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Thermodynamics of the $MgO–SiO_2$ liquid system in Earth's lowermost mantle from first principles

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ABSTRACT

Knowledge of the multi-component thermodynamics and phase equilibria of silicate melts in Earth's deep interior are key to understanding the thermal and chemical evolution of the planet, yet the melting phase diagram of the lower mantle remains poorly constrained, with large uncertainties in both eutectic composition and temperature. We use results from first-principles molecular dynamics of nine compositions along the $MgO–SiO_2$ binary to investigate the compositional dependence of liquid state thermodynamics, applying our results to describe incongruent melting for the system at deep lower mantle pressures. Our phase diagram is bi-eutectic throughout the lower mantle, with no liquid immiscibility. Accounting for solid–liquid partitioning of Fe, we find partial melts of basaltic and peridotitic lithologies to be gravitationally stable at the core–mantle boundary, while liquidus density contrasts predict that perovskite will sink and periclase will float in a crystallizing pyrolytic magma ocean.

1. Introduction

Melting at high pressure is a ubiquitous process in the formation and evolution of terrestrial planets. The moon forming giant impact alone would have melted the entire Earth (Canup, 2004; Ke and Solomatov, 2006), while seismic ultra-low velocity zones atop the core–mantle boundary (CMB) are often associated with patches of partial melt (Williams and Garnero, 1996). As the vector of chemical differentiation during magma ocean crystallization and melting of the solid mantle, the buoyancy contrast between liquid and solid phases is a critical factor in planetary dynamics and evolution. These contrasts can differ notably among mineral phases, so that the crystallization sequence is just as important for understanding these processes. Most models describing crystallization of a magma ocean assume perovskite to be the liquidus phase, with crystallization starting from the base and crystals forming at shallower depths sinking to the bottom (Solomatov, 2007).

Very little data on incongruent melting at lower mantle pressures is available to test these assumptions. Indeed, high pressure experiments indicate that the sequence of crystallization depends on pressure (Fiquet, 2010), while it was recently shown that the adiabatic thermal gradient in a magma ocean will be notably steeper than previously thought (Mosenfelder et al., 2007; Stixrude and Karki, 2005), so that crystallization may in fact initiate at depths shallower than the base (Stixrude et al., 2009). High pressure studies of congruent melting indicate that the Clapeyron slope of melting for MgO is likely higher than that of $MgSiO_3$ perovskite, which could potentially result in a strong pressure dependence in the $MgO–MgSiO_3$ eutectic composition.

The ambient pressure $MgO–SiO_2$ phase diagram, first mapped out by Bowen and Andersen (1914), suggests a number of intriguing questions regarding potential high pressure phenomena. The system exhibits liquid immiscibility in high-silica compositions (Hageman and Oonk, 1986), a very large contrast between the liquidus temperatures at intermediate (geological) compositions and MgO (Riley, 1966), a eutectic between MgO periclase and $MgSiO_4$ forsterite, another eutectic between $MgSiO_3$ enstatite and SiO_2 cristobalite, and a peritectic by which enstatite melts into a slightly more SiO_2-rich liquid phase co-existing with forsterite.

Low pressure liquid immiscibility, notably also observed in the $CaO–SiO_2$ (Hageman and Oonk, 1986) and $FeO–SiO_2$ (Bowen and Schairer, 1935) systems, has been shown to vanish by around 5 GPa (Dalton and Presnall, 1997). If this phenomenon reappears at lower mantle pressures, an idea as yet untested by experiment

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or simulation, the geochemical evolution of a cooling magma ocean, and subsequently the mantle, would be significantly more complex than current models assume.

Description of incongruent melting in the deep mantle requires knowledge of the liquid Gibbs free energy as a function not only of pressure and temperature, but also of composition, $G(P,T,X)$. Numerous studies have considered congruent melting of mantle phases, thus implicitly taking account of $G(P,T)$, but our knowledge of the behavior of liquid free energy with composition at deep mantle pressures remains sparse. Some clues to the nature of $G(X)$ are obtained from comparisons between measurements of shock compressed liquid volume (Asimow and Ahrens, 2010), and studies of the crystallization sequence at deep mantle conditions (Fiquet, 2010; Ito et al., 2004).

Here we use first-principles molecular dynamics (FPMD) to describe the thermodynamics of mixing in the MgO–SiO_2 system, and subsequently derive the chemical potential for the system. We apply this description to constrain incongruent melting equilibria for the lower mantle.

2. Theory

FPMD has proven to be a powerful and robust tool for investigating silicate melts at extreme pressures, reliably reproducing shock compression data to very high pressures and temperatures (de Koker, 2010; de Koker and Stixrude, 2009; Sun, 2011). Our simulation approach has been discussed extensively in our previous work (de Koker, 2010; de Koker et al., 2008; Stixrude and Karki, 2005). Density functional theory (DFT; Hohenberg and Kohn, 1964; Kohn and Sham, 1965) implemented in the VASP plane-wave code (Kresse and Furthmüller, 1996) is used to perform *NVT*-ensemble first-principles molecular dynamics (FPMD), with ultra-soft pseudopotentials (Kresse and Hafner, 1994) and the local density approximation (LDA). We combine existing simulation results for liquid MgO (de Koker and Stixrude, 2009; Karki et al., 2006), Mg_2SiO_4 (de Koker et al., 2008), $MgSiO_3$ (de Koker and Stixrude, 2009; Stixrude and Karki, 2005) and SiO_2 (Karki et al., 2007), together with MgO periclase (de Koker and Stixrude, 2009), $MgSiO_3$ perovskite (de Koker and Stixrude, 2009; Stixrude and Karki, 2005), and SiO_2 stishovite (Karki et al., 2007), with new simulations for liquids of intermediate composition: Mg_5SiO_7, $Mg_3Si_2O_7$, $MgSi_2O_5$, $MgSi_3O_7$ and $MgSi_5O_{11}$. More details on these simulations are given in the online supplement.

