Lower mantle composition and temperature from mineral physics and thermodynamic modelling

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SUMMARY

A generalized inverse method is applied to infer the radial lower mantle composition and temperature profile from seismological models of density and bulk sound velocity. The computations are performed for a five components system, MgO-FeO-CaO-Al₂O₃-SiO₂ and three phases: (Mg,Fe,Al)(Si,Al)O₃ perovskite, (Mg,Fe)O magnesiowüstite, and CaSiO₃ perovskite. A detailed review of the elasticity data set used to compute the elastic properties of mineral assemblages is given. We consider three different a priori compositional models - pyrolite, chondritic, and a model based on cosmic abundances of elements - as starting points for the inversions in order to investigate the sensitivity of any given best-fit solution to the assumed initial composition. Consistent features in all inversions, independent of the starting model, are a total iron content of \( X_{Fe} \approx 0.10 \pm 0.06 \) and a subadiabatic temperature gradient over most of the lower mantle depth range. A peculiar
correlated behavior of the two most sensitive parameters (iron content and temperature) is found below the 660 km discontinuity: over the depth range from 660 km down to 1300 km, $X_{Fe}$ decreases and the temperature profile is strongly subadiabatic. Significantly, we find that the bulk composition inferred from any given inversion is strongly dependent on the choice of starting model. Equally satisfactory fits to the lower mantle bulk sound velocity and density profiles can be obtained using any of the a priori models. However, the thermal structure associated with these compositional models differ significantly. Pyrolite yields a relatively cool geotherm ($T_{660} \approx 1800$ K and $X_{Pv} \approx 0.64$), while perovskite-rich models such as chondritic or cosmic models yield hot geotherms ($T_{660} \approx 2500$ K and $X_{Pv} \approx 0.84$ for the latter), but all of the geotherms are subadiabatic. The results of inversions are virtually unaffected by the partitioning of iron between perovskite and magnesiowüstite. Out of the five oxide components considered in our models, the bulk Al$_2$O$_3$ and CaO contents of the mineral assemblages are least well constrained from our inversions. Our results show that the major shortcoming of lower mantle compositional and thermal models based on inversions of bulk sound velocity and density is the strong dependence of the final solution on the starting model. That is, a wide variety of best-fit compositional and thermal models can be obtained, all of which provide satisfactory fits to global average seismic models. It is, in fact, this non-uniqueness that dominates the resulting a posteriori uncertainties and prevents a clear discrimination between different compositional models. Independent constraints on the thermal structure or on the shear properties of lower mantle assemblages are needed to infer lower mantle composition with a higher degree of certainty.

**Key words:** Bulk modulus, Density, Inverse problem, Mantle, Mineralogy, Seismic velocities.

1 **INTRODUCTION**

The lower mantle accounts for nearly half of the mass the Earth. It is generally accepted that its mineralogy mostly consists of magnesium silicate perovskite (Mg,Fe,Al)(Si,Al)O$_3$, magnesiowüstite (Mg,Fe)O, and calcium silicate perovskite CaSiO$_3$ (*e.g.* Irifune 1994, Kesson et al. 1998). However,
the exact proportions of these phases as well as the distribution of the elements between them (e.g. the partitioning of iron between perovskite and magnesiowüstite) are not exactly known and the details of the lower mantle chemical composition are still under debate. Whether or not the lower mantle has the same bulk composition as the upper mantle is fundamental for understanding the global mantle dynamics, the thermal structure of the Earth and the nature and location of various geochemical reservoirs.

Since the 60’s, a large number of lower mantle compositions have been proposed. They range from essentially pure perovskite (Mg/Si~1) to compositions with Mg/Si ratio as high as 1.3. The perovskite-rich type was introduced in order to keep the Mg/Si ratio for the bulk mantle close to that of chondrites (e.g. Hart & Zindler 1986 with the CI chondrite hypothesis, and Javoy 1995 with EH chondrite model). These compositional models imply that the upper and lower mantle are chemically distinct. The second group of models corresponds to pyrolite-like composition. The original pyrolite model was proposed by Ringwood (1962a), Ringwood (1962b) and Green and Ringwood (1963) as a fictitious mixture of olivine and pyroxene capable of producing the observed mid oceanic basaltic magmas during partial melting. There now exist a large number of refined pyrolite models based on geochemical and petrological analysis (e.g. LOSIMAG1 of Hart & Zindler 1986, PRIMA of Allègre et al. 1995, pyrolite model of McDonough & Sun 1995). The hypothesis of an entire pyrolitic mantle implies that the mantle is depleted in silicon compared to chondrites. To explain a possible silicon depletion several scenarios have been proposed invoking either siderophile behavior of Si at moderate pressures or volatilization at high temperatures. Allègre et al. (1995) and McDonough & Sun (1995) put the missing silicon budget into the core whereas Ringwood (1979) suggested that Si was volatilized during Earth accretion.

In the past, a stratified mantle with independent reservoirs was proposed to explain geochemical observations such as the rare gas budget (e.g. Allègre et al. 1986). Such a model is however in contradiction with other geochemical observations, such as the ubiquitous signature of recycled material in all hotspots (Hofmann 1997) and with various geophysical observations: large scale gravity field (e.g. Richards & Hager 1984, Ricard et al. 1993) and modern seismic tomography. The latter indicates that some subducting slabs penetrate deep into the mantle (e.g. Van der Hilst et al. 1997, Grand et al. 1997) suggesting some degree of mass exchange between the upper mantle and the lower mantle. Neither simple one layer model nor two layers model of mantle convection can satisfy both the geophysical and the geochemical observations. More refined patterns of mantle convection have been proposed over the last decade (e.g. Tackley 2000 for a review). Kellogg et al. (1999) argue that large mass transfer between the upper mantle and the lower mantle does not exclude inhomogeneous layers in the lowermost mantle. Coltice & Ricard (1999) and Ferrachat & Ricard (2001) show that
one layer mantle convection is not necessarily in contradiction with geochemical observations. Recent laboratory experiments carried out on two superimposed fluids suggest that the lower mantle may be in a convective transient state allowing both a regime of oscillating domes, a stable stratified regime and a large-scale mixing regime (see Davaille et al. 2003 for a review). Consequently, the mode of convection is still questionable.

Most constraints on lower mantle composition and thermal structure come from comparing seismic velocities with experimentally measured properties of various mineral assemblages. The seismological parameters of primary interest are the compressional wave velocities, $V_P$, and the shear wave velocities, $V_S$, and their lateral variations. However, the most abundant experimental results from mineral physics are for the density $\rho$, and the isothermal bulk modulus, $K_T$ (by static compression) or adiabatic bulk modulus, $K_S$ (by acoustic methods). It is therefore more difficult to utilize shear properties as a constraint on mantle composition. For phases stable only at lower mantle conditions (e.g. silicate perovskite), results on $V_P$ and $V_S$ and shear properties are becoming available by Brillouin spectroscopy (Sinogeikin et al. 2004, Jackson et al. 2004) and ultrasonics techniques (Aizawa et al. 2004, Sinelnikov et al. 1998) but such data are still comparatively few in number. A more often used approach is therefore to combine seismological models of $V_P$ and $V_S$ to generate bulk sound velocity $V_\phi$ and density $\rho$ models for comparison to mineralogically properties. $V_\phi$ is related to the two seismic velocities via $V_\phi^2 = V_P^2 - 4/3 V_S^2 = K_S/\rho$, which leaves $V_\phi$ independent of the shear modulus.

Seismological and mineralogical properties must of course be compared at similar pressure and temperature conditions. This can be done either: (1) by adiabatic decompression of seismologically determined mantle properties for comparison at zero pressure with laboratory data (e.g. Bukowinski & Wolf 1990, Jackson 1998, Stacey & Isaak 2001), or (2) by extrapolation of measured mineral properties to lower mantle $P$-$T$ conditions for comparison with seismologically determined bulk sound velocity and density profiles. Among the latter studies, some proposed that a pyrolitic composition can reasonably match the seismological models without any iron or silicon enrichment (e.g. Fiquet et al. 2000, Jackson 1998, Wang et al. 1994, Wang & Weidner 1994). At the same time, other studies (e.g. Ita & Stixrude 1992) disagreed with the idea of a uniform mantle and therefore favored layered convection. Jeanloz & Knittle (1989), Bina & Silver (1990), Stixrude et al. (1992) argued that the lower mantle should rather be chondritic or even pure perovskite. Several authors attempted to better constrain the lower mantle composition and its temperature by also including shear properties. Nevertheless, no clear consensus has emerged from these studies: Vacher et al. (1998) did not discriminate between homogeneous and stratified mantle models, Marton & Cohen (2002) preferred a pyrolic lower mantle, and Wentzcovitch et al. (2004) suggested radially heterogeneous lower mantle models. Most of these studies only consider a three components system (MgO-FeO-SiO$_2$), neglecting
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the CaO and Al₂O₃ contents. However, all petrological models contain significant amounts of calcium and aluminum (at least 5 wt.%). The latter are especially relevant for the mineralogy of the upper mantle, since they control the phase relationships in the pyroxene-garnet component. In addition, as suggested by several studies (see Daniel et al. 2001 and Andrault et al. 2001 for reviews) aluminum oxide, even in small proportions, seems to drastically change the bulk properties of the magnesium silicate perovskite phase. Contrary to aluminum, calcium does not enter the orthorhombic Mg-rich perovskite phase (e.g. Hirose et al. 1999) but instead is incorporated into a separate cubic CaSiO₃ perovskite phase. This phase has been often disregarded due to its lesser abundance in the lower mantle (expected to be less than 5 mol%), and CaSiO₃ perovskite is believed to be an invisible phase in terms of density and bulk modulus at lower mantle conditions (e.g. Shim et al. 2000). However, Karki & Crain (1998) suggested that shear properties can allow the calcium budget of the lower mantle to be constrained. These points show that the exact role of CaSiO₃ perovskite in the lower mantle is not yet clearly identified.

