



# High-temperature miscibility of iron and rock during terrestrial planet formation



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## ABSTRACT

The accretion of a terrestrial body and differentiation of its silicate/oxide mantle from iron core provide abundant energy for heating its interior to temperatures much higher than the present day Earth. The consequences of differentiation on the structure and composition of planets are typically addressed considering only the interaction of molten iron with an immiscible ‘rocky’ phase. We demonstrate that mixing in a representative system of liquid or solid MgO and liquid iron to a single homogeneous liquid occurs at sufficiently low temperature to be present in the aftermath of a giant impact. Applying the thermodynamic integration technique to density functional theory molecular dynamics simulations, we determine the solvus closure temperature for the Fe–MgO system for pressures up to 400 GPa. Solvus closure occurs at  $\sim 4000$  K at low pressure, and has a weak positive pressure dependence, such that its gradient with respect to depth is less steep than an adiabatic temperature profile. This predicts a new mode of core–mantle differentiation following the most energetic giant impacts, with exsolution of iron from the mixture beginning in the outer layers of the planet. We demonstrate that high-temperature equilibration results in delivery of nominally insoluble Mg-rich material to the early core. Since MgO is the least soluble major mantle component in iron at low temperatures, these results may represent an upper bound on temperature for mixing in terrestrial planets.

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## 1. Introduction

Terrestrial planets are, to the first order, made up of a metallic iron core and a mantle composed of silicate and oxide minerals. Chondritic meteorites show that these materials initially condensed together from the protoplanetary nebula, but became free to separate and gravitationally stratify as planetesimals grew. Numerous scenarios have been put forward to describe how these reservoirs interact depending on the pressure, extent of melting, and the specific assumptions of rocky phases (Stevenson, 1990; Solomatov, 2007; Rubie et al., 2007). These typically assume the major components occur in two immiscible phases. Additionally, most studies assume that element partitioning between the two phases is similar to that observed in experiments performed at much lower temperatures (McDonough and Sun, 1995). In the case of a hot early history of a growing planet, neither assumption is necessarily correct. At sufficiently high temperatures, entropic effects dominate and any mixture of materials will form a single, homogeneous phase. It is therefore necessary to consider a high

temperature mixture of the ‘rocky’ and metallic terrestrial components. The presence of such a mixed phase will affect the chemistry of iron–silicate differentiation on the early Earth.

Here we consider a simple representative material for the mixed rock–metal phase as a mixture of Fe and MgO formed via the reaction  $\text{MgO}_{\text{sol/liq}} + \text{Fe}_{\text{liq}} \Rightarrow \text{FeMgO}_{\text{liq}}$ . We determine the stability of these phases using first-principles calculations. At a given pressure, a system with two separate phases can be described in terms of a miscibility gap. At low temperatures, homogeneous mixtures with intermediate compositions are thermodynamically unstable and a heterogeneous mixture of two phases with compositions near the endmembers is preferred. The exsolution gap is bounded by a solvus that marks the temperature above which a single mixed phase is stable, and the maximum temperature along the solvus is referred to as the solvus closure temperature. Here we calculate the Gibbs free energy of the mixture and the endmembers to determine the solvus closure temperature for mixture similar to the bulk-composition of a terrestrial planet. These results can inform future work, by providing the conditions where rock–metal miscibility plays a role in the differentiation of terrestrial planet interiors.

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An order of magnitude calculation shows the gravitational energy released in the formation of an Earth-mass body, if delivered instantaneously, is sufficient to raise temperatures inside the body by  $\sim 40,000$  K. Redistribution of mass within the body during core formation can account for another  $\sim 4000$  K increase. This energy is released over the timescale of accretion,  $\sim 10^8$  years (Chambers and Wetherill, 1998), with efficient surface heat loss through a liquid–atmosphere interface (Abe, 1997; Elkins-Tanton, 2012). However, simulations of the final stages of planet growth (Cameron and Benz, 1991; Chambers and Wetherill, 1998; Canup and Agnor, 2000) suggest that near-instantaneous release of large quantities of energy through giant impacts is the rule rather than the exception. Simulations of the ‘canonical’ moon-forming impact hypothesis (Canup, 2004), in which a Mars-sized body collides with the protoearth, find fractions of the target’s interior shocked well above 10,000 K. More recently, dissipation of angular momentum from the Earth–Moon system by the evection resonance has loosened physical constraints on the impact, suggesting that the formation of the moon is better explained by an even more energetic event than the ‘canonical’ one (Canup, 2012; Cuk and Stewart, 2012). It is, therefore, difficult to precisely constrain the temperature of the Earth’s interior in the aftermath of the moon forming impact, much less that of other terrestrial planets with even more uncertain impact histories. Regardless, there is evidence for giant impacts throughout the inner solar system, implying temperatures significantly higher than the present day Earth may have been common. In addition to high temperatures, giant impacts involve significant physical mixing of iron and rocky materials (Dahl and Stevenson, 2010). Thus, miscibility may be important even if the impacting bodies have iron cores that differentiated at lower temperatures and pressures.

Differentiation and core formation is a key event or series of events in terrestrial planet evolution. The timing and conditions of differentiation have important consequences for the evolution of the planet, through its effect on the distribution of elements throughout the planet’s interior. The distribution of elements affects the gravitational stability of solid layers in the mantle, the location of radioactive heat sources, and the nature of the source of buoyancy driving core convection and magnetic field generation. Each of these subsequently affect the thermal evolution of the planet. If this process occurs near the solvus closure temperature, there are likely to be physical and chemical differences from the processes at conditions where the phases are completely immiscible. We include a discussion of some of these processes in Section 4.

