



Contents lists available at ScienceDirect

Physics of the Earth and Planetary Interiors

journal homepage: www.elsevier.com/locate/pepi

Ferrous iron partitioning in the lower mantle



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ARTICLE INFO

Article history:

Received 18 June 2015

Received in revised form 4 April 2016

Accepted 12 May 2016

Available online 21 May 2016

Keywords:

Ferropericase

Bridgmanite

Partitioning

Lower mantle

ABSTRACT

We used density functional theory (DFT) to examine the partitioning of ferrous iron between pericase and bridgmanite under lower mantle conditions. To study the effects of the three major variables – pressure, temperature and concentration – these have been varied from 0 to 150 GPa, from 1000 to 4000 K and from 0 to 100% total iron content. We find that increasing temperature increases K_D , increasing iron concentration decreases K_D , while pressure can both increase and decrease K_D . We find that K_D decreases slowly from about 0.32 to 0.06 with depth under lower mantle conditions. We also find that K_D increases sharply to 0.15 in the very lowermost mantle due to the strong temperature increases near the CMB. Spin transitions have a large effect on the activity of ferropericase which causes K_D to vary with pressure in a peak-like fashion. Despite the apparently large changes in K_D through the mantle, this actually results in relatively small changes in total iron content in the two phases, with $X_{\text{Fe}}^{\text{fp}}$ ranging from about 0.20 to 0.35, before decreasing again to about 0.28 at the CMB, and $X_{\text{Fe}}^{\text{bd}}$ has a pretty constant value of about 0.04–0.07 throughout the lower mantle. For the very high Fe concentrations suggested for ULVZs, Fe partitions very strongly into ferropericase.

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1. Introduction

The presence of iron and its oxidation state has a major effect on the structure and dynamics of minerals in the Earth's interior. For instance, the concentration of iron affects the density, elasticity, electrical conductivity, melting temperature and melt compositions, diffusion rates and the rheological properties of the host mineral. Iron concentrations also affect the sharpness of phase transitions (see for example pv to ppv (Catalli et al., 2009)), and the onset and width of spin transitions. In addition, spin transitions in ferropericase have been suggested to cause strong depletions of Fe in bridgmanite and strong enrichments in ferropericase (e.g. (Auzende et al., 2008; Badro et al., 2003; Holmstrom and Stixrude, 2015; Lin et al., 2005; Vilella et al., 2015)). This in turn changes the physical properties of the mantle in those areas (see for example Lin et al. (2013)).

The lower mantle is over 90% bridgmanite (bd) and ferropericase (fp) with typical iron concentrations of around 10% by weight. Although the partitioning of iron between these phases at pressures ~20–110 GPa and at ~2000–2600 K has been studied experimentally and with thermodynamic modelling a number of times (Auzende et al., 2008; Guyot et al., 1988; Katsura and Ito, 1996; Mao et al., 1997; Nakajima et al., 2012; Narygina et al.,

2011; Sakai et al., 2009; Sinmyo et al., 2008), there are still discrepancies between different studies. The partitioning reaction is defined as:



and the partition coefficient K_D is defined at equilibrium as:

$$K_D = \frac{\frac{X_{\text{FeSiO}_3}^{\text{bd}}}{X_{\text{MgSiO}_3}^{\text{bd}}}}{\frac{X_{\text{FeO}}^{\text{fp}}}{X_{\text{MgO}}^{\text{fp}}}} \quad (1)$$

where X_i^a is the mole fraction ratio of component i in phase a . All studies show that iron prefers fp to bd but there are some differences as to what degree fp is favoured. For instance, at 100 GPa and about 2000 K, K_D varies between about 0.07 and 0.25 depending on the particular study in Mg_2SiO_4 mixtures (Auzende et al., 2008; Nakajima et al., 2012; Narygina et al., 2011; Sakai et al., 2009; Sinmyo et al., 2008; Tange et al., 2009). There are also small differences on the effect of pressure on K_D ; pressure tends to decrease K_D at a rate of around 0.001–0.002 K_D/GPa , but this again depends upon the particular study. Most studies only have a small temperature range but thermodynamic modelling shows that increasing temperature tends to increase K_D on the order of ~0.1 K_D for every 1000 K (Nakajima et al., 2012). Increasing the overall iron concentration has the effect of reducing K_D (Nakajima et al., 2012), although individual studies tend to have small ranges in

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concentration and so the magnitude of this effect is subject to some uncertainty when extrapolated away from the experimental compositions.

