



Spin state transition and partitioning of iron: Effects on mantle dynamics



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ABSTRACT

Experimental studies at pressure and temperature conditions of the Earth's lower mantle have shown that iron in ferroprecipitate (Fp) and in Mg-silicate perovskite (Pv) undergoes a spin state transition. This electronic transition changes elastic and transport properties of lower mantle minerals and can play an important role in mantle convection. Here we focus on the geodynamic effect of the spin-induced density modifications caused by the volume collapse of Fp and by the variation of Fe partitioning (K^{Pv-Fp}) between Fp and Pv. Since K^{Pv-Fp} behavior strongly depends on alumina content, we explore two end-member compositions, one Al-bearing (with 4.7 wt% Al_2O_3 in Pv) and the other Al-free. We use the theoretical model by Sturhahn et al. (2005) to calculate the spin configuration of Fp over a range of pressure–temperature conditions, and use experimental results to model Fe partitioning. We then apply the Mie–Grüneisen–Debye equation of state to obtain the density of the mineral assemblages. The calculated amplitude of the density change across the spin state transition is less than 1%, consistent with experiments by Mao et al. (2011); our density profiles differ from PREM by less than 1.5%. The spin-induced density variations are included in a three dimensional convection code (Stag3D) for a compressible mantle. We find small temperature differences between models with and without spin state transitions, since over billions of years the relative temperature difference is less than 50 K. However the relative RMS vertical velocity difference is up to 15% for an Al-free system, but only less than 6% for an Al-bearing system.

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1. Introduction

The widely accepted pyrolytic compositions consist of approximately 18 vol% ferroprecipitate (Mg,Fe)O (hereafter called Fp), 75 vol% Mg-silicate perovskite (Mg,Fe)(Al,Si)O₃ (hereafter called Pv), and 7 vol% Ca-silicate perovskite CaSiO₃ (hereafter called CaPv) (Ringwood, 1982; Irifune, 1994; Irifune et al., 2010). Even if the uncertainties in the composition of the lower mantle are considered, current experiments at high pressure and temperature, coupled with equations of state (Jackson, 1998; Ricolleau et al., 2009; Murakami et al., 2012) cannot fully explain density and seismic velocities inferred by seismic models such as PREM (Dziewonski and Anderson, 1981). The disagreement reveals the large uncertainties that still affect composition, temperature, and physical properties in the lower mantle.

Fyfe (1960) suggested that the electronic structure of Fe²⁺ in the octahedral coordination can change at high pressure. For example, the 3d orbitals of Fe²⁺ in Fp, which is surrounded by six oxygen atoms, split in two different groups with different energies: three orbitals (t_{2g}) with a lower energy and two orbitals (e_{2g}) with a higher energy (see Li et al., 2004, Fig. 4). Following Hund's rule, at ambient condition, the stable state has two unpaired electrons in two t_{2g} orbitals, two unpaired electrons in two e_{2g} orbitals, and two paired electrons in a t_{2g} orbital. This configuration is the high spin (HS) state. With compression, the splitting of the two energy levels can increase and at some point the energy gap becomes large enough to stabilize the state with six paired electrons in the t_{2g} orbitals. This configuration is the low spin (LS) state. Sherman (1988) and Burns (1993), with a crystal field theory, as well as Cohen et al. (1997), with a band theory, predicted the occurrence of such change in spin state at the pressure–temperature conditions of the Earth's lower mantle. Badro et al. (2003) found a spin state transition in Fp at a pressure range ~60–70 GPa and at ambient temperature. At higher temperatures, theoretical models (Sturhahn et al., 2005; Tsuchiya et al., 2006) predicted that the

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spin state transition should occur at higher pressure and over a broad range of pressure, as confirmed by Lin et al. (2007a). Iron spin state transitions occur also in Pv (Badro et al., 2004; Jackson et al., 2005), but it is more complex because of two different crystallographic sites, an octahedral and a dodecahedral, and two different oxidation state of iron, Fe²⁺ and Fe³⁺ (see Lin et al., 2013; Badro, 2014, and reference therein).

Spin state transitions alter the elastic and transport properties (Jackson et al., 2006; Lin et al., 2006, 2007b, 2013; Crowhurst et al., 2008; Goncharov et al., 2008, 2009; Antonangeli et al., 2011; Ammann et al., 2011) thereby affecting mantle dynamics. Moreover the lower mantle density is modified by the volume collapse due to the lower volume of Fe²⁺ in LS state, and by the spin state induced modification of Fe partitioning between Fp and Pv. Bower et al. (2009) and Shahnas et al. (2011) calculated the property changes induced by the Fe²⁺ spin state transition in Fp, and conducted numerical simulations to quantify the effect on mantle dynamics. Both studies found increased mantle temperature and enhanced flow velocity. However, Bower et al. (2009) assumed a pure Fp composition and Shahnas et al. (2011) neglected Fe partitioning, so that both studies use a simplified lower mantle composition.

Here we use a theoretical model (Sturhahn et al., 2005) coupled to an equation of state (Jackson and Rigden, 1996) to build a density model including the Fe²⁺ spin state transition in Fp. The dominant chemical components (e.g., FeO, MgO, MgSiO₃, Fe₂O₃, Al₂O₃, etc.) are included in order to provide realistic thermodynamic properties of the mineral assemblages (Fp, Pv, and CaPv). We apply an equation of state to these minerals to obtain their density as a function of pressure and temperature. This approach enables us to explore different compositions and to calculate the corresponding density profile.

