Thermochemical State of the Lower Mantle: New Insights From Mineral Physics

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We report recent findings in the field of high-pressure mineral physics with important implications for Earth’s lower mantle. We show that the two main constituents of the lower mantle, namely, (Mg,Fe)SiO$_3$—magnesium silicate perovskite—and (Mg,Fe)O—ferropericlase—undergo electronic transitions at lower mantle pressures (70 and 120 GPa), in which iron transforms from the high-spin state to the low-spin state. The transformations modify the thermochemical state of Earth’s lower mantle. Minerals bearing high-spin iron have characteristic absorption lines in the near-infrared, hindering radiative conductivity at lower-mantle temperatures. These absorption lines shift to the visible (green to violet) range in the low-spin state, and their intrinsic intensities decrease; the minerals thus become increasingly transparent in the near-infrared and their radiative and total thermal conductivities rise. Thus, the heat conductivity of the lowermost mantle could be higher than previously thought. Moreover, the spin-driven partitioning of iron between the two mineral phases can explain large-scale chemical heterogeneities in the mantle that are driven by regional temperature variations. It is noteworthy that the transition pressures correspond to the bottom third of the lower mantle (70 GPa, 1700-km depth), and to the last 300 km above the core–mantle boundary (120 GPa, 2600-km depth); these regions have very special geophysical signatures, as chemical heterogeneities have been reported by seismology in the first case and the bottom 300 km of Earth’s mantle constitutes the D” layer. Our observations provide a mineral physics basis for these features in Earth’s lower mantle.

INTRODUCTION

Seismic wave analysis is the main tool for studying Earth’s structure [Jeffreys and Bullen, 1940], whether on the shallow (crustal seismology, oil exploration) or the deep (Earth’s inner structure) scale [Birch, 1952]. Radial seismological models, such as PREM [Dziewonsky and Anderson, 1981], obtained from inversion of seismic travel times and normal mode spectra, give the density, bulk and shear moduli, compressional and shear sound velocities in the Earth as a function of depth. In terms of seismic wave travel times, structurally different entities are determined on the basis of discontinuities in density, bulk, and shear properties [Birch, 1952; Jeffreys and Bullen, 1940]. Seismological profiles show without any doubt that the most severe discontinuity in material properties occurs at a depth of 2890 km; this is the core–mantle boundary (CMB) that separates the dense iron-rich core below from the lighter silicate-rich mantle above. In the mantle, the sharpest discontinuity occurs at a depth of 660 km, followed by a broader one at 410 km; the 660-km discontinuity separates the lower mantle below from the upper mantle above, whereas the 410-km discon-
tinuity further separates the uppermost mantle above from the transition zone below. In one of its major achievements, high-pressure mineral physics has shown that these seismic discontinuities are a direct consequence of phase transformations in candidate mantle minerals (e.g. Ringwood [1975]; Jackson and Rigden [1998]; and a review article by Fiquet [2001] and references therein). Although the question of a difference in chemical composition between the upper and lower mantle is still a matter of debate, the mineralogy of these two reservoirs is in any case fundamentally different; the upper mantle is mainly constituted of fourfold-coordinated silicate framework minerals (olivine, pyroxene, garnet, and their high-pressure modifications), whereas the lower mantle consists mainly of sixfold coordinated silicates—magnesium silicate perovskite (Mg-pv) and calcium silicate perovskite (Ca-pv)—and dense oxides such as ferropericlase (fp) [Fiquet, 2001; Liu, 1974].

Although apparent changes in the lower mantle cannot be observed using radial (one-dimensional) seismological models, the recent developments [Fukao et al., 2001; Grand, 2002; Romanowicz, 2003; Trampert and van der Hilst, this volume] of seismic tomography as well as high-precision modelling of seismic anisotropy [Garnero and Lay, 2003] have revealed more subtle phenomena in the deepest parts of the lower mantle. For instance, lateral velocity anomalies at depths around 1700 km have been ascribed to chemical heterogeneities [Karato and Karki, 2001; van der Hilst and Kárason, 1999], as thermal heterogeneities alone cannot reasonably explain the magnitude of these anomalies. Such effects cannot be addressed by mineral physics by probing structural transformations, because the absence of sharp discontinuity withdraws all chances for the phenomenon to be related to a structural phase transformation. Of course, past reports of chemical reactions in the lower mantle, such as the breakdown of Mg-pv into silica and fp [Saxena et al., 1996] could have brought a logical mineral-chemical basis to these observations. However, it appears today that this breakdown was not observed in any of the numerous studies performed since [Fiquet, 2001; Fiquet et al., 2000; Kesson et al., 1998; Serghiou et al., 1998; Shim and Jeanloz, 2002], and it is widely accepted today that Mg-pv is chemically stable (i.e. it does not break down into its simple constituents) under the pressure and temperature (P–T) conditions of Earth’s mantle. Given that geophysical observations tend to show a chemical origin for lower-mantle heterogeneities, a deeper insight in the chemistry of minerals in the lower mantle is necessary. This has led us to investigate directly the properties that control the chemistry in these compounds, namely, their electronic structure, by carrying out x-ray emission spectroscopy (XES) measurements on the lower mantle’s most abundant minerals [Badro et al., 2003, 2004] at high pressure.

A mysterious and uncharacterised geophysical entity, the D’ layer, is a 300-km thick layer at the bottom of the mantle that sits right above the CMB [Lay, 1983]. The highest resolution seismic studies even locally suggest another very thin layer (on the order of tens of km) characterized by very low seismic wave velocities between the D’ layer and the CMB: the ultra-low velocity zone (ULVZ). If the top of the D’ layer represents a discontinuity, it could have a structural signature in terms of mineral transformations. But as very little is known about the chemical balance (and therefore about the chemistry) at those depths, with the chemical input of cold downwellling slabs and the chemical output through upwelling plumes, there is a possibility that D’ and the ULVZ constitute a chemical layer different from the surrounding mantle and core; in this case again, and this time because the chemistry of the reservoir (and therefore the mineralogical composition) is not known, little can be obtained from structural studies stricto sensu to help address this issue.

Until very recently, high pressure and high temperature (HP–HT) experiments performed in the laser-heated diamond anvil cell in the P-T conditions of Earth’s lower mantle have shown the stability of lower-mantle phases (Mg-pv, fp, and Ca-pv) up to 110 GPa (2450-m depth) [e.g. Fiquet, 2001], with possible small distortions (and minor phase changes) of the Mg-pv phase [Shim et al., 2001]. However, a recent x-ray diffraction study showed that Mg-pv undergoes a transformation to a denser high-pressure modification named post-perovskite phase (Mg-pp), at the P–T conditions of the D’ layer [Murakami et al., 2004a]. This mineral physics observation directly addresses the question of the origin of the D’ layer in terms of a structural mineralogical transformation. In order to constrain and provide input for geophysical and geochemical models, and also to cross-check the validity of the new material’s properties with geophysical observations, various physical and chemical properties (beyond crystal structure) of this new phase need to be known (Clapeyron slope, electronic and transport properties, etc. We have performed a XES study that shows that the properties of Mg-pv are severely modified in the same pressure range as the Mg-pv to Mg-pp transformation [Badro et al., 2004], partly addressing issues related to the properties of that phase.

In this article, we present a study of the electronic properties of lower-mantle minerals subject to extreme conditions, using x-ray spectroscopy to gain insight in important physical and chemical properties that cannot otherwise be obtained. The rationale lies in the fact that the strong changes in the properties of the lower mantle’s main minerals, Mg-pv, fp, and Ca-pv, should likely be determined by their iron (and to a lesser degree aluminium) content. Indeed, the alkali-earth end-member minerals MgO (periclase), MgSiO₃-pv and CaSiO₃-pv do not seem to exhibit any physical or chemical
peculiarity with increasing pressure and temperature. They remain mostly transparent broad-band-gap ionically bonded insulators. In the presence of iron oxide, periclase and Mg-pv readily form solid solutions by Mg/Fe exchange, giving rise to electronically complex compounds (Mg,Fe)O-fp and (Mg,Fe)SiO$_3$-pv, whereas Ca-pv remains essentially iron-free. Because Mg is a more abundant major element than Fe in Earth’s mantle, all the present (oxidized) iron is accommodated in the solid solution fp and Mg-pv phases, and no pure (oxidized) iron end-member minerals should exist.

