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Thermodynamics of the MgO–SiO₂ 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–SiO₂ 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.

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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 MgSiO₃ perovskite, which could potentially result in a strong pressure dependence in the MgO–MgSiO₃ eutectic composition.

The ambient pressure MgO–SiO₂ 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 MgSiO₄ forsterite, another eutectic between MgSiO₃ enstatite and SiO₂ cristobalite, and a peritectic by which enstatite melts into a slightly more SiO₂-rich liquid phase co-existing with forsterite.

Low pressure liquid immiscibility, notably also observed in the CaO–SiO₂ (Hageman and Oonk, 1986) and FeO–SiO₂ (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–SiO₂ 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), Mg₂SiO₄ (de Koker et al., 2008), MgSiO₃ (de Koker and Stixrude, 2009; Stixrude and Karki, 2005) and SiO₂ (Karki et al., 2007), together with MgO periclase (de Koker and Stixrude, 2009), MgSiO₃ perovskite (de Koker and Stixrude, 2009; Stixrude and Karki, 2005), and SiO₂ stishovite (Karki et al., 2007), with new simulations for liquids of intermediate composition: Mg₅SiO₇, Mg₃Si₂O₇, MgSi₂O₅, MgSi₃O₇ and MgSi₅O₁₁. 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).

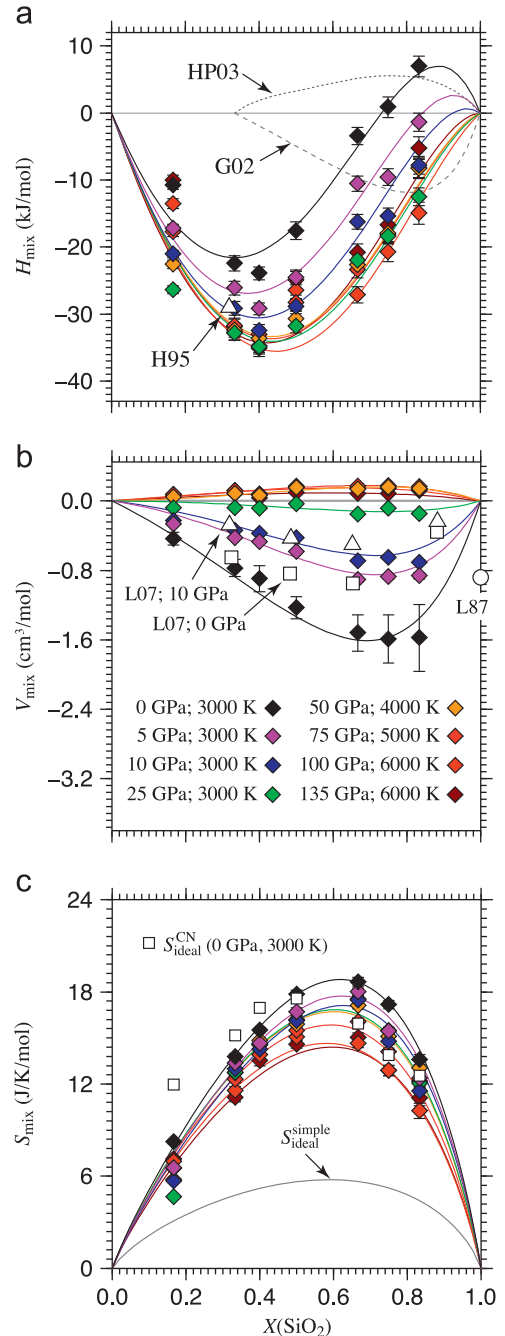


Fig. 1. (a) Enthalpy, (b) volume and (c) entropy of mixing. Diamonds – values computed using the individual thermodynamic models for each simulated composition; lines – model values determined from $G(P,T,X)$ (Eq. (2)). Change of S_{mix} with pressure is constrained from H_{mix} through Eq. (1); S_{mix} at ambient pressure is constrained from phase equilibria (refer to online supplement), and existing estimates at MgO, Mg₂SiO₄, MgSiO₃ and SiO₂. S_{mix} is higher than the configurational value for mixing of the endmembers (MgO, SiO₂; $S_{\text{ideal}}^{\text{simple}} = Nk_B \sum X \ln X$; Ghiorso et al., 2002), yet comparable to configurational values determined from the distribution of Mg and Si coordination species, $S_{\text{ideal}}^{\text{CN}} = Nk_B \sum_{ij} y_{ij} \ln y_{ij}$, 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 SiO₂ (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

and Ahrens, 2010). Negative volumes of mixing seen at ambient pressure highlight the fact that applying constant partial molar volumes to a large compositional range must be done with caution (Ghiorso et al., 2002; Lange and Carmichael, 1987).

Together, V_{mix} and the pressure dependence of H_{mix} constrain the pressure dependence of the entropy of mixing S_{mix} through

$$T \left(\frac{\partial S_{mix}}{\partial P} \right)_T = \left(\frac{\partial H_{mix}}{\partial P} \right)_T - V_{mix} \quad (1)$$

S_{mix} itself is determined by integrating Eq. (1), with the integration constant fixed by matching to experimental phase equilibria at ambient pressure (refer to online supplement). The variation of S_{mix} with pressure relative to this fixed point is fully constrained by our FPMD results.

We find that prominent liquid immiscibility at low pressure in the MgO–SiO₂ system, known to vanish with increasing pressure, remains absent throughout the lower mantle. The increasingly linear nature of mixing of volume and enthalpy as pressure increases is consistent with results from shock compression of liquid silicates, although these experiments were conducted in somewhat different compositions over a notably smaller variations of silica contents (Asimow and Ahrens, 2010).

We fit the excess Gibbs free energy of mixing using an asymmetric regular solution model (Haselton and Newton, 1980; Thompson Jr., 1967)

$$G_{mix} = G_{ideal} + W_A Y^2 (1-Y) + W_B Y (1-Y)^2, \quad (2)$$

with W_i interaction parameters, and $Y = X/[X + \lambda(1-X)]$, so that $Y=X$ when $\lambda=1$, and $\lambda \neq 1$ allows for additional asymmetry in G_{mix} . Taking $X = X(\text{SiO}_2)$, our low pressure enthalpy of mixing results require $\lambda=1.43$. Previous studies of thermodynamics of mixing in silicate systems have also suggested $\lambda \neq 1$ (Burnham, 1975; Hess, 1995; Zhou and Miller, 1997). Although more complex and ostensibly more physical models have been developed, we choose (2) for its simplicity, continuity, and the empirical fact that it works very well in representing our FPMD results. We note that some previous studies have interpreted values of λ different from unity in terms of the compositions of complexes that are mixing, for example Si₂O₄ instead of SiO₂, or Mg₂O₂ instead of MgO (Hess, 1995). However, we find no simple relationship between the value of λ required to match our FPMD results and the liquid structures observed in our simulations, which contain multiple species at all temperatures (de Koker, 2010; de Koker et al., 2008; Stixrude and Karki, 2005) that change with compression.

With G_{mix} constrained, we can derive all other thermodynamic properties at any composition along the join, including H , V , S , (Fig. 1) and the chemical potential μ ,

$$\mu_A = \frac{\partial G}{\partial X_A} \quad (3)$$

3.2. High pressure MgO–SiO₂ phase diagram

We find that the MgO–SiO₂ phase diagram at lower mantle conditions is bi-eutectic (Fig. 2). The compositions of the two eutectic points vary only weakly with pressure, corresponding closely to values characteristic of peridotite and basalt, respectively. The periclase-perovskite eutectic shifts by about 2 mol % towards MgO between 25 and 60 GPa, consistent with experimental observations (Fiquet, 2010; Ito et al., 2004). For a peridotitic magma ocean, this signals a change in the liquidus phase from periclase at shallow depths to perovskite at greater depth, with the position of the transition depending sensitively on composition.

Solidus temperatures for the MgO–SiO₂ system at the base of Earth's mantle (136 GPa) are 4930 ± 170 K and 4580 ± 210 K for

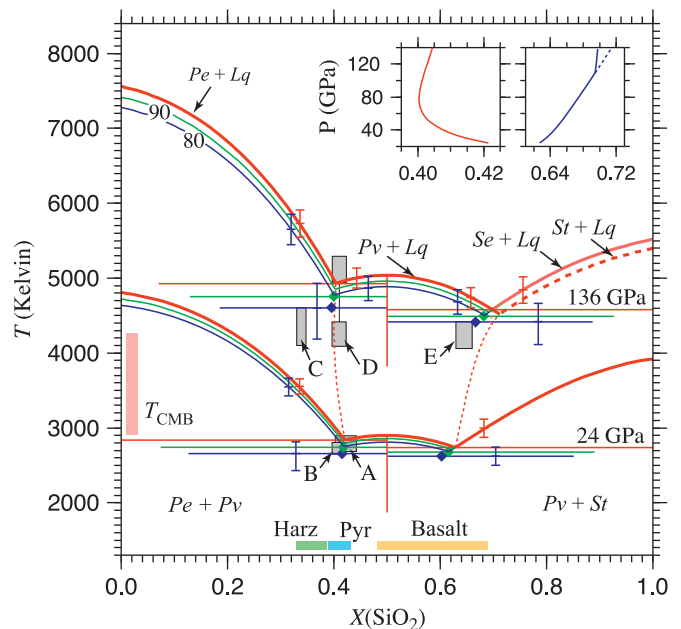


Fig. 2. Melting phase diagram for the MgO–SiO₂ system in the lower mantle (heavy red lines). Thinner green and blue lines indicate liquidus adjusted for indicated Mg# values (refer to online supplement); diamonds indicate the corresponding solidus points on the cotectic. Error bars represent uncertainty due to FPMD simulations and the partition coefficient used in adjusting for Fe (Trønnes and Frost, 2002). Stishovite metastability above 40 GPa is negligible in the CaCl₂-structure stability field, with the change to seifertite above 110 GPa (Oganov et al., 2005) resulting in a small increase in melting temperature (pink line, determined using the Clapeyron relation). Experimental measurements are shown by grey boxes; at 24 GPa, (A) MgO–SiO₂ eutectic (Presnall et al., 1998), (B) peridotite eutectic (Ito et al., 2004); at 136 GPa, (C) shock melting of Fo90 (Holland and Ahrens, 1997), (D) peridotite solidus and liquidus (Fiquet, 2010), (E) extrapolated high P melting of MORB (Hirose et al., 1999). Pe—periclase, Se—seifertite, St—stishovite, Pv—perovskite, Lq—liquid, Harz—harzburgite, Pyr—pyrolyte. Inset: Variation of Pe–Pv (red, left) and Pv–St (blue, right) eutectic compositions with pressure. Depending on the composition of a peridotitic magma ocean, Pe or Pv will be the liquidus phase at different depths in the mantle. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

$X < 0.5$ and $X > 0.5$, respectively. Based on scaling arguments, we estimate that replacement of 10 mol% MgO by FeO (Mg#=90) will lower the periclase-perovskite solidus temperature by 180–320 K; for Mg#=80, representative of basaltic oceanic crust, the silica-perovskite solidus will be decreased by a similar amount. These estimates are determined by adjusting the chemical potential of liquid and solid for a given FeO concentration (refer to online supplement), using $K_{MF}=0.40 \pm 0.15$ as an estimate of the partition coefficient between solid and melt (Trønnes and Frost, 2002). The theoretical basis for this adjustment in the chemical potential is explained in detail in section S4 of the online supplement.