All inversions of lower mantle composition are limited by the lack of information on the temperature profile. There is indeed a wide spectrum of proposed thermal structures. Brown & Shankland (1981) advocated for a nearly adiabatic profile based on calculation of entropy. da Silva et al. (2000) deduced a strongly superadiabatic profile from mineral physics calculations (temperature as high as 4000 K below 2500 km depth). These models are in contrast to numerical simulations of mantle convection mostly heated from within (Bunge et al. 2001, Monnereau & Yuen 2002), reporting a subadiabatic lower mantle (up to 400 K below an adiabat) except in a hot boundary layer above the core-mantle-boundary (CMB).

Given the uncertainties on mantle minerals elastic and shear properties, and on thermal structure, the interpretation of 1-D seismic profiles is far from straightforward and is still controversial. In this study, we first select the most recent and high-quality experimental data, then we apply a generalized inverse method to deduce the lower mantle composition and temperature profile. This method allows us to determine the composition and the temperature which best match global 1-D density and bulk sound velocity profiles reported by PREM (Dziewonski & Anderson 1981) and ak135 (Kennett et al. 1995). We also precisely evaluate which are the best constrained inverted parameters and study the impact of experimental uncertainties on the resulting mineralogy and temperature. The shear properties are not considered for two reasons. First, bulk modulus and density are the most numerous and presumably best constrained parameters from experimental studies. Even though the experimental measurements of mineral rigidities are becoming available, their pressure and temperature dependence is still poorly constrained. Indeed, for MgSiO₃ perovskite (the most abundant lower mantle mineral) only a few studies are available in a limited P-T range (Sinelnikov et al. 1998, Sinogeikin et al. 2004).
Second, the results can be compared to previous studies that used density and bulk sound velocity (or bulk modulus) as constraints for lower mantle properties. The formal inversion defined in this way allows us to study the effect of Al and Ca as well as the possible non-uniqueness of the results, taking into account all available experimental elastic data and their uncertainties.

2 ELASTICITY DATA SET

The major features of the lower mantle mineralogy can be described by using three distinct phases: silicate perovskite \((\text{Mg,Fe,Al})(\text{Si,Al})\text{O}_3\) (Pv), magnesiowüstite \((\text{Mg,Fe})\text{O}\) (Mw) and calcium-bearing perovskite \(\text{CaSiO}_3\) (CaPv). Two perovskites form separate phases with limited solubility between them (e.g Hirose et al. 1999). On the other hand, the solubility of aluminum in CaPv is not negligible (at maximum 10 mol%) as reported by Hirose et al. (1999) and Takafuji et al. (2002). These results come from experiments on MORB-like composition and grossular samples (and all Al-rich compositions).

In the case of pyrolite-like composition (magnesium-rich), aluminum enters the magnesium-rich perovskite and only negligible amount of Al is found in CaPv (less than 2 mol%, Irifune 1994). Perovskite and magnesiowüstite phases form solid solutions which can be modeled by a mixture of the following end-members: \(\text{MgSiO}_3\) (MgPv), \(\text{FeSiO}_3\) (FePv), \(\text{Al}_2\text{O}_3\) (AlPv) in the case of silicate perovskite and \(\text{MgO}\) (periclase, MgMw), \(\text{FeO}\) (wüstite, FeMw) in the case of magnesiowüstite. FePv is a virtual end-member since iron content of perovskite \((\text{Mg}_{1-x}\text{Fe}_x)\text{SiO}_3\) does not exceed \(~0.2\) (Fei et al. 1996). Real wüstite is in fact a non-stoichiometric compound, \(\text{Fe}_{1-x}\text{O}\). The stoichiometric extrapolation \(x = 1\) used in this study leads to the purely fictitious end-member \(\text{FeO}\) (FeMw). It should be noted that the purpose of the fictive Fe end-members is to reproduce the elastic properties in the range of lower mantle iron contents and they are not intended to obtain the actual properties of the pure iron end-members (FePv and FeMw).

In order to compute density and bulk sound velocity in the lower mantle (see appendix A for details), we use a third-order Birch Murnaghan equation of state (EoS). The following elastic properties of each end-member are required (see appendix A for details): molar volume at ambient conditions, \(V_0\), isothermal bulk modulus, \(K_{0,T}\), with its pressure and temperature derivatives, \(K'_{0,T}\), \((\partial K_{0,T}/\partial T)_P\), respectively, and thermal expansion coefficient as a function of temperature, \(\alpha(T)\). The elastic properties used in this study are listed in Table 1. In spite of significant progress in experimental techniques, not all of these properties are well constrained and a detailed discussion of their uncertainties is useful.

In this section, we review the elastic dataset of all important phases in the lower mantle. We see that for each parameter considered separately, the experimental uncertainties are still very large, compared to the accuracy of the seismological models. These apparent discrepancies are however misleading. Due to the very trade-off between elastic parameters inverted from experiments, very
different parameter sets can reproduce very similar $P$-$V$-$T$ measurements at mantle conditions. We illustrate this point in details in the case of MgPv (see Fig. 1).

### 2.1 Molar volume $V_0$

This is the best constrained parameter. The most accurate and precise values of $V_0$ come from conventional diffraction measurements made outside any high pressure device at ambient conditions. These values are more accurate than those deduced from high $P$-$T$ experiments in a high pressure device by simultaneously inverting experimental $P$-$V$-$T$ data for $V_0$ and other EoS parameters. For periclase, $V_0$ can be directly measured at ambient conditions (Jackson & Niesler 1982). Due to the non-stoichiometry of wüstite, $V_0$ of pure fictive FeMw is obtained by extrapolation of experimental results on Fe$_{1-x}$O, for $x$ varying from 0.019 to 0.073 (Will et al. 1980, Hazen 1981, Yagi et al. 1985, Jeanloz & Sato-Sorensen 1986, Liu & Liu 1987). When $V_0$ can not be obtained independently and more accurately, such as for unquenchable CaSiO$_3$ perovskite, the value of $V_0$ is deduced from $P$-$V$-$T$ inversions of compression data (e.g. Wang et al. 1996, Shim et al. 2000). For MgSiO$_3$ perovskite the value of $V_0$ is constrained by direct diffraction measurements at ambient conditions (e.g. Fiquet et al. 1998). Value of $V_0$ for the pure virtual FePv end-member is determined by extrapolation of measured volume of perovskite samples with variable iron content, (Mg$_{1-x}$Fe$_x$)SiO$_3$: Parise et al. (1990) ($x=0.1$), Mao et al. (1991) ($x=0.1, 0.2$), Wang et al. (1994) ($x=0.1$), Andrault et al. (2001) ($x=0.05$). For $V_0$ of AlPv, we use the value recently determined by Jackson et al. (2004) on aluminous MgSiO$_3$ perovskite (5 mol.% Al$_2$O$_3$) by X-ray measurement. We also consider an alternative value deduced from extrapolation of volumes reported for perovskite samples with variable aluminum content, $x$Al$_2$O$_3$+(1$-x$)MgSiO$_3$: Zhang & Weidner (1999) ($x=0.05$), Andrault et al. (2001) ($x=0.11$), Daniel et al. (2001) ($x=0.077$), Daniel et al. (2004) ($x=0.05$), Jackson et al. (2004) ($x=0.05$), Yagi et al. (2004) ($x=0.012, 0.103$).

### 2.2 Bulk modulus $K_{0,T}$ and its pressure derivative $K'_{0,T}$

The volume (and density) at standard conditions is generally not controversial. However, with the bulk modulus and its pressure and temperature derivatives there are sometimes significant discrepancies between values when multiple measurements are available. Therefore, we had to prioritize the data from various sources. Where available, the results from ultrasonic techniques and Brillouin spectroscopy performed on single crystals are preferred over data from static compression or acoustic measurements on polycrystalline specimens. In many cases, the two approaches give quite similar results (e.g. for MgPv, Sinogeikin et al. 2004 gives $K_{0,S} = 253(9)$ GPa whereas Fiquet et al. (2000)
gives $K_{0,T} = 253(3)$ GPa. In cases where there are substantial differences (for example for AlPv EoS data) we use diffraction results as alternative set of parameters.

The compressibility of periclase MgO has been widely studied and is well constrained either by Brillouin scattering (Sinogeikin & Bass 2000) or by ultrasonic (e.g. Jackson & Niesler 1982) measurements. Compatible results are obtained from X-ray diffraction measurements in the diamond anvil cell (e.g. Dewaele et al. 2000). The values for FeO are obtained from measurements on a non-stoichiometric wüstite, e.g. Fe$_{0.943}$O (Jackson et al. 1990), or from extrapolation of measurements on MgO-FeO join (Fei 1999, Kung et al. 2002). These studies suggest that $K_{0,T}$ of wüstite is lower than that of periclase. However, a recent study by Jacobsen et al. (2002) shows that the bulk modulus of (Mg$_{1-x}$Fe$_x$)O remains constant (within the experimental uncertainties) up to at least $x = 0.3$. Therefore, to simulate properly lower mantle magnesiowüstite (i.e. with $x < 0.3$), we choose bulk modulus of FeMw equal to bulk modulus of MgMw. The two recent studies on CaSiO$_3$ perovskite based on X-ray diffraction measurements (Wang et al. 1996, Shim et al. 2000) give similar incompressibilities even though they propose numerically different sets of $K_{0,T}$ and $K_{0,T}'$ (see Table 1). The two sets equally describe very similar $P$-$V$-$T$ measurements and the apparent differences are only due to strong trade-offs between inverted elastic parameters.