## 2. Theory and methodology

Modern high pressure experimental techniques, using static or dynamic compression techniques, can reach megabar pressures (Boehler, 2000). However, experiments at simultaneous high pressures and temperatures have limitations. Interpretation of mixing processes during shock wave experiments is difficult, and the samples are not recoverable. Meanwhile, laser heated diamond anvil cells experience extreme temperature gradients and require survival of quenched texture to interpret. In both cases, the methods only cover a small fraction of the  $P$ – $T$  range expected in the aftermath of a giant impact. As a result, simulations based on first-principles theories are an appropriate means of constraining material properties over a range of such extreme conditions.

### 2.1. Simulated system

We performed density functional theory molecular dynamics (DFT-MD) simulations for phases in a model reaction between liquid iron, and solid (B1) or liquid magnesium oxide. The change in

Gibbs free energy of this system per formula unit FeMgO is described as

$$\Delta G_{\text{mix}} = \frac{1}{24} G_{(\text{FeMgO})_{24}} - \frac{1}{32} [G_{(\text{MgO})_{32}} + G_{\text{Fe}_{32}}] \quad (1)$$

where  $G_{(\text{MgO})_{32}}$  and  $G_{\text{Fe}_{32}}$  are the Gibbs free energies of a pure MgO and iron endmembers with subscripts referring to the number of atoms in the periodic simulation cell.  $G_{(\text{FeMgO})_{24}}$  is the Gibbs free energy of 1:1 stoichiometric liquid solution of the two endmembers. Comparing Gibbs free energies among a range of compositions, we find the temperature for mixing of the phases in the 1:1 ratio to be a good approximation for the solvus closure temperature.

MgO is the simplest mantle phase to simulate, and a reasonable starting point for a study of the miscibility of terrestrial materials. Up to  $\sim 400$  GPa, MgO remains in the cubic B1 (NaCl) structure (Boates and Bonev, 2013), meaning simulations of only one solid phase were necessary for the rocky endmember. In order to describe a similar reaction for MgSiO<sub>3</sub> perovskite, the Gibbs free energy of MgO and SiO<sub>2</sub> must also be calculated to address the possibility of incongruent dissolution of the solid phase (Boates and Bonev, 2013). More importantly, high pressure experiments observing reactions of silicates with iron have demonstrated the MgO component has by far the lowest solubility in iron up to  $\sim 3000$  K (Knittle and Jeanloz, 1991; Ozawa et al., 2008). This suggests our results can be interpreted as an upper bound for the solvus closure temperature with more realistic compositions.

It is worth emphasizing that the mixed FeMgO phase is unlike any commonly studied rocky phase, in that it does not have a balanced oxide formula. This is by design and is necessary for the mixing of arbitrary volumes of the metallic and oxide phases. This is a separate process from the reaction of the FeO component which transfers O to the metallic phase at lower temperature, and which is primarily controlled by oxygen fugacity rather than temperature (Tsuno et al., 2013). We treat the mixed phase as a liquid at all conditions. Although we cannot absolutely rule out the possibility of a stable solid with intermediate composition, such a phase would require a lower Gibbs free energy, and therefore is consistent with treating our results as an upper bound on the solvus closure temperature.

### 2.2. Computation of Gibbs free energies

The Gibbs free energy of a material includes a contribution from entropy of the system. Since entropy is not determined in the standard DFT-MD formalism, we adopt a two step thermodynamic integration method, used in previous studies (Wilson and Militzer, 2010, 2012; Wahl et al., 2013; González-Cataldo et al., 2014). The thermodynamic integration technique considers the change in Helmholtz free energy for a transformation between two systems with governing potentials  $U_a(\mathbf{r}_i)$  and  $U_b(\mathbf{r}_i)$ . We define a hybrid potential  $U_\lambda = (1 - \lambda)U_a + \lambda U_b$ , where  $\lambda$  is the fraction of the potential  $U_b(\mathbf{r}_i)$ . The difference in Helmholtz free energy is then given by

$$\Delta F_{a \rightarrow b} \equiv F_b - F_a = \int_0^1 d\lambda (U_b(\mathbf{r}_i) - U_a(\mathbf{r}_i))_\lambda \quad (2)$$

where the bracketed expression represents the ensemble-average over configurations,  $\mathbf{r}_i$ , generated in simulations with the hybrid potential at constant volume and temperature. This technique allows for direct comparisons of the Helmholtz free energy of DFT phases,  $F_{\text{DFT}}$ , by finding their differences from reference systems with a known analytic expression,  $F_{\text{an}}$ .

In practice, it is more computationally efficient to perform the calculation  $\Delta F_{\text{an} \rightarrow \text{DFT}}$  in two steps, each involving an integral of

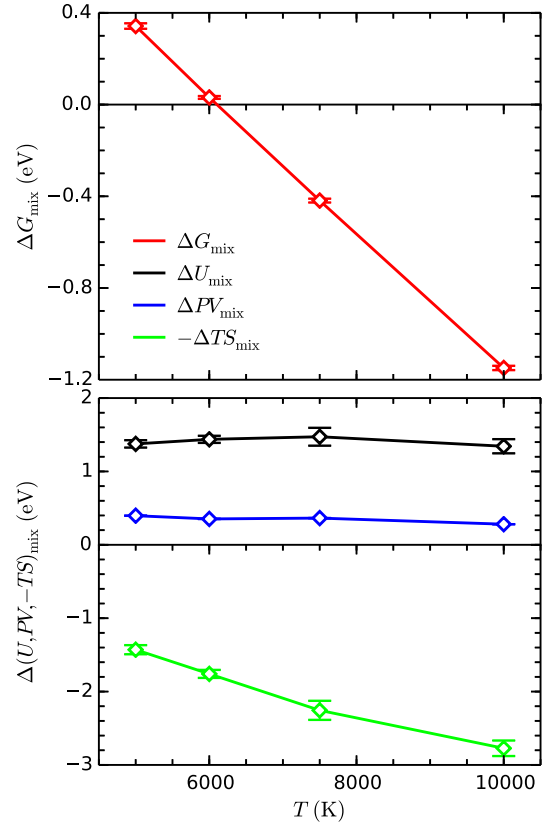
the form of Eq. (2). We introduce an intermediate system governed by classical pair potentials,  $U_{cl}$ , found by fitting forces to the DFT trajectories (Wilson and Militzer, 2010; Izvekov et al., 2004). For each pair of elements, find the average force in bins of radial separation and fit the shape of a potential using a cubic spline function. We constrain the potential to smoothly approach zero at large radii and use a linear extrapolation at small radii, where the molecular dynamics simulations provide insufficient statistics. Examples of these potentials are included in the online supplementary information. The full energetics of the system is then described as