3.3. Liquid structure as a function of composition

Structural adjustment in response to compression is most readily expressed in terms of the coordination of O around Si atoms, $Z_{\text{Si-O}}$, while the nature and extent of polymerization is best considered through $Z_{\text{O-Si}}$, the coordination of Si around O atoms. Coordination numbers are computed as the appropriately normalized area under the first peak of the radial distribution function (de Koker et al., 2008; McQuarrie, 1984). $Z_{\text{O-Si}}$ values of intermediate compositions vary continuously along the binary, with multiple O-coordination species present at each composition (Fig. 3). For a given degree of compression relative to the volume at ambient pressure, $Z_{\text{Si-O}}$ values do not vary notably along the binary, but do

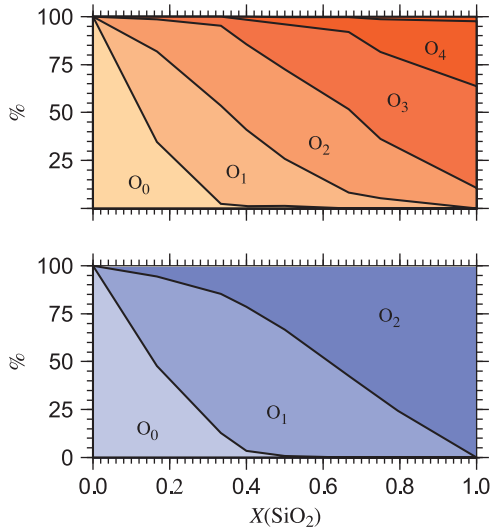


Fig. 3. The distribution of oxygen species at 6000 K and 136 GPa (top), and 3000 K and 0 GPa (bottom). $O_F-Z_{O-Si}=0$, $O_N-Z_{O-Si}=1$, $O_B-Z_{O-Si}=2$, $O_3-Z_{O-Si}=3$, $O_4-Z_{O-Si}=4$.

show a stark contrast with pure SiO_2 (Fig. 4a). Z_{Si-O} increases uniformly from 4 to 6 over a two-fold compression range relative to V_0 , the volume at 0 GPa and 3000 K, i.e. $V/V_0=1.0$ to $V/V_0=0.5$. However in pure SiO_2 compression is initially accommodated by an increase in the mean framework ring-size (Karki et al., 2007; Stixrude and Bukowinski, 1990), with coordination change becoming the primary compression mechanism around $V/V_0=0.8$ (~ 4 GPa, depending on T), from where coordination changes dominate strongly.

The changes in liquid structure with pressure and composition are strongly reflected by the thermodynamic properties. The Grüneisen parameter (γ) increases with compression for all liquids along the join, albeit delayed in SiO_2 , and highlights the relation between γ and Z_{Si-O} (Fig. 4b). In solids, high pressure phase transitions involving an increase in Z_{Si-O} result in notable increases in γ , with similar effects predicted for other cations, including Mg^{2+} (Jeanloz and Roufousse, 1982). The increase of γ with MgO content, and its notably weaker volume dependence in MgO suggests that Mg–O bonds have intrinsically higher γ values, less sensitive to changes in bond length. Density decreases with increasing silica content at low pressure, but increases with increasing silica content at high pressure. The greater compressibility at the silica rich end is consistent with the collapse of the initially open framework structure for silica rich compositions and is reflected in the decrease of the values of the reference bulk modulus K_0 from 24 GPa in the Mg-rich compositions to 12.5 GPa in silica-rich compositions. This decrease in bulk modulus is accompanied by an increase in K_0' from ~ 5.6 to ~ 6.5 (Table 1), consistent with the K_0-K_0' anti-correlation observed in silicate liquids (Lange, 2007) Fig. 5.

The differences in compressibility and partial molar volume at different compositions are also reflected in the disappearance of liquid immiscibility with pressure. Liquid immiscibility is often ascribed to the Coulombic effects (Hudon and Baker, 2002; McGahay and Tomozawa, 1989), by which the small size and high charge of the Mg^{+2} ion is difficult to accommodate in the high SiO_2 compositions, resulting in energetically less favorable structures in the liquid with increased internal energy values (Hudon and Baker, 2002). However, the volumetric advantage of a single phase assemblage grows dominant with pressure, so that two less dense liquid phases has a higher enthalpy than a single dense phase with somewhat unfavorable structural species.

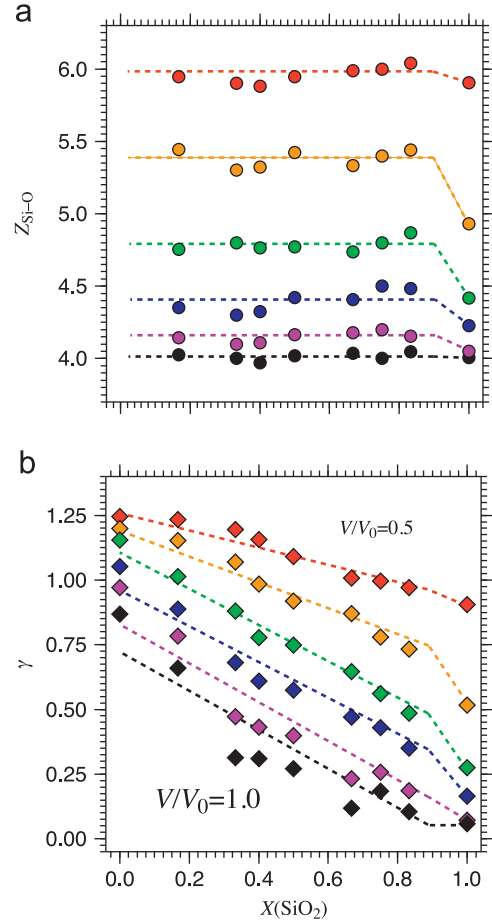


Fig. 4. (a) Silicon coordination Z_{Si-O} increases from 4 to 6 for all species considered upon two fold compression relative to V_0 , the volume at 0 GPa and 3000 K as determined from fitting the equation of state along the join. However the increase is notably delayed in SiO_2 . (b) The Grüneisen parameter γ for all liquids on the join increases with compression and MgO content. The delay in its increase for SiO_2 reflects the delayed increase in Z_{Si-O} . T increases from 3000 K at V_0 to 6000 K at $0.5V_0$. Note that here individual colors denote degrees of compression: red— $0.5V_0$, yellow— $0.6V_0$, green— $0.7V_0$, blue— $0.8V_0$, magenta— $0.9V_0$, black— $1.0V_0$. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Therefore, immiscibility arising due to similar structural accommodation problems is unlikely to arise in liquids at high pressures.

4. Geophysical implications

The fact that the MgO–MgSiO₃ eutectic composition changes little over the entire lower mantle pressure range may at first seem a simple and unsurprising result. Yet the increasing contrast between congruent melting curves of MgO and MgSiO₃ has led to large differences in speculated eutectic compositions (Boehler, 1996; Miller et al., 1991; Zhou and Miller, 1997). A high MgO melting temperature relative to MgSiO₃ could potentially even express itself as a peritectic, with MgSiO₃ melting incongruently into an SiO_2 -rich liquid and MgO periclase as residuum. If the similarity of the eutectic composition to that of peridotite is not simply a coincidence, the fact that it does not change much as a function of pressure raises the enticing possibility that extrasolar planets with non-volatile bulk compositions similar to that of the sun could also have mantles that are Earth-like in composition.

Computed eutectic temperatures are similar to estimates of temperatures reached in the thermal boundary layer at the base

Table 1
Thermodynamic properties of liquids on the MgO–SiO₂ binary at 0 GPa and 3000 K.

	MgO	Mg ₅ SiO ₇	Mg ₂ SiO ₄	Mg ₃ Si ₂ O ₇	MgSiO ₃	MgSi ₂ O ₅	MgSi ₃ O ₇	MgSi ₅ O ₁₁	SiO ₂
V/V_0	16.46 (1)	107.50 (1)	58.40 (8)	100.50 (8)	41.8 (1)	67.50 (9)	93.50 (8)	146.00 (1)	27.8 (2)
K_T (GPa)	33.49 (5)	24.33 (2)	19.50 (9)	18.35 (4)	17.2 (1)	12.92 (6)	12.53 (6)	13.06 (5)	6.2 (3)
K_S (GPa)	41.75 (9)	29.49 (7)	20.70 (7)	19.55 (4)	18.1 (1)	13.10 (6)	12.96 (10)	13.20 (3)	6.2 (4)
K_T'	4.81	5.61	5.99	5.97	6.17	6.9	6.72	5.16	14.94
α (10^{-6} K^{-1})	95 (1)	107 (1)	65 (2)	71 (1)	65 (2)	40 (1)	63 (2)	35 (3)	39 (3)
S (J/mol K) ^a	174.1 (2)	1125.4 (5)	595.1 (3)	1010.8 (5)	415.3 (2)	641.1 (5)	859.3 (7)	1283.2 (17)	205.5 (5)
C_V (Nk _B)	3.6 (2)	3.9 (1)	4.1 (4)	4.2 (2)	4.2 (4)	4.5 (3)	4.4 (3)	4.5 (2)	4.6 (2)
C_P (Nk _B)	4.5 (3)	4.8 (2)	4.4 (5)	4.5 (3)	4.4 (4)	4.5 (4)	4.6 (4)	4.6 (3)	4.6 (2)
γ	0.87 (1)	0.66 (1)	0.31 (1)	0.31 (1)	0.27 (1)	0.12 (1)	0.18 (1)	0.10 (1)	0.06 (2)

^a Based on entropy of mixing, anchored on Mg₂SiO₄ and SiO₂.