As well as the somewhat inconsistent results from different experimental studies and the limited range of compositions and temperature in experiments which makes extrapolation difficult, additional complications arise with more realistic systems. For instance, ferric iron does not affect ferrous iron partitioning when it is monitored and removed from calculations of iron content (Frost and Langenhorst, 2002; Kesson et al., 2002; Mao et al., 1997; McCammon et al., 2004), but the concentration of ferric iron can be affected by total iron concentration, oxygen fugacity, aluminium content and ferric and ferrous spin transitions and thus can drastically vary K_D (Fujino et al., 2014; Nakajima et al., 2012; Prescher et al., 2014; Sinmyo and Hirose, 2013). In addition, spin transitions in both bd and fp are known to affect iron partitioning (Auzende et al., 2008; Fujino et al., 2014; Irifune et al., 2010; Nakajima et al., 2012; Prescher et al., 2014; Sakai et al., 2009; Sinmyo and Hirose, 2013) and so the spin state needs to be known when extrapolating to different conditions. Pyrolytic compositions, as opposed to Mg_2SiO_4 compositions, tend to have larger K_D values of around ~ 0.4 – 1 (Fujino et al., 2014; Irifune et al., 2010; Prescher et al., 2014; Sinmyo and Hirose, 2013).

In this work we use DFT methods to calculate the partitioning of Fe^{2+} between ferro-periclase and bridgmanite. This method has the benefit of being free from the issues of ferric iron contamination, and spin states can be explicitly known and varied. We can also examine the effect of large concentrations of iron on K_D , which are potentially important in some regions of the mantle (Bower et al., 2011; Dobson and Brodholt, 2005; Mao et al., 2006; Muir and Brodholt, 2015a; Wicks et al., 2010). Moreover, we can also study higher pressures and temperature than have been achieved experimentally before (up to 150 GPa and 4000 K).

2. Methods

2.1. Theoretical details

All simulations were carried out with the DFT code VASP (Kresse and Furthmüller, 1996) using the projector-augmented-wave (PAW) method (Kresse and Joubert, 1999) and the PBE formulation of GGA corrected for solids (Perdew et al., 2008). The core radii of the PAW spheres are O 0.80 Å ($2s^2 2p^4$), Si 1.00 Å ($3s^2 3p^2$), Mg 1.06 Å ($2p^6 3s^2$), Fe 1.22 Å ($3d^7 4s^1$). 14 electron Fe potentials were also tested and the results are similar. To account for GGA's inability to correctly reproduce iron spin states we used a GGA+U functional with Hubbard U parameters set to 3 eV. This value has been estimated for fp from optical spectroscopy (Goncharov et al., 2006) and has been used theoretically to produce spin crossovers similar to experiments (Persson et al., 2006). A slightly smaller value (2.5 eV) has also been used to replicate experimental results (Holmstrom and Stixrude, 2015). Similarly this same value has been used to replicate experimental spin crossovers in bd (Huang and Pan, 2012).

For ferropericlase we used a cubic 64 atom unit cell ($2a^*2a^*2a$) and for bridgmanite an 80 unit cell ($2a^*2b^*c$). To calculate the variation in free energy of reaction 1, both enthalpies and entropies have to be determined.

Enthalpies were determined statically (i.e. at 0 K) with an energy cutoff of 850 eV, $6 \times 6 \times 6$ k points and self-consistent runs that were relaxed to within 10^{-6} eV.