$$F_{DFT} = F_{an} + \Delta F_{an \rightarrow cl} + \Delta F_{cl \rightarrow DFT} \quad (3)$$

where  $\Delta F_{cl \rightarrow DFT}$  requires a small number of DFT-md simulations, and  $\Delta F_{an \rightarrow cl}$  numerous, but inexpensive classical Monte Carlo (CMC) simulations. The method depends on a smooth integration of  $\Delta F_{cl \rightarrow DFT}$  and avoiding any first order phase transitions with  $\lambda$ . We use five  $\lambda$  points, for all  $\Delta F_{cl \rightarrow DFT}$  integrations. For solid MgO we use a combination of classical pair and one-body harmonic oscillator potentials for  $U_{cl}$  (Wilson and Militzer, 2012; Wahl et al., 2013). Liquids we use only pair potentials. For solids the analytical reference system is an Einstein solid with atoms in harmonic potentials centered on a perfect lattice, while a gas of non-interacting particles is used for liquids. We found integrating over 5 lambda points to be sufficiently accurate, with an increase to 9 lambda points changing our results by  $<0.003$  eV per formula unit. In the online supplementary information we include two additional tests of the thermodynamic integration method, demonstrating that our results are not sensitive use of different classical potentials or the integration path with respect to the interaction between different species in the multicomponent systems.

All DFT simulations presented here were performed using the Vienna *ab initio* simulation package (VASP) (Kresse and Furthmüller, 1996). VASP uses projector augmented wave pseudopotentials (Blochl, 1994) and the exchange-correlation functional of Perdew, Burke and Ernzerhof (1996). Although the DFT formalism is based on a zero-temperature theory, DFT-MD simulations at high temperatures have been shown to agree with theory developed for warm dense matter (Driver and Militzer, 2012). We use an iron pseudopotential with valence states described by a  $[Mg]3pd^64s^2$  electron configuration. For consistency, all simulations use Baldereschi point sampling, a 600 eV cutoff energy for the plane wave expansion and temperature dependent Fermi-smearing to determine partial orbital occupations. A time step of between 0.5 and 1.0 fs is used depending on the temperature, with the smaller time step used for all simulations with temperatures above 6000 K. We confirmed that the resulting molecular dynamics results are well-converged with respect to the energy cutoff and time step. All presented results involve molecular dynamics simulation lengths of at least 2 ps simulated time at each, with longer simulation times having an insignificant effect on the results of the thermodynamic integration. The largest source of uncertainty was the finite size effect, which we discuss in detail in Section 3.

The workflow for the calculation is as follows: 1) Determine the density of the system at the target pressure and temperature by iteratively correcting the volume until the calculated DFT pressure matches the target pressure with a 1% tolerance. 2) Perform DFT simulations to determine the internal energy, and fit classical potentials for the thermodynamic integration. 3) Perform the thermodynamic integration with the classical potentials with DFT simulations, 4) and CMC simulations to complete the Helmholtz free energy (Eq. (3)), and by extension the entropy and Gibbs free energy. 5) Calculate the differences in these values at given  $P$  and  $T$ , using Eq. (1) to determine whether the system mixes or not.

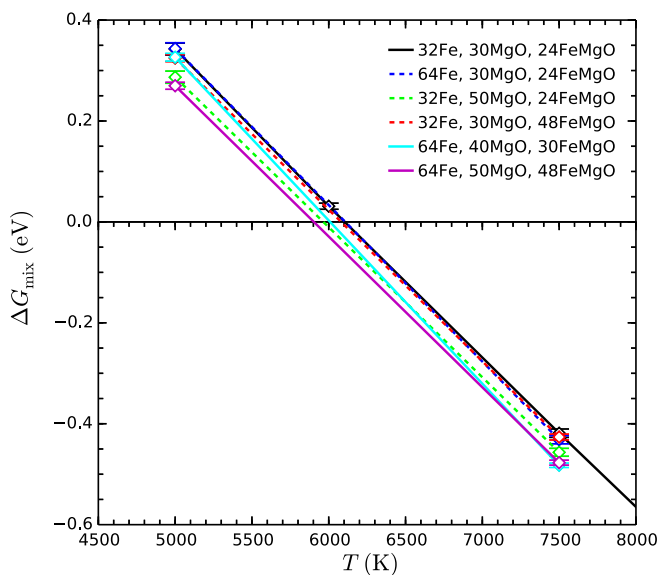


**Fig. 1.** Gibbs free energy change per formula unit,  $G_{mix}$  of the reaction  $MgO_{liq} + Fe_{liq} \rightarrow FeMgO_{liq}$  at  $P = 50$  GPa (red). Independently calculated components of  $\Delta G_{mix}$ :  $\Delta U$  (black),  $\Delta PV$  (blue), and  $-\Delta TS$  (green). Positive values favor separation into endmember phases, while negative values favor a single mixed phase.  $\Delta PV$  values presented here use the target pressure. Error bars represent the integrated error from the  $1\sigma$  statistical uncertainty of the molecular dynamics simulations. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