A new aspect of our work is to consider the spin state induced Fe partitioning between Pv and Fp (K^{Pv-Fp}). Recent experiments have shown different behaviors of K^{Pv-Fp} for an olivine composition (Kobayashi et al., 2005; Sinmyo et al., 2008; Auzende et al., 2008; Sakai et al., 2009) and pyrolitic compositions (Irifune, 1994; Kesson et al., 1998; Wood, 2000; Murakami et al., 2005; Irifune et al., 2010; Sinmyo and Hirose, 2013). Therefore we study two end-member compositions, an Al-bearing and an Al-free pyrolite, with their corresponding Fe partitioning. We assume that in the Al-free system Fe partitioning follows the same behavior as in the olivine composition. The calculated density profile in the lower mantle fits PREM density (Dziewonski and Anderson, 1981) within 1.5%, using Brown and Shankland (1981) geotherm, and it is consistent with high temperature experiments (Mao et al., 2011). The density models are then included in the convection code Stag3D (Tackley, 1996) to quantify the long term impact of the Fe spin state transition on mantle convection.

2. Density models

This paragraph presents how we calculate: (a) the average spin state of Fe²⁺ in Fp, (b) the iron content of Fp and Pv, considering Fe partitioning, and (c) the density variations induced by the spin state transition for two end-member lower mantle compositions.

2.1. Average spin state of iron in ferroperricase

Following Sturhahn et al. (2005) we calculate the average Fe²⁺ spin configuration in Fp by minimizing the Helmholtz free energy: $F = U - TS$. Note that by considering the Helmholtz free energy, rather than the Gibbs free energy, Sturhahn et al. (2005) implicitly neglect work variations during the spin state transition. Only LS state Fe²⁺ ions interact with each other, thus the internal energy is

$$U = -N J_{LS} \eta_{LS}^2 + N(\eta_{LS} E_{LS} + \eta_{HS} E_{HS}), \quad (1)$$

where N is the number of Fe²⁺ in Fp, E_{LS} and E_{HS} are the energy levels of LS state and HS state, respectively, J_{LS} is the coupling LS state–LS state, η_{LS} and η_{HS} the fractions of Fe²⁺ in LS state and HS state, respectively, with $\eta_{LS} + \eta_{HS} = 1$. The entropy of the crystal can be written as

$$S = -k_B N \left[\eta_{LS} \ln \left(\frac{\eta_{LS}}{g_{LS}} \right) + \eta_{HS} \ln \left(\frac{\eta_{HS}}{g_{HS}} \right) \right], \quad (2)$$

where k_B is the Boltzmann constant, g_{LS} and g_{HS} are the energy degeneracies of the electronic configuration. The free energy is then:

$$F = N \left\{ -J_{LS} \eta_{LS}^2 + \eta_{HS} E_{HS} + \eta_{LS} E_{LS} + k_B T \left[\eta_{LS} \ln \left(\frac{\eta_{LS}}{g_{LS}} \right) + \eta_{HS} \ln \left(\frac{\eta_{HS}}{g_{HS}} \right) \right] \right\}. \quad (3)$$

To find the equilibrium state at a given condition we solve

$$\frac{\partial F}{\partial \eta_{LS}} = 0. \quad (4)$$

By using the normalized equation, we express Eq. (4) as:

$$0 = \eta_{LS} \left[1 + \frac{g_{HS}}{g_{LS}} \exp(-2\beta J_{LS} \eta_{LS}) \exp(\beta(E_{LS} - E_{HS})) \right] - 1, \quad (5)$$

with $\beta = k_B T$. J_{LS} depends on the iron content and volume, E_{LS} and E_{HS} depend on volume (Sturhahn et al., 2005), the remaining parameters are assumed to be constant. The solution of Eq. (5) provides the fraction of LS state as a function of iron content, volume, and temperature. For further details on the parameters values please refer to Sturhahn et al. (2005).

The next step is to convert volume to pressure using the Mie–Grüneisen–Debye equation of state (Jackson and Rigden, 1996) and the parameters listed in Tables 1 and 2. At ambient temperature we use the third order Birch–Murnaghan equation of state:

$$P = \frac{3K_{T0}}{2} \left[\left(\frac{V_0}{V} \right)^{7/3} - \left(\frac{V_0}{V} \right)^{5/3} \right] \left\{ 1 - \frac{3}{4} (4 - K'_{T0}) \left[\left(\frac{V_0}{V} \right)^{2/3} - 1 \right] \right\} + \Delta P_{th}, \quad (6)$$

while the effect of temperature is added via a thermal pressure:

$$\Delta P_{th} = \frac{\gamma(V)}{V} [E_{th}(V, T) - E_{th}(V, T_0)], \quad (7)$$

where the subscript zero indicates ambient conditions for volume V_0 , temperature T_0 , isothermal bulk modulus K_{T0} and its pressure derivative K'_{T0} . The Grüneisen parameter depends on volume:

$$\gamma(V) = \gamma_0 \left(\frac{V}{V_0} \right)^q, \quad (8)$$

where q is assumed to be a constant. The vibrational energy is calculated from the Debye model,

$$E_{th} = \frac{9nRT^4}{\theta^3} \int_0^{\theta/T} \frac{x^3}{e^x - 1} dx, \quad (9)$$

n is the number of atoms per formula unit, R is the gas constant, and θ is the Debye temperature:

$$\theta = \theta_0 \exp \left(\frac{\gamma_0 - \gamma(V)}{q} \right). \quad (10)$$

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