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 ~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 $MgO_{sol/liq} + Fe_{liq} \Rightarrow FeMgO_{liq}$. 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

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

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 $MgSiO_3$ perovskite, the Gibbs free energy of MgO and SiO_2 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 λ is the fraction of the potential $U_b(\mathbf{r_i})$. The difference in Helmholtz free energy is then given by

$$\Delta F_{a \to b} \equiv F_b - F_a = \int_0^1 d\lambda \langle U_b(\mathbf{r_i}) - U_a(\mathbf{r_i}) \rangle_\lambda \qquad (2)$$

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_{DFT}, by finding their differences from reference systems with a known analytic expression, F_{an}.

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