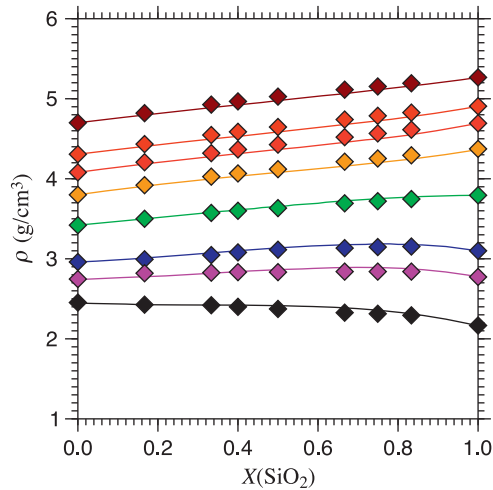


Fig. 5. Liquid density along lines of constant pressure along the MgO–SiO₂ join reveals the greater compressibility of high SiO₂ mixtures, with the compressibility of pure SiO₂ notably higher. Colors are coded as in Fig. 1, with lines obtained from the thermodynamic model. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

of Earth's mantle (T_{CMB}), and after the likely decrease due to other chemical elements on the solidus are taken into account, consistent with the proposal that seismic ultra-low velocity zones represent regions of partially molten mantle (Labrosse et al., 2007; Williams and Garnero, 1996). Consistent with previous analyses (Zhou and Miller, 1997), we find that the solidus of enriched materials ($X > 0.5$) is substantially less than that of primitive material, and will likely bracket the upper part of the range of estimates for T_{CMB} . The presence of relatively small scale enriched mantle heterogeneities may therefore explain the observation that ultra-low velocity zones are relatively localized (Williams and Garnero, 1996).

Analysis of solid-melt density contrasts indicate that partial melts of both basalt and peridotite will be gravitationally stable at the base of Earth's mantle. In the Fe-free system, liquids of eutectic composition are less dense than the isochemical solid aggregate, but inclusion of appropriate concentrations of Fe renders melts in both these systems negatively buoyant. These findings are consistent with previous analyses of the melting of perovskite (Stixrude and Karki, 2005), and are strengthened by recent indications that changes in spin state of Fe in silicate melts facilitates Fe partitioning into the liquid (Nomura et al., 2011).

Liquidus density contrasts relevant to a crystallizing pyrolytic magma ocean show that newly crystallized perovskite will sink, while periclase will float (Fig. 6). With perovskite enriched in incompatible elements relative to ferropericlase, this contrast can act as a vector for chemical differentiation. CaSiO₃ perovskite is

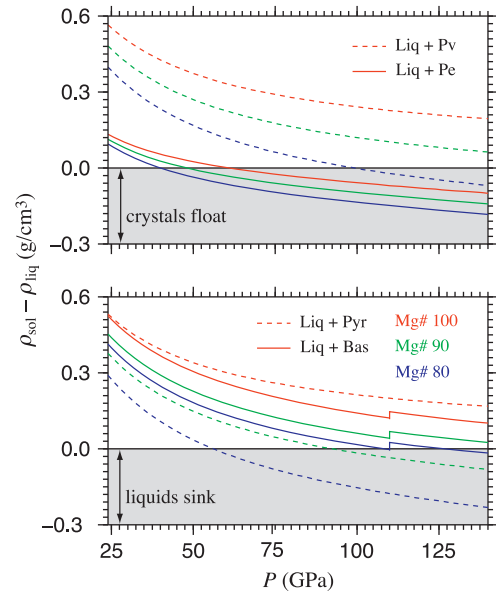


Fig. 6. (top) Density contrasts between solid and cotectic melt predicted during crystallization of a pyrolytic magma ocean. Note the opposing density contrasts of melt with perovskite (Pv) and periclase (Pe), and that a large degree of liquid fractionation is required for Pv to float. (bottom) Contrasts associated with melting indicate that partial melts of peridotitic (Pyr) and basaltic (Bas) lithologies will be gravitationally stable at the core-mantle boundary. Densities are computed at the corresponding eutectic temperatures.

about 4% denser than MgSiO₃ perovskite (Stixrude and Lithgow-Bertelloni, 2005), so that its additional affinity for incompatible elements will enhance this divergence; only after significant fractionation and enrichment of the liquid in iron will the remaining liquid phase be dense enough for perovskite to float.

The density contrast between crystal and liquid is a fundamental parameter controlling the process of crystal settling in a magma ocean. The fluid dynamics of this process are however still poorly understood and it is unclear to what extent slowly sinking crystals would gradually settle out or remain entrained in a the background flow (Solomatov, 2007). Stokes settling velocities determined from these density contrasts are between 10^{-2} and 10^{-6} m/s, depending on the crystal size and liquid viscosity (Karki and Stixrude, 2010; Martin and Nokes, 1989; Sparks et al., 1984), much smaller than plausible convective velocities associated with a vigorously convecting magma ocean.

5. Conclusions

First principles molecular dynamics simulations based on density functional theory is now capable of treating chemically rich systems

with multiple stable phases and extensive solution. Our results on the MgO–SiO₂ join show bi-eutectic melting throughout the lower mantle with a slightly lower eutectic temperature on the enriched side. The eutectic compositions are remarkably stable with increasing pressure and correspond closely to basaltic and peridotitic bulk compositions. The simulations simultaneously and self-consistently predict the density contrast between co-existing liquid and crystals. At the mantle solidus, liquids are denser than co-existing solids, providing a plausible explanation for the origin of ultra-low velocity zones at the base of the mantle in terms of partial melt. At the magma ocean liquidus, crystal buoyancy varies with phase, with perovskites tending to sink and periclase tending to float. These results place important constraints on the presence of melt at the base of the present-day mantle and on the chemical evolution of the putative magma ocean.

Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at <http://dx.doi.org/10.1016/j.epsl.2012.11.026>.

References

- Asimow, P.D., Ahrens, T.J., 2010. Shock compression of liquid silicates to 125 GPa: the anorthite-diopside join. *J. Geophys. Res.* 115, B10209, <http://dx.doi.org/10.1029/2009JB007145>.
- Boehler, R., 1996. Melting temperature of the Earth's mantle and core: Earth's thermal structure. *Annu. Rev. Earth Planet. Sci.* 24, 15–40.
- Bowen, N.L., Andersen, O., 1914. The binary system MgO–SiO₂. *Am. J. Sci.* 37, 487–500.
- Bowen, N.L., Schairer, J.F., 1935. The system, MgO–FeO–SiO₂. *Am. J. Sci.* 29, 151–217.
- Canup, R.M., 2004. Simulations of a late lunar-forming impact. *ICARUS* 168, 433–456.
- Dalton, J.A., Presnall, D.C., 1997. No liquid immiscibility in the system MgSiO₃–SiO₂ at 5.0 GPa. *Geochim. Cosmochim. Acta* 61, 2367–2373.
- de Koker, N., 2010. Structure, thermodynamics, and diffusion in CaAl₂Si₂O₈ liquid from first-principles molecular dynamics. *Geochim. Cosmochim. Acta* 74, 5657–5671.
- de Koker, N., Stixrude, L., 2009. Self-consistent thermodynamic description of silicate liquids, with application to shock melting of MgO periclase and MgSiO₃ perovskite. *Geophys. J. Int.* 178, 162–179.
- de Koker, N., Stixrude, L., Karki, B.B., 2008. Thermodynamics, structure, dynamics, and freezing of Mg₂SiO₄ liquid at high pressure. *Geochim. Cosmochim. Acta* 72, 1427–1441, <http://dx.doi.org/10.1016/j.gca.2007.12.019>.
- Fiquet, G., 2010. Melting of peridotite to 140 gigapascals. *Science* 329, 1516–1518.
- Ghiorso, M.S., Hirschmann, M.M., Reiners, P.W., Kress, V.C., 2002. The pMELTS: a revision of MELTS for improved calculation of phase relations and major element partitioning related to partial melting of the mantle to 3 GPa. *Geochem. Geophys. Geosyst.* 3, <http://dx.doi.org/10.1029/2001GC000217>.
- Hageman, V.B.M., Onk, H.A.J., 1986. Liquid immiscibility in the SiO₂+MgO, SiO₂+SrO, SiO₂+LaO₃, and SiO₂+Y₂O₃ systems. *Phys. Chem. Glasses* 27, 194–198.
- Haselton, H.T., Newton, R.C., 1980. Thermodynamics of pyrope-grossular garnets and their stabilities at high temperatures and high pressures. *J. Geophys. Res.* 85, 697306982.
- Hess, P.C., 1995. Thermodynamic mixing properties and the structure of silicate melts. In: Stebbins, J.F., McMillan, P.F., Dingwell, D.B. (Eds.), *Structure, Dynamics and Properties of Silicate Melts*. Mineralogical Society of America, Washington, D.C.
- Hirose, K., Fei, Y., Ma, Y., Mao, H.K., 1999. The fate of subducted basaltic crust in the Earth's lower mantle. *Nature* 397, 53–56.
- Hohenberg, P., Kohn, W., 1964. Inhomogeneous electron gas. *Phys. Rev. B* 136, B864.
- Holland, K.G., Ahrens, T.J., 1997. Melting of (Mg,Fe)₂SiO₄ at the core–mantle boundary of the Earth. *Science* 275, 1623–1625.
- Holland, T., Powell, R., 2003. Activity–composition relations for phases in petrological calculations: an asymmetric multicomponent formulation. *Contrib. Mineral. Petrol.* 145, 492–501.
- Hudon, P., Baker, D.R., 2002. The nature of phase separation in binary oxide melts and glasses. I. Silicate systems. *J. Non-Cryst. Solids* 303, 299–345.
- Ito, E., Kubo, A., Katsura, T., Walter, M.J., 2004. Melting experiments of mantle materials under lower mantle conditions with implications for magma ocean differentiation. *Phys. Earth Planet. Interiors* 143–144, 397–406.
- Jeanloz, R., Roufousse, M., 1982. Anharmonic properties—ionic model of the effects of compression and coordination change. *J. Geophys. Res.* 87, 763–772.
- Karki, B., Stixrude, L., 2010. Viscosity of MgSiO₃ liquid at Earth's mantle conditions: implications for an early magma ocean. *Science* 238, 740–743.
- Karki, B.B., Bhattarai, D., Stixrude, L., 2006. First principles calculations of the structural, dynamical and electronic properties of liquid MgO. *Phys. Rev. B* 73, 174208.
- Karki, B.B., Bhattarai, D., Stixrude, L., 2007. First-principles simulations of liquid silica: structural and dynamical behavior at high pressure. *Phys. Rev. B* 76, 104205.
- Ke, Y., Solomatov, V.S., 2006. Early transient superplumes and the origin of the Martian crustal dichotomy. *J. Geophys. Res.*, 111, <http://dx.doi.org/10.1029/2005JE002631>.
- Kohn, W., Sham, L.J., 1965. Self-consistent equations including exchange and correlation effects. *Phys. Rev.* 140, 1133.
- Kresse, G., Furthmüller, J., 1996. Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set. *Comput. Mater. Sci.* 6, 15–50.
- Kresse, G., Hafner, J., 1994. Norm-conserving and ultrasoft pseudopotentials for first-row and transition-elements. *J. Phys. Condens. Matter* 6, 8245–8257.
- Labrosse, S., Hernlund, J., Coltice, N., 2007. A crystallizing dense magma ocean at the base of the Earth's mantle. *Nature* 450, 866–869.
- Lacks, D.J., Rear, D.B., Van Orman, J.A., 2007. Molecular dynamics investigation of viscosity, chemical diffusivities and partial molar volumes of liquids along the MgO–SiO₂ join as functions of pressure. *Geochim. Cosmochim. Acta* 71, 1312–1323.
- Lange, R.A., 2007. The density and compressibility of KAlSi₃O₈ liquid to 6.5 GPa. *Am. Mineral.* 92, 114–123.
- Lange, R.A., Carmichael, I.S.E., 1987. Densities of Na₂O–K₂O–CaO–MgO–FeO–Fe₂O₃–Al₂O₃–TiO₂–SiO₂ liquids—new measurements and derived partial molar properties. *Geochim. Cosmochim. Acta* 51, 2931–2946.
- Martin, D., Nokes, R., 1989. A fluid-dynamical study of crystal settling in convecting magmas. *J. Petrol.* 30, 1471–1500.
- McGahay, V., Tomozawa, M., 1989. The origin of phase separation in silicate melts and glasses. *J. Non-Cryst. Solids* 109, 27–34.
- McQuarrie, D.A., 1984. *Statistical Mechanics*. University Science Books, Sausalito, CA.
- Miller, G.H., Stolper, E.M., Ahrens, T.J., 1991. The equation of state of a molten Komatiite. 2. Application to Komatiite petrogenesis and the Hadean mantle. *J. Geophys. Res.* 96, 11849–11864.
- Mosenfelder, J.L., Asimow, P.D., Ahrens, T.J., 2007. Thermodynamic properties of Mg₂SiO₄ liquid at ultra-high pressures from shock measurements to 200 GPa on forsterite and wadsleyite. *J. Geophys. Res.*, 112, <http://dx.doi.org/10.1029/2006B004364>.
- Nomura, R., Ozawa, H., Tateno, S., Hirose, K., Hernlund, J., Muto, Y., Ishii, H., Hiraoka, N., 2011. Spin crossover and iron-rich silicate melt in the Earth's deep mantle. *Nature* 473, 199–202.
- Oganov, A.R., Gillan, M., Price, G.D., 2005. Structural stability of silica at high pressures and temperatures. *Phys. Rev. B* 71, 064104.
- Presnall, D.C., Weng, Y.-H., Milholland, C.S., Walter, M.J., 1998. Liquidus phase relations in the system MgO–MgSiO₃ at pressures up to 25 GPa—constraints on crystallization of a molten Hadean mantle. *Phys. Earth Planet. Interiors* 107, 83–95.
- Riley, B., 1966. The Determination of melting points at temperatures above 2000° Celsius. *Revue internationale des hautes températures et des réfractaires* 3, 327–336.
- Solomatov, V.S., 2007. Magma oceans and primordial mantle differentiation. In: Schubert, G. (Ed.), *Treatise on Geophysics*, vol. 9. Evolution of the Earth. Elsevier, Amsterdam.
- Sparks, R.S.J., Huppert, H.E., Turner, J.S., 1984. The fluid dynamics of evolving magma chambers. *Philos. Trans. R. Soc. London Ser. A* 310, 511–534.
- Stixrude, L., Bukowinski, M.S.T., 1990. A novel topological compression mechanism in a covalent liquid. *Science* 250, 541–543.
- Stixrude, L., de Koker, N., Sun, N., Mookherjee, M., Karki, B.B., 2009. Thermodynamics of silicate liquids in the deep Earth. *Earth Planet. Sci. Lett.* 278, 226–232.
- Stixrude, L., Karki, B., 2005. Structure and freezing of MgSiO₃ liquid in Earth's lower mantle. *Science* 310, 297–299.
- Stixrude, L., Lithgow-Bertelloni, C., 2005. Thermodynamics of mantle minerals—I. Physical properties. *Geophys. J. Int.* 162, 610–632.
- Sun, N., 2011. First principles molecular dynamics simulations of diopside (CaMgSi₂O₆) liquid to high pressure. *Geochim. Cosmochim. Acta* 75, 3792–3802.
- Thompson Jr., J.B., 1967. Thermodynamic properties of simple solutions. *Res. Geochim.* 2, 340–361.
- Trønnes, R.G., Frost, D.J., 2002. Peridotite melting and mineral–melt partitioning of major and minor elements at 22–24.5 GPa. *Earth Planet. Sci. Lett.* 197, 117–131.
- Williams, Q., Garnero, E.J., 1996. Seismic evidence for partial melt at the base of Earth's mantle. *Science* 273, 1528–1530.
- Zhou, Y., Miller, G.H., 1997. Constraints from molecular dynamics on the liquidus and solidus of the lower mantle. *Geochim. Cosmochim. Acta* 61, 2957–2976.