Molecular dynamics (MD) simulations were run to obtain properties at high T using an NVT ensemble with the Nosé thermostat (Nosé, 1984) and with Nosé frequencies of ~ 20 THz. MD calculations were run at the gamma point with a cutoff of

500 eV, relaxation to within 10^{-4} eV and were run for 10 ps. The electronic entropy was determined directly from VASP. Magnetic entropy was determined using Eq. (2):

$$S_{\text{mag}} = \ln(\mu + 1) \times R \times n_{\text{Fe}} \quad (2)$$

where R is the gas constant and μ is the average absolute magnetic moment of an individual iron atom determined from VASP. Note that this does not contain a term for magnetic degeneracy since that is already contained in the electronic entropy. It is assumed that iron states are fully paramagnetic.

To determine vibrational entropy contribution to fp and bd we used thermodynamic integration with the blue-moon algorithm in VASP (Bucko, 2008). This calculates the difference between two states (here different temperatures) by calculating the free-energy gradient along a constrained reaction path. This is done by calculating the restoring force between the constrained and unconstrained reaction path. The restoring force is then integrated to give a free energy difference between the initial and final state. The reaction path constraints were placed on the Fe–O and Fe–Fe bond lengths in iron-bearing systems and Mg–O and Mg–Mg in iron-free systems, as these lengthen upon heating. However, the choice of reaction path is irrelevant when calculating the free energy between 2 final states as the free energy is a state function. At each temperature, pressure and composition (i.e. concentration of Fe) investigated, the free energy was calculated between a system (fp or bd) at 0 K and the same system at the temperature of interest using 6 image paths (different temperatures) and the path energies were integrated to give a vibrational free energy difference (ΔG) between the 0 K and the heated system. This is fundamentally identical to calculating the variation of heat capacity divided by temperature between fp and bd systems.

2.2. Calculating K_D

The enthalpy and entropy were determined for $Fe_xMg_{1-x}O$ and $Fe_xMg_{1-x}SiO_3$ with $x = 0, 0.25, 0.5, 0.75$ and 1 at 30, 60, 90, 130 and 150 GPa and at 1000, 2000 and 4000 K. Fp calculations involve a mixed spin state and the method of calculating the free energy of this state is outlined in Muir and Brodholt, 2015a. As calculating the free energy of every possible arrangement of iron in each concentration would be computationally onerous, all calculated arrangements had iron at the maximum separation from each other and it is assumed that the possible formation of iron clusters does not overly affect the partitioning (atom positions at 0 GPa are included in File S1 and S2).

Once enthalpy and entropies of fp and bd systems were obtained the K_D of Reaction 1 was calculated with Eq. (3):

$$RT \ln K_D = -\Delta G_{p,T}^0 - RT \ln \frac{\gamma_{\text{Fe}}^{\text{bd}} / \gamma_{\text{Mg}}^{\text{bd}}}{\gamma_{\text{Fe}}^{\text{fp}} / \gamma_{\text{Mg}}^{\text{fp}}} \quad (3)$$

where R is the gas constant, T is temperature, $-\Delta G_{p,T}^0$ is the standard state Gibbs free energy change between the end members at the pressure, temperature and composition of interest and includes magnetic, vibrational and electronic entropy, and γ_i^a is the activity coefficient of Fe or Mg in either phase and accounts for the non-ideality of Fe–Mg mixing in each solid solution.

To calculate the activity coefficients we first calculated a set of Margules parameters (Walas, 1985) using the equation:

$$\frac{G_{\text{mix}}}{RT} = X_{\text{Fe}}X_{\text{Mg}}(X_{\text{Mg}}W_{\text{Fe-Mg}} + X_{\text{Fe}}W_{\text{Mg-Fe}}) \quad (4)$$

where G_{mix} is the difference in energy between a linear mixture of FeO and MgO (or $FeSiO_3$ and $MgSiO_3$) and the calculated energy of $Fe_xMg_{1-x}O$ (or $Fe_xMg_{1-x}SiO_3$). For each phase (bd or fp) this was solved simultaneously for $x = 0.25$, $x = 0.5$ and $x = 0.75$ to get both

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