Although (Mg,Fe,Al)-bearing perovskite is the most abundant phase in the lower mantle, there is no general agreement on its incompressibility. The reported experimental values of $K_{0,T}$ for pure MgSiO$_3$ perovskite range from 246 GPa to 261 GPa (Yeganeh-Haeri et al. 1989, Sinogeikin et al. 2004 both using Brillouin scattering, Mao et al. 1991, Wang et al. 1994, Utsumi et al. 1995, Funamori et al. 1996, Fiquet et al. 1998, Saxena et al. 1999, Fiquet et al. 2000, Andrault et al. 2001 using X-ray diffraction technique). A value of $K_{0,S} = 253(5)$ GPa, which corresponds to $K_{0,T} \simeq 250(5)$ GPa taking into account the appropriate correction (see appendix A), has been recently measured by Brillouin spectroscopy (Sinogeikin et al. 2004) agreeing within the error-bars with $K_{0,T} = 253(9)$ GPa obtained from previous $P$-$V$-$T$ data by Fiquet et al. (2000). As for $K'_{0,T}$, its value is often fixed more or less arbitrary to 4. A better resolution of $K'_{0,T}$ would require a larger number of precise simultaneous high-$P$ and high-$T$ measurements to reduce the strong correlations between $V_0$, $K_{0,T}$ and $K'_{0,T}$. Fiquet et al. (2000) considered all available $P$-$V$-$T$ measurements to perform a generalized inversion and obtained $K'_{0,T} = 3.7$ together with $K_{0,T} = 260$ GPa. Given the uncertainties on $K_{0,T}$, $(\partial K_{0,T}/\partial T)_P$ (see discussion below) and intrinsic correlations, we keep $K'_{0,T}$ equal to 4. The effect of iron on the bulk modulus of perovskite is not clearly identified yet. Several studies suggest that small amounts of iron (less than 10%) have only a negligible effect on $K_{0,T}$ and $K'_{0,T}$ of iron-bearing perovskite, within the experimental error-bars (Mao et al. 1991 and Knittle & Jeanloz 1987). However, there are some indications that iron could make perovskite somewhat stiffer but there is no agreement
on the magnitude of this phenomenon. Andrault et al. (2001) reported that 5 mol.% of iron increases the bulk modulus by 2.7% whereas Kiefer et al. (2002) calculated using first-principles method that 25 mol.% of iron increases $K_{0,T}$ by only 1.9%.

As for aluminum, both theoretical (Brodholt 2000, Yamamoto et al. 2003) and experimental studies (Zhang & Weidner 1999, Daniel et al. 2001, Daniel et al. 2004, Jackson et al. 2004, Yagi et al. 2004) showed that the dissolution of ~5% of Al$_2$O$_3$ into the perovskite structure decreases its incompressibility. There is however no agreement on the amplitude and physical basis for this phenomenon: some experimental results on Al-bearing perovskite (5% mol. Al$_2$O$_3$) show a decrease of between 0-1% (Daniel et al. 2004, Jackson et al. 2004) whereas others show a decrease of 7% (Zhang & Weidner 1999) compared to bulk modulus of pure MgSiO$_3$ perovskite. It should also be noticed that Andrault et al. (2001) reported contrasting behavior suggesting a stiffer Al-bearing perovskite structure. In this study, we choose the most recent Brillouin results on Al-bearing perovskite (with 5 mol.% of Al$_2$O$_3$) by Jackson et al. (2004). We also assume as in the case of iron that aluminum has no significant effect on $K_{0,T}$ supported by recent experiments by Daniel et al. 2004.

2.3 $(\partial K_{0,T}/\partial T)_P$ and thermal expansion $\alpha$

These parameters are often obtained by inversion of $P$-$V$-$T$ measurements. As a result, they are highly correlated. $(\partial K_{0,T}/\partial T)_P$ is considered being constant with temperature. Thermal expansion is usually given as a non-linear function with empirically determined coefficients. It can be shown that within the actual experimental uncertainties, a linear increase of $\alpha$ with temperature is sufficient to fit experimental observations.

The values reported by separate $P$-$V$-$T$ studies can differ significantly even though they have been obtained matching similar observed densities. In order to assess the effect of uncertainties on these correlated parameters in a self consistent way, we need to know the associated covariance matrix. However, the latter is not usually reported. We revisited the data from Fiquet et al. (1998) and Fiquet et al. (2000) to compute $(\partial K_{0,T}/\partial T)_P$ and $\alpha$ of MgPv using a generalized inverse method (Tarantola & Valette 1982). In addition to the inverted parameters and their uncertainties (which we found in agreement with Fiquet et al. 2000), we also computed the complete associated covariance matrix. We notice that the inverted value of -0.021 GPa/K for $(\partial K_{0,T}/\partial T)_P$ is in agreement with several other studies (Wang et al. 1994, Utsumi et al. 1995, Funamori et al. 1996, Fiquet et al. 1998, Fiquet et al. 2000, Gillet et al. 2000).

For MgPv, Fig. 1 depicts the resulting confidence ellipses within the 2$\sigma$ range in the simultaneous determination of $\alpha$ and $(\partial K_{0,T}/\partial T)_P$, with fixed $V_0$, $K_{0,T}$, $K_{0,T}'$. We perform three inversions by fixing $K_{0,T}$ either to 246 GPa (Yeganeh-Haeri et al. 1989), or 250 GPa (preferred value, Sinogeikin...
et al. 2004) or 261 GPa (e.g. Mao et al. 1991). $V_0$ and $K_{0,T}^'$ are fixed to previously discussed values. Fig. 1 also shows that increasing the nominal value of $K_{0,T}$ shifts the inverted $\alpha$ and $(\partial K_{0,T}/\partial T)_P$ towards lower values. It clearly reveals strong anticorrelations between the inverted elastic parameters. These three parameter sets will be used to study the influence of uncertainties on elastic parameters of MgPv, by random sampling of $(\partial K_{0,T}/\partial T)_P$ and $\alpha$ within these $2\sigma$ ellipses.

The effect of aluminum on the thermal equation of state of perovskite has been studied by Zhang & Weidner (1999) who reported a value of $(\partial K_{0,T}/\partial T)_P$ close to -0.06 GPa/K. This value is significantly higher than reported values for any other mantle minerals, and it is in particular above the experimental values of MgPv. Due to the intrinsic trade-offs, this value can not be considered alone because it was obtained together with a significantly low value of $K_{0,T}$ (234 GPa) and unusually high value of $\alpha$ (which gives $\sim 6 \times 10^{-5}$ K$^{-1}$ at 2000 K). We note that high (negative) values of $(\partial K_{0,T}/\partial T)_P$ were also reported by Mao et al. (1991) and Stixrude et al. (1992) for MgSiO$_3$ perovskite. Wang et al. (1994) suggested that these high values are likely due to partial back-transformation, or even to partial amorphization. We choose this parameter set as an alternative one. In the case of iron-bearing perovskite, there is no evidence for a change of either $(\partial K_{0,T}/\partial T)_P$ or thermal expansivity due to dissolution of iron in perovskite structure (Hama & Suito 1998, Anderson & Hama 1999). Therefore, we choose the same values for FePv as those for MgPv.

In the case of CaSiO$_3$ perovskite, the available $(\partial K_{0,T}/\partial T)_P$ comes from two previously mentioned studies (Wang et al. 1996 and Shim et al. 2000) but the thermal expansion is not well constrained. Wang et al. (1996) obtained the best fit to their measurements by assuming a constant thermal expansion coefficient equal to $3 \times 10^{-5}$ K$^{-1}$. Extrapolation of this value using the Birch-Murnaghan EoS leads to a negative thermal expansion at high pressure (above $\sim 75$ GPa) and high temperature (above $\sim 2200$ K) for CaPv. Therefore, we reevaluate the thermal expansion of these two studies using the same inversion of $P$-$V$-$T$ measurements as previously described for MgPv. We set $V_0$, $K_{0,T}$ and $(\partial K_{0,T}/\partial T)_P$ to respective values of Wang et al. (1996) and Shim et al. (2000) and invert for thermal expansion coefficients, $\alpha_0$, and $\alpha_1$. Data of Shim et al. (2000) does not allow to constrain $\alpha_1$. The best fit is then obtained when $\alpha_1 = 0$. The inversion of the two datasets leads to thermal expansions higher than the fixed value of $3 \times 10^{-5}$ K$^{-1}$ reported by Wang et al. (1996) and have a reasonable behavior at lower mantle $P$-$T$ conditions.