Supplimentary Online Material:
Multi-Component Melting of Earth's Lowermost Mantle
from First Principles

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S1 Details of FPMD Simulations

The new intermediate compositions simulated are Mg_5SiO_7 , $\text{Mg}_3\text{Si}_2\text{O}_7$, MgSi_2O_5 , MgSi_3O_7 , and $\text{MgSi}_5\text{O}_{11}$. Simulation cells have 78, 72, 72, 66, and 75 atoms, respectively. These intermediate systems are initiated by removing and/or transforming an appropriate number of atoms from either MgSiO_3 or Mg_2SiO_4 and evolving the resulting high energy configuration to a favorable state at 10000 K for at least 6000 time steps by FPMD; in all calculations in this work 1 time step = 1 femto second. Results obtained in test simulations initiated using geometries generated by classical molecular dynamics runs of 1 nano second differed negligibly from the FPMD production runs.

For compositions with no stable solid phases with which to compute the correction for the systematic overbinding in LDA, values are interpolated along the join using the known values for MgO , Mg_2SiO_4 , MgSiO_3 and SiO_2 (Figure S1; Karki and Stixrude, 2010; de Koker and Stixrude, 2009; de Koker et al., 2008; Karki et al., 2007, 2006; Stixrude and Karki, 2005).

S2 Fundamental Thermodynamic Relations

S2.1 Description of Liquids

The liquid-state fundamental relation (LFTR) we use to model the thermodynamics of each simulated liquid composition was described in detail in de Koker and Stixrude (2009). The relation uses the Helmholtz free energy as thermodynamic potential, expressed as a function of its natural variables

$$F(V, T) = F_{\text{ig}}(V, T) + F_{\text{el}}(V, T) + F_{\text{xs}}(V, T), \quad (\text{S1})$$

by considering three separate contributions due to atomic momenta $F_{\text{ig}}(V, T)$, electronic excitation $F_{\text{el}}(V, T)$, and bonding $F_{\text{xs}}(V, T)$, respectively.

$F_{\text{xs}}(V, T)$ is written as a two-dimensional expansion in terms of functions $f(V)$ (Eulerian finite strain) and $\theta(T)$ about the reference volume and temperature V_0 and T_0 ,

$$F_{\text{xs}}(V, T) = \sum_{i=0}^{\mathcal{O}'_f} \sum_{j=0}^{\mathcal{O}'_\theta} \frac{a_{ij}}{i!j!} f^i \theta^j; \quad (\text{S2})$$

$$f = \frac{1}{2} \left[\left(\frac{V_0}{V} \right)^{\frac{2}{3}} - 1 \right]; \quad \theta = \left[\left(\frac{T}{T_0} \right)^m - 1 \right]. \quad (\text{S3})$$

s28 F_{el} is given by

$$F_{\text{el}}(V, T) = -\zeta \left[\frac{1}{2} (T^2 - T_{\text{el}}^2) - TT_{\text{el}} \ln \frac{T}{T_{\text{el}}} \right], \quad (\text{S4})$$

s29 which follows by integration of the electronic heat capacity for a conductor, modified
s30 to account for the liquid being conductive only above T_{el} , with ζ the electronic heat
s31 capacity coefficient. The volume dependence of ζ and T_{el} is described using power
s32 law relations

$$\zeta = \zeta_0 \left(\frac{V}{V_0} \right)^\xi; \quad T_{\text{el}} = T_{\text{el}0} \left(\frac{V}{V_0} \right)^\eta, \quad (\text{S5})$$

s33 with ζ_0 , ξ , $T_{\text{el}0}$, and η free parameters to be determined.

s34 F_{ig} is the free energy of an ideal gas with a composition corresponding to that of
s35 the liquid (eg. Callen, 1985; McQuarrie, 1984)

$$F_{\text{ig}}(V, T) = -k_{\text{B}}T \sum_i N_i \ln \frac{e q_i}{N_i}, \quad (\text{S6})$$

s36 with the partition function

$$q_i = V \left(m_i k_{\text{B}} / 2\pi \hbar^2 \right)^{3/2}, \quad (\text{S7})$$

s37 with m_i the atomic mass element i .

s38 To obtain the level of accuracy in fitting of the LFTR to our FPMD results
s39 required for considering the thermodynamics of mixing, we use second order tem-
s40 perature fits ($\mathcal{O}_\theta = 2$). We find that MgO, Mg₅SiO₇, Mg₂SiO₄, Mg₃Si₂O₇, MgSiO₃,
s41 MgSi₂O₅, and MgSi₃O₇ are well fit by a third order finite strain expansion ($\mathcal{O}_f = 3$),
s42 while MgSi₅O₁₁ requires $\mathcal{O}_f = 4$, and SiO₂ $\mathcal{O}_f = 5$, consistent with our previous
s43 findings (de Koker and Stixrude, 2009). Fits for each composition are shown in Fig-
s44 ures S2-S10, with thermodynamic properties at 0 GPa and 3000 K reported in Table
s45 1 of the main text.

s46 S2.2 Description of Solids

s47 Thermodynamics of FPMD solids are described using the anharmonic relation for
s48 high T solids (SFTR) explained in de Koker and Stixrude (2009); for completeness
s49 we briefly summarize it here. The Helmholtz free energy of the solid is written as

$$F(V, T) = F(V_0, T_0) + F_{\text{cmp}}(V, T_0) + F_{\text{th}}(V, T), \quad (\text{S8})$$

s50 with $F(V_0, T_0)$ the free energy at reference volume V_0 and temperature T_0 , $F_{\text{cmp}}(V, T_0)$
s51 the contribution due to isothermal compression, and $F_{\text{th}}(V, T)$ that due to isochoric
s52 temperature differences relative to T_0 .