The specificity of iron comes from the fact that it is a transition metal; unlike the other major elements (Mg, Ca, Si, Al) of the bulk silicate Earth [BSE; McDonough and Sun, 1995], it has partially filled 3d orbitals that give rise to a series of possible energy configurations depending on its atomic environment. Notably, iron adopts different valences, for instance, ferrous (Fe$^{2+}$) and ferric (Fe$^{3+}$) iron, and different electronic configurations, for instance, high-spin and low-spin states. The energy differences in 3d orbitals are small compared to those in s and p orbitals, implying that the sensitivity of iron-bearing compounds to energy changes induced by pressure and temperature is more dramatic. Properties such as electrical, thermal, and radiative conductivity can vary significantly with pressure or temperature in such compounds, whereas they remain almost unperturbed in the iron-free end-members. The physical and chemical complexity of lower-mantle mineralogical assemblages is undoubtedly linked to the presence of iron.

ELECTRONIC STRUCTURE OF IRON— THERMODYNAMICS

Iron is a 3d transition metal, and its ionic electronic structure is (Ar)3d$^6$ for ferrous iron (Fe$^{2+}$) and (Ar)3d$^5$ for ferric iron (Fe$^{3+}$). The 3d orbitals are constituted of a subset of five orbitals with different symmetry. Three of these ($d_{x^2}, d_{y^2}, d_{z^2}$) make up a set of orbitals named $t_{2g}$ and the two others ($d_{x^2-y^2}, d_{xy}$) make up a set of orbitals named $e_g$. Iron can be in the high-spin (HS) or low-spin (LS) states, as defined by the occupation of that outermost 3d orbital. Their energetic fine structure is shown in Figure 1 in the case of an octahedral (sixfold coordination) field, within the framework of crystal field theory [Burns, 1993]. The latter is a simple yet sound theoretical framework, for estimating the electronic contributions to internal energy and entropy of a HS or LS state. All thermodynamic calculations presented in this paper are based on this simple theory, and should only be considered as first-order approximations. More precise theoretical modelling is required to obtain increased precision or insight into more complex effects. Depending on the values of the pairing energy ($E_p$) and the $t_{2g}$—$e_g$ splitting (known as 10 Dq or $\Delta$) — often referred to as the crystal field stabilisation parameter — the lowest energy configuration can either be the HS state (high $E_p/\Delta$ ratio or weak field) where the spin quantum number is maximum or the LS state (low $E_p/\Delta$ ratio or strong field). The crystal field stabilisation parameter (CFSP) $\Delta$ increases with decreasing iron–oxygen bond-length, and thus with increasing density, whereas the pairing energy remains essentially unchanged; in this respect, an iron-bearing mineral consisting of HS iron at low pressure (at the surface of the globe) can undergo a HS to LS (or spin pairing) transition at higher pressure (at depth in the Earth). Obviously, such a transformation has an effect on various properties linked to the energetics (energy and entropy) of the compound. A striking example of the effects of spin transitions is the colour change of haemoglobin, the substance in red blood cells that bonds oxygen to its octahedral ferrous iron site, making it the oxygen carrier in the body: iron in this molecule undergoes a HS to LS transition upon release of the oxygen atom (and the opposite upon capture) and transforms in color from red (oxygen-rich arterial blood) to purple (oxygen-depleted venous blood). Other band-structure effects can induce spin-pairing transitions (for instance, an increase of $e_g$ and $t_{2g}$ bandwidth), but these only apply in

![Figure 1. Electronic fine-structure of ferrous iron in the high-spin and low-spin states. The figure on the left shows the population of both states in terms of orbital symmetry ($t_{2g}$ and $e_g$), whereas the figure on the right shows the energetic diagram as a function of the crystal field splitting energy $\Delta$ and coulomb repulsion energy $E_p$.](image-url)
the case of band-like systems, which is irrelevant to the case of diluted iron in lower-mantle minerals.

The internal energy in the HS and LS states of Fe\(^{2+}\) is obtained by summing the energies of all six electrons, depending on their energy level and pairing, which yields (see Figure 1)

\[
U_{HS} = 4 \times (-0.4\Delta) + 2 \times (0.6\Delta) + E_p = -0.4\Delta + E_p \tag{1a}
\]

\[
U_{LS} = 6 \times (-0.4\Delta) + 3E_p = -2.4\Delta + 3E_p \tag{1b}
\]

and similarly for Fe\(^{3+}\), one obtains

\[
U_{HS} = 3 \times (-0.4\Delta) + 2 \times (0.6\Delta) = 0 \tag{1c}
\]

\[
U_{LS} = 5 \times (-0.4\Delta) + 2E_p = -2.0\Delta + 2E_p \tag{1d}
\]

The (configurational) entropy is given by \(S = k_B \ln(n \cdot (2s + 1))\) where \(s\) is the total spin, \(n\) the orbital degeneracy, and \(k_B\) the Boltzmann constant [Sherman, 1991]. For ferrous iron (Fe\(^{2+}\)), the total spin is \(s_{HS} = 2\) and \(s_{LS} = 0\); the degeneracy term is \(n_{HS} = 1\) in the LS state and \(n_{LS} = 3\) in the HS state but should be considered \(n_{HS} = 1\) at low temperatures because the degeneracy could be lifted. Therefore, the entropy of LS state is \(S_{LS} = 0\) (there is a single microstate), and the entropy of the HS state is \(S_{HS} = k_B \ln 5\) at high temperature and \(S_{HS} = k_B \ln 5\) at low temperature. For ferric iron (Fe\(^{3+}\)), the total spin is \(s_{HS} = 2.5\) and \(s_{LS} = 0.5\); the degeneracy term is \(n_{HS} = 1\) in the HS state, and \(n_{LS} = 3\) in the LS state at high temperature but should be considered \(n_{LS} = 1\) at low temperatures because, once again, the degeneracy could be lifted. Therefore, the entropy of HS state is equal to \(S_{HS} = k_B \ln 6\), and the entropy of the LS state is equal to \(S_{LS} = k_B \ln 6\) at high temperature and to \(S_{LS} = k_B \ln 2\) at low temperature. It is interesting to note that \(\Delta S = 0\) at high temperature for the spin-pairing transition in ferric iron.

A spin transition occurs when the overlap in electronic orbitals is such that \(\Delta\) reaches a critical value thermodynamically favouring the LS state. \(\Delta\) increases with compression following pressure according to Burns [1993]:

\[
\Delta(V) = \Delta^0 \left( \frac{V_0}{V} \right)^{5/3} \tag{2}
\]

and reaches a critical value \(\Delta_c\), defined by thermodynamic equilibrium in the canonical \((T,V)\) ensemble, minimising the Helmholtz free energy \(F = U - TS\). This is what we will call hereafter a density-driven transition, although the term may not be perfectly correct because it doesn’t reflect the entropy dependence but rather has the meaning that the transition is due to increasing electronic overlap, which is a sole function of density. Therefore, at the spin transition \(F_{HS} = F_{LS}\), and incorporating the terms detailed above, one obtains at the transition

\[
\Delta_c = E_p + \frac{1}{2}k_B T \ln 15 \tag{3a}
\]

at mantle temperatures and

\[
\Delta_c = E_p + \frac{1}{2}k_B T \ln 5 \tag{3b}
\]

at room temperature (for ferrous iron).

In a system at a fixed pressure and temperature [canonical \((P,T)\) ensemble], a spin transition is thus followed by a local volume collapse around the concerned ionic species. This is of course accompanied by an increase in \(\Delta\) according to equation (2), and this reduced volume for iron in the LS state with respect to the HS state affects partitioning of iron between various phases coexisting in the HS and LS state. It is also partially responsible for the important changes expected in the transport properties as indicated above. Whether this volume collapse, following the spin transition, should be accounted for in the equilibrium condition \((\Delta G = 0)\) is still a matter of debate and depends on whether the transition is cooperative in character or not. Therefore, two cases will be discussed below: (i) taking this volume change into account at equilibrium (a first-order transition with phase coexistence) and (ii) considering the volume collapse occurs only afterwards (a cooperative first-order transition with no phase coexistence). Of course, one must keep in mind that we are dealing with a multicomponent system and that our one-component thermodynamic treatment is not rigorously exact.