As for periclase, we average the thermal expansion obtained by Suzuki (1975) from dilatometric measurements and by Fiquet et al. (1999) from X-ray diffraction measurements. $(\partial K_{0,T}/\partial T)_P$ is inverted from $P$-$V$-$T$ measurements of Dewaele et al. (2000), fixing the values of $V_0$, $K_{0,T}$, $K_{0,T}^'$ and $\alpha$. It is in agreement with previous values reported by Isaak et al. (1989), Isaak et al. (1990), Utsumi et al. (1998), Fei (1999), Zhang (2000), Sinogeikin et al. (2000). We notice that the resulting
uncertainty is small. It is not surprising since \((\partial K_{0,T}/\partial T)_P\) is the only free parameter. To take into account experimental uncertainties, we choose the parameters given by Dewaele et al. (2000) as an alternative set. Finally, there is a little information on the behavior of MgO-FeO solid solutions at high temperature, leaving \((\partial K_{0,T}/\partial T)_P\) and \(\alpha\) of these compositions poorly constrained. In this study, we use the value of \((\partial K_{0,T}/\partial T)_P\) of wüstitie given by Sumino et al. (1980) who conducted experiments on adiabatic bulk modulus on non-stoichiometric wüstitie Fe\(_{0.92}\)O. The value of \(\alpha\) of FeMw has been measured by X-ray diffraction measurements by Skinner (1966).

3 INVERSION TECHNIQUE

The density and bulk sound velocity profiles in the lower mantle reflect its mineralogical composition as well as its thermal structure. We can therefore formulate an inverse problem in order to extract these characteristics from seismological observations. In this study, we use the generalized inverse method proposed by Tarantola & Valette (1982).

The observations (the data vector \(d_0\)) consist of values of density and bulk sound velocity. They are deduced from PREM (Dziewonski & Anderson 1981) and ak135 (Kennett et al. 1995) at various depths. The molar abundances of each end-member and the temperature at these depths are the model parameters (the vector \(p\)). The forward problem, mathematically expressed as \(d = g(p)\), relates any set of model parameters to a data vector \(d\), which is generally different from \(d_0\). The operator \(g\) reflects the procedure of computing density and bulk sound velocity for a given mantle mineralogy. \(g\) can not be expressed as a simple expression and we use a numerical code to compute the direct problem.

The inverse problem is to derive a parameter set \(\hat{p}\) that explains the observations within their uncertainties and remains reasonably close (depending on our knowledge) to an \emph{a priori} guess \(p_0\). In other words, we are looking for \(\hat{p}\) that minimizes the following misfit function:

\[
S(p) = (d_0 - g(p))^T C_{d_0d_0}^{-1} [d_0 - g(p)] + (p - p_0)^T C_{p_0p_0}^{-1} (p - p_0)
\]

where \(C_{d_0d_0}\) and \(C_{p_0p_0}\) are covariance matrices corresponding to our \emph{a priori} confidence to data and \emph{a priori} knowledge of model parameters. In this study, we assume that data and parameters are uncorrelated. Therefore, the covariance matrices are diagonal and contain the squares of uncertainties on observations, \(C_{d_0d_0}\), and on parameters, \(C_{p_0p_0}\). We adopt the reported uncertainties on density and bulk sound velocity of 0.5% (Silver et al. 1988) and 0.1% (Kennett et al. 1995), respectively. Our \emph{a priori} model \(p_0\) corresponds to pyrolite-like mineralogy, which is often assumed to be an average lower mantle composition (\textit{e.g.} Ringwood 1982), and temperature profile proposed by Brown & Shankland (1981). The latter is a reasonable approximation of a mantle adiabat. However, it should
be noted that there is no physical reason that the actual geotherm should correspond to an isentrope. The uncertainty on each molar abundances is set to 50% and to ∼400 K for temperature.

The minimization is performed iteratively using standard procedures (for details see Tarantola & Valette 1982). Besides the best fitting model \( \hat{p} \), this method allows us to evaluate the associated \( a posteriori \) uncertainties and covariance matrix. We choose the starting model to coincide with the \( a priori \) model.

4 RESULTS

In this section, we perform several numerical experiments to test a series of possible sets of elastic constants and of partitioning coefficients. We also study the effect of various \( a priori \) models of global chemical composition and of thermal structure.

The best fitting model of lower mantle composition and temperature depends on our confidence in the \( a priori \) parameters (i.e. values of \( C_{d0d0} \)), in the seismological data (i.e. values of \( C_{d0d0} \)) but also in the physical modelling of \( g \) (i.e. modelling errors, Tarantola 1987). Modelling uncertainties come from the non-uniqueness in estimating averaged properties (e.g. Stacey 1998), from the inaccuracies of the elastic constants and from not precisely constrained models of the iron partitioning between perovskite and magnesiowüstite. While the effect of the parameter and data uncertainties is automatically expressed by the \( a posteriori \) covariance matrix, the influence of the model uncertainty is not straightforward to evaluate. Our approach will be to randomly test a series of possible sets of elastic constants and partitioning coefficients.

To represent the inverted mineralogy of the lower mantle, we use the common representation in terms of molar fraction of magnesium-rich silicate perovskite, \( X_{Pv} \), and calcium silicate perovskite, \( X_{Ca} \), defined as follows:

\[
X_{Pv} = \frac{Pv}{Pv + Mw + CaPv} \quad \text{and} \quad X_{Ca} = \frac{CaPv}{Pv + Mw + CaPv} \tag{2}
\]

where \( Pv \), \( Mw \) and \( CaPv \) are the molar abundances of perovskite, magnesiowüstite and calcium-perovskite phases. The molar fraction of magnesiowüstite is then simply given by:

\[
X_{Mw} = 1 - X_{Pv} - X_{Ca} \tag{3}
\]

The iron content of the mantle is characterized by the molar ratio:

\[
X_{Fe} = \frac{Fe}{Fe + Mg} \tag{4}
\]

For the \( a priori \) pyrolite composition, \( X_{Pv} = 0.622 \), \( X_{Mw} = 0.327 \), \( X_{Ca} = 0.051 \) and \( X_{Fe} = 0.104 \).

We perform calculations from 800 km to 2700 km depth to avoid effects due to either phase
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changes associated with 660-km discontinuity and with thermal and compositional boundary layer at the base of the mantle. The transition from garnet to perovskite is likely extended far below 660 km (i.e. Hirose et al. 1999, Irifune et al. 1996) enhanced by presence of Al-rich subducting slabs. At the bottom of the mantle, the radial seismic profiles are perturbed due to the topography and the complex nature of D" (e.g. Lay et al. 1998). These effects may introduce a significant bias to radial seismic profiles (e.g. by changing their slopes).

4.1 Influence of iron partitioning

The partitioning of iron between perovskite and magnesiowüstite relates molar abundances of four among six end-member abundances in the lower mantle (MgPv, FePv, MgMw, FeMw). The corresponding partition coefficient $K_D$ is usually defined by:

$$K_D = \frac{X_{Pv}^{Fe}}{X_{Pv}^{Mg}} \frac{X_{Mw}^{Mg}}{X_{Mw}^{Fe}}$$  \hspace{1cm} (5)

It has been reported that in Al$_2$O$_3$-free systems, Fe goes preferentially into magnesiowüstite rather than into perovskite giving values of $K_D$ around 0.25 (Frost & Langenhorst 2002, Mao et al. 1997, Martinez et al. 1997, Katsura & Ito 1996). The influence of pressure, temperature and bulk iron content on $K_D$ is however not clearly quantified (e.g. Mao et al. 1997). It has also been shown that the iron partitioning is strongly coupled to the Al$_2$O$_3$ content, but this effect remains poorly constrained. Wood & Rubie (1996) reported a $K_D$ value of 1 at 25 GPa and 1873 K in a peridotitic sample containing 4 to 5 wt% of Al$_2$O$_3$ whereas Andrault (2001) proposed a $K_D$ at 2200 K ranging from 0.8 at 51 GPa to 3.2 at 94 GPa for the same Al$_2$O$_3$ content but on olivine sample.

To cover this large experimental range, we choose two characteristic values of $K_D$: $K_D^{(1)}=1.0$ and $K_D^{(2)}=0.25$. We also consider the value of partition coefficient, $K_D^{(3)}$, obtained assuming thermodynamic equilibrium. In that case, we solve the following equation:

$$\mu_{MgPv}(P,T) + \mu_{FeMw}(P,T) = \mu_{FePv}(P,T) + \mu_{MgMw}(P,T)$$  \hspace{1cm} (6)

where the $\mu_i$ are the chemical potentials at pressure $P$ and temperature $T$ of each end-member $i$, MgPv, FePv, MgMw and FeMw. Each chemical potential $\mu_i$ is given by:

$$\mu_i(P,T) = \mu_i^0(P,T) + RT \ln a_i(P,T, n_i)$$  \hspace{1cm} (7)

$n_i$ is the molar abundance of the end-member $i$. The standard chemical potentials $\mu_i^0$ are computed using thermodynamical data summarized in Table 1, Table 2 and Table A1 (see appendix A). The activity-composition relationships $a_i$ are poorly constrained for lower mantle assemblages. The non-ideality of solid solutions is usually expressed in terms of empirical Margules parameters $W$. $W$'s
however depend on the particular choice of standard chemical potentials and reference mixing models (e.g. Fei 1991). We can not use at the same time standard chemical potentials and Margules parameters taken from two distinct studies. In this paper, we thus assume an ideal on-site mixing model (Spear 1995) for perovskite and magnesiowüstite phases. The computed equilibrium partition coefficient $K_D^{(3)}$ is almost constant around 0.8 throughout the lower mantle.

The three inversions with the three different partitioning coeffi cients lead to uniform compositions throughout the lower mantle (see Fig. 2). The inverted bulk composition is rather similar to the pyrolite composition (see Table 3). For $K_D = 1$, resulting $X_{Pv} = 0.643$ is higher by 3% and $X_{Ca} = 0.054$ by 7% whereas $X_{Fe} = 0.096$ is lowered by 7% compared to the original pyrolite composition. The temperature profi le is subadiabatic and colder by 180 K in the mid-mantle compared to Brown & Shankland’s geotherm. The results obtained with $K_D^{(1)}$ and $K_D^{(3)}$ are indistinguishable. In the case of $K_D^{(2)}$, inverted geotherm is closer to the a pri ori estimation than in the two other cases, but the composition remains very similar. The insensitivity of the inversion to the iron partitioning was already discussed by Marton & Cohen (2002), Stacey & Isaak (2001) and Jackson (1998).