553 F_{cmp} is expressed as an expansion in terms of the Eulerian finite strain (f) (Birch,
554 1952, 1978)

$$F_{\text{cmp}} = 9K_{T0}V_0 \left[\frac{1}{2}f^2 + \frac{1}{6}a_3f^3 + \dots \right], \quad (\text{S9})$$

$$a_3 = 3(K'_{T0} - 4), \quad (\text{S10})$$

555 V_0 , K_{T0} , and K'_{T0} being the volume, bulk modulus, and its first pressure derivative
556 at zero pressure and a reference temperature T_0 .

557 F_{th} is obtained by integration of the entropy as

$$F_{\text{th}}(V, T) = -S_0 [T - T_0] - C_V \left[T \ln \frac{T}{T_0} - [T - T_0] \right] - C_V [T - T_0] \int_{V_0}^V \frac{\gamma(V', T_0)}{V'} dV', \quad (\text{S11})$$

558 where S_0 is the entropy at zero pressure and reference temperature, C_V is the heat
559 capacity at volume V , assumed to be constant as a function of T though not con-
560 strained to a harmonic value of $3Nk_B$, and γ is the Grüneisen parameter, described
561 as (Stixrude and Lithgow-Bertelloni, 2005)

$$\gamma = \frac{\gamma'_0 + (2\gamma'_0 + \gamma'_1) f + 2\gamma'_1 f^2}{3(2 + 2\gamma'_0 f + \gamma'_1 f^2)}, \quad (\text{S12})$$

562 with

$$\gamma_0 = \frac{1}{6}\gamma'_0; \quad q_0 = \frac{\gamma'_1 + 2\gamma'_0 - \gamma_0'^2}{-3\gamma'_0}. \quad (\text{S13})$$

563 For MgO periclase, Mg_2SiO_4 forsterite, MgSiO_3 perovskite, and SiO_2 stishovite
564 we use a third order finite strain expansion for F_{cmp} . Fits for each solid composition
565 considered are shown in Figures S11-S14.

566 **S3 Constraining Reference Entropy Values for Thermo-** 567 **dynamic Relations of Simulated Phases**

568 Complete description of the free energy in the liquid and solid fundamental relations
569 requires the entropy at one reference point for each system to be known, i.e. 13
570 values of S_0 have to be specified, 9 for liquids and 4 for solids. Our description of
571 the thermodynamics of mixing (eq. 2) gives the total entropy along the binary at
572 constant P and T as

$$S = YS_{\text{SiO}_2} + (1 - Y)S_{\text{MgO}} + S_{\text{ideal}} + W'_A Y^2(1 - Y) + W'_B(1 - Y)^2 Y, \quad (\text{S14})$$

573 with

$$S_{\text{ideal}} = R[Y \ln Y + (1 - Y) \ln(1 - Y)], \quad (\text{S15})$$

S74

$$Y = X/(X + \lambda(1 - X)), \quad (\text{S16})$$

S75

$$W' = -(\partial W/\partial T)_P. \quad (\text{S17})$$

S76

Constraining S_0 for the 9 liquid compositions therefore requires λ , W'_A , W'_B , S_{SiO_2} ,
S77 and S_{MgO} to be specified at a single chosen reference state, the P and T dependence
S78 of these quantities being fixed by our FPMD simulations. λ is determined from
S79 fitting to H_{mix} (Figure 1). W'_A and W'_B are constrained by optimizing with respect
S80 to three invariant points on the MgO–SiO₂ phase diagram (Figure S15) associated
S81 with the ambient pressure liquid for periclase and forsterite together with the liquid
S82 immiscibility field. The three invariant points are i) the critical temperature of liquid
S83 immiscibility ($T = 2250$ K, $X = 0.87$; Hageman and Oonk, 1986), ii) the forsterite-
S84 periclase eutectic ($T = 2136$ K; $X = 0.30$ Bowen and Andersen, 1914), and iii) the
S85 forsterite-clinoenstatite peritectic ($T_{\text{liquidus}} = 1830$; $X = 0.52$ Bowen and Andersen,
S86 1914). Values for S_{SiO_2} and S_{MgO} are chosen to optimize agreement with the available
S87 estimates of liquid entropy along the binary (Figure S16), obtained as

$$S_{\text{liq}}(T, P) = S_{\text{sol}}(T_m, P) + \Delta S_m(P) + \Delta S_{\text{liq}}(T_m \rightarrow T, P), \quad (\text{S18})$$

S88

where $\Delta S_{\text{liq}}(T_m \rightarrow T, P) = C_P \ln(T/T_m)$, and the subscript m indicates melting.

S89

To constrain S_0 values in the crystalline phases in a manner that is consistent with
S90 the liquid entropies through their measured melting temperatures, we constrain the
S91 crystalline S_0 values by matching liquid Gibbs free energies at chosen experimental
S92 melting points. These fixed points are: 3070 K, 0 GPa for periclase (Riley, 1966);
S93 2163 K, 0 GPa for forsterite (Bowen and Andersen, 1914); 2900 K, 25 GPa for
S94 perovskite (Stixrude and Karki, 2005, and references therein); 3120 K, 14 GPa for
S95 stishovite (Zhang et al., 1993; Shen and Lazor, 1995). Entropy values in our SFTRs
S96 are therefore not directly constrained from calorimetry data; a comparison between
S97 experimental entropy values and the values in our description is made in Table S1.

S98

Our computed ambient pressure phase diagram agrees very well with the ex-
S99 perimental data. The optimal S_{mix} model gives the periclase-forsterite eutectic at
S100 $X = 0.31$, $T = 2136$ K, and the forsterite-clinoenstatite peritectic at $X = 0.52$.
S101 We further obtain the critical point of immiscibility at $T = 2250$ K, $X = 0.92$, al-
S102 though our computed immiscibility field is narrower than the experimental curve.
S103 We find that the shape of the computed immiscibility field is sensitive to H_{mix} , but
S104 not to S_{mix} . Using a different mixing model will not increase the width of the field
S105 width, and the discrepancy likely results from the approximations made in treating
S106 the exchange-correlation energy at the first-principles level.

s107 **S4 Estimating the Influence of FeO**

s108 We estimate the influence of the addition of FeO on our results as

$$\mu_{\alpha}^{\beta}(X^*, Z) = \mu_{\alpha}^{\beta}(X^*) + RT \ln \gamma^{\beta} Z, \quad (\text{S19})$$

s109 where μ_{α}^{β} is the chemical potential of component α in phase β , γ is the activity
s110 coefficient, and the compositional variables

$$X^* = \frac{N_{\text{SiO}_2}}{N_{\text{SiO}_2} + N_{\text{MgO}} + N_{\text{FeO}}}, \quad (\text{S20})$$

s111

$$Z = \frac{N_{\text{MgO}}}{N_{\text{MgO}} + N_{\text{FeO}}}. \quad (\text{S21})$$

s112 Motivated by the expectation that Fe will substitute primarily for Mg, we assume
s113 that

$$\mu_{\alpha}^{\beta}(X^*) = \mu_{\alpha}^{\beta}(X), \quad (\text{S22})$$

s114 where

$$X = \frac{N_{\text{SiO}_2}}{N_{\text{SiO}_2} + N_{\text{MgO}}}. \quad (\text{S23})$$

s115 From our FPMD results, we know the first term on the right-hand side of eq. S19
s116 for the components in the liquid phase (Lq), and for the solid phases stishovite (St)
s117 (or seifertite), ferropericlase (Fp) and perovskite (Pv) for which $\mu_{\alpha}^{\beta}(X^*)$ is simply the
s118 chemical potential of the pure end-member in the MgO-SiO₂ system. We can then
s119 find the influence of the FeO component on the phase diagram by equating chemical
s120 potentials in coexisting phases. In order to specify the solution completely, we further
s121 assume values of the Mg-Fe partition coefficients for the pairs liquid-ferropericlase
s122 and perovskite-ferropericlase. The system of equations to be solved is then

$$\mu_{\text{MgO}}^{\text{Lq}}(X^*, Z) = \mu_{\text{MgO}}^{\text{Fp}} + RT \ln \frac{Z^{\text{Fp}}}{Z^{\text{Lq}}}, \quad (\text{S24})$$

$$\mu_{\text{MgSiO}_3}^{\text{Lq}}(X^*, Z) = \mu_{\text{MgSiO}_3}^{\text{Pv}} + RT \ln \frac{Z^{\text{Pv}}}{Z^{\text{Lq}}}, \quad (\text{S25})$$

$$\mu_{\text{SiO}_2}^{\text{Lq}}(X^*, Z) = \mu_{\text{SiO}_2}^{\text{Pv}}, \quad (\text{S26})$$

$$K^{\text{Lq-Fp}} = \frac{Z^{\text{Lq}}(1 - Z^{\text{Fp}})}{Z^{\text{Fp}}(1 - Z^{\text{Lq}})}, \quad (\text{S27})$$

$$K^{\text{Pv-Fp}} = \frac{Z^{\text{Pv}}(1 - Z^{\text{Fp}})}{Z^{\text{Fp}}(1 - Z^{\text{Pv}})}, \quad (\text{S28})$$

s123 where $K^{\beta-\delta}$ is the Mg-Fe partition coefficient between phases β and δ , and we have
s124 further assumed that ratios of activity coefficients, e.g. $\gamma^{\text{Pv}}/\gamma^{\text{Lq}} \approx 1$ because Mg-Fe

s125 solution is found to be close to ideal in many silicate and oxide systems (eg. Stixrude
s126 and Lithgow-Bertelloni, 2011, and references therein). For example, for a given value
s127 of temperature T and Z^{FP} of the bulk system, we may solve eqs. S24 and S27 for X^* ,
s128 the silica fraction on the liquidus in the FeO-bearing system, along which $Z^{\text{Lq}} = Z^{\text{FP}}$.

s129 **References**

- s130 Alfè D. (2005) Melting curve of MgO from first-principles simulations. *Physical*
s131 *Review Letters* **94**, 235701.
- s132 Birch F. (1952) Elasticity and Constitution of the Earth's Interior. *Journal of Geo-*
s133 *physical Research* **57**, 227–286.
- s134 Birch F. (1978) Finite Strain Isotherm and Velocities for Single-Crystal and Poly-
s135 crystalline NaCl at High Pressures and 300 K. *Journal of Geophysical Research*
s136 **83**, 1257–1268.
- s137 Bowen N.L. and Andersen O. (1914) The binary system MgO – SiO₂. *American*
s138 *Journal of Science* **37**, 487–500.
- s139 Callen H.B. (1985) *Thermodynamics and an Introduction to Thermostatistics*. John
s140 Wiley & Sons, New York, 2nd edition.
- s141 de Koker N. and Stixrude L. (2009) Self-Consistent Thermodynamic Description of
s142 Silicate Liquids, with Application to Shock Melting of MgO Periclase and MgSiO₃
s143 Perovskite. *Geophysical Journal International* **178**, 162–179.
- s144 de Koker N., Stixrude L. and Karki B.B. (2008) Thermodynamics, Structure, Dynam-
s145 ics, and Freezing of Mg₂SiO₄ Liquid at High Pressure. *Geochimica et Cosmochimica*
s146 *Acta* **72**, 1427–1441, doi:10.1016/j.gca.2007.12.019.
- s147 Ferguson J.B. and Merwin H.E. (1918) The Melting Points of Cristobalite and
s148 Tridymite. *American Journal of Science* **46**, 417–426.
- s149 Ghiorso M.S. and Carmichael I. (1980) A Regular Solution Model for Met-Aluminous
s150 Silicate Liquids: Applications to Geothermometry, Immiscibility, and the Source
s151 Regions of Basic Magmas. *Contributions to Mineralogy and Petrology* **71**, 323–342.
- s152 Hageman V.B.M. and Oonk H.A.J. (1986) Liquid immiscibility in the SiO₂ + MgO,
s153 SiO₂ + SrO, SiO₂ + LaO₃, and SiO₂ + Y₂O₃ systems. *Physics and Chemistry of*
s154 *Glasses* **27**, 194–198.