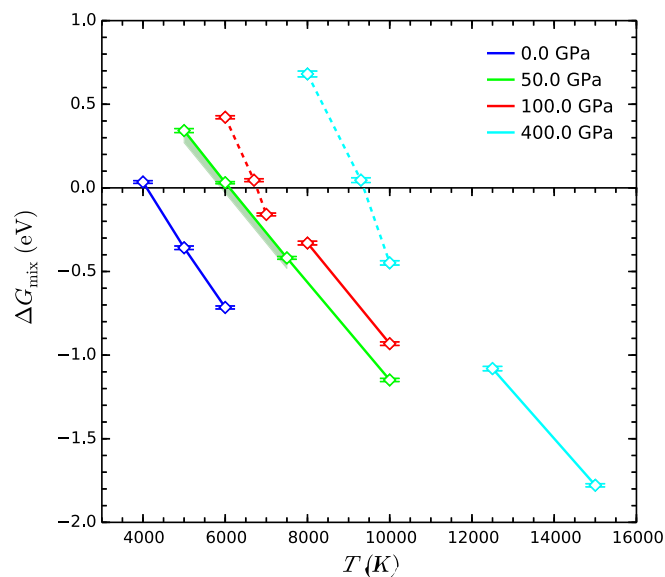
### 3. Results

The online supplementary material includes a table with the results of the calculations for each composition and  $P$ - $T$  condition. It includes the density along with the calculated pressure, internal energy, entropy and Gibbs free energy. The stable phase at each condition is determined using Eq. (1). The point at which the trend in  $\Delta G_{mix}$  at constant  $P$  changes sign is the inferred solvus temperature at the 1:1 stoichiometric composition. Fig. 1 shows an example of this trend in  $\Delta G$  for the 1:1 mixture at  $P = 50$  GPa, along with its components  $\Delta U$ ,  $\Delta PV$  and  $-\Delta TS$ . Using the convention from Eq. (1), positive values favor the separation of the material into the endmember phases, while negative values favor the single homogeneous mixed phase. The contributions of the internal energy and volumetric terms are positive, while the entropy provides the negative contribution that promotes mixing at sufficiently high temperature.

Using additional calculations at  $P = 50$  GPa, we estimated uncertainties in our calculated Gibbs free energies. The most significant contribution to the uncertainty comes from the finite size of the simulation cells. We estimate the magnitude of this uncertainty by comparing results from larger simulated cells to those of the original system. Fig. 2 compares the values of  $\Delta G_{mix}$  for Fe and FeMgO cells with up to twice the number of atoms, and MgO with up to 100 atoms per cell. From this, we estimate a maximum shift of  $<0.1$  eV per formula unit. This corresponds to an uncertainty in temperature of  $\sim 200$  K, roughly an order of magnitude larger than the statistical precision of the calculation. The combined effect



**Fig. 2.** Quantifying the finite size effect on  $\Delta G_{\text{mix}}$  for simulations of the reaction  $\text{MgO}_{\text{liq}} + \text{Fe}_{\text{liq}} \rightarrow \text{FeMgO}_{\text{liq}}$  at  $P = 50$  GPa with different cell sizes. In black are the results for the systems  $\text{Fe}_{32}$ ,  $\text{Mg}_{32}\text{O}_{32}$  and  $\text{Fe}_{24}\text{Mg}_{24}\text{O}_{24}$  used at the other  $P$ - $T$  conditions. The other lines show the shift in  $\Delta G_{\text{mix}}$  obtained when the calculation is repeated for with a larger cell for one (dashed lines) or all (solid lines) of the systems.



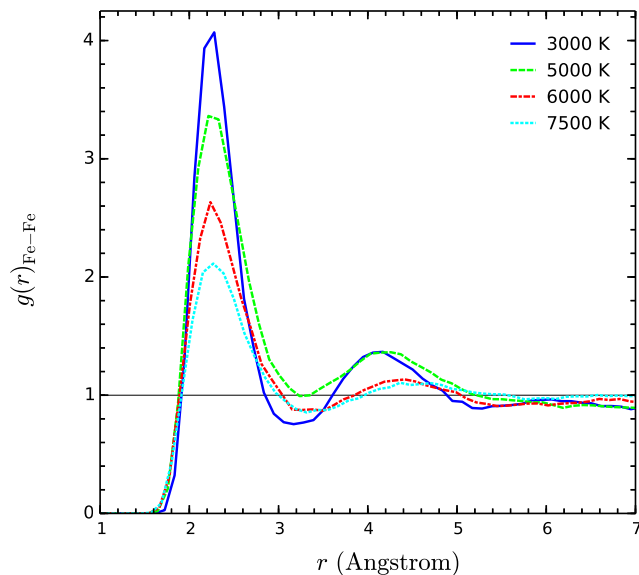
**Fig. 3.** Gibbs free energy of mixing for MgO and liquid Fe. Solid lines show conditions where MgO was simulated as a liquid, and dashed lines where MgO is in its (B1) solid phase. The filled green region shows an estimate of the uncertainty from finite size effects, taken as the maximum shifts in  $\Delta G_{\text{mix}}$  observed our tests of larger cells (Fig. 2). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

of increasing cell size for all systems leads consistently to lower values of  $\Delta G_{\text{mix}}$  at both temperatures, and thus, lower predicted solvus closure temperatures. For the subsequent analysis, we consider an estimated uncertainty defined as the largest (positive or negative) shift in the Gibbs free energy for each phase. It should be noted that these estimated error bars cannot be strictly viewed as statistical uncertainties, since they are unidirectional and based on a small number of independent calculations. They suggest the likely magnitude by which similar shifts in the calculated Gibbs free energies will effect the calculated transition temperature at different  $P$ - $T$  conditions.

The effect of pressure and temperature on  $\Delta G_{\text{mix}}$  is shown in Fig. 3. As pressure increases, the slope of  $\Delta G_{\text{mix}}$  with  $T$  remains nearly constant for all simulations with liquid MgO, but the values are shifted to higher temperatures. This means that the solvus closure temperature has a positive slope with pressure over the entire range of conditions considered. There is a noticeable change in the slope of this quantity when MgO melts. This corresponds with a weaker dependence on pressure at high pressures, where the solvus temperature is below the melting temperature of MgO.

