natural systems and have long been studied (e.g., Roedder, 1951; Philpotts, 1976). There is now growing interest in a more unusual behavior. This phenomenon, whereby a one-component system can exist as two liquid or amorphous phases having an identical chemical composition but distinct density and structure, is termed polyamorphism (Grimsditch, 1984). Phase transitions between such distinctly structured liquids occur without change in composition but instead with a change in density (Tanaka, 2000). Experimental evidence for polyamorphism has been found in molten silica, H_2O, and binary melts in the system Al_2O_3–Y_2O_3 among other compositions (e.g., Aasland and McMillan, 1994; Debenedetti 1996; Senker and Rossler, 2001; Brazhkin and Lyapin, 2003; Skibinsky et al., 2004). Polyamorphism for a given composition can be predicted from thermodynamic analysis provided a robust EOS is available. Due to advances in both hardware and software within the last decade a sufficient number ($\sim$70) of state points for a single composition can now be routinely investigated by MD simulation thereby enabling accurate construction of an EOS consistent with a given effective pair potential.

The liquid state arises from a delicate balance between the 'packing' of atoms (related to the configurational entropy) and the 'cohesive' forces between atoms (related to the internal energy). The details of this balance determine liquid structure, its dependence on temperature and density (pressure) and material properties-both thermodynamic and transport (Barrat and Hansen, 2003). Two specific aspects are particularly noteworthy. The first is the work of Rosenfeld and Tarazona (1998) who have developed free energy functionals for systems characterized by continuous ('soft') potentials such as those used to study silicate geoliquids. Their model posits that the fluid Madelung (potential) energy scales with T according to $T^{3/5}$. Rosenfeld–Tarzona (RT) scaling can be tested using MD results and has been found quite robust and hence extremely useful in EOS construction from MD simulations (Ghiorso et al., 2008) because it provides a rationale for interpolation and extrapolation. A second point, now widely appreciated, is that pressure has a dramatic effect on melt structure (e.g., Nevins and Spera, 1998; Bryce et al., 1999; Lacks et al., 2007; Guillot and Sator, 2007b). An advantage of the MD method is that complete coordination number statistics are available at each state point, essential information for constraining mixing models. The combination of coordination statistics with RT scaling provides a framework for a multicomponent model of the thermodynamics of molten silicates. For multicomponent systems, entropic effects associated with the mixing of various coordination polyhedra are crucial to the development of accurate