- s155 Hudon P., Jung I.H. and Baker D.R. (2002) Melting of β -quartz up to 2.0 GPa and
s156 thermodynamic optimization of the silica liquidus up to 6.0 GPa. *Physics of the*
s157 *Earth and Planetary Interiors* **130**, 159–174.
- s158 Karki B.B., Bhattarai D. and Stixrude L. (2006) First principles calculations of the
s159 structural, dynamical and electronic properties of liquid MgO. *Physical Review B*
s160 **73**, 174208.
- s161 Karki B.B., Bhattarai D. and Stixrude L. (2007) First-principles simulations of liquid
s162 silica: Structural and dynamical behavior at high pressure. *Physical Review B* **76**,
s163 104205.
- s164 Karki B.B. and Stixrude L. (2010) First-principles study of enhancement of transport
s165 properties of silica melt by water. *Physical Review Letters* **104**, 215901.
- s166 McQuarrie D.A. (1984) *Statistical Mechanics*. University Science Books, Sausalito,
s167 CA.
- s168 Navrotsky A., Ziegler D., Oestrike R. and Maniar P. (1989) Calorimetry of Sili-
s169 cate Melts at 1773K - Measurement of Enthalpies of Fusion and of Mixing in
s170 the Systems Diopside-Anorthite-Albite and Anorthite-Forsterite. *Contributions to*
s171 *Mineralogy and Petrology* **101**, 122–130.
- s172 Richet P., Bottinga Y., Denielou L., Petitet J.P. and Tequi C. (1982) Thermodynamic
s173 properties of quartz, cristobalite and amorphous SiO₂: drop calorimetry measure-
s174 ments between 1000 and 1800 K and a review from 0 to 2000 K. *Geochimica et*
s175 *Cosmochimica Acta* **46**, 2639–2658.
- s176 Riley B. (1966) The Determination of Melting Points at Temperatures Above 2000°
s177 Celcius. *Revue internationale des hautes temperatures et des refractaires* **3**, 327–336.
- s178 Robie R.A. and Hemingway B.S. (1995) *Thermodynamic Properties of Minerals and*
s179 *Related Substances at 298.15 K and 1 Bar (10⁵ Pascals) Pressure and at Higher*
s180 *Temperatures*, volume 2131 of *USGS Bulletin*. Eastern Region, Reston, Va.
- s181 Shen G. and Lazor P. (1995) Measurement of melting temperatures of some minerals
s182 under lower mantle pressures. *Journal of Geophysical Research* **100**, 17699–17713.
- s183 Stebbins J.F., Carmichael I.S.E. and Moret L.K. (1984) Heat-Capacities and En-
s184 tropies of Silicate Liquids and Glasses. *Contributions to Mineralogy and Petrology*
s185 **86**, 131–148.

- s186 Stixrude L. and Karki B.B. (2005) Structure and Freezing of MgSiO₃ liquid in the
s187 Earth's lower mantle. *Science* **310**, 297–299.
- s188 Stixrude L. and Lithgow-Bertelloni C. (2005) Thermodynamics of mantle minerals -
s189 I. Physical properties. *Geophysical Journal International* **162**, 610–632.
- s190 Stixrude L. and Lithgow-Bertelloni C. (2011) Thermodynamics of mantle minerals -
s191 II. Phase equilibria. *Geophysical Journal International* **in press**.
- s192 Tangeman J.A., Phillips B.L., Navrotsky A., Weber J.K.R., Hixson A.D. and Key
s193 T.S. (2001) Vitreous forsterite (Mg₂SiO₄): Synthesis, structure, and thermochem-
s194 istry. *Geophysical Research Letters* **28**, 2517–2520.
- s195 Zhang J., Liebermann R.C., Gasparik T. and Herzberg C.T. (1993) Melting and
s196 Subsolidus Relations of SiO₂ at 9 – 14 GPa. *Journal of Geophysical Research* **98**,
s197 19785–19793.

Table S1: Entropy of FPMD simulated solid phases at the respective fixed melting points used to constrain their free energy by matching to liquid values.

	Periclase MgO	Forsterite Mg ₂ SiO ₄	Perovskite MgSiO ₃	Stishovite SiO ₂
<i>P</i> (GPa)	0	0	25	14
<i>T</i> (Kelvin)	3070	2163	2900	3120
<i>S</i> (J/mol K)	145.3 (2)	440.7 (5)	306.0 (3)	163.5 (2)
Previous estimates	144 (1) [†]	419 (2) [†]	308 (2) [‡]	178 (2) [‡]

[†] Robie and Hemingway (1995);

[‡] Stixrude and Lithgow-Bertelloni (2011)

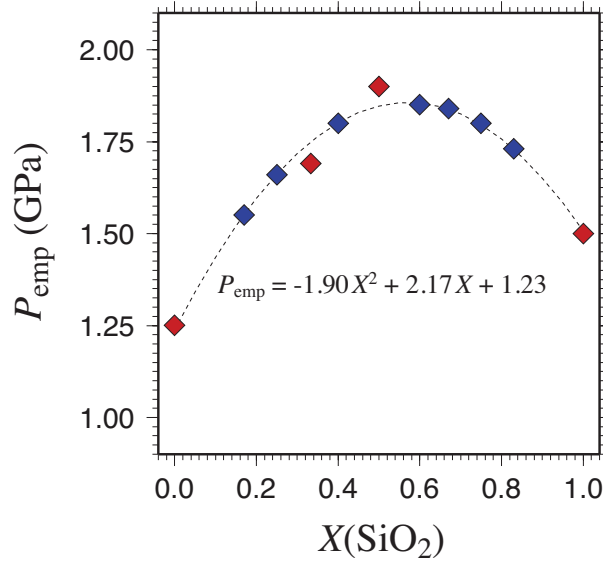


Figure S1: Interpolation of the pressure correction for systematic overbinding of LDA from phases for which it can be computed (red) to phases with no corresponding solid phases (blue).

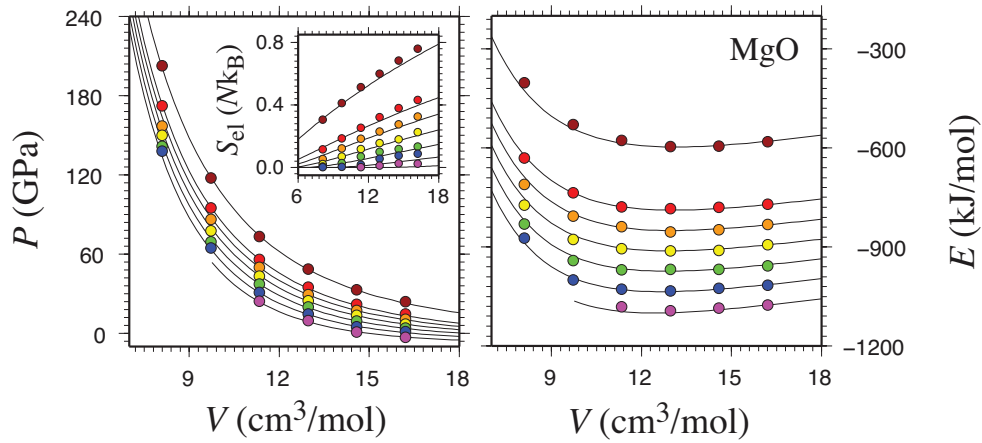


Figure S2: FPMD results (circles) and LFTR fit (lines) for MgO liquid. Purple - 2000 K; blue - 3000 K; green - 4000 K; yellow - 5000 K; orange - 6000 K; red - 7000 K; maroon - 10000 K.

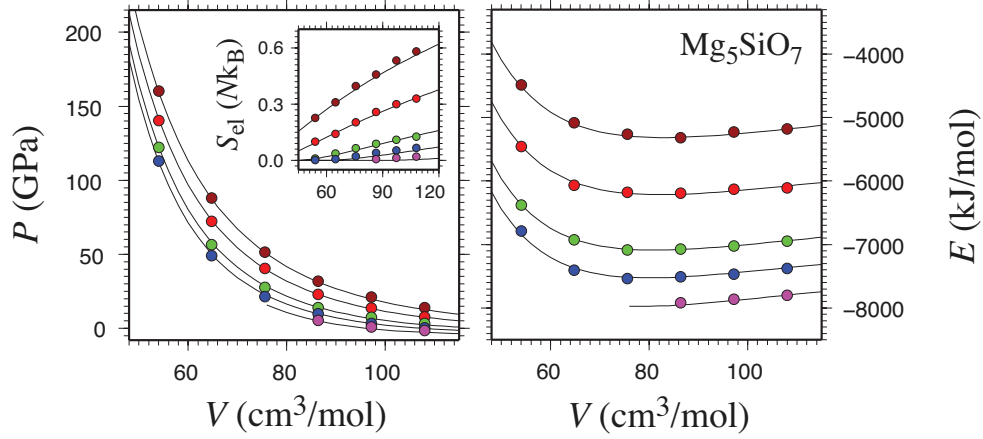


Figure S3: FPMD results (circles) and LFTR fit (lines) for Mg_5SiO_7 liquid. Purple - 2000 K; blue - 3000 K; green - 4000 K; red - 6000 K; maroon - 8000 K.