When determining the energetics of the mixed FeMgO phase, it is important to verify that the simulation remain in a single mixed phase. At temperatures sufficiently close to the solvus closure temperature the system should behave as a super-cooled homogeneous mixture, while at sufficiently low temperatures the simulations could, in principle, spontaneously separate into two phases. This would bias the results as interfacial energies between the separating phases would be included in the calculated Gibbs free energy. We were unable to detect phase separation by visual inspection of various of snapshots as has been seen for hydrogen-helium mixtures in (Soubiran, 2012). The pair correlation function,  $g(\mathbf{r})$ , can be used as a proxy for separation of phases (Soubiran, 2012).

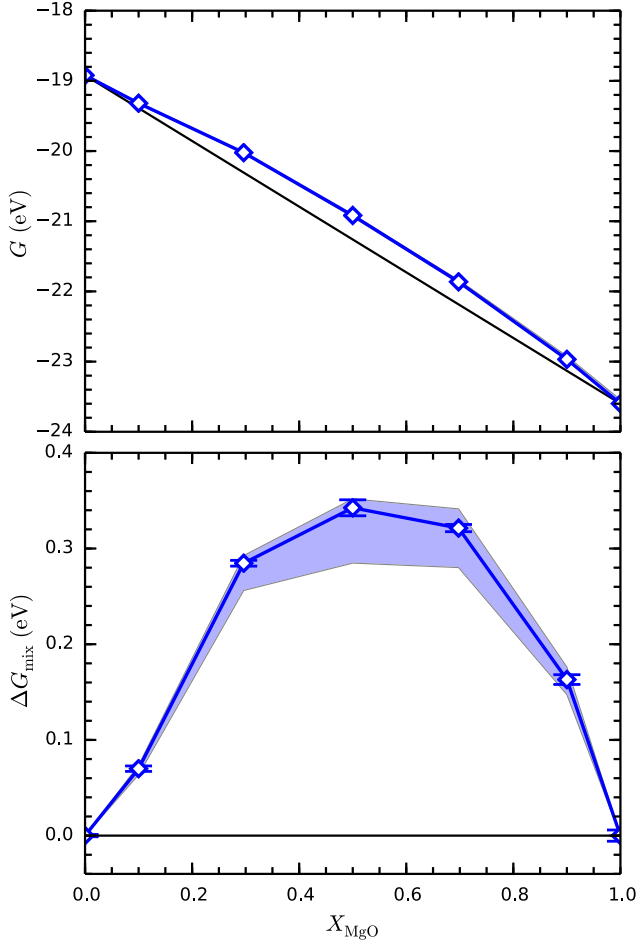
Fig. 4 shows the Fe-Fe  $g(r)$  for simulations of the mixed FeMgO phase at 50 GPa. For temperatures significantly below solvus closure temperature, 3000 and 5000 K, there are slight negative deviations of the  $g(r)_{\text{Fe-Fe}}$  at large  $r$  from their expected asymptote to unity. This is consistent with clustering into MgO and Fe-rich regions, and may indicate spontaneous phase separation at temperatures well below the inferred solvus closure temperature. These



**Fig. 4.** Fe-Fe pair correlation functions for mixed Fe + MgO phase. Compares the spatial distribution of atoms in simulations at 50 GPa with different temperatures. The 3000 K and 5000 K asymptote to values notably less than one, while temperatures near or above the solvus closure temperature do not show such a deviation at large  $r$ .

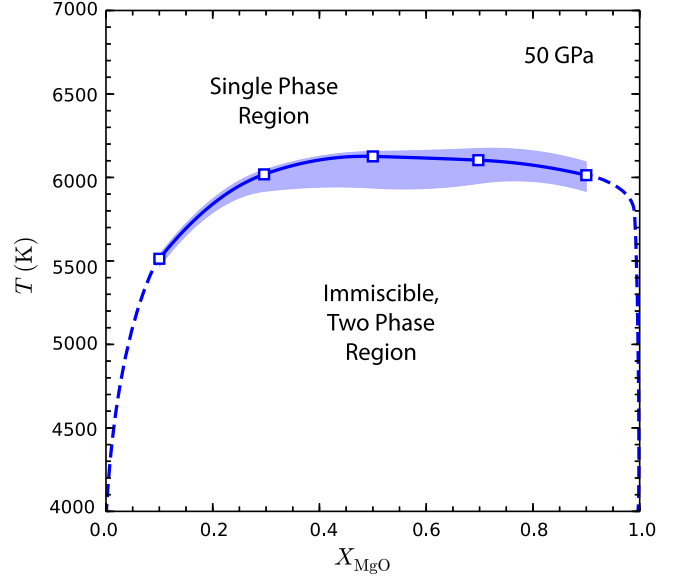
deviations are minimal or not observed in simulations near or above the inferred solvus closure temperature. We performed additional simulations at temperatures close to the solvus closure temperature to verify that the Gibbs free energy changes linearly as a function of temperature, which is the expected behavior without spontaneous phase separation. In spite of deviations in  $g(r)$ , we note that including the low temperature simulations in our calculation of the solvus closure temperature does not significantly change the result at any pressure.