These global results are a little different from previously published conclusions. For example, Jackson (1998) proposed a pyrolite-like composition with $X_{Pv} = 0.67$ and $X_{Fe} = 0.11$. The direct comparison of his results is not straightforward since he limited the inversion to a three components system MgO-FeO-SiO$_2$. Our values when transformed from fi ve to three components system by putting CaPv=AlPv=0 in equation 2, give $X_{Pv} = 0.73$ and $X_{Fe} = 0.10$. We think that these differences may mainly be due to a different choice of elastic parameters. Jackson (1998) used higher $K_{0,T}$ for perovskite and for magnesiowüstite. He chose $K_{0,S} = 264$ GPa for perovskite instead of 253 GPa in this study and $K_{0,S} = 162.5$ GPa with $K_{0,S}^t = 4.13$ for magnesiowüstite instead of 161 GPa and 3.83, respectively, in this study (see further discussion in section 4.5).

As for the temperature, we obtain a value at the 660-km discontinuity $T_{660}$ of $\sim 1800$ K which is very close to $T_{660} \simeq 1900 \pm 100$ K obtained from experimental study by Ito & Katsura (1989). The temperature at the core mantle boundary $T_{CMB}$ is close to 2250 K. These results are also in agreement with $T_{660} \simeq 1850$ K and $T_{CMB} \simeq 2300$ K proposed by Jackson (1998).

Fig. 2 also suggests some anomalous behavior of iron content from 660 km down to about 1300 km depth. One can observe a progressive transition from an iron enriched top of the lower mantle to a mid-mantle (from 1000 km and deeper) having the same iron content as pyrolite. This behavior is correlated with strongly subadiabatic temperature gradient (the geotherm is basically flat down to 1000 km). Is it a real behavior or an artifact of our inversion? One can wonder if it can be a signature of a complex phase change at 660 km (structural changes, elemental exchanges between various phases, effect of latent heat) that is smeared by seismic profi les. Indeed, one can observe a larger velocity
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Gradient in both PREM and ak135 models to about 1300 km depth, which may be related to the anomalous behavior of iron content and the subadiabatic temperature profile in this region. We also notice that the anomalous behavior of iron is not observed at the base of the mantle. A mild flattening of the geotherm appears again from 2600 km depth. In general, the inverted temperature profile is not as smooth as that proposed by Jackson (1998). This may be due to the fact that we do not use an adiabatic decompression.

In the following sections, we fix $K_D = 1$. This model with the a priori pyrolite composition and Brown & Shankland’s geotherm is denoted M1 model, and its associated inverted model IM1 (“Inverted Model 1”).

4.2 Resulting a posteriori uncertainties

The results discussed above should be considered carefully in light of a posteriori uncertainties. In Fig. 3, we compare the a priori and a posteriori uncertainties assuming an iron partitioning equal to 1. We can see that the inversion does not allow us to equally constrain all parameters. $X_{PV}$, $X_{Fe}$ and temperature profile are better constrained than $X_{Ca}$ since their a posteriori uncertainties are significantly smaller than their a priori ones (see Fig. 3). The same a posteriori error bars are shown in Fig. 4 in terms of uncertainties on the six end-members. These two figures reveal that the resolution of all parameters is constant with depth and that density and bulk sound velocity put significant constraints neither on calcium nor on aluminum content of the lower mantle. Moreover, one can read in Table 3, that even though the inversion gives results close to pyrolite composition, other possible compositions of the lower mantle such as silicon-enriched are acceptable due to large error bars.

Our approach also makes possible to compute appropriate a posteriori covariance matrix which provides information on correlations and trade-offs between inverted parameters. Fig. 5 depicts the covariance matrix in the mid-mantle. Since the global formula for the lower mantle assumes one mole of MgPv and since FePv is given by the partition coefficient $K_D$, only 5 independent parameters are plotted in this matrix (molar abundances of MgMw, FeMw, CaPv, AlPv and temperature $T$). It shows that MgMw is strongly correlated to FeMw, whereas the temperature is anticorrelated to both MgMw and FeMw. In other words, the possible values are located within associated confidence ellipses. CaPv and AlPv are not significantly correlated with any other parameters. We also notice that the correlation matrix does not significantly change with depth.

4.3 Influence of a priori composition

Since several different models for bulk composition have been proposed, we have also tested the influence of a priori composition model on the inverted parameters. We have chosen two additional a
priori compositions of the lower mantle that are often discussed. First, a chondritic model (CI carbonaceous chondrite from McDonough & Sun 1995) denoted here as model M2 and second, a model derived from cosmic abundance analysis by Anderson & Bass (1986), denoted here as model M3. Inverted profiles are depicted in Fig. 6 and associated average parameters are summarized in Table 4. As previously observed for the pyrolite M1 model, the most sensitive parameters for the two new models M2 and M3 are also $X_{Fe}$ and temperature. Therefore the inversion tends to preferentially modify these two values to minimize the misfit function, whereas $X_{Pv}$ and $X_{Ca}$ remain close to their original values (that is M2 or M3).

Inversion of the two additional compositions M2 and M3 also reveals the peculiar behavior of $X_{Fe}$ down to 1300 km depth. The progressive depletion in iron is again associated with strongly subadiabatic temperature profiles. This result seems to support the idea that the gradient of iron content as well as subadiabatic temperature is related to higher velocity gradient in seismic profiles. In the case of inverted chondritic model, one can clearly observe a decrease of temperature by 150 K between 800 and 1200 km depth. In the mid-mantle, all three geotherms have almost the same adiabatic gradient. The absolute values are however very different. At 1800 km depth, one found 2000 K for inverted pyrolite model, 2300 K for inverted chondritic model and 2600 K for inverted cosmic model. At the base of the mantle, all of the best-fit geotherms flatten.

Fig. 6 highlights trade-off between $X_{Pv}$ and temperature. A highly perovskitic lower mantle can be reconciled with observed density and bulk sound velocity profiles only if the mantle geotherm is very hot (~2600 K) whereas pyrolitic values of $X_{Pv}$ yield temperature slightly colder than Brown & Shankland’s geotherm. The inversion of cosmic M3 composition indeed gives on average isothermal lower mantle with $T \sim 2600$ K. Since the a posteriori uncertainties on temperature of M3 model are ~100 K, this hot geotherm can cross over neither the geotherm of Brown & Shankland (1981) nor that inverted from M1 model, which makes this conclusion robust. The interpretation of high temperature at 660 km depth in terms of thermal boundary layer depends on the value of the Clapeyron slope of all phase changes taking place in that region. If we only consider the ringwoodite to perovskite plus magnesiowüstite transition and if we believe the highly negative value of -3.2 MPa/K proposed by Ito & Takahashi (1989), $T_{660} \simeq 2500$ K would be too high to correspond to a discontinuity governed by this phase change and would call for the presence of a pronounced thermal and chemical boundary layer. On the contrary, if the Clapeyron slope is around -0.4 MPa/K as suggested by Katsura et al. (2003), a temperature as high as 2500 K would not necessarily imply any boundary layer at this depth.
4.4 Influence of temperature

The previous inversions indicate that the temperature is a sensitive parameter. If the geotherm were known, one could significantly increase the resolution of other parameters by imposing real lower mantle geotherm. However, there is no general agreement on the lower mantle thermal regime. Recent numerical simulations of mantle convection (e.g. Bunge et al. 2001) shows that the mantle geotherm is not adiabatic, whereas the usual analysis of the seismological profiles (e.g. PREM and ak135) suggests it is close to an adiabatic profile.

In order to study the influence of various geotherms on our inversion, we perform several numerical experiments where the temperature profile is kept fixed (its covariance is strongly reduced). In other words, we invert for the mineralogy only. We consider the geotherm proposed by Brown & Shankland (1981), \( T_1 \), modified by \( \pm 400 \) K and that extracted from Bunge et al. (2001), \( T_2 \). Fig. 7 shows that the inverted mineralogy depends on the choice of the geotherm. This is not surprising because the inversion has to modify other less sensitive parameters (such as \( X_{PV} \) and \( X_{Ca} \)) to match observed density and bulk sound velocity. Variations of \( \pm 400 \) K of Brown & Shankland’s adiabat induce modifications of \( X_{PV} \) by 16%, of \( X_{Ca} \) by 17% and of \( X_{Fe} \) by 12% (shaded areas in Fig. 7). Although \( X_{Fe} \) is the most sensitive parameter, due to the correlation with Mg-bearing end-members, all changes cannot be done only on \( X_{Fe} \). Since the convective geotherm from Bunge et al. (2001) is included within the shaded area, the inverted mineralogy does not exceed those obtained previously. Therefore, the precise evaluation of effects due to imposing subadiabatic gradients is beyond the resolution of the inversion.

Fig. 7 confirms the trade-off between \( X_{PV} \) and temperature that was discussed in section 4.3. It also highlights trade-offs between other parameters: hot lower mantle is likely to be consistent not only with high \( X_{PV} \) but also with high iron content and high calcium perovskite content. Extrapolating this trend, an entirely perovskitic lower mantle \((X_{PV}+X_{Ca}=1)\) would require a temperature higher by \( \approx 900 \) K compared to Brown & Shankland’s geotherm and a corresponding iron content around 0.13. This would lead to a temperature at 660-km discontinuity close to 2800 K. As discussed previously, the existence of a thermal boundary layer between the upper mantle and the lower mantle strongly depends on the Clapeyron slopes of phase changes taking place in this region.