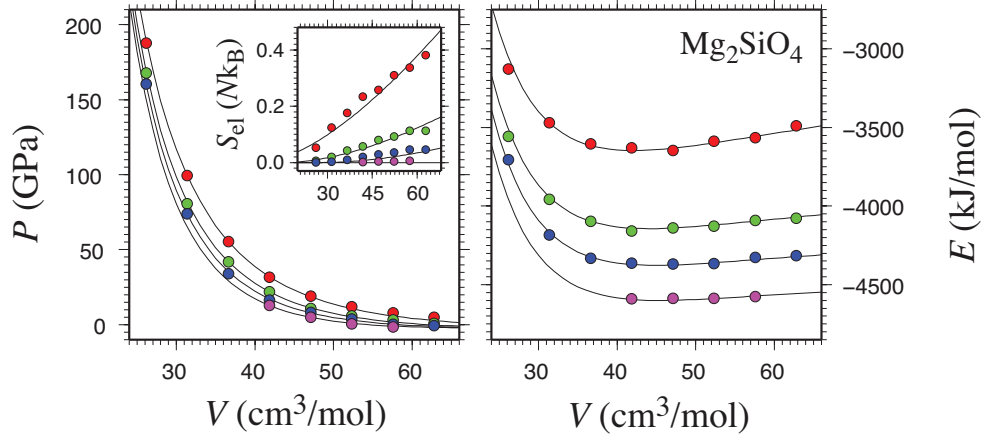


Figure S4: FPMD results (circles) and LFTR fit (lines) for Mg_2SiO_4 liquid. Purple - 2000 K; blue - 3000 K; green - 4000 K; red - 6000 K.

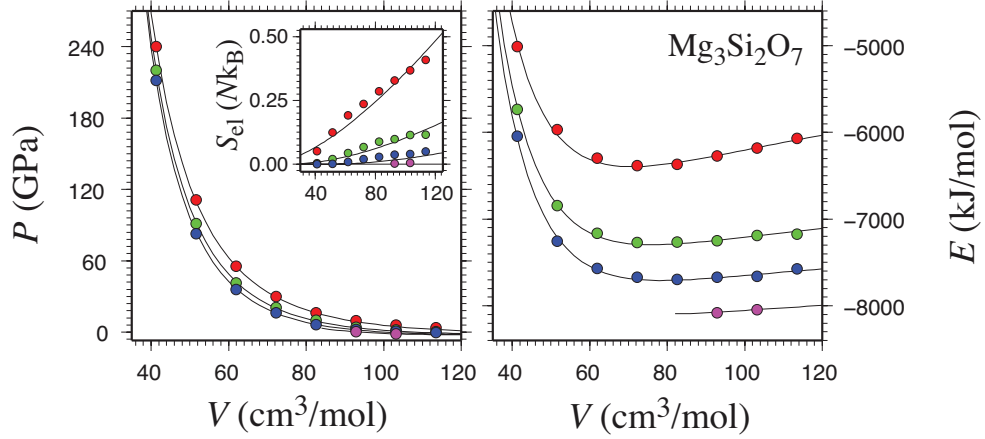


Figure S5: FPMD results (circles) and LFTR fit (lines) for $\text{Mg}_3\text{Si}_2\text{O}_7$ liquid. Purple - 2000 K; blue - 3000 K; green - 4000 K; red - 6000 K.

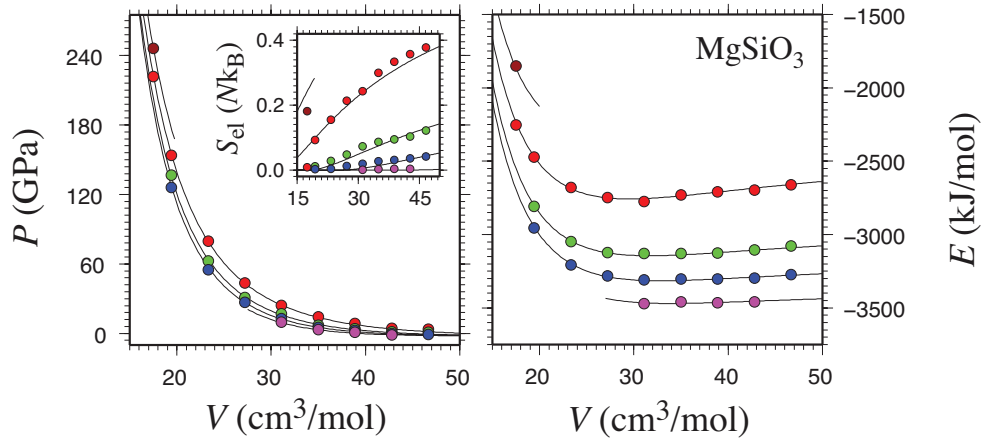


Figure S6: FPMD results (circles) and LFTR fit (lines) for MgSiO_3 liquid. Purple - 2000 K; blue - 3000 K; green - 4000 K; red - 6000 K; maroon - 8000 K.

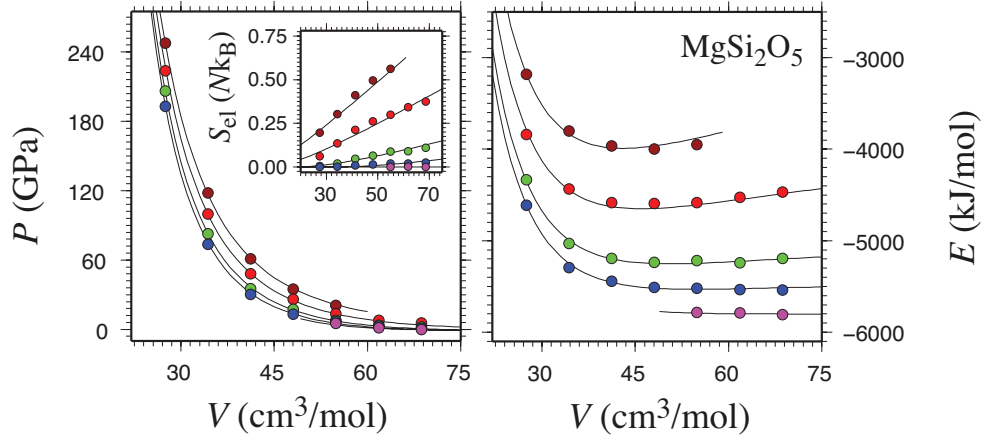


Figure S7: FPMD results (circles) and LFTR fit (lines) for MgSi_2O_5 liquid. Purple - 2000 K; blue - 3000 K; green - 4000 K; red - 6000 K; maroon - 8000 K.

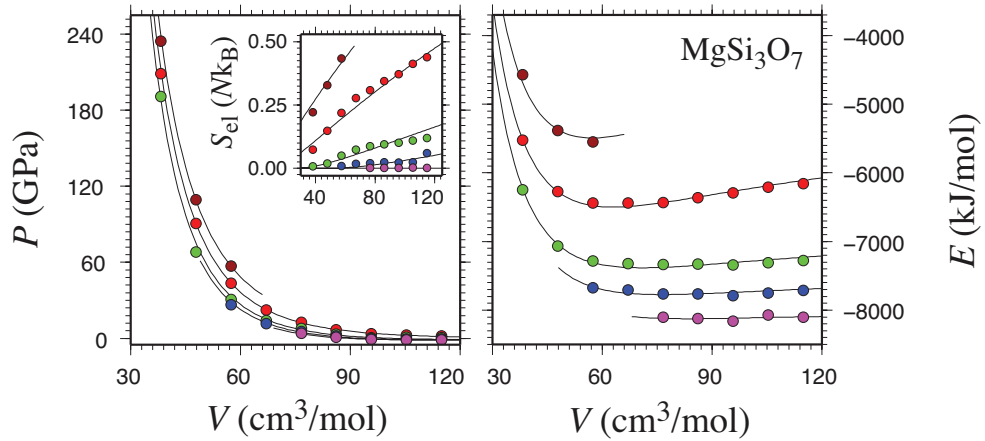


Figure S8: FPMD results (circles) and LFTR fit (lines) for MgSi_3O_7 liquid. Purple - 2000 K; blue - 3000 K; green - 4000 K; red - 6000 K; maroon - 8000 K.

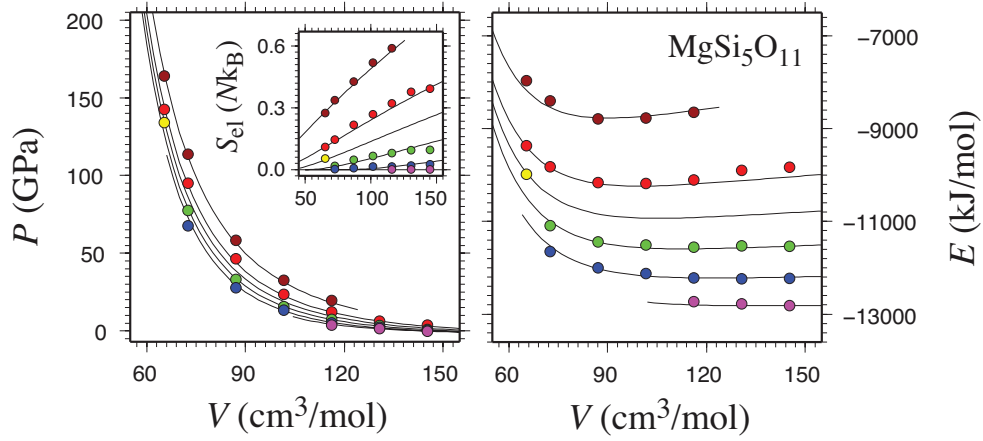


Figure S9: FPMD results (circles) and LFTR fit (lines) for $\text{MgSi}_5\text{O}_{11}$ liquid. Purple - 2000 K; blue - 3000 K; green - 4000 K; yellow - 5000 K; red - 6000 K; maroon - 8000 K.

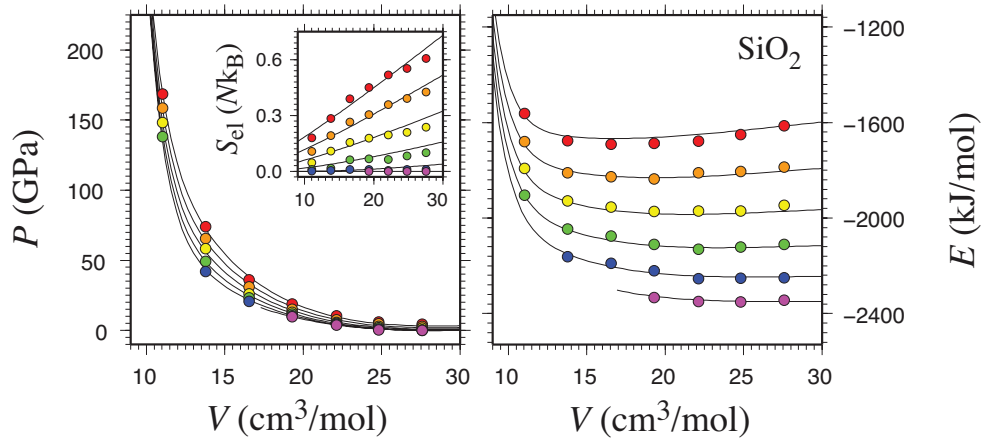


Figure S10: FPMD results (circles) and LFTR fit (lines) for SiO_2 liquid. Purple - 2000 K; blue - 3000 K; green - 4000 K; yellow - 5000 K; orange - 6000 K; red - 7000 K.