We also studied the effect of composition on the solvus temperature. Calculations were performed on four additional intermediate compositions between the Fe and MgO endmembers. Fig. 5 shows

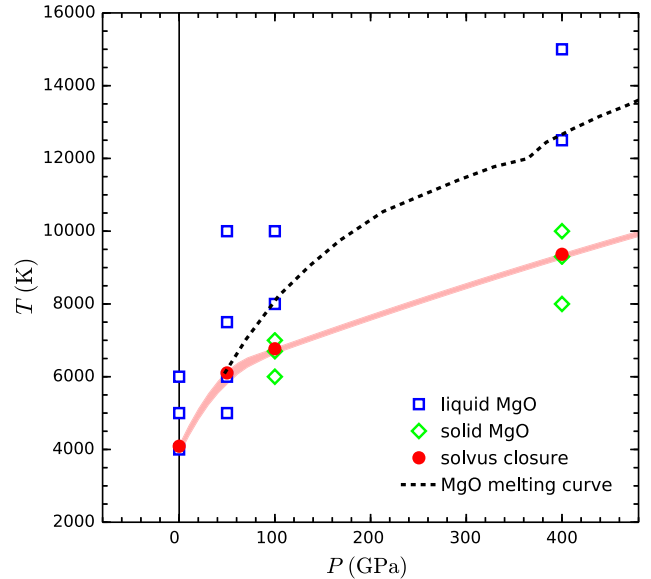


**Fig. 5.** Convex hull of  $\Delta G_{\text{mix}}$  versus formula unit fraction,  $X_{\text{MgO}}$ , for the Fe-MgO system at  $P = 50$  GPa and  $T = 5000$  K (top). Difference between  $\Delta G_{\text{mix}}$  and a mixing line between the endmembers (bottom). The filled region shows an estimate of the uncertainty from finite size effects, taken as the maximum shifts in  $\Delta G_{\text{mix}}$  from our tests of larger Fe, MgO and FeMgO simulations. The estimated error is weighted as a function of composition since the finite size effects will cancel with that of the endmember as the compositions become more similar.

a convex-hull in  $G_{\text{Fe}_{1-x}\text{MgO}_x}$  and  $\Delta G_{\text{mix}}$  at 50 GPa and 5000 K. This corresponds to a temperature below the calculated solvus temperature. The Gibbs free energies of all intermediate components are above the mixing line between the end members, and form a smooth function with composition. This is consistent with a binary system with a miscibility gap. Using linear interpolation between this convex hull and one at 7500 K, we estimate the shape of the miscibility gap at 50 GPa, as shown in Fig. 6. The miscibility gap is notably asymmetric, with temperatures decreasing faster towards the Fe-rich endmember than the MgO-rich end. A similar, more pronounced asymmetry has been experimentally determined for the Fe-FeO system at lower pressures (Ohtani et al., 1984; Kato and Ringwood, 1989). In spite of this, the shape of the solvus at intermediate compositions,  $\sim 0.3$ – $0.9$  molar fraction MgO, is relatively flat. As a result, the temperatures predicted for a 1:1 mixture provide a good estimate for the solvus closure temperature. We note, however, that the shape of miscibility gap may be sensitive to uncertainties from the finite size effect. Considering the estimated errors from the finite size effect test, we can only constrain to be within that  $\sim 0.3$ – $0.9$   $X_{\text{MgO}}$  range. Regardless of this composition our uncertainty in the temperature of solvus closure remains  $\sim 200$  K.



**Fig. 6.** Solvus phase diagram of the Fe-MgO system at  $P = 50$  GPa. The shape is consistent with the composition  $X_{\text{MgO}} = 0.5$  being representative for estimating the solvus closure temperature at other pressures. The filled region shows an estimate of the uncertainty in transition temperature arising from the uncertainties in  $G$  in Fig. 5.



**Fig. 7.** Pressure dependence of the solvus closure. The  $P$ - $T$  condition of all thermodynamic integration calculations are included. Blue markers denote conditions where MgO was treated as a liquid. Green markers denote conditions where MgO was treated as a solid (B1). Red circles show the solvus closure temperature inferred from simulations at the same pressure. The estimated uncertainty in the solvus closure temperature from finite size effects is shown by the filled red region. The dashed, black line shows the MgO melting temperature from molecular dynamics from DFT-md with PBE exchange correlation function (Boates and Bonev, 2013), which is consistent with other first-principles calculations (Alfè, 2005; Belonoshko et al., 2010). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Fig. 7 summarizes the results, showing all the conditions at which simulations were performed. We find the solvus closure at ambient pressure to be  $4089^{+25}_{-235}$  K. While there is little experimental work on this exact system, our results are superficially consistent with extrapolations of the phase diagram for the Fe-FeO system from low temperatures (Ohtani et al., 1984; McCammon et al., 1983), and with the ‘accidental’ discovery of

the Fe-silicate solvus by Walker et al. (1993). We find that the solvus temperature increases with pressure to  $6010_{-204}^{+28}$  K at 50 GPa, but its slope decreases significantly at higher pressures, with a temperatures of  $6767_{-135}^{+14}$  K at 100 GPa and  $9365_{-130}^{+14}$  K at 400 GPa. This transition also corresponds roughly to the pressure where the trend crosses the MgO melting curve (Alfè, 2005; Belonoshko et al., 2010; Boates and Bonev, 2013). Indeed, the simulations used to infer the closure temperature at these pressures used the solid (B1) structure of MgO. Unfortunately, it is difficult to check whether the change in slope is a direct result of this phase transition, as liquid MgO simulations rapidly freeze at temperatures far below the melting curve. Conversely, the liquidus of a deep magma ocean might be below the solvus at these temperatures due to the effect of a SiO<sub>2</sub> or FeO component in the silicate/oxide endmember (de Koker et al., 2013; Zerr, 1998). However, extrapolation of  $\Delta G_{\text{mix}}$  from simulations with liquid MgO at higher temperatures (Fig. 3) suggest that the change in slope occurs in liquids as well. We estimate shifts in the inferred solvus closure temperature from finite size effects on the order of 200 K. The actual solvus closure temperature may also be shifted by up to a couple hundred Kelvin, if we also consider the uncertainty in the solvus shape (Fig. 5), since our results refer specifically the solvus temperature for a 1:1 stoichiometric mixture. The observed change in slope of the solvus temperature and the relation to the pure MgO melting curve are, however, robust against uncertainties of this magnitude.