In all cases, the inverted composition seems to be homogeneous throughout the mantle (except the peculiar iron behavior already mentioned). One can estimate that a gradient of bulk composition is only obtained either if the temperature is constant in the mantle or if the temperature gradient is extremely superadiabatic.
4.5 Influence of elastic data

The previous computations have been performed assuming the perfect knowledge of thermodynamical data. However, as discussed in section 2, the equations of state of lower mantle minerals still remain uncertain (see Table 1). In order to take into account these inaccuracies (modelling uncertainties), we have performed several inversions changing the parameter sets of MgSiO$_3$ perovskite, Al$_2$O$_3$ perovskite, CaSiO$_3$ perovskite and periclase.

We first study the effect of bulk modulus of MgPv. Due to the already discussed correlations between elastic parameters, we consider the three different confidence ellipses obtained by assuming three values of $K_{0,T}$ (246, 250, and 261 GPa) and shown in Fig. 1. Inverted composition and temperature profiles are plotted in Fig. 8. The most significant variations are found for temperature and iron content (the two most sensitive parameters): 10% for $X_{Fe}$ and almost 200 K for temperature. In case of $X_{Pv}$ and $X_{Ca}$, only small effects are observed (less than 4%). It should be noticed here that if we do not use the confidence ellipses, in other words, if we do not consider elastic parameters as correlated parameters, but instead if we independently use comparable error bars on $K_{0,T}$, $(\partial K_{0,T}/\partial T)_P$, and $\alpha$, the difference of inverted composition and temperature can be extremely important and significantly increased with depth. In that case, the EoS standing behind such deviations is inconsistent with experimental $P$-$V$-$T$ measurements at high pressure and high temperature (predicted densities deviate from experimental values far beyond their error bars).

Second, we analyze the influence of uncertainties on bulk modulus of AlPv. As discussed in section 2, aluminum is likely to decrease the bulk modulus of perovskite. No general agreement on the amplitude has however been found. We consider the set of elastic parameters given by Zhang & Weidner (1999) as an alternative (extreme) case. The results are very different from those obtained within uncertainties on MgPv (see Fig. 8). Although the temperature profile obtained with Zhang & Weidner’s EoS lies within the uncertainties of MgPv, $X_{Fe}$ is surprisingly low. The iron content decreases from the top ($X_{Fe}=75\%$ of pyrolite value) to the bottom of the mantle where $X_{Fe}$ is divided by a factor 2. This behavior is likely due to the fact that EoS of Al-bearing perovskite by Zhang & Weidner (1999) differs very significantly from that of MgPv. Indeed, the bulk modulus deduced from Zhang & Weidner (1999) is lower than our preferred value by 20% in the mid-mantle ($K_{0,T} \approx 420$ GPa instead of 520 GPa). Small uncertainties on the major phase such as MgPv ($\sim 55$ mol%) has the same effect as large uncertainties on the minor phase such as AlPv ($\sim 4$ mol%).

We have also verified that the EoS obtained for periclase from Dewaele et al. (2000) and for calcium perovskite from Shim et al. (2000) give very similar results compared to our preferred set of parameters. This is because both alternative EoS explain almost equally high pressure and high
temperature $P-V-T$ measurements. We do not think that any further improvement of EoS of MgMw and CaPv will affect our conclusions.

5 DISCUSSION AND CONCLUSION

The Fig. 9 shows the relative differences between the computed density and bulk sound velocity, and those given by PREM and ak135, before and after inversion. As required by the a priori covariances (see equation 1), the inverted parameters match the seismological models within 0.5% for the density and 0.1% for the bulk sound velocity. Although this figure was obtained using pyrolite as an a priori model, similar a posteriori fits are computed for all the inversions discussed in this paper. This is due to the fact that we are dealing with an under-determined inversion and that at least two model parameters are sufficiently sensitive to observed data. We have seen in this study that the iron content and the temperature were the most sensitive parameters of the inversion.

Our results support a uniform chemical composition throughout the lower mantle, except a peculiar behavior of iron content down to $\sim 1300$ km depth. Whatever the a priori compositional model (M1, M2 or M3), the inversion changes the most sensitive parameters (temperature and iron content) in order to match seismic profiles (see Table 4). The inverted compositions $X_{Pv}$ and $X_{Ca}$ are only slightly modified compared to their associated a priori models. In all cases, the iron content is found with very similar values: $X_{Fe}=0.096$ for IM1, $X_{Fe}=0.103$ for IM2 and $X_{Fe}=0.109$ for IM3. The iron content appears as the most robust feature of the inversion.

We find no clear indication for a deep chemically distinct layer or compositional boundary as proposed by Kellogg et al. (1999) and van der Hilst & Kàrason (1999). Recently, Čížkovà & Matyska (2004) have reported that stable layered convection can exist with a net density contrast due to thermal and chemical effects of only about 1%. Such low value of $\Delta \rho$ associated with an undulated boundary located in the lower mantle may be difficult to detect in 1-D seismic profiles and therefore may not be detected by our inversion. In order to rule out or confirm the existence of such boundary, the resolution of the inversion needs to be significantly improved by adding other independent observations.

The average geotherm is not very different from an adiabat. In the case of IM1 model (inverted pyrolite), the resulting temperature profile is colder than the a priori geotherm of Brown & Shankland (1981), ranging from $\sim 1800$ K at the 660-km discontinuity to $\sim 2300$ K at the core-mantle boundary (within $\pm 250$ K of uncertainties). The main difference from the Brown & Shankland’s geotherm is the subadiabaticity observed from 660 km to 1300 km and above 2500 km. This temperature characteristic is correlated with a decreasing iron down to $\sim 1300$ km depth. Although these results are biased by large a posteriori uncertainties, we obtain the same behavior in all numerical experiments performed in this study. We have tested that this combined behavior is due to higher velocity gradients present
both in PREM and ak135. This could be a signature of complex discontinuity at 660 km depth. As previously mentioned, the decomposition of garnets to perovskites can take place over a large region below the 660-km discontinuity (e.g. Hirose et al. 1999). The tomographic imaging also reports complex slab morphology in this region (e.g. Albarède & van der Hilst 2002 for a review). Mantle cross sections reveal that some subducting slab does not penetrate immediately into the lower mantle but instead may flatten at the 660-km discontinuity. Since the iron content is significantly higher in basaltic crust than in the surrounding mantle ($X_{Fe} \sim 0.5$, e.g. Hirose et al. 1999), the slab trapping could lead to an accumulation of iron enriched material in that depth region. These features can be in addition smeared by seismic observation and by averaging when computing radial profiles.

The inverted temperature and composition characteristics can also be expressed using the Bullen parameter $\eta$. Since it is defined as the ratio between compressibilities of real mantle ($d\rho/dz$) and of perfectly homogeneous and adiabatic model, the Bullen parameter measures the departure of the mantle from homogeneity and adiabaticity. We have computed $\eta$ associated with the inverted lower mantle model IM1 (see Fig. 10). Similar values of $\eta$ were found in all numerical experiments performed in this study. Below 1300 km depth, the Bullen parameter is very close to 1 which is consistent with the homogeneous and adiabatic mantle as already discussed. In the region from 800 to 1300 km, the Bullen parameter is significantly lower than one, ranging from 0.95 to 0.99. Since the temperature is found subadiabatic in this region, this value may seem surprising. Indeed, if the bulk composition is constant, subadiabatic temperature induces $\eta > 1$. The values lower than 1 are due to the associated depletion of iron content observed in this region. Since the iron end-members are always denser than the magnesian end-members, the non-homogeneity contribution to $\eta$ is negative and large enough to overcome the positive subadiabatic temperature contribution.

The geotherm is not superadiabatic in any of performed numerical experiments. The temperature obtained at the CMB is at most 3000 K (for entirely perovskite lower mantle). These conclusions are in contradiction with those obtained by da Silva et al. (2000). This is likely because they considered the radial profile of $K_S$ only and had a significantly different set of elastic parameters. They also kept chemical composition fixed and tried to match the $K_S$ seismic profile by changing the temperature only. However, the generalized inversion demonstrates that iron content is equally a sensitive parameter and thus the temperature profile needs to be modified to a much lower gentler gradient and lower values.

This study highlights several important trade-offs between inverted parameters. Fig. 6 demonstrates the positive trade-off between $X_{Pv}$ and temperature. Seismic density and bulk sound velocity may be equally explained either by a “cold” (~2000 K) pyrolite-like composition or by a “hot” (~2600 K) perovskite-rich composition. This results is robust since the two temperature profiles do not overlap.
within their \textit{a posteriori} uncertainties. Fig. 7 shows that a hot geotherm is also associated with a high calcium perovskite content as well as a high iron ratio. A hot lower mantle would imply the existence of a thermal and chemical boundary between the lower and the upper mantle and would favor a layered convection, if the transition from ringwoodite to perovskite is responsible for the seismic 660-km discontinuity and if its associated Clapeyron slope is as steep as suggested by Ito & Takahashi (1989). To discriminate between different models from radial profiles, more accurate independent observations such as shear properties are required. Since the latter also seem to be more sensitive to presence of minor elements (Karki & Crain 1998, Jackson et al. 2004), they should help to constrain not only temperature but also abundances of calcium and aluminum.