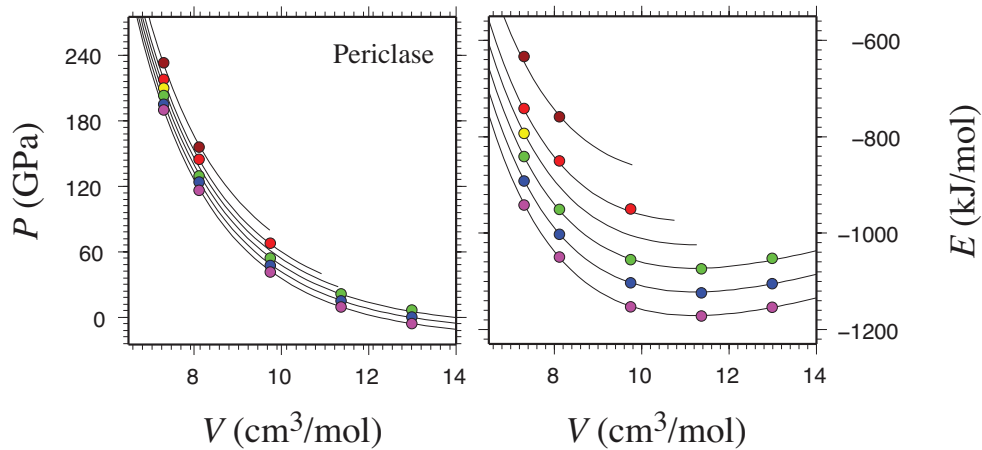


Figure S11: FPMD results (circles) and SFTR fit (lines) for MgO periclase. Purple - 2000 K; blue - 3000 K; green - 4000 K; yellow - 5000 K; red - 6000 K; maroon - 8000 K.

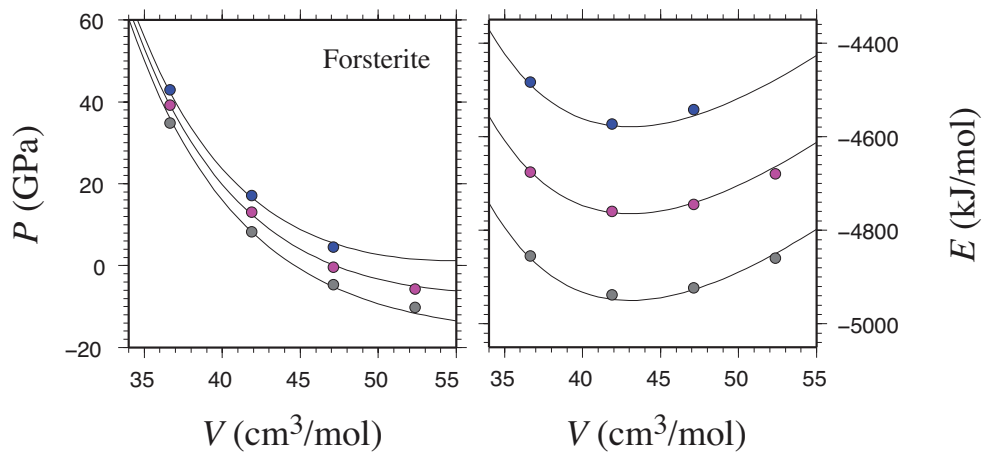


Figure S12: FPMD results (circles) and SFTR fit (lines) for Mg₂SiO₄ forsterite. Grey - 1000 K; purple - 2000 K; blue - 3000 K.

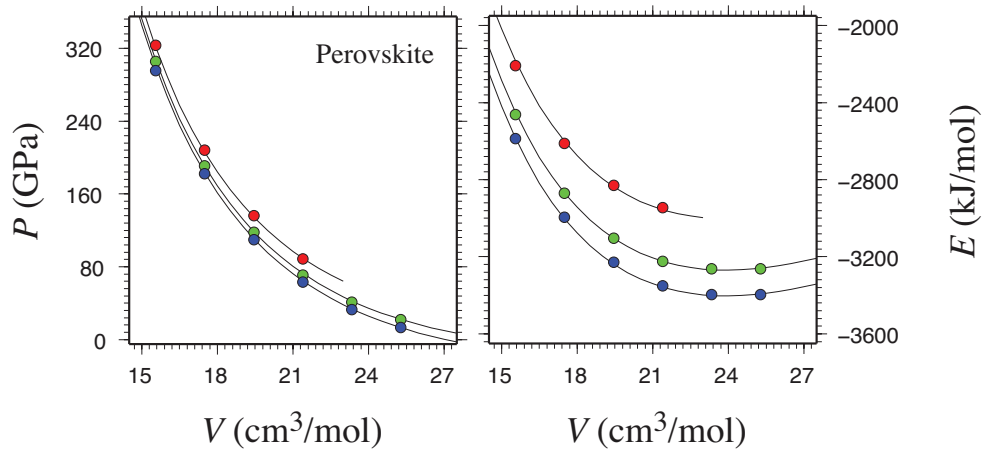


Figure S13: FPMD results (circles) and SFTR fit (lines) for MgSiO₃ perovskite. Blue - 3000 K; green - 4000 K; red - 6000 K.

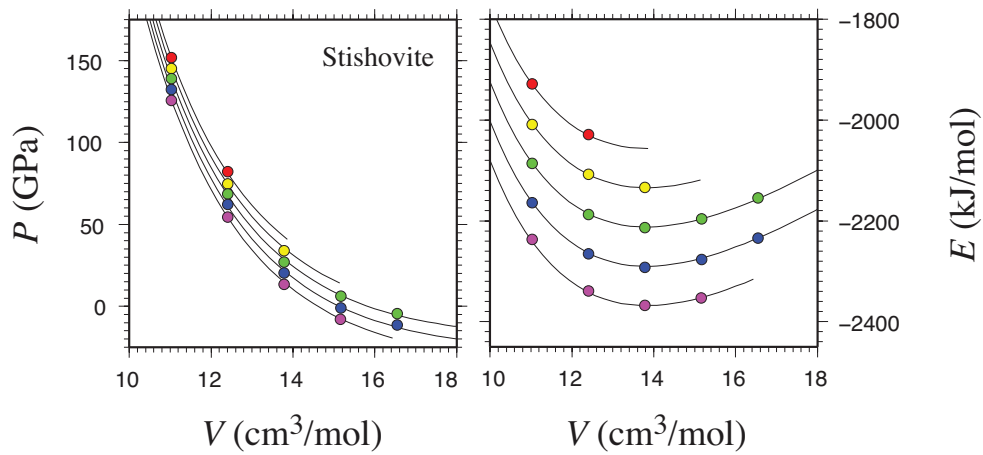


Figure S14: FPMD results (circles) and SFTR fit (lines) for SiO₂ stishovite. Purple - 2000 K; blue - 3000 K; green - 4000 K; yellow - 5000 K; red - 6000 K.

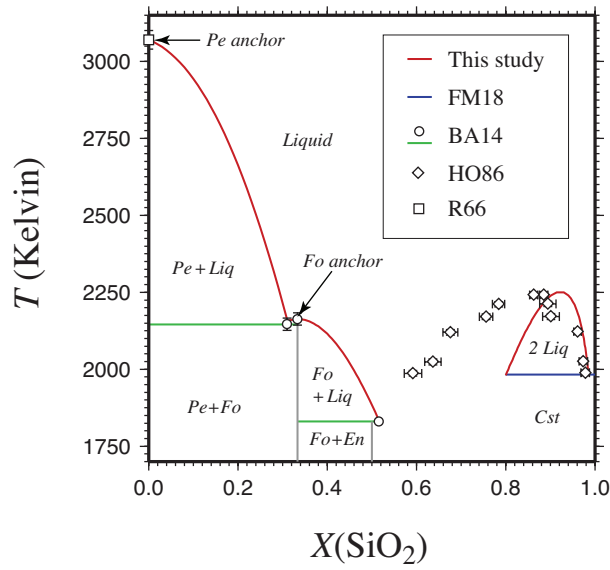


Figure S15: Ambient pressure phase equilibria used to constrain the reference entropy of mixing. Red curves are computed using our thermodynamic model; *Liq* - liquid, *Pe* - periclase, *Fo* - forsterite, *En* - enstatite, *Cst* - cristobalite; FM18 - Ferguson and Merwin (1918), BA14 - Bowen and Andersen (1914), HO86 - Hageman and Oonk (1986), R66 - Riley (1966). Points used to anchor free energies in thermodynamics models for periclase and forsterite are indicated (from left to right: periclase melting; periclase-forsterite eutectic; forsterite melting; forsterite+enstatite peritectic; liquid immiscibility field).

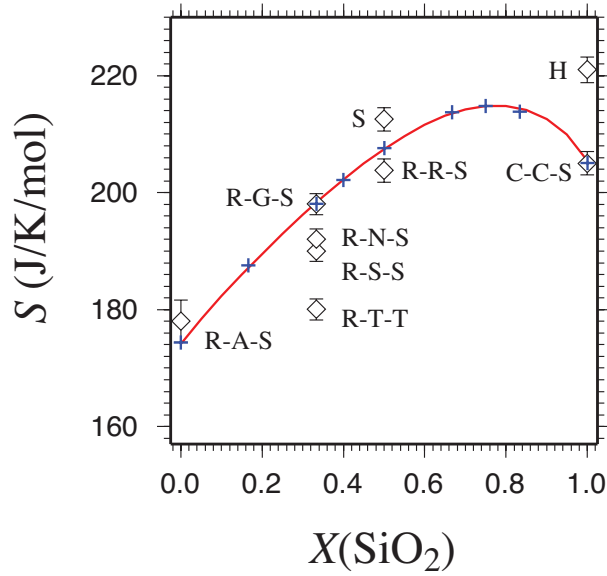


Figure S16: Reference third law entropy of the respective liquid compositions along the join (blue crosses) and the optimal entropy of mixing (red line) at ambient pressure and 3000 K, constrained via eq. S18 by optimizing agreement with the available estimates of the entropy of individual compositions (diamonds). Except where a single letter is noted, labels list the references used for the various components of eq. S18: $[S_{\text{sol}}(T_m, P)] - [\Delta S_{\text{fus}}(P)] - [\Delta S_{\text{liq}}(T_m \rightarrow T, P)]$. Labels are: A - Alfe (2005), C - Richet et al. (1982), G - Ghiorso and Carmichael (1980), H - Hudon et al. (2002), N - Navrotsky et al. (1989), R - Robie and Hemingway (1995), S - Stebbins et al. (1984), T - Tangeman et al. (2001). Unit is per mol of oxides.