**X-RAY EMISSION SPECTROSCOPY**

XES is a spectroscopic technique that allows probing of the structure of the low-energy outermost electronic levels or orbitals of a chemical element [Jenkins, 1999]. It is a chemically sensitive local technique in the sense that it probes only the local environment around a given chemical species. The process is schematically described in Figure 2. When a primary x-ray excitation source strikes a sample, the x-ray can either be absorbed by the atom or scattered through the material. The process in which an x-ray is absorbed by the atom by transferring all of its energy to an electron is called the “photoelectric effect” [Ashcroft and Mermin, 1976; Jenkins, 1999]. During this process, if the primary x-ray had sufficient energy, electrons are ejected from the inner shells (e.g. 1s electrons), creating core-holes (vacancies). These holes present an unstable condition for the atom. As the atom returns to its stable condition, electrons from the outer shells are transferred to the inner shells and, in
the process, give off a characteristic x-ray whose energy is the difference between the two binding energies of the corresponding shells. Because each element has a unique set of energy levels, each element produces x-rays at a unique set of energies, allowing one to nondestructively measure the elemental composition of a sample. The process of emissions of characteristic x-rays is called x-ray fluorescence or x-ray spectroscopy. Their analysis is called x-ray fluorescence spectroscopy, or x-ray emission spectroscopy (XES).

The characteristic x-rays are labelled K, L, M, or N to denote the shells from which they originated. Another designation, α, β, or γ, is made to mark the x-rays that originated from the transitions of electrons from higher shells. Hence, a Kα x-ray is produced from a transition of an electron from the L to the K shell (or 2p to 1s), and a Kβ x-ray is produced from a transition of an electron from the M to a K shell (or 3p to 1s), etc. Given that within the shells there are multiple orbits of higher and lower binding-energy electrons, a further designation is made as α1, α2 or β1, β2, etc. to denote transitions of electrons from these orbits into the same lower shell. Now, the hole left in the upper levels interacts with the outermost electronic shell (3d in the case of iron), an exchange interaction that gives rise to small energy shifts (on the order of a few electron volts) of the emission line [Jenkins, 1999]. These shifts, and the lineshapes accompanying them, depend on the specific electronic configuration and structure of that outermost shell; their analysis in turn allows determining these, which as we said earlier, is responsible for the electronic complexity of transition metals.

The Kβ emission line originates from the 3p to 1s decay. Kβ spectra can be interpreted using atomic multiplet calculations [Hermsmeier et al., 1988] and configuration interactions. The spectral shape of Kβ emission line in 3d transition metal compounds is dominated by final state interaction between the 3p core-hole and the electrons of the partially filled 3d shell (see Figure 3). Qualitatively, the main effect is due to the exchange interaction between the core-hole and the local moment, which results in the splitting of the Kβ spectrum into HS and LS final states. This simple picture also predicts that the energy separation between the two peaks is given by the product of the exchange integral J and (2S + 1), where S is the total spin of the 3d shell; and that the intensity ratio between the two is given by S/(S + 1) [Tsutsumi et al., 1976]. Both the energy splitting and intensity ratio are modified when configuration interaction is taken into account.

**Figure 2.** Schematic representation of the shell structure of a Fe$^{2+}$ ion as well as an illustration of the x-ray absorption (left) followed by the Kα and Kβ emission processes (right).

**Figure 3.** Schematic illustration of the various states in the Fe$^{2+}$ Kβ x-ray emission process: the initial state (left panel) is a K-edge x-ray absorption process ejects an electron (arrow), which leaves an empty core-hole (circle) in the 1s shell. This is followed by a Kβ x-ray emission process in the intermediate state (middle panel), which is associated with the collapse of a 3p electron onto the 1s shell to fill the core-hole. The final state (right panel) corresponds to a core-hole in the 3p shell, which strongly interacts with the 3d magnetic moment. That interaction in the final state, in turn, allows the determination of the structure of that 3d shell.
These detailed calculations show that the $3p^43d^1$ final state is characterized by a single peak, which constitutes the most of the intensity of the main emission line. On the other hand, the $3p^33d^1$ final state is further split into two components, one at significantly lower energy than predicted by simple theory and one at slightly lower energy than the main emission line ($3p^33d^1$), which appears as a shoulder to the main emission line. However, the simplified picture does point out the qualitative changes one would expect as the 3$d$ electrons go from HS state to LS state, namely, smaller energy splitting between the main peak and the satellite as well as reduction of the intensity ratio of the satellite peak to the main peak. Figure 4 reports two Kβ emission spectra from iron in wüstite (FeO) and pyrite (FeS$_2$) at room conditions [Badro et al., 1999], which are archetypes of HS- and LS-bearing iron, respectively. The difference is quite striking in terms of lineshape. Indeed, the emission spectrum of HS Fe is characterized by a main peak Kβ$_{1,3}$ with an energy of 7058 eV and a satellite peak Kβ' located at lower energy appearing as a result of the 3$p$ core-hole–3$d$ exchange interaction in the final state as described above. Given that the LS state of Fe$^{2+}$ ($d^6$ configuration) is characterized by a total magnetic moment equal to zero, it should lead to the disappearance of the low-energy satellite, a very clear spectral signature that can be seen in Figure 4.

As we will see later, not only do the intensities on the satellite and widths of the main line change between the HS and LS configurations, but so does the position of the main line [Peng et al., 1994]. This has been given less attention in recent studies because of the difficulty of making absolute energy measurements. Indeed, in most studies, the position of the main line is taken as a reference and is set to the default value of 7058 eV. This has the advantage of not needing to calibrate the geometry of the x-ray spectrometer for every measurement, but its drawback is that one cannot use that additional information (main line position) to detect, constrain, and quantify the spin transition.

**EXPERIMENTAL DETAILS**

In order to probe the electronic properties of lower-mantle minerals in the pressure and temperature conditions of the lower mantle, all our samples were loaded in specially designed diamond anvil cells. These had radial openings with respect to the compression axis, through which the XES spectra were measured. The incoming x-rays were monochromatised with a high-resolution (approximately 100-mev bandwidth) fixed exit monochromator at 15 keV for $fp$ and 14 keV for Mg-pv. The beam was focused into the sample through one of the diamond anvils, and the emitted x-rays were measured at 90° through the radial openings in the diamond anvil cell, thanks to x-ray–transparent high-strength beryllium gaskets. Pressure was measured using the ruby fluorescence technique, and one of the samples (Mg-pv) was heated with the single-mode TEM$_{00}$ fundamental harmonic of a Nd:YAG infrared laser. Both the very small size of the samples (50 mm diameter, 10 mm thickness) and their low-iron content are responsible for the very weak signals. In turn, this rules out the use of a pressure medium, in order to maximise signal. Even in these conditions, every spectrum required accumulation times of 6 h for $fp$ to 18 h for Mg-pv.

![Figure 4](https://example.com/figure4.png)

**Figure 4.** Example of two Kβ x-ray emission spectra of a low-spin (left) and a high-spin (right) compound, namely, FeS$_2$ (pyrite) and FeO (wüstite), respectively. The characteristic lineshape of the low-spin compound consists of a single main line (position marked by a long vertical line), whereas that of a high-spin compound consists of two smaller lines (positions marked by short lines) in addition to that same main line. One of them is at significantly lower energy and constitutes the Kβ' satellite, whereas the second is a weak feature at slightly lower energy than the main line and appears as a shoulder in the peak.
The spectrometer for the x-ray emission measurement is an 80-cm Rowland circle instrument laid out in the horizontal plane. Emission was measured using the (531) reflection of a spherically bent (focusing) silicon crystal-stopper analyzer. The incoming x-ray beam was focused using a pair of Kirkpatrick–Baez mirrors to increase photon density on the microscopic sample.