We fit an updated version of the fundamental thermodynamic relation of de Koker and Stixrude (2009) to the simulation results to obtain a thermodynamic model $G(P,T)$ for each composition considered, and combine these to construct a single representation of $G(P,T,X)$ in the system. These thermodynamic interpolation formulae are specified in the online supplement.

3. Results

3.1. Thermodynamics of mixing

Multi-component thermodynamics is expressed through the comparison of model values obtained for each simulated intermediate composition to the oxide end-members. Values of the enthalpy of mixing (H_{mix}) show positive values for silica rich compositions at low pressure. As pressure increases, values become negative and increasingly independent of pressure (Fig. 1). H_{mix} values are consistent with observed immiscibility at ambient pressure (Hageman and Oonk, 1986), as well as its disappearance by 5 GPa (Dalton and Presnall, 1997).

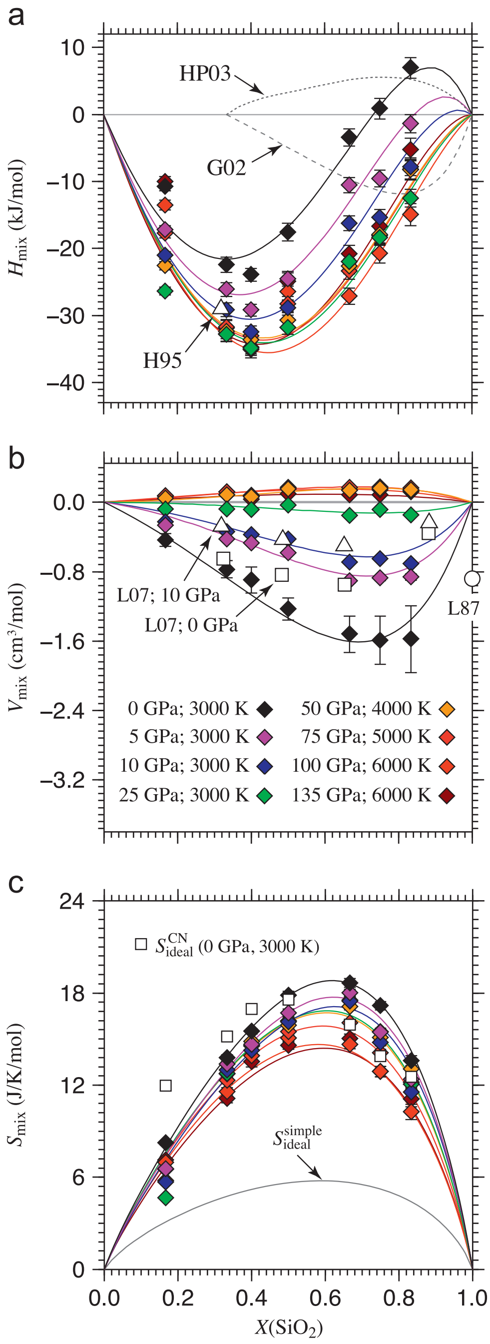

Fig. 1. (a) Enthalpy, (b) volume and (c) entropy of mixing. Diamonds – values computed using the individual thermodynamic models for each simulated composition; lines – model values determined from $G(P,T,X)$ (Eq. (2)). Change of S_{mix} with pressure is constrained from H_{mix} through Eq. (1); S_{mix} at ambient pressure is constrained from phase equilibria (refer to online supplement), and existing estimates at MgO, Mg_2SiO_4, $MgSiO_3$ and SiO_2. S_{mix} is higher than the configurational value for mixing of the endmembers (MgO, SiO_2; $S^{simple}_{ideal} = Nk_B \sum X \ln X$; Ghiorso et al., 2002), yet comparable to configurational values determined from the distribution of Mg and Si coordination species, $S^{CN}_{ideal} = Nk_B \sum_{ij} y_{ij} \ln y_{ij}$, where y_{ij} denotes the fraction of cations of type i (Mg or Si) in coordination state j (de Koker et al., 2008). Units in mol of oxides; H95—H_{mix} based on combining solid enthalpies of mixing and fusion (Hess, 1995); HP03—H_{mix} values determined by Holland and Powell (2003) based on phase equilibria; G02—H_{mix} from extrapolating multi-component parameterization of Ghiorso et al. (2002); L87—the experimental partial molar V of SiO_2 (Lange and Carmichael, 1987); L07—V_{mix} results obtained by Lacks et al. (2007) using empirical potentials. (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)

The volume of mixing (V_{mix}) becomes increasingly ideal at elevated pressure. Indeed, V_{mix} is essentially zero over most of the lower mantle, consistent with shock compression results (Asimow