Despite taking particular care in selecting elastic parameters, \textit{a posteriori} uncertainties resulting from their inaccurate knowledge remain large. The inverted composition and temperature are sensitive to the selected data. We believe that differences in conclusions between most previous studies are coming from different choice of elastic parameters. It is therefore delicate to compare directly results from various studies without checking their database. Although MgPv is about ten times more abundant than AlPv, the inaccuracy of the EoS of AlPv, especially of its \( (\partial K_{0,T}/\partial T)_P \) and \( \alpha \), is a predominant source of uncertainties. It should be noticed here that we have also tested the influence of various models when averaging \( K_S \) (Reuss, Voigt, Reuss-Voigt-Hill average). \( X_{Pv} \) and \( X_{Ca} \) are not sensitive to this averaging. Assuming Voigt average instead of Hill average leads to an iron content higher by 7% and a temperature higher by at most 150 K. The resulting uncertainties are however of less importance than those induced by inaccuracy of EoS of MgPv.

We demonstrated that the iron partitioning coefficient is not a crucial parameter in constraining the lower mantle composition and temperature since the resulting inverted parameters do not depend on the value of \( K_D \). It can be explained by the fact that moderate iron content has small effect on thermoelastic properties. This result \textit{a posteriori} validates our choice of ideal solid solution model as well as our choice of calorimetric data (\( \Delta H_f^0 \), \( S_0 \) and \( C_P \)) of perovskite and magnesiowüstite. A more sophisticated solid solution model seems unnecessary. Even an extreme \( K_D \) variation within the lower mantle (Badro et al. 2003) would not significantly change our conclusions. This conclusion will however not be valid anymore if observations sensitive to iron partitioning are used as may be the case of the shear properties.

Indeed, the analysis of the inversion results calls for the incorporation of the shear properties into the inversion. They could potentially give additional constraints on the inversion features, and for instance, could confirm or rule out the peculiar behaviors of iron and temperature at the top of the lower mantle. Shear properties may also be more sensitive to minor elements. Previous studies have suggested that CaPv behaves as an invisible component in the lower mantle in terms of density
and bulk modulus (Wang et al. 1996, Shim et al. 2000). Karki & Crain (1998) have proposed that analysis of its shear properties can be used to constrain the abundance of calcium in the lower mantle. Aluminum and iron seem to have significant effect on shear properties (Jackson et al. 2004, Kiefer et al. 2002). The complete $P$-$T$-$\mu$ data set for the six lower mantle end-members is not available yet. In order to use high quality measurements of shear properties for an inverse problem, a careful analysis of the effect of anelastic attenuation (e.g Karato 1993) is also required. This is beyond the scope of our paper and will be treated in a forthcoming study.
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Table 1. Elastic properties of lower mantle minerals: MgSiO$_3$ perovskite (MgPv), FeSiO$_3$ perovskite (FePv), Al$_2$O$_3$ perovskite (AlPv) for the perovskite phase, MgO periclase (MgMw), FeO wüstite (FeMw) for the magnesiowüstite phase and CaSiO$_3$ perovskite (CaPv) for the calcium perovskite phase.

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<td></td>
<td>cm$^3$.mol$^{-1}$</td>
<td>GPa</td>
<td>GPa.K$^{-1}$</td>
<td></td>
<td>10$^{-5}$ K$^{-1}$</td>
<td>10$^{-8}$ K$^{-2}$</td>
</tr>
<tr>
<td>MgPv</td>
<td>24.43$^1$</td>
<td>250$^2$</td>
<td>4.0$^3$</td>
<td>-0.021$^{\pm}$0.004$^4$</td>
<td>2.461$^{\pm}$0.119</td>
<td>0.165$^4$</td>
</tr>
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<td></td>
</tr>
<tr>
<td>FePv</td>
<td>25.34$^4$</td>
<td>250$^7$</td>
<td>4.0$^7$</td>
<td>-0.021$^{\pm}$0.004$^7$</td>
<td>2.461$^{\pm}$0.119</td>
<td>0.165$^7$</td>
</tr>
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<td></td>
<td></td>
</tr>
<tr>
<td>AlPv*</td>
<td>24.58$^8$</td>
<td>249$^8$</td>
<td>4.0$^9$</td>
<td>-0.021$^7$</td>
<td>2.461</td>
<td>0.165$^7$</td>
</tr>
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<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MgMw</td>
<td>11.25$^{11}$</td>
<td>160.1$^{12}$</td>
<td>3.83$^{12}$</td>
<td>-0.022$^{\pm}$0.001$^4$</td>
<td>3.265</td>
<td>1.065$^4$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>FeMw</td>
<td>12.26$^4$</td>
<td>160.1$^4$</td>
<td>3.83$^4$</td>
<td>-0.020$^{14}$</td>
<td>3.203</td>
<td>0.629$^{15}$</td>
</tr>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CaPv</td>
<td>27.45$^{16}$</td>
<td>232$^{16}$</td>
<td>4.8$^{16}$</td>
<td>-0.033$^{16}$</td>
<td>3.133</td>
<td>0.388$^4$</td>
</tr>
<tr>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>27.45$^{17}$</td>
<td>236$^{17}$</td>
<td>3.9$^{17}$</td>
<td>-0.028$^{17}$</td>
<td>3.690</td>
<td>0.000$^4$</td>
</tr>
</tbody>
</table>

If multiple choice, the preferred values are in bold. $V_0$, molar volume, $K_{0,T}$, isothermal bulk modulus, $K'_{0,T}$ and $(\partial K_{0,T}/\partial T)_P$, its pressure and temperature derivatives; $\alpha(T) = \alpha_0 + \alpha_1 T$, thermal expansion coefficients.

* Al-bearing MgSiO$_3$ perovskite with 5 mol% Al$_2$O$_3$.

1 e.g. Fiquet et al. (1998); 2 after Sinogeikin et al. (2004); 3 fixed to 4 as Fiquet et al. (1998); 4 see text; 5 Yeganeh-Haeri et al. (1989); 6 e.g. Mao et al. (1991); 7 same as MgPv; 8 after Jackson et al. (2004); 9 Daniel et al. (2004); 10 Zhang & Weidner (1999); 11 Jackson & Niesler (1982); 12 after Sinogeikin & Bass (2000); 13 Dewaele et al. (2000); 14 Sumino et al. (1980); 15 Skinner (1966); 16 Wang et al. (1996); 17 Shim et al. (2000).
Table 2. Enthalpy of formation $\Delta H_{0}^{f}$, and entropy $S_{0}$, at standard conditions, $P_{0} = 1$ bar and $T_{0} = 298$ K.

<table>
<thead>
<tr>
<th></th>
<th>$\Delta H_{0}^{f}$</th>
<th>$S_{0}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>kJ.mol$^{-1}$</td>
<td>J.mol$^{-1}$.K$^{-1}$</td>
</tr>
<tr>
<td>MgPv</td>
<td>-1442.50$^{1}$</td>
<td>58.29$^{2}$</td>
</tr>
<tr>
<td>FePv</td>
<td>-1090.10$^{1}$</td>
<td>100.77$^{1}$</td>
</tr>
<tr>
<td>MgMw</td>
<td>-601.49$^{1}$</td>
<td>26.94$^{1}$</td>
</tr>
<tr>
<td>FeMw</td>
<td>-267.27$^{1}$</td>
<td>57.59$^{1}$</td>
</tr>
</tbody>
</table>

$^{1}$ Fei et al. (1991); $^{2}$ Vibrational approach after Gillet et al. (2000).

Table 3. Average inverted compositions assuming different iron partitioning $K_{D}$ and compared to a priori pyrolite composition (Ringwood 1982). See equations 2 and 4 for definitions of $X_{Pv}$, $X_{Ca}$ and $X_{Fe}$.

<table>
<thead>
<tr>
<th></th>
<th>$X_{Pv}$</th>
<th>$X_{Ca}$</th>
<th>$X_{Fe}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyrolite</td>
<td>0.622</td>
<td>0.051</td>
<td>0.104</td>
</tr>
<tr>
<td>$K_{D}^{(1)} = 1$</td>
<td>0.643 ± 0.172</td>
<td>0.054 ± 0.036</td>
<td>0.096 ± 0.062</td>
</tr>
<tr>
<td>$K_{D}^{(2)} = 0.25$</td>
<td>0.664 ± 0.159</td>
<td>0.057 ± 0.038</td>
<td>0.097 ± 0.050</td>
</tr>
</tbody>
</table>
Table 4. Average inverted compositions for several *a priori* models and associated estimation of the temperature at the 660-km discontinuity, $T_{660}$, and at the core mantle boundary, $T_{CMB}$. Except for model M11 (see below), the temperature is a free parameter and the *a priori* temperature profile is the geotherm of Brown & Shankland 1981.

<table>
<thead>
<tr>
<th></th>
<th>$X_{Pv}$</th>
<th>$X_{Ca}$</th>
<th>$X_{Fe}$</th>
<th>$T_{660}$ (K)</th>
<th>$T_{CMB}$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyrolite*</td>
<td>0.622</td>
<td>0.051</td>
<td>0.104</td>
<td>1873</td>
<td>2450</td>
</tr>
<tr>
<td>IM11</td>
<td>0.643 ± 0.172</td>
<td>0.054 ± 0.036</td>
<td>0.096 ± 0.062</td>
<td>1800</td>
<td>2300</td>
</tr>
<tr>
<td>IM11</td>
<td>0.687 ± 0.103</td>
<td>0.059 ± 0.033</td>
<td>0.101 ± 0.027</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

* Ringwood (1982), M1 model; 1 IM1, inverted M1 model: inverted composition when pyrolite is the *a priori* composition and the temperature is free; 2 IM11: inverted composition when pyrolite is the *a priori* composition and the temperature is fixed to the Brown & Shankland’s geotherm.