LOWE MANTLE MINERALS

(Mg,Fe)SiO$_3$ Perovskite

We probed the spin state and measured the spin magnetic moment of iron in (Mg$_{0.9}$Fe$_{0.1}$)SiO$_3$ perovskite from 20 to 145 GPa using high-resolution K$\beta$ XES. To release stresses and to avoid any presence of disordered or amorphous phases, the sample was heated with a Nd:YAG laser operating in TEM$_{00}$ mode (as indicated above) at each pressure point between 30 and 120 GPa. At higher pressure, laser radiation did not couple with the sample and heating of the sample was no longer possible.

The spectra (Figure 5), which have been vertically shifted by groups for clarity, reveal two transitions associated with a decrease of K$\beta'$ peak intensity (Figure 6a) and shifting of the K$\beta_{1,3}$ peak to lower energy (Figure 6b), occurring around 70 and 120 GPa, respectively. The intensity decrease of the K$\beta'$ peak (Figures 5 and 6a) is directly proportional to the relative abundances of the HS and LS species (Figure 6a, right scale). Moreover, the energy shift of the K$\beta_{1,3}$ line (by $-0.75$ eV) measured in Mg-$p$ between 20 and 145 GPa (Figure 6b) is consistent with predicted values for a HS to LS transition (and also linearly scales to the relative abundance of the species as shown in Figure 6b); indeed, the transfer of spectral weight to the satellite region in the HS state, compared to the LS state in which the satellite is largely reduced, is balanced by a displacement of the main peak in the opposite direction, to keep fixed the centre of mass of the emission line [Peng et al., 1994]. The pressure dependence of the iron magnetic

![Figure 5. X-ray emission spectra collected on magnesium silicate perovskite (Mg$_{0.9}$Fe$_{0.1}$)SiO$_3$ between 20 and 145 GPa. The presence of a satellite structure (K$\beta'$ line) on the low-energy side of the iron main emission line (K$\beta_{1,3}$ line) is characteristic of a high spin 3$d$ magnetic moment. The spin state of iron transforms twice at 70 and 120 GPa, as indicated by the changes in K$\beta$ line intensity. Moreover, the position of the K$\beta_{1,3}$ line shifts at each transition, and by a total of $-0.75$ eV between 20 and 145 GPa, which is in agreement with a HS–LS transition in iron. The spectra have been vertically shifted (each group separately) for clarity. The first (bottom) group is characteristic of the HS state, the second (middle) is characteristic of the mixed state (mixture of HS and LS iron), and the third (top) is characteristic the LS state. Note that all spectra within one group are close to identical in terms of both K$\beta$ intensity and K$\beta_{1,3}$ position. The solid lines are models constructed from reference molecular compounds (see text and Figure 7), and are not fitted to the data; in this respect, the agreement with the data is excellent and brings a totally independent confirmation of the three-state scenario with a fully HS state, a mixed state, and a fully LS state.](image-url)
state derived from the data analysis (Figures 6a and 6b) shows the two successive transitions at around 70 and 120 GPa. Unfortunately, we cannot state whether the first transition is sharp or gradual due to the limited pressure sampling in the range of the first transition (70 GPa), although recent studies have shown that it is a gradual transition that ends at 70 GPa [Jackson et al., 2005]. However, the precision at the onset of the second transition (120 GPa) clearly indicates a sharp transition. Interestingly, our measurements show a nearly constant Kβ' peak intensity (Figure 6a) and Kβ1,3 peak position (Figure 6b) as well as a similar lineshape (Figure 5) for all spectra in a given spin-state (HS, mixed state, LS). Therefore, iron in a HS state at low pressure and around 70 GPa undergoes a first transition that is completed to a “mixed” state where the relative amount of the HS and LS iron species is roughly 55% and 45% (Figures 6a and 6b, right scale). At 120 GPa, a second sharp transition occurs, transforming the remaining HS iron to the LS state; above this pressure, all iron in Mg-pv is in the LS state.

Iron in Mg-pv can be in the ferrous (Fe2+) or ferric (Fe3+) valence-state and can occupy one of two crystallographic sites [McCannmon, 1997]. Although the exact partitioning behaviour of ferrous and ferric iron between these two sites is poorly characterized, current interpretation [McCannmon, 1997] indicates that the large “dodecahedral” A site (actually a bicapped trigonal prism, but referred to as dodecahedral hereafter for consistency with the generally accepted nomenclature) is the host of ferrous iron, whereas the smaller octahedral B site is the host of ferric iron. In the conditions of synthesis and with 2 mol% iron [Fe/(Fe + Mg) = 0.1] in
our sample, Mg-pv should contain about 80% Fe$^{2+}$ and 20% Fe$^{3+}$ [Fei et al., 1994], although it has been shown recently [Jackson et al., 2005] that a similar synthesis yields 60% ferrous iron and 40% ferric iron.

The changes up to 70 GPa could be related to a recently reported transition [Jackson et al., 2005] concerning ferric iron and observed by nuclear forward scattering (a synchrotron time-resolved Mössbauer spectroscopy technique), which shows that Fe$^{3+}$ undergoes a gradual spin-pairing transition between room pressure and 70 GPa. Given that we observe the transition of 45% of the Fe ions at that pressure, this could indicate that the amount of Fe$^{3+}$ in our Mg-pv sample is actually higher than we expected and closer to that measured by Jackson et al. [2005] than that by Fei et al. [1994]. Unfortunately, we have no analysis of the redox state of our sample to address this issue, and relating these populations, whether on a site-specific basis or on a valence-specific basis, is beyond the scope of this study; it should, however, be considered in the future. A careful characterisation of the samples has to be undertaken in order to ascribe the transitions to either valences or sites. Studying the electronic properties of Al-bearing Mg-pv [Li et al., 2004] is a way to address this issue, because the Fe$^{3+}$/Fe ratio increases with Al content [McCamm, 1997]. Although this study [Li et al., 2004] does not cover the entire lower-mantile pressure range, it indicates that the transitions in Al-bearing Mg-pv could be shifted to higher pressures. On the other hand, the presence of large stresses could have increased the observed pressure of transition, or even smeared the pressure range in which it occurred (the samples in that study were not annealed at high pressure). The work by Li et al. [2004] nevertheless shows that it is important to gage the effect of aluminium on the transition pressure, as one should bear in mind that the transition will lose all geophysical relevance if its pressure shifts for any given reason above 136 GPa (CMB).

With this in hand, support for our interpretation of the two transitions can be obtained from a direct comparison (i.e. without fitting, Figures 5 and 7) with reference spectra of molecular spin crossover compounds [Vankó et al., 2002] containing ferrous or ferric iron in the HS and LS states. In these systems, which are used as references in XES [Vankó et al., 2002], iron is in a localized state and adopts a band-free atomic behaviour, as in Mg-pv, which

![Figure 7](image_url)

Figure 7. Fit of the a priori models to the x-ray emission spectra collected on magnesium silicate perovskite (Mg$_{0.9}$Fe$_{0.1}$)$_2$O$_3$ between 20 and 145 GPa. These models, constructed from reference molecular spin crossover compounds, are not fitted to the data, but only overlain. The spectra (and models) have been vertically shifted (each group separately) for clarity; the first (bottom) group is characteristic of the HS state, the second (middle) is characteristic of the mixed state (mixture of HS and LS iron), and the third (top) is characteristic of the LS state. The solid lines are models based on 55% Fe$^{2+}$ and 45% Fe$^{3+}$ (close to the composition found in Jackson et al. [2005]) and the dashed lines are models based on 80% Fe$^{2+}$ and 20% Fe$^{3+}$ (close to the composition found in Fei et al. [1994]). The agreement with the data suggests that the prior (55% Fe$^{2+}$ and 45% Fe$^{3+}$) is more self-consistent than the latter. The larger discrepancy in the intermediate “mixed” model suggests that more complex phenomena might occur in that state.
contains only 10 mol% of iron. Given that x-ray emission spectroscopy is a locally sensitive technique (depending on local environment of atoms, and not on the general structure), such model spectra can be used to interpret those obtained in Mg-\(\text{pv}\). Composite spectra can thus be constructed from these reference spectra by linear combination of the spectra of the four components (ferrous HS and LS, ferric HS and LS) weighted by the fractions of the individual states. Using two models with different Fe\(^{3+}/\text{Fe}^{2+}\) ratios, one with 80% Fe\(^{2+}\) and 20% Fe\(^{3+}\) (according to Fei et al. [1994], dashed lines), and one with 55% Fe\(^{2+}\) and 45% Fe\(^{3+}\) (close to Jackson et al. [2005], solid lines), we created model spectra for a fully HS (low pressure), a fully LS (high pressure), and a mixed state (Fe\(^{2+}\) HS and Fe\(^{3+}\) LS) Mg-\(\text{pv}\). These models (Figure 7) agree (intensity of the K\(\beta\) line and position of the K\(\beta_{1.3}\) line) with the measured spectra and confirm that the LP spectra have the signature of a full HS state and that the highest pressure spectra have the signature of a full LS state. Comparison of the spectra in the “mixed” state do not show as good an agreement as the two extremes states, indicating that more complex phenomena may be taking place, but strengthens the idea (this can already be seen in the LS state) that the model with 55% Fe\(^{2+}\) and 45% Fe\(^{3+}\) composition shows a better agreement with the experiment (Figure 7) than does the model with the 80% Fe\(^{2+}\) and 20% Fe\(^{3+}\). This could confirm the transition in Fe\(^{3+}\) at 70 GPa (as shown in Jackson et al. [2005]) and that in Fe\(^{2+}\) at 120 GPa.

(Mg,Fe)O Ferropericlase

The case of \(\text{fp}\) is simpler, because it contains one species of iron (i.e. ferrous iron) and one site in the structure which is the standard octahedral site in the cubic \(\text{fcc}\) structure. We monitored the spin state and measured the spin magnetic moment of iron in (Mg\(_{0.83}\) Fe\(_{0.17}\))O \(\text{fp}\) as a function of pressure, from 0 to 80 GPa, by high-resolution K\(\beta\) XES. As described above, two features are identified in the emission spectrum as a main peak (K\(\beta_{1.3}\)) and a satellite peak (K\(\beta^\prime\)).

The spectra of the micrometer-sized samples were measured at different pressures (Figure 8) and the spectrum of a larger sample at ambient pressure was measured outside the cell. The spectra show that there is a decrease of the satellite peak intensity at 49 GPa and that it vanishes at 75 GPa, indicating a HS to LS transition in iron in \(\text{fp}\) between those pressures. Upon decompression, the spectrum at 64 GPa shows a partial reversal from HS to LS (a mixture of phases) and at 41 GPa, the spectrum shows the presence of only the HS state (indicating a complete transformation). The sample was probably subject to large radial pressure gradients in the absence of a pressure-transmitting medium and without laser-annealing. Whether the transition is gradual (occurring over a large pressure range) or whether this observation is an artefact due to pressure gradients is still an open question. Measurements will need to be carried out either in a hydrostatic environment or along with laser annealing of the sample (e.g. in the experiment in Mg-\(\text{pv}\)) in order to fully address this important issue.

Similar measurements on FeO [Badro et al., 1999] have shown there is no transition to a low-spin state to at least 143 GPa. Very recent experimental work [Lin et al., 2005] shows that the transition pressure decreases with decreasing iron content. This has also been suggested by theoretical calculations [Brodholt, 2003]. The transition could thus be accompanied by phase separation between an iron-rich high-spin and a magnesium-rich low-spin \(\text{fp}\), as shown by some experimental reports [Dubrovinsky et al., 2000, 2001], although opposing claims have also been reported [Lin et al., 2003]. Recent high-temperature equation of state measurements [Fei et al.] show a volume collapse at around 60 GPa, which is possibly a signature of the spin transition. Whether phase separation occurs at the onset of this transition at high temperature remains to be elucidated.
CRYSTAL-FIELD SPLITTING AND TEMPERATURE EFFECT

Although the effect of temperature still needs to be probed directly in order to transfer these laboratory observations to the real-Earth system, one can estimate that effect by using simple thermodynamic arguments. Recent experimental work [Lennartsson et al., 2004] has shown the way with the in situ study of \( f_{p} \) and needs to be extended to higher pressures and temperatures and other systems (e.g. Mg-\( pv \)). As explained above, electronic transitions are most of the time density-driven transition, i.e. they occur at a given critical density. Therefore, the effect of temperature, apart from entropy contributions that have been estimated earlier, would be to increase the transition pressure so as to counterbalance the effect of thermal expansion with that of isothermal compressibility. At a given pressure, the thermal expansion is given by:

\[
\alpha = \left( \frac{1}{V} \frac{\partial V}{\partial T} \right)_p = \left( \frac{\partial \ln V}{\partial T} \right)_p
\]

and at a given temperature, the isothermal compressibility is given by:

\[
\chi_T = \frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T = \left( \frac{\partial \ln V}{\partial P} \right)_T = \frac{1}{K_T}.
\]

Counterbalancing the effect of thermal expansion with that of pressure means that

\[
d\ln V = \left( \frac{\partial \ln V}{\partial T} \right)_p dT + \left( \frac{\partial \ln V}{\partial P} \right)_T dP = 0
\]

hence obtaining

\[
\frac{dP}{K_T} = \alpha \cdot dT = 0,
\]

the differential equation which can be expressed in an integral form as follows:

\[
\int_{P_0}^{P} \frac{1}{K_T} \cdot dP = \int_{T_0}^{T} \alpha \cdot dT.
\]

\((\text{Mg,Fe})O\) Ferropericlase

Given that this compound contains only one species of iron in one site, estimating the temperature-dependence is simpler in the case of \( f_p \) than for Mg-\( pv \). \( \Delta h^0 \) in this compound has been measured by spectroscopy and is equal to 1.34 eV [Burns, 1993] at room conditions. At room temperature, the molar volume \( V_e \) at the transition (70 GPa and 300 K) is 9.15 cm\(^3\)/mol [Knittle, 1995]. Therefore

\[
\left( \frac{V_0}{V_e} \right) = 1.30
\]

(for \( f_p \) as well as for the octahedral site in \( f_p \)) and

\[
\Delta(V) = \Delta h^0 \left( \frac{V_0^{1/3}}{V_e} \right) = 2.07 \text{ eV}
\]

at the transition. One can therefore estimate the value of \( E_p \) by using equation (3b), because the transition occurs at low temperature (300 K), yielding \( E_p = 2.05 \text{ eV} \), which is in excellent agreement with the accepted value in dense oxides and silicates of 2.09 eV in \( f_p \) [Burns, 1993].

At 2500 K (average lower-mantle geotherm at 70 GPa [Brown and Shankland, 1981]), the transition should occur for a CFSP

\[
\Delta_c = E_p + \frac{1}{2} k_B T \ln 15 = 2.34 \text{ eV}.
\]

Using equation (2), we obtain

\[
\left( \frac{V_0(T_0)}{V_e(T)} \right) = 1.40.
\]

The pressure corresponding to this compression can be calculated by using the thermal equation of state

\[
P(T) = \frac{3}{2} K_0(T) \left[ \left( \frac{V(T)}{V_0(T)} \right)^{7/3} - \left( \frac{V_0(T)}{V_0(T)} \right)^{5/3} \right] =
\]

\[
\frac{3}{2} K_0(T) \left[ \frac{V(T) V_0(T_0)}{V_0(T_0) V_0(T)} \right]^{7/3} \left( \frac{V(T) V_0(T)}{V_0(T_0) V_0(T)} \right)^{5/3}
\]

(7)

where

\[
V_0(T) = V_0(T_0) \exp \left( \int_{T_0}^{T} \alpha(T) dT \right),
\]

\[
\alpha(T) = \alpha_0 + \alpha_1 T + \alpha_2 T^2,
\]

and

\[
K_0(T) = K_0 + \frac{\partial K_0}{\partial T} \Delta T.
\]

[Fei, 1995; Knittle, 1995]. At 2500 K (\( \Delta T = 2200 \text{ K} \)), this is equal to 104 GPa and yields a Clapeyron slope

\[
\frac{dP}{dT} = \frac{\Delta S}{\Delta V} = 1.6 \text{ MPa/K}.
\]

Another way to estimate the temperature effect is to calculate directly the Clapeyron slope from the entropy and volume variation at the transition. The entropy change for one iron atom, that is, one octahedron, is \( \Delta S = k_B \ln 15 \), and the volume change can be calculated by using the tabulated contraction of the Fe\(^{2+}\) ionic radius in an octahedral site between a HS and LS transition, which is 0.17 Å. The octahedral volume is 13.44 Å\(^3\) at ambient pressure and reaches 9.60
Å³ at the transition pressure. That volume corresponds to a Fe–O bond length of 1.93 Å. When iron transforms to the LS state, the Fe–O bond length shortens by 0.17 Å to reach 1.76 Å, corresponding to an octahedral volume of 7.30 Å³, and the volume contraction is therefore $\Delta V = V_LS - V_TR = 2.3$ Å³ per octahedron, or 1.39 cm³/mol. This gives a Clapeyron slope

$$\frac{dP}{dT} = \frac{\Delta S}{\Delta V} = 16.2 \text{ MPa/K},$$

which is very close to the value obtained above.

**Mg,FeSiO₃ Perovskite**

As there are two transitions in Mg-pv, there have to be two sites/species with two different values of $\Delta$. Information on the electronic structure of iron in the perovskite structure is very scarce [Burns, 1993; Keppeler et al., 1994]. Given that crystal field theory is a first-order approximate theory, we will consider from here on an “average” model that has the following characteristics: Two quasi-octahedral sites in Mg-pv contain ferric and ferrous iron, respectively, and undergo spin pairing at 70 and 120 GPa, respectively. The use of a quasi-octahedral model for the “dodecahedral” site is justified by its bccapped trigonal prism geometry and can be understood in terms of Mg–O bond-lengths in that site [Wentzovich et al., 1995]: At 100 GPa, there are six bonds that have an average length of 1.90 Å, two with a length of 2.213 Å, and four others with lengths longer than 2.5 Å. This means that the close oxygen environment is quasi-octahedral, with the bonds at 1.90 Å responsible for most of the electronic overlap on the atom in the site.

For Fe²⁺, at the spin transitions (70 and 120 GPa, 300 K),

$$\Delta_c = E_p + \frac{1}{2} k_B T \ln(5) = 2.07 \text{ eV}$$

and

$$\left(\frac{V_0}{V_{c,B}}\right) = 1.20, \text{ and } \left(\frac{V_0}{V_{c,A}}\right) = 1.31$$

yielding

$$\Delta_{p,B}^0 = \Delta_c \left(\frac{V_0}{V_{c,B}}\right)^{-5/3} = 1.53 \text{ eV}$$

and

$$\Delta_{p,A}^0 = \Delta_c \left(\frac{V_0}{V_{c,A}}\right)^{-5/3} = 1.32 \text{ eV},$$

the latter being surprisingly close to the value of 1.34 eV in $f_p$.

The A and B subscripts to the CFSP denote that these could be related to sites A and B of the structure. Nevertheless, there is no direct proof of this yet, and this nomenclature can also represent two virtual sites “A” and “B”.

The effect of temperature is obtained from the Clapeyron slope

$$\frac{dP}{dT} = \frac{\Delta S}{\Delta V}$$

of the transition, where entropy and volume changes need to be estimated as shown above. For ferrous iron, $\Delta S$ between the LS state and the HS state is $\text{per atom}$ [Sherman, 1991] at high temperature (restored orbital degeneracy), whereas for ferric iron, $\Delta S=0$. Thus the Clapeyron slope for a spin-pairing transition involving ferric iron (possibly that at 70 GPa) at high temperature is null, and the transition pressure should not vary with temperature. The volume variation of an octahedral site at the transition can be approximated as follows. Using tabulated values, the ionic radius difference between octahedrally coordinated HS and LS Fe³⁺ is 0.17 Å. In the HS phase, the volume of the A and B sites at 100 GPa [Wentzovich et al., 1995] is 15.73 cm³/mol (26.1 Å³ per site) and 3.73 cm³/mol (6.19 Å³ per site), respectively, corresponding to average Fe–O bond lengths of 1.97 Å (average for the six closest oxygen atoms) in the A site and 1.67 Å in the B site. The 0.17 Å contraction yields $\Delta V$ of 3.74 and 1.02 cm³/mol for the A and B sites, respectively. With 75% Fe in the dodecahedral site and 25% in the octahedral site, the average $\Delta V$ is 3.06 cm³/mol. Finally one obtains a Clapeyron slope

$$\frac{dP}{dT} = 7.4 \text{ MPa/K},$$

which is obtained by taking into account only Fe²⁺; the effect of Fe³⁺ will be to decrease that slope because it contributes to $\Delta V$ but not to $\Delta S$. But it can be estimated only if the proportion of Fe³⁺ is known.

A linear extrapolation to 2500 K ($\Delta T=2200$ K) gives a pressure correction of 15 GPa. Whether this value is to be added to the experimental transition pressure of 120 GPa determined remains to be elucidated; because the LS spin state was quenched from a high-temperature annealing, the actual pressure could reflect the transition at high temperature. Ideally, such measurements should be performed in situ at high pressures and temperatures [Lennartsson et al., 2004].

**DISCUSSION**

In this study, we showed that iron in both of these phases undergoes spin-pairing transitions at lower-mantle depths. Of the many aspects these transitions can bear, two seem of utmost importance: the heat conductivity of the minerals and
mineral assemblages, and the partitioning or iron between the two phases.

**Thermal Conductivity in the Lower Mantle**

Heat can be transported in the mantle by conduction, radiation, or convection. Convection in the lower mantle is initiated only if the other two processes fail to transfer heat produced from the secular cooling of the core and by radioactive decay, through the lower mantle, e.g. if the ratio of heat transport through convection to heat transport through conduction and radiation, is high enough. Changes in the conduction or radiation properties of lower-mantle mineral assemblages will therefore strongly affect lower-mantle dynamics [Clark, 1957; Dubuffet et al., 2000; Goto et al., 1980; Kellogg et al., 1999; Shankland et al., 1979; Tackley, 2002; van den Berg et al., 2001]. We have shown that iron in both major phases of the lower mantle undergoes spin-pairing transitions between 70 and 120 GPa [Badro et al., 2003, 2004]. One of the main and intrinsic characteristics of LS iron-bearing minerals resides in the blue-shift [Burns, 1993; Sherman, 1991] of iron absorption bands (the absorption bands initially in the infrared [IR] and red region shift to the green–blue region).

A HS–LS transition should increase the intrinsic radiative thermal conductivity of Mg-pv and fp [Burns, 1993; Sherman, 1991]. Indeed, radiative conductivity in HS iron-bearing lower-mantle minerals is hindered by light absorption in the near IR spectral region, due to intraband transitions [Clark, 1957; Goto et al., 1980; Keppler et al., 1994; Shankland et al., 1979; Williams et al., 1990]. An HS–LS transition of iron in these minerals is accompanied by a blue-shift of these absorption bands, from the near IR to the visible (blue-green) spectrum, as has been shown for octahedral Fe²⁺-bearing minerals [Burns, 1993] and is likely in the case of dodecahedral coordination. In turn, light with wavelengths in the red to near IR spectral range should radiate through the assemblages with a longer mean absorption length. This spectral range corresponds to the maximum of blackbody emission for temperatures between 2000 K and 3000 K (970 nm at 3000 K), meaning that most of the radiative energy emitted from the core and lowermost mantle should be affected by the HS–LS transition.

Figure 9 shows the normalized blackbody thermal radiation as a function of wavelength at three different temperatures (2000, 2500, and 3000 K) that can be considered as bounds for the lower-mantle geotherm.

**Figure 9.** Normalized blackbody thermal radiance as a function of wavelength at three different temperatures (2000, 2500, and 3000 K) that can be considered as bounds for the lower-mantle geotherm. The absorption bands of (Mg₀.₉Fe₀.₁)SiO₂ perovskite are reported in the HS state (solid black vertical line) and in the LS state (solid gray vertical line), whereas those of fp are similarly represented by dashed black and gray lines. In the HS state, the most intense absorption bands are in the near IR region, where blackbody radiation is maximal at these temperatures; this makes these compounds bad radiative thermal conductors. In the LS state, these same bands undergo a blue-shift to the visible region, where blackbody radiation is weaker. The total radiative power throughput in both minerals should significantly increase after the transition.
Iron Partitioning in the Lower Mantle

We have seen that both fp and Mg-pv undergo a spin-pairing transition in the 70 GPa range. Although our study does not offer the resolution required to accurately determine which compound undergoes the transition first, there is necessarily a pressure region where the two samples are in different states, i.e. one of them is in the LS state and the other in the HS state. Even if the transition pressures were identical to start with, the Clapeyron slopes are different enough so that lateral temperature variations at depth in the mantle would create such conditions.

Considering this eventuality is important, because a spin-pairing transition in one only of the minerals should alter the chemical behaviour of the assemblage as a whole, in the sense that the partition coefficient (of that species undergoing the transition, e.g. iron) between the minerals of the assemblage should be affected [Burns, 1993; Malavergne et al., 1997]. This is due to the fact that the LS iron atom occupies a smaller volume than the HS species, and that at high pressure, the \( PAV \) energy term is all the stronger and favours iron in the LS site: One therefore expects an exchange of Fe with Mg between the phases in order to minimize the system’s Gibbs free energy.

Crystal field theory [Burns, 1993] is a sound theoretical framework for estimating the electronic contributions to enthalpy and entropy of a HS or LS state, which in turn provides the Gibbs free energy change for the substitution reaction of Mg and ferrous Fe between Mg-pv and fp given by:

\[
(Mg^{2+})_{fp} + (Fe^{2+})_{pv} \rightleftharpoons \ (Mg^{2+})_{pv} + (Fe^{2+})_{fp}
\]  

(8)

At thermodynamic equilibrium, this Gibbs free energy is proportional to the logarithmic partition coefficient of iron between the two phases defined by

\[
\ln(K) = \ln\left(\frac{x_{Fe}}{x_{Mg}}\right)_{fp} - \ln\left(\frac{x_{Fe}}{x_{Mg}}\right)_{pv} = -\frac{\Delta G}{RT}
\]  

(9)

where \( R = \frac{Nk_B}{3} \) is the universal gas constant, and \( x \) the molar fractions. As proposed above, we will consider two thermodynamic models for the transition.

1. Cooperative phase transition. The first case we consider is that of a cooperative phase transition, as developed in Badro et al. [2003]. In this case, the Gibbs free energy of the system varies dramatically during the spin transition, and the effective \( \Delta G \) between the two phases is finite in a similar fashion as Landau-type transitions. This effective free energy difference can be estimated as \( \Delta G = \Delta F_{\text{electron}} + PAV \). The Helmholtz free energy term can be readily cal-
culated from the equations given above, and we estimate the $\Delta V$ term hereafter.

We will consider only the case of ferrous (Fe$^{2+}$) iron, because it is the only species we followed in both compounds. As the ferrous iron content of our $fp$ sample in the conditions of synthesis is almost null, the transition occurring in $fp$ can be attributed to that of ferrous iron. The partitioning of ferric iron according to the relationship above introduces an additional term like the creation of a hole to accommodate the charge balance, as well as that of a defect, which are both unknown and too complex to account for here. For all these reasons, we shall limit the scope of this chapter to ferrous iron in the A site (which undergoes the spin-pairing transition at 120 GPa), keeping in mind that the framework used here can only be considered qualitatively, not quantitatively.

At 70 GPa,

$$\left(\frac{\nu}{\nu_0}\right)_{fp} = 0.77$$

and

$$\left(\frac{\nu}{\nu_0}\right)_{pv} = 0.83$$

gives CFSP values $\Delta_{fp} = 2.07$ eV and $\Delta_{pv,A} = 1.80$ eV according to equation (2). This implies, using equations (1a) and (1b), that

$$U_{fp}^{HS} = 1.222 \text{ eV} \quad U_{pv,A}^{HS} = 1.330 \text{ eV}$$
$$U_{fp}^{LS} = 1.182 \text{ eV} \quad U_{pv,A}^{LS} = 1.830 \text{ eV} \tag{10}$$

and allows us to estimate the partition coefficient with the Gibbs free energy change upon iron substitution given by

$$\Delta G = G_{Fe,fp} - G_{Fe,pv} = U_{fp} - U_{pv} - T(S_{fp} - S_{pv}) + P(V_{fp} - V_{pv}) \tag{11}$$

where the volume difference can be calculated as shown above to be $\Delta V = -1.39 \text{ cm}^3/\text{mol}$. We see that the estimated partition coefficient of ferrous iron between $fp$ and Mg-pv's A site at 70 GPa and 2500 K (approximately 1700 km depth) is 1.7 in the case where iron is in the HS in both phases (as $\Delta S$ and $\Delta V$ are both identically 0, and partitioning is driven only by internal energy minimisation), and is in agreement with measurements [Kesson, et al., 2002; Mao, et al., 1997; Murakami, et al., 2004b] performed on recovered samples. This partition coefficient increases to 13.3 when Fe$^{2+}$ undergoes the transition in $fp$, enriching that phase in iron with respect to (and to the detriment of) Mg-pv. The numerical values are condensed in Table 1.

At 120 GPa (approximately 2600 km depth),

$$\left(\frac{\nu}{\nu_0}\right)_{fp} = 0.70$$

and

$$\left(\frac{\nu}{\nu_0}\right)_{pv} = 0.765$$

gives CFSP values $\Delta_{fp} = 2.43$ eV and $\Delta_{pv,A} = 2.07$ eV according to equation (2). It is at that pressure that Mg-pv becomes fully LS. This implies, using equations (1a) and (1b), that

$$U_{fp}^{HS} = 1.078 \text{ eV} \quad U_{pv,A}^{HS} = 1.222 \text{ eV}$$
$$U_{fp}^{LS} = 0.318 \text{ eV} \quad U_{pv,A}^{LS} = 1.182 \text{ eV} \tag{12}$$

The partition coefficients are also reported in Table 1. We see that the partition coefficient increases to 28 when both compounds are in the LS state and remains 15 times higher than in the top part (fully HS) of the lower mantle.

2. Noncooperative phase transition. Here we consider that the HS–LS phase transition is noncooperative in nature and that both phases coexist in a finite pressure range. Thermodynamic equilibrium is classically defined by minimization of the Gibbs free energy. In this case, the transition is defined by $G_{HS} = G_{LS}$, and there is no discontinuity of the Gibbs free energy at the transition, meaning that the parti-

<table>
<thead>
<tr>
<th>$P$ (GPa)</th>
<th>$T$ (K)</th>
<th>$Fe^{2+}$ in $fp$</th>
<th>$Fe^{2+}$ in pv</th>
<th>$\Delta U$ (eV)</th>
<th>$\nu \Delta V$ (eV)</th>
<th>$T \Delta S$ (eV)</th>
<th>$\Delta G$ (eV)</th>
<th>$K$</th>
</tr>
</thead>
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<tr>
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</tr>
<tr>
<td>120</td>
<td>3000</td>
<td>LS</td>
<td>LS</td>
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<td>0</td>
<td>0</td>
<td>-0.864</td>
<td>28</td>
</tr>
</tbody>
</table>
tion coefficient is constant at the transition, and equal to 1.7 (Figure 10) as shown above. The effect on partitioning is only afterwards revealed. As pressure increases above the transition, we move into the field where iron occupies a lower volume in the LS state and partitions preferentially in the LS phase. This is driven once again by $P\Delta V$, except that $P$ here is actually corrected for the transition pressure $P_{tr}$ and the energetic term is $(P - P_{tr})\Delta V$.

This can be formally obtained from a Taylor development of the Gibbs free energy above the transition pressure. Given that $\Delta G = 0$ at the transition, this can be developed to the first order as follows:

$$\Delta G(P) = \left[ G_{LS}(P_{tr}) - G_{HS}(P_{tr}) \right] - \left( \frac{\partial G_{LS}}{\partial P} - \frac{\partial G_{HS}}{\partial P} \right) (P - P_{tr}) + \mathcal{O}^2 \quad (13)$$

and since

$$\frac{\partial G}{\partial P} = V,$$

this can be rewritten as $\Delta G(P) = \left[ G_{LS}(P_{tr}) - G_{HS}(P_{tr}) \right] - \left( V_{LS} - V_{HS} \right) (P - P_{tr}) + \mathcal{O}^2$. The difference in the first bracket is identically null by definition of thermodynamic equilibrium and therefore the relation becomes simply $\Delta G = \Delta V \cdot (P - P_{tr})$.

The partition coefficient can be written as:

$$\ln(K) = -\frac{\Delta G}{RT} = \ln(K_0) - \frac{\Delta V \cdot (P - P_{tr})}{RT}$$

or

$$K = K_0 \cdot \exp\left( -\frac{\Delta V \cdot (P - P_{tr})}{RT} \right) \quad (14)$$

and is plotted in Figure 10. We see that the partition coefficient increases by 17-fold to reach 28.8 ($K_0 = 1.7$). After the second transition in perovskite, and within this thermodynamical framework, the partition coefficient should stabilize at that value.

3. Discussion. The partition coefficients calculated by both models are reported in Figure 10. Both models described above show that the spin transitions reported in both minerals should have the same effect on the partition coefficient of iron between these minerals, which is to enrich the oxide phase and deplete the silicate phase. They are in qualitative agreement in the intermediary regime and in perfect agreement at both transition pressures. In particular, they both

![Figure 10](image-url)

**Figure 10.** The predicted Fe–Mg partition coefficient between ferropericlase and magnesium silicate perovskite. Shown are the two transition models developed in the text. The lower curve is calculated considering a noncooperative phase transition (phase coexistence of HS and LS species). This is the standard thermodynamic theory. The four dots are calculated considering that the volume collapse in the LS state is not part of the equilibrium conditions (cooperative transition) and shows discontinuities in $\Delta G$ and therefore in $K$. The upper curve is also a guide to the eye. We see that both models predict an enrichment of iron in the oxide (ferropericlase) phase and depletion in the perovskite phase. Moreover, they both predict very close values at 120 GPa, with $K = 28$, that is, a 16-fold enrichment with respect to the standard lower mantle (below 70 GPa). In the intermediate region between 70 and 120 GPa, only a qualitative agreement is found. This effect and its magnitude still need to be confirmed experimentally or through more precise theoretical models.
show that $K_{\text{Fe-Mg}} \sim 30$ at 120 GPa, that is, at the onset of the D' layer in the post-perovskite phase.

This is in very good agreement with recent experimental results [Murakami et al., 2004b] obtained from an analytical transmission electron microscopy (ATEM) study of recovered samples, that shows a large increase of the partition coefficient between $fp$ and the post-perovskite phase. These recent results, as well as our predictions, are at odds with the conclusions of previous work, whether based on ATEM studies [Kesson et al., 2002] or on indirect assessment using equations of state [Andraul, 2001]. The latter was performed prior to the discovery of the spin transitions and assumes a constant compressibility and zero-pressure volume for the phases at high pressure. This assumption is not consistent with the observed spin transitions [Badro et al., 2003, 2004] and more recently with the high-temperature equation of state measurement on $fp$ [Fei et al., 2004], which shows an important volume discontinuity at 60 GPa.

Obviously, more quantitative calculations based on quantum modelling of electronic interactions in both phases would be very useful for refining this qualitative prediction. Moreover, in a real mineralogical assemblage, the effect of partitioning will affect the spin-pairing transition pressures, and the whole interaction can be seen as a negative feedback loop: As $fp$ is enriched in iron, its transition pressure increases and smooths and constrains the partition coefficient values between the phases. Again, state-of-the-art experimental investigation [Murakami et al., 2004b] and modelling of these phenomena is required to obtain a self-consistent image of the processes occurring at these depths in the lower-mantle assemblage.

Nevertheless, we see qualitatively that such phenomena can have a major chemical impact. At depths around 1800 km, they indicate that lateral temperature variations can be responsible of tremendous large-scale chemical variations; indeed, because the spin-pairing transitions have different Clapeyron slopes in both compounds, it is possible for lateral (constant pressure) temperature heterogeneities on the order of a few hundred degrees to drive the $fp$ phase in and out of the LS state. This in turn would induce the strong partitioning behaviour giving rise large-scale thermally induced lateral chemical heterogeneities, as suggested recently by tomographic modelling [Trampert et al., 2004].

CONCLUSION

We have shown experimentally through high-pressure x-ray spectroscopy measurements on its major constituents (magnesium silicate perovskite and ferropericlase, accounting for 90–100% of its mass) that Earth’s lower mantle is in a fundamentally different thermochemical state at pressures exceeding 70 to 90 GPa [Badro et al., 2003, 2004], corresponding to depths greater than 1700 to 2000 km. This is due to a change of the electronic properties of iron in these phases at those pressures. Indeed, iron in perovskite undergoes two successive spin transitions at about 70 and 120 GPa, to a partially and fully spin-paired (low-spin) state, respectively. On the other hand, iron in ferropericlase undergoes one transition between 60 and 70 GPa to a fully LS state. These changes can have major implications on the chemistry and dynamics of the lowermost mantle. They indicate that the lower mantle could be separated into three distinct regions in different thermochemical states:

- above 1700 km (below 70 GPa), the “normal” state, where iron is in the HS state in both lower-mantle compounds.
- between 1700 and 2600 km (between 70 and 120 GPa), the “transitional” state, where iron can be in the LS state in ferropericlase, and partially in the HS state in perovskite.
- below 2600 km and to the CMB (between 120 and 135 GPa), the “deep” state, where iron is in the LS state in both lower-mantle compounds.

Interestingly, these distinct regions have geophysical signatures that have been previously reported. The “transitional” region corresponds to depths where chemical heterogeneities have been observed by seismic tomography [van der Hilst and Karason, 1999]. Thermodynamic modelling of the partitioning of iron in this state indicates that the spin transitions at 70 GPa could promote large-scale chemical heterogeneities due to lateral temperature heterogeneities.

The depths and pressures of the “deep” region are in concordance with that of the D' layer [Lay, 1983]. The transition pressure (120 GPa) is also in accord with a recently reported crystallographic transition in perovskite [Murakami et al., 2004a], and so is our estimated Clapeyron slope of 8.5 MPa/K [Itaka et al., 2004; Oganov and Ono, 2004; Tsuchiya et al., 2004]. The latter value is also in agreement with the seismically derived value of the Clapeyron slope at the D' layer of 6 MPa/K [Sidorin et al., 1999].

All these concordances strengthen the suggestion that the spin-transition in perovskite at 120 GPa can very likely be linked to the pv-to-ppv transition [Murakami et al., 2004a]. These studies do provide a mineral-physics basis for Earth's D' layer. In the “deep” state, the lower-mantle mineralogical assemblage has an increased radiative conductivity, and iron in that assemblage has an increased affinity to the oxide phase (ferropericlase), as proposed here and shown very recently in a groundbreaking [Murakami et al., 2004b] analysis of a KLB-1 composition synthetic peridotite recovered from these pressures and temperatures. That assemblage
should be associated with a strong dynamical signature because the increase in thermal conductivity may hinder convection and favour layering in the lowermost mantle [Anderson, 2004; Dubuffet and Yuen, 2000], and the depletion of iron from the silicate phase should alter the electrical conductivity of the layer [Dobson and Brodholt, 2000; Katsura et al., 1998; Shankland et al., 1993]. These state-of-the-art measurements should stimulate discussions and further studies as to their geophysical consequences. Indeed, all of these recent observations pertaining to the properties of the minerals [Badro et al., 2003, 2004; Dubrovinsky et al., 2000; Iitaka et al., 2004; Murakami et al., 2004a, 2004b; Oganov and Ono, 2004; Tsuchiya et al., 2004] that constitute the D* layer indicate that complex physical and chemical processes are undoubtedly taking place in this lowermost silicate envelope of the Earth.

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