#### 4. Discussion

In the extreme case where a significant fraction of the planet is in a mixed iron-rock phase, the early evolution will be quite different than prevailing theories. Differentiation of material accreted onto the planet is delayed until the planet cools to below the solvus closure temperature, allowing iron to exsolve and sink to the core. This study provides an estimate of the temperatures required to mix the Mg-rich rocky mantle with the core of a terrestrial planet. At the surface, the complete mixing of Fe and MgO is achieved at  $\sim 4000$  K (Fig. 7), which is well above the melting point of silicates. At core-mantle boundary pressures, the critical temperature would be  $\sim 7000$  K. This is below higher estimates for the melting temperature of pure MgO (Alfè, 2005; Belonoshko et al., 2010; Boates and Bonev, 2013) and MgSiO<sub>3</sub> perovskite (Zerr and Boehier, 1993). There are significant disparities among calculations and experiments on the melting (Belonoshko, 1994; Belonoshko and Dubrovinsky, 1997; Alfè, 2005; Zerr, 1998) temperatures in the lower mantle, disagreeing even on which phases represent the solidus and liquidus. The melting behavior in our MgO simulations are consistent with the high-temperature melting curve of recent first-principles simulations (Alfè, 2005; Belonoshko et al., 2010; Boates and Bonev, 2013). Regardless, the solvus remains well above the solidus for more realistic compositions of the silicate mantle (de Koker et al., 2013; Zerr, 1998; Holland, 1997).

##### 4.1. Evolution of a fully mixed planet

For a sufficiently energetic impact, or series of impacts, a planet might be heated to such high temperatures, that the entire planet maybe be an approximately homogeneous mixture of the iron and rock components. Such an extreme scenario is unlikely for an Earth-sized planet, and likely violates geochemical observations that preclude complete mixing of the Earth's primitive mantle (Mukhopadhyay, 2012). Nonetheless, considering the evolution of a planet from a fully-mixed state is useful for demonstrating the effects our phase diagram on the mixing behavior in a planet. A fully

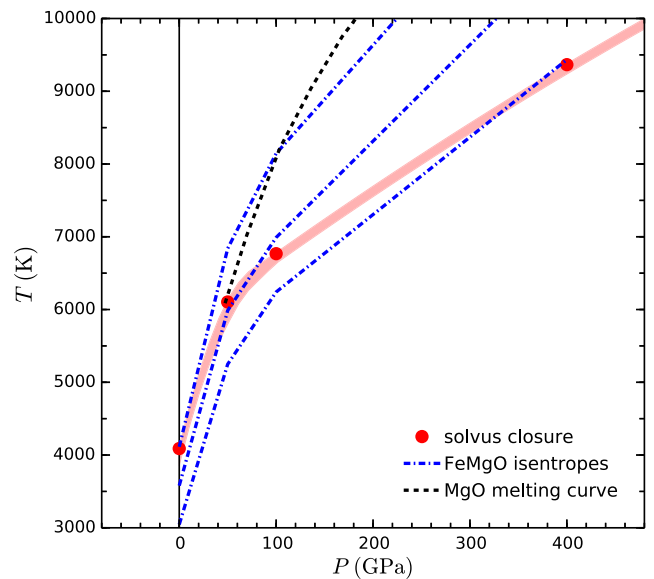


Fig. 8. Calculated isentropes for the mixed FeMgO liquid phase compared to the solvus closure temperature. These results favor the mixed phase to remain stable at depth. The dashed, black line shows the MgO melting temperature from (Boates and Bonev, 2013). The filled regions represent the propagation of estimated errors from finite size effects.

mixed state is also not so far-fetched for super-Earths since heating from release of gravitational energy scales as roughly  $M^{2/3}$ .

The depth at which the phases separate from the fully mixed state is determined by the pressure dependence of solvus closure. Following such a large impact, the planet will quickly evolve to a magma ocean state, and a higher-temperature adiabat will be rapidly re-established. Fig. 8 compares the solvus closure temperature to the calculated isentropes of the mixed FeMgO phase. For a homogeneous, vigorously convecting liquid layer of the planet, these approximate adiabatic temperature profiles of the interior of the planet at different points in its evolution. The comparison is qualitatively the same if the isentropes for either endmember is used instead of the mixed phase. At pressures above 50 GPa, the isentropes have a notably steeper slope than the solvus closure temperature. At lower pressures,  $< 50$  GPa the slopes are identical within the estimated uncertainty. As a result, separation begins in the exterior of the planet and proceeds inwards as the planet cools. Since iron separating in the outer portion of the planet is denser than the rocky phase, it would sink until it reached a depth where it dissolves into the mixed phase again. This may promote compositional stratification, and possibly multi-layer convection between an upper iron-poor and deeper iron-rich layer. The extent to which this process can stratify the planet depends on the competition between growth of liquid Fe droplets and their entrainment in convective flows (Solomatov, 2007).

Based on the Fe–MgO solvus closure temperature presented here, transition of a planet from a fully mixed state to separated rocky and metallic phases would occur while the entire planet is at least partially molten. Consequently, a fully mixed state in an Earth-mass planet would be short lived, since cooling timescales for a deep magma ocean are short in comparison to the timescale of accretion (Abe, 1997; Elkins-Tanton, 2012). This also means little record of such an event is likely to survive to the present day Earth. Indeed, there is little unambiguous evidence for a magma ocean, despite it being a seemingly unavoidable consequence of the moon-forming impact hypothesis. The high surface temperatures of some rocky exoplanets (Pepe et al., 2013) might allow for prolonged cooling times from a such a mixed state.