<table>
<thead>
<tr>
<th></th>
<th>$X_{Pv}$</th>
<th>$X_{Ca}$</th>
<th>$X_{Fe}$</th>
<th>$T_{660}$ (K)</th>
<th>$T_{CMB}$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chondrite CI*</td>
<td>0.761</td>
<td>0.048</td>
<td>0.113</td>
<td>1873</td>
<td>2450</td>
</tr>
<tr>
<td>IM2</td>
<td>0.741 ± 0.174</td>
<td>0.047 ± 0.031</td>
<td>0.103 ± 0.067</td>
<td>2200</td>
<td>2500</td>
</tr>
<tr>
<td>Cosmic</td>
<td>0.830</td>
<td>0.041</td>
<td>0.068</td>
<td>1873</td>
<td>2450</td>
</tr>
<tr>
<td>IM3</td>
<td>0.843 ± 0.184</td>
<td>0.039 ± 0.025</td>
<td>0.109 ± 0.077</td>
<td>2500</td>
<td>2700</td>
</tr>
</tbody>
</table>

* McDonough & Sun (1995), M2 model; c Anderson & Bass (1986), M3 model; 3 IM2, inverted M2 model: inverted composition when chondrite composition is the *a priori* composition and the temperature is free; 4 IM3, inverted M3 model: inverted composition when cosmic composition is the *a priori* composition and the temperature is free.
LIST OF FIGURES

1 Values of \( \left( \partial K_{0,T} / \partial T \right)_P \) and \( \alpha_0 \) of MgSiO\(_3\) perovskite (MgPv) deduced from generalized inversion of \( P-V-T \) measurements assuming \( K_{0,T} \)(MgPv) is either equal to 246 GPa, or 250 GPa, or 261 GPa. The \( P-V-T \) measurements are taken from Fiquet et al. (1998), Fiquet et al. (2000). The associated confidence ellipses (2\( \sigma \) level) indicate strong anti-correlation between the two parameters. An increase of the nominal value of \( K_{0,T} \) shifts the confidence ellipse towards lower \( \alpha \) and \( \left( \partial K_{0,T} / \partial T \right)_P \) values (towards lower left corner) revealing strong trade-offs between elastic parameters.

2 Influence of iron partitioning on lower mantle mineralogy (a, b, c) and temperature (d). The dashed curves represent the \textit{a priori} model: the pyrolite composition and the geotherm given by Brown & Shankland (1981). Other curves corresponds to different values of partitioning coefficient \( K_D^{(1)} = 1 \) (solid), \( K_D^{(2)} = 0.25 \) (long dashed), \( K_D^{(3)} \) computed from thermodynamical equilibrium (light dot-dashed). The predicted geotherms are subadiabatic and below the \textit{a priori} temperature profile by \( \sim 180 \) K in the mid-mantle.

3 Inverted depth dependent profiles of \( X_{Pv} \), \( X_{Ca} \), \( X_{Fe} \) and temperature \( T \) with their \textit{a priori} and \textit{a posteriori} uncertainties (light and dark gray shading). \textit{A priori} model is pyrolite composition and geotherm of Brown & Shankland (1981). Due to large \textit{a priori} uncertainties, scale of subfigures (c) and (d) have been extended. \( X_{Fe} \) and temperature are rather well resolved. \( X_{Ca} \) is not constrained by inversion of density and bulk sound velocity.

4 Depth dependence of inverted molar fractions of individual end-members: MgSiO\(_3\) perovskite (MgPv), FeSiO\(_3\) perovskite (FePv), Al\(_2\)O\(_3\) perovskite (AlPv), CaSiO\(_3\) perovskite (CaPv), periclase (MgMw) and wüsite (FeMw). \textit{A priori} model is pyrolite composition and geotherm of Brown & Shankland (1981). Shaded areas depict their \textit{a priori} and \textit{a posteriori} uncertainties (light and dark gray shading). Iron-bearing end-members are better constrained than others. Aluminum and calcium perovskite are poorly resolved by the join inversion of \( \rho \) and \( V_p \).

5 Normalized coefficients \( c \) of correlation matrix between inverted end-members : periclase (MgMw), wüsite (FeMw), CaSiO\(_3\) perovskite (CaPv), Al\(_2\)O\(_3\) perovskite (AlPv) molar abundances and temperature (T). The two oxides end-members are strongly correlated and anticorrelated with temperature. The values are taken in the mid-mantle when the \textit{a priori} model M1, pyrolite composition and Brown & Shankland (1981) geotherm, is inverted. A similar matrix holds throughout the mantle.
Influence of a priori compositional model on inverted lower mantle mineralogy (a,b,c) and temperature (d). In all cases, the temperature is inverted from the a priori Brown & Shankland’s geotherm (dotted line on graph d). M1 (circle): a priori pyrolite composition (Ringwood 1982); IM1 (solid line): associated inverted model. M2 (square): a priori chondritic CI composition (McDonough & Sun 1995); IM2 (dot-dashed line): associated inverted model. M3 (triangle): a priori cosmic composition (Anderson & Bass 1986); IM3 (long dashed line): associated inverted model. $X_{\text{Fe}}$ and temperature are the most sensitive parameters, whereas $X_{\text{Pv}}$ and $X_{\text{Ca}}$ remain close to their a priori values. There is a strong positive trade-off between $X_{\text{Pv}}$ and temperature. Seismic density and bulk sound velocity profiles can be explained either by a “cold” (i.e. ~2000 K) pyrolite-like lower mantle ($X_{\text{Pv}}$~0.64) or by a “hot” (i.e. ~2600 K) perovskitic lower mantle ($X_{\text{Pv}}$~0.84). The resulting uncertainties on temperature profiles do not allow these two profiles to cross over, making this observation a robust result.

Influence of fixed temperature profile (d) on inverted mineralogy (a, b, c) using pyrolite as an a priori composition. In order to study effect of hot and cold geotherms, Brown & Shankland’s geotherm ($T_1$, solid line) is plotted with error-bars of ±400 K (shaded area). An example of geotherm from convection modelling is taken from Bunge et al. 2001 ($T_2$, dot-dashed line). Fixing temperature implies significant modifications of all compositional parameters. A hot lower mantle is associated with high values of $X_{\text{Pv}}$, $X_{\text{Ca}}$ and $X_{\text{Fe}}$. A pure perovskitic lower mantle (i.e. $X_{\text{Pv}}+X_{\text{Ca}}$=1) would call for a geotherm hotter by ~900 K compared to profile $T_1$. This would lead to the existence of a thermal and chemical boundary layer between the upper mantle and the lower mantle. In all cases, the composition is uniform throughout the lower mantle, except the peculiar behavior of $X_{\text{Fe}}$ down to ~1300 km depth. A non-uniform composition would be obtained if the lower mantle were either isothermal or superadiabatic.
Influence of elastic data of MgPv and AlPv on inverted parameters. Uncertainties on bulk modulus $K_{0,T}$ of MgPv are considered, using values of 246, 250 and 261 GPa, with associated correlated parameters $(\partial K_{0,T}/\partial T)_P$ and $\alpha_0$ within the three ellipses of Fig. 1 (corresponding results with shading area). $X_{Fe}$ and temperature are the most sensitive parameters. Equation of state parameters given by Zhang & Weidner (1999) are taken as an alternative extreme set for AlPv (dot-dashed line). This leads to unusual values of $X_{Fe}$, decreasing from the top, where $X_{Fe}\approx 75\%$ of the pyrolite value, to the bottom of the lower mantle, where $X_{Fe}$ reaches surprising low value of $\sim 0.04$. The temperature remains within the area resulting of uncertainties on MgPv. Alternative sets for MgMw (Dewaele et al. 2000) and for CaPv (Shim et al. 2000) give very similar results as those obtained with preferred elasticity datasets. Despite the fact that considerable attention has been given to experiments on MgPv, the uncertainties still significantly impact our conclusions.

Profiles of density ($\rho$) and bulk sound velocity ($V_\theta$) before and after inversion. These properties are plotted as residuals relative to the seismic models PREM (Dziewonski & Anderson 1981) and ak135 (Kennett et al. 1995). As required by our inversion, the inverted parameters match both PREM and ak135 models, within 0.5% for density and within 0.1% for bulk sound velocity. All the inversions discussed in this paper lead to similar a posteriori fits.

Computed Bullen parameter $\eta$ associated with the inverted lower mantle model IM1 (pyrolite composition and Brown & Shankland’s geotherm as an a priori model). Below 1300 km, $\eta$ is close to 1, in agreement with a homogeneous and adiabatic lower mantle as discussed in the text. From 800 km to 1300 km, it is significantly lower than 1, ranging from 0.95 to 0.99. Since in this region the associated temperature profile is subadiabatic, this is due to the iron depletion. Its contribution to $\eta$ is negative and large enough to counterbalance the positive subadiabatic contribution. Similar Bullen parameters are computed in all the numerical experiments performed in this study.
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Composition and temperature of the lower mantle

Figure 5. Normalized coefficients $c$ of correlation matrix between inverted end-members: periclase (MgMw), wustite (FeMw), CaSiO$_3$ perovskite (CaPv), Al$_2$O$_3$ perovskite (AlPv) molar abundances and temperature (T). The two oxides end-members are