First-principles study of diffusion and viscosity of anorthite (CaAl₂Si₂O₈) liquid at high pressure

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ABSTRACT

We have carried out equilibrium molecular dynamics simulations of CaAl₂Si₂O₈ (anorthite) liquid as a function of pressure (up to 160 GPa) and temperature (2500 to 6000 K) within density functional theory. Along the 3000 K isotherm, the Ca self-diffusivity varies most (decreasing by two orders of magnitude between 0 and 50 GPa), whereas the self-diffusion coefficients of Al, Si, and O vary anomalously—they initially increase with pressure, reach the broad maxima (around 5 GPa), and then decrease upon further compression. The calculated melt viscosity also shows a weak anomalous behavior with a local minimum around a similar pressure. Temperature suppresses the dynamical anomalies as well as the overall pressure variations. Therefore, the curvatures of the diffusivity (viscosity) isotherms change from a concave (convex) shape at 3000 K to a convex (concave) shape at 6000 K. We find that anorthite liquid is much more mobile than silica liquid because of its high content of non-bridging oxygen atoms (NBO) and oxygen triclusters (O₃). The predicted pressure variations can be associated with structural changes consisting of the pressure-induced maximum in the abundance of pentahedral states (fivefold Al/Si-O coordination) and rapid increase in the O₃ abundance. Finally, our predicted first-principles results compare favorably with the available experimental data.

Keywords: Anorthite liquid, diffusion, viscosity, first-principles simulations, high pressure

INTRODUCTION

Knowledge about molten silicates is crucial for our understanding of the cooling and crystallization of Earth’s early magma ocean as well as for our understanding of present day mantle dynamics (e.g., Rigden et al. 1984; Solomatov 2007). The analysis of xenoliths (e.g., Haggerty and Sautter 1990) and seismic observations (Revenaugh and Sipkin 1994; Lay et al. 2004) suggest that melts can exist at various depths in the mantle including the core-mantle boundary and can have a broad range of composition. In recent years, we have carried out first-principles simulations of melts in the MgO-SiO₂ (binary) system at high pressure and temperature to study their structural and dynamical properties (e.g., Stixrude and Karki 2005; Karki et al. 2006, 2007, 2010; de Koker et al. 2008) including viscosity (Karki and Stixrude 2010a, 2010b).

We chose to study anorthite (CaAl₂Si₂O₈) liquid for several reasons: First, it represents a composition in ternary (CaO-Al₂O₃-SiO₂) system. Naturally occurring melts are indeed multi-component silicates. Second, it is considered as a highly polymerized liquid. Such melts are known to show the non-Arrhenian dependence on temperature and also anomalous increase (decrease) of diffusivity (viscosity) with pressure (Bottinga and Richet 1995; Giordano and Dingwell 2003; Tinker et al. 2003, 2004). Third, amorphous anorthite, particularly, in glass form has widely been studied experimentally. Since the experimental measurements are confined to relatively low pressures (Urbain et al. 1982; Taniguchi 1992), to apply these results for the deep mantle requires long extrapolations. In addition, the ways in which the microscopic (atomic) characteristics control the macroscopic (bulk) properties is still an unsolved issue. Fourth, previous computational studies were based mostly on semi-empirical force fields (Nevins and Spera 1998; Morgan and Spera 2001a, 2001b; Winkler et al. 2004; Spera et al. 2009). A first-principle approach based on quantum mechanical formulation has been recently applied to anorthite liquid, with the main focus on the structure and thermodynamics (de Koker 2010).

In this paper, we report equilibrium molecular dynamics (MD) simulations of molten CaAl₂Si₂O₈ to study from first-principles diffusion and viscosity as a function of pressure (up to 160 GPa) and temperature (2500 to 6000 K). First, we introduce the methodology in the context of simulations, and derivation and analysis of dynamical properties. Then, we present the specific results and discussion on the equation of state, self-diffusivities, and viscosity of the melt.

METHODOLOGY

The first-principles molecular dynamics method, Vienna ab initio simulation package (VASP) (Kresse and Furthmüller 1996), was used within the local density approximation (Ceperley and Alder 1980). The projector augmented wave (PAW) method (Kresse and Joubert 1999) was used with a plane wave cutoff of 400 eV and γ point. Simulations based on the canonical (NVT) ensemble were performed.