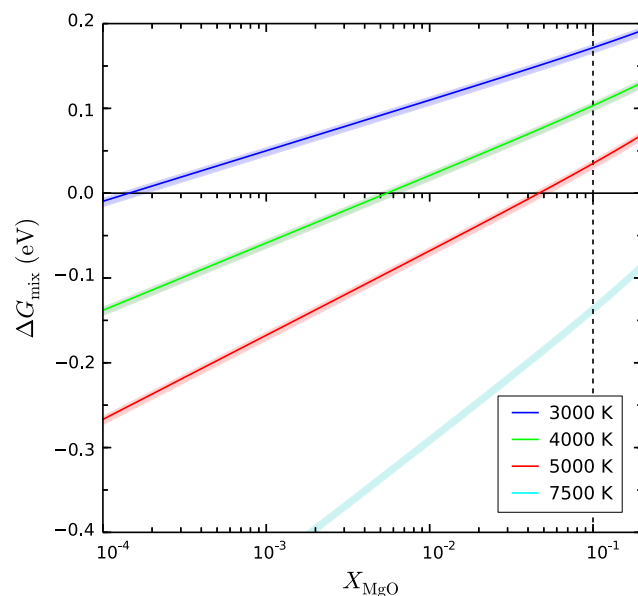
At the relatively low pressures of growing planetesimals (Kleine et al., 2002; Šrámek et al., 2012; Weiss and Elkins-Tanton, 2013),

these results predict that core formation begins at temperatures well below the solvus. As a result, complete mixing of a planet must overcome the gravitationally stable differentiated structure. This will impede upward mixing of a dense core even at temperatures above solvus closure, leading to an inefficient double-diffusive convection state like that proposed for the giant planets (Chabrier and Baraffe, 2007). Material accreted while the planet was above the solvus would, however, remain in a fully mixed outer layer, and evolve according to the picture presented in Fig. 8. Substantial mechanical mixing during giant impact events (Canup, 2004, 2012; Cuk and Stewart, 2012) would also enhance mixing prior to the setup of a double-diffusive state.

#### 4.2. Consequences of localized heating

Despite the implausibility of a fully-mixed earth, related processes may become important as material is added by impacts with smaller differentiated bodies at temperatures near or above solvus closure. Since peak shock temperatures are related to the velocity of the impact rather than the size of the impactor, smaller-scale events can create localized regions where the temperature exceeds the solvus closure temperature. Assuming iron from the shocked region can be rapidly delivered to the core without significant cooling (Monteux et al., 2009), material equilibrated near or above the solvus can be delivered to the core, through a mantle of lower average temperature. In the case that heat transfer from the sinking iron diapir is negligible, the comparison between the solvus closure temperature and adiabats is valid for the fraction of the planet in contact with the sinking iron. In other words, the temperature in the sinking iron will follow a nearly adiabatic path, with Fe and MgO becoming more soluble as the pressure rises. This means that a fraction of the iron delivered to the core could have equilibrated with the rocky mantle at much higher temperatures than on average. The differentiation of a fraction of the planet in the presence of a mixed phase would likely effect partitioning of both major and minor elements between the core and mantle. Walker et al. (1993) suggested that deviations in siderophile element partitioning behavior occur near the solvus closure temperature for iron–silicate mixtures. However, this interpretation has been questioned in light of the confounding effect of drastic changes in oxygen partitioning with pressure (Frost et al., 2010). Better characterization of element-partitioning at such high temperatures could constrain what fraction of the mantle could have been equilibrated in this fashion.

One important consequence of high-temperature equilibration is the delivery of excess, nominally insoluble, light components to the core. This will occur if iron is equilibrated with rocky materials at near-solvus temperatures, and rapidly delivered to the core before it can cool and re-equilibrate with the mantle at lower temperatures. This would be followed by exsolution of a Mg-rich material at the top of the cooling core. This process has been suggested as a possible solution to the problem of the Earth's core having insufficient energy to generate a magnetic field before nucleation of the inner core (Stevenson, 2012). If the interpretation of Fig. 8 can be extended to more iron rich compositions, then exsolution will occur at the top of the core, depositing sediments of Mg-rich material at the core–mantle boundary (Buffett, 2000). As a result, the effect of this sedimentation on core convection is analogous to the exclusion of light elements from the growing inner core. Fig. 9 shows an extrapolation of our results to predict the saturation of MgO in Fe at 50 GPa as a function of temperature. This is done using a function for  $G$  in terms of the cell volumes derived in the low-concentration limit (Wilson and Militzer, 2012; Wahl et al., 2013), and details are presented in the supplemental material. From this we predict a >1% MgO saturation limit down to 4200 K, with concentrations steeply decreasing to be below detec-



**Fig. 9.** Extrapolated saturation limits of MgO in Fe at 50 GPa at various temperatures. Extrapolation is under the assumption that the solution behaves in the low-concentration limit. The dashed vertical line is the most Fe-rich composition from Fig. 5, from which the extrapolation is made. The filled regions represent the propagation of estimated errors from finite size effects.

tion limits in high-pressure experiments by ~3000 K (Knittle and Jeanloz, 1991; Ozawa et al., 2008). In principle, high-temperature equilibration could also explain a bulk-mantle iron concentration in disequilibrium with the present-day core (Ozawa et al., 2008; Tsuno et al., 2013). However, the shape of the MgO-rich side of the calculated exsolution gap (Fig. 6) contradicts this, since the Fe content of the MgO endmember shows a significant deviation for only a small range of temperatures.

## 5. Conclusions

The solvus closure temperatures for material with the bulk terrestrial planet composition marks the transition to a regime where miscibility is a dominant effect in the evolution of the planet. These results present an estimate of those temperatures based on the simplified Fe–MgO system. Where possible, our simulated system was chosen to provide an upper limit for these temperatures, so we expect miscibility for realistic terrestrial compositions at possibly lower temperatures than those found here. **The solvus closure temperature found here for the Fe–MgO system is at temperatures low enough, that it was likely overcome for some fraction of the planet during accretion.** Energetic impact events are now thought to have been commonplace during the formation of the terrestrial planets, and the role of miscibility between the most abundant rocky and metallic materials should be considered to adequately assess their early evolution.

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## Appendix A. Supplementary material

Supplementary material related to this article can be found online at <http://dx.doi.org/10.1016/j.epsl.2014.11.014>.

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