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Role of iron-spin transition in ferropericlase on seismic interpretation: A broad thermochemical transition in the mid mantle?

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[1] Most of the lower mantle is relatively simple in terms of seismic structure. Lateral variations are weaker compared to its bottom part and to the upper mantle and seismic velocities increase smoothly with depth. To a first order, these features appear consistent with the adiabatic compression of a homogeneous medium. Here we show, instead, that seismic data require a change of chemical and/or thermal state with depth below ~1600 km, if the effect of the spin-transition of Fe^{2+} in ferropericlase on the elastic signature of a typical lower mantle assemblage is taken into account. The inferred thermochemical structure helps to reconcile geochemical and geophysical observations and has profound implications on the dynamical evolution of our planet. **Citation:** Cammarano, F., H. Marquardt, S. Speziale, and P. J. Tackley (2010), Role of iron-spin transition in ferropericlase on seismic interpretation: A broad thermochemical transition in the mid mantle?, *Geophys. Res. Lett.*, *37*, L03308, doi:10.1029/2009GL041583.

1. Introduction

[2] Knowledge of thermal and compositional conditions of the lower mantle is of primary importance to understand the dynamics of the Earth's interior. The best constraint on current conditions comes from the interpretation of seismic models (or data) based on elasticity of mantle minerals measured at appropriate pressures and temperatures [*Birch*, 1952; *Cammarano et al.*, 2005; *Matas et al.*, 2007; *Cobden et al.*, 2009].

[3] For possible average chemical compositions of the mantle [*O'Neill and Palme*, 1997], the mineralogy of the lower mantle is rather simple and is dominated by a magnesium rich perovskite phase (~80% in volume) plus ferropericlase (or magnesiowüstite, (Mg, Fe)O), as secondary component. Laboratory experiments and theoretical computations constantly improve our knowledge on elastic properties of the lower mantle minerals and thus help to refine the seismic interpretation.

[4] The spin transition of Fe^{2+} in ferropericlase has been well documented in recent years [*Badro et al.*, 2003; *Speziale et al.*, 2005; *Lin et al.*, 2007]. It is only very recently that the elastic properties have been measured at pressures relevant to the Earth's lower mantle [*Crowhurst et al.*, 2008; *Marquardt et al.*, 2010]. During the spin crossover, the bulk modulus reduces significantly its value, but the shear modulus does not change much. Seismic velocities (V_P and V_S) have been estimated from a combined study of Brillouin scattering and x-ray diffraction experiments on ($Mg_{0.9}$, $Fe_{0.1}$)O [*Marquardt et al.*, 2010] (Figure 1). Based on this study, the spin transition in ferropericlase occurs between pressures of 45 and 63 GPa, at ambient temperature. Theoretical computations and experimental data show that the transition broadens as temperature increases [*Tsuchiya et al.*, 2006; *Wentzcovitch et al.*, 2009; *Lin et al.*, 2007, 2009] (Figure 1). In addition, high temperature promotes disorder and thus high-spin state becomes relatively more stable than low-spin state. Therefore, the transition may start deeper [*Hofmeister*, 2006; *Wentzcovitch et al.*, 2009]. There are, certainly, several open questions on the modality of the spin transition. For example, iron may cluster in ferropericlase (at the microscopic scale) [*Kantor et al.*, 2009] and thus affecting the width of spin crossover. Furthermore, it must be recalled that perovskite can also have similar transition and thus the relation between the two main mineralogical phases of the lower mantle are not yet well known. Finally, expected nonlinear feedback between temperature, pressure and compositional factors can complicate the picture even further. There is a qualitative consensus, however, on the two fundamental aspects that are treated in this paper, i.e., the softening of the bulk modulus and the broadening of the spin transition at high temperature. The new elasticity data of ferropericlase are included in mineralogical models to assess their effects on seismic interpretation. We show that including such effects modifies radically the inferred thermal and/or compositional gradient of the lower mantle. In order to test whether the inferred thermochemical average structure is dynamically feasible, potential dynamical consequences of the iron-spin transition are discussed as well.

2. Revised Thermochemical Interpretation

2.1. Seismic Constraints

[5] Average seismic velocities and their gradients with depth are sufficiently well constrained throughout the lower mantle. For example, arrivals of P and S seismic phases at epicentral distances larger than 30° (i.e., teleseismic distances) are particularly useful to estimate the average V_P and V_S throughout the lower mantle (see methods in auxiliary material).[3] In general, models that are only slightly, but systematically slower (or faster) than what required by the data, accumulate significant delays in travel times (or arrive earlier)

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[3]Auxiliary materials are available in the HTML. doi:10:1029/2009GL041583.

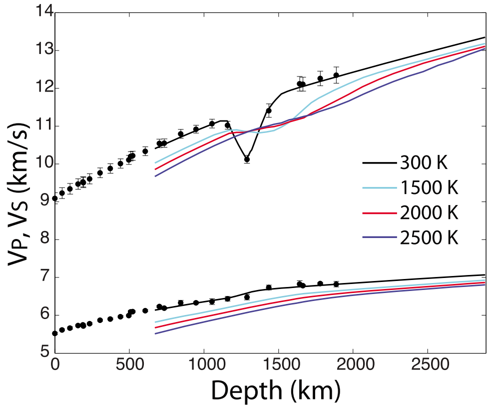

Figure 1. Seismic velocities of ($Mg_{0.9}$, $Fe_{0.1}$)O as a function of depth and temperature. Data points and error bars refer to measurements at ambient temperature [*Marquardt et al.*, 2010]. Pressures are converted to depths by using the PREM [*Dziewonski and Anderson*, 1981] pressure profile. Velocities are computed along 4 isotherms (see legend). The broadening of the iron-spin transition with temperature is modeled on the basis of a theoretical computation [*Tsuchiya et al.*, 2006]. The elastic properties are corrected at high temperature using the Debye model with parameters from *Matas et al.* [2007].

as data are recorded at longer epicentral distances, that is as rays turn deeper in the lower mantle (Figure 2). The baseline shift of the residuals at teleseismic distances is due to crustal and upper mantle structure [*Cammarano et al.*, 2005]. Deviations between the required seismic velocities in the lower mantle and the modeled ones result in a "non horizontal" shape of the residuals in Figure 2.

2.2. Mineral Physics Constraints and Interpretation

[6] In spite of advances in laboratory experiments and theoretical computations, uncertainties on the elastic properties of lower mantle minerals are still large and preclude a precise interpretation in terms of absolute temperature (T) or composition (C). For example, at 850 km depth, uncertainties in T, for a given composition and V_P, have been estimated to be around ±350 K [*Cammarano et al.*, 2003]. Some properties, such as the temperature dependence of the shear modulus at high pressure, are mostly unknown. Therefore, the adoption of different extrapolation schemes at high P and T conditions can also be a source of discrepancy between available mineral physics models [*Matas et al.*, 2007; *Cobden et al.*, 2009]. In general, it is not unusual that seismic velocities predicted by mineral physics models at the same T-C conditions differ by several percent (Figure 3). Details on the computations of seismic velocities from the mineralogical models are given in auxiliary material. Most of the current pyrolite models predict lower velocities than seismic ones in a large part of the lower mantle when the geotherm proposed by Brown and Shankland or a similar mantle adiabatic profile with potential T of 1300°C (albeit only slightly, the adiabats are model dependent) is assumed (Figure 3). For completeness, we briefly discuss the density profiles predicted by the mineralogical models and the seismic constraints on density in the auxiliary material.

[7] Despite the large uncertainties in absolute velocities, the velocity gradients with depth show small deviations from each other. The change in dV_S/dz with or without spin transition in ferropericlase is not significant due to the large uncertainties of shear properties and the small effect of iron spin transition on isotropic aggregate shear modulus. The large uncertainties in shear properties also imply a less precise interpretation of the seismic dV_S/dz. We will therefore focus our attention on the effect of the iron spin transition in (Mg,Fe)O on the gradient of V_P. dV_P/dz along the Brown and Shankland geotherm [*Brown and Shankland*, 1981] is surprisingly similar for all the models which do not include the iron-spin transition (Figure 3). This is mostly due to the apparently well constrained pressure dependence of the bulk modulus (K′) for lower mantle minerals. To reduce the velocity gradients with depth in order to match the seismic velocities, previous studies have found the need for either a superadiabatic gradient throughout the lower mantle or a compositional gradient with depth with more Fe-enriched material toward

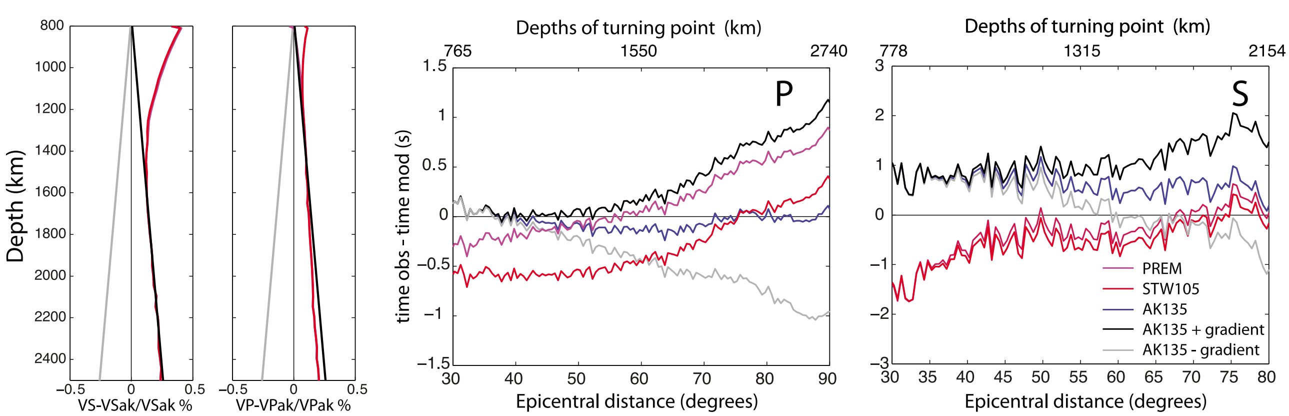

Figure 2. P and S residual times at teleseismic distances. Time differences with observations are computed for the seismic models AK135 [*Kennett et al.*, 1995], PREM [*Dziewonski and Anderson*, 1981], and STW105 [*Kustowski et al.*, 2008] (see legend for color scheme) and for 2 models for which the gradients with depth of AK135 have been slightly modified. (left) Relative velocity variations with respect to AK135 are given. (middle) P and (right) S residuals at teleseismic distances are given as function of epicentral distance and turning point of the seismic rays in the lower mantle. Turning depths are slightly different between models. Here we show the ones computed with the AK135 model. See methods in supporting material for further details.

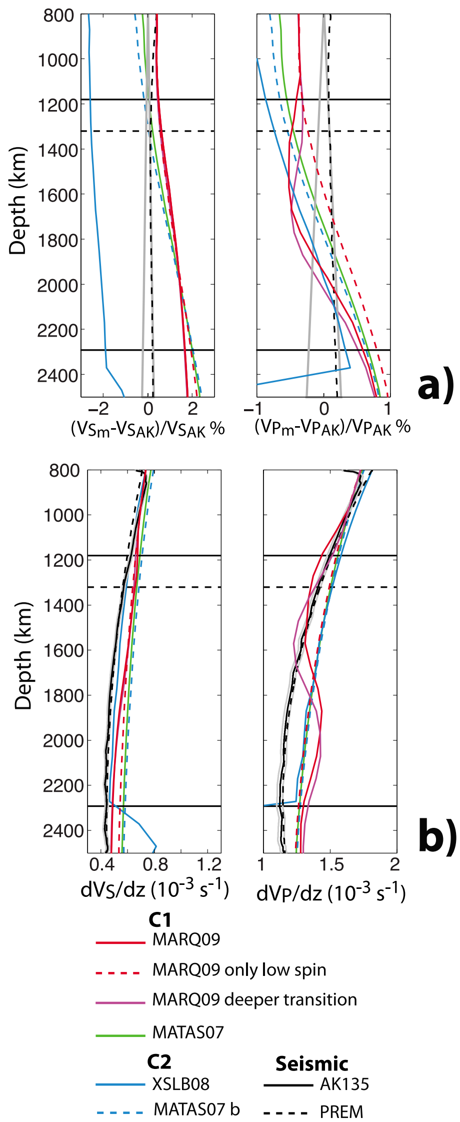

Figure 3. (a) Deviations of seismic velocities from AK135 and (b) velocity gradients with depth. Predicted velocities from mineralogical models are computed along the *Brown and Shankland* [1981] geotherm. The models labeled C1 have 80% perovskite (0.11 iron) and 20% ferropericlase (0.1 iron). Elastic properties for the green model are from *Matas et al.* [2007]. MARQ09 model is obtained replacing the ferropericlase with the new elasticity data [*Marquardt et al.*, 2010]. Dashed-red model is obtained by extrapolating the high-spin ferropericlase properties down to 2500 km. Purple model assumes that the transition starts and terminates deeper than what was predicted by *Tsuchiya et al.* [2006]. The XSLB08 model (in blue) is from a self-consistent thermodynamical model with a pyrolite composition [*Xu et al.*, 2008]. Dashed blue model has similar mineralogy (i.e., 75% $(Mg_{0.92}, Fe_{0.08})SiO_3$, 18% $(Mg_{0.83}, Fe_{0.17})O$, and 7% of $CaSiO_3$), but properties are from *Matas et al.* [2007]. The differences between the two blue models are mostly due to the different elastic properties of mantle minerals.

the bottom [e.g., *Cammarano et al.*, 2005; *Matas et al.*, 2007; *Cobden et al.*, 2009]. Of course, a combination of the two factors is not precluded. Based on the new data on ferropericlase, the interpretation changes radically. The discovery of the iron spin transition makes V_P vary with depth in a way that is not reproducible with any equation of state, whatever set of parameters are used. As shown in Figure 3, the dV_P/dz for a given geotherm markedly changes with depth. The gradients with depth are now consistent with an adiabatic pyrolite down to a depth of ~1600 km. Below this depth, dV_P/dz increases dramatically (Figure 3). Consequently, the change in thermochemical structure is required to be sharper and more pronounced compared to what inferred in previous studies. A more iron-rich ferropericlase, which is a better candidate for lower mantle mineralogy, would have even larger effects. Finally, note that even with a composition of only 10% of ferropericlase, the interpretation of velocity gradients with depth in terms of T and/or C gradients is significantly affected (Figure S1).

[8] Assuming that the $(Mg_{0.9}Fe_{0.1})O$ properties used in this study [*Marquardt et al.*, 2010] are the ones relevant to the lower mantle, we estimated a thermal gradient larger than 0.9 K/km below 1600 km for a composition with 15% of ferropericlase (Figure S2). At the other extreme, if temperature is assumed to be adiabatic, we can explain the seismic data with an enrichment in material that is slower at same P, T conditions. Owing to the uncertainties in the elastic parameters of mantle minerals, a compositional explanation is more uncertain. An increase in iron content or a decrease in Mg/Si ratio with depth go in the right direction [*Cobden et al.*, 2009], but a quantification is difficult. An additional complexity is given by the partitioning behaviour of iron in the lower mantle. It is still debated whether the iron-spin transition may lead to preferentially partitioning of iron in ferropericlase [*Auzende et al.*, 2008] or not [*Sinmyo et al.*, 2008]. In any case, if we use the simple two-minerals composition of the MARQ09 model (and its elastic properties), an increase in ferropericlase from 20% in volume to ~30% would be required to explain the data (Figure S2). Thermal and compositional factors should both play a role, obviously, as they are both related to the dynamics that have shaped the mantle.

[9] A more realistic ferropericlase, with 20% of iron, has lower velocities and therefore contributes to get higher temperatures (for the same composition), but also predicts large iron spin effects. Hence, the variations in the thermochemical structure across the spin cross-over would be even larger. Residual uncertainties in mineral physics data preclude a precise determination of the average thermochemical gradient along the lower mantle. However, our results depend on qualitative aspects of the iron-spin transition in ferropericlase. In our analysis, we also tried to take into account the uncertainties in thermal effects by enlarging the predicted width of the spin crossover based on a theoretical study [*Tsuchiya et al.*, 2006]. Moreover, we used the results on a ferropericlase specimen with only 10% of iron. Even in this extreme case, we found a significant change in thermochemical interpretation also if only 10% of ferropericlase is present.

[10] In conclusion, including the effects of the iron-spin transition in ferropericlase, requires a lower mantle that is separated in two different regimes. Specifically, the required thermochemical gradient to explain the data is reduced above ~1600 km and increased below this depth (Figure S2). Standing to current mineral physics data, it turns out that the upper part of the lower mantle is now more consistent with the adiabatic compression of a homogeneous medium (well-mixed mantle?) compared to previous studies that did not include

the iron-spin transition effects. Instead, the lower mantle below ~1600 km is characterized by a large thermochemical gradient, on average, probably indicating the presence of a less well-mixed mantle.

3. A Broad Thermochemical Transition in the Lower Mantle?

[11] The presence of a thermochemical boundary within the Earth's mantle has been suggested in the past on the basis of geochemical arguments [*Tackley*, 2000]. A logical place to look for such a boundary was at the transition between the upper and lower mantle, i.e., at ~660 km. Seismic tomography, however, shows that some slabs penetrate into the lower mantle [*van der Hilst*, 2004]. A chemical boundary within the lower mantle would explain several observations, such as the high heat flow through the surface or anomalously high ratio of $^3He/^4He$ at some hotspots, suggesting the existence of a primitive reservoir [*Hofmann*, 1997]. Nevertheless, the smooth increase of seismic velocities with depth and the absence of structural changes in the main forming mineralogical phases throughout most of the lower mantle were indeed consistent with a homogeneous adiabatic mantle. In order to reconcile geochemical and geophysical observations, different hypotheses have been presented [*Tackley*, 2000]. For example, the presence of a chemical boundary with strong topography has been proposed [*Kellogg et al.*, 1999], which was argued to be difficult to detect by geophysical observations, and to be consistent with geochemical constraints. Non-horizontal thermochemical boundaries, however, are not consistent with the weak lateral variations in seismic structure that characterize the central part of the lower mantle. In general, it is difficult to generate geodynamical models where the heterogeneity is seismically invisible. Based on the recently measured elasticity effects of the iron-spin transition in ferropericlase, we found here that the seismic data are instead consistent with the presence of a broad thermochemical transition in the mid lower mantle (~1600 km).

[12] Key dynamic factors, such as thermal expansion, viscosity and thermal conductivity may be also affected by the iron-spin transition [*Goncharov et al.*, 2006; *Wentzcovitch et al.*, 2009]. The pressure dependence and, more important, the temperature dependence of the transition have the potential to affect mantle dynamical evolution. The fate of slabs of subducted lithosphere, for example, may change. According to current knowledge, cold slabs could become relatively denser, but more buoyant compared to the surrounding material when crossing the iron spin transition (the maximum effects are expected around 1300–1400 km depth). It is not known whether the effects may inhibit the further descent of the slabs. Seismic tomography [see, e.g., *van der Hilst*, 2004; *Sigloch et al.*, 2008; *Boschi et al.*, 2007] does not contradict the possibility of a broadening and/or flattening of the slab material in the mid-lower mantle. At a shorter length scale, scattering profiles below pacific subduction zone also show a sharp decrease in intensity at mid mantle depths [*Kaneshima and Helffrich*, 2009]. Effects on shear anisotropy and variations in heterogeneity ratios dV_P/dV_S, discussed elsewhere [*Marquardt et al.*, 2010, 2009], can also affect the signature of the seismic anomalies. If the slabs that reach into the lower mantle are continuous from the surface to the "stagnation zone" in the mid lower mantle, it is theoretically possible to look for effects at surface, e.g., look for the possible signature in plate motion reconstructions based on paleo kinematics data [*Goes et al.*, 2008]. A future class of dynamical models that include the complexities related to the iron-spin transition (G. Morra et al., Geodynamics implications of a viscosity and density peak in the mid lower mantle, submitted to *Physics of the Earth and Planetary Interiors*, 2009) will probably help to understand how the inferred thermochemical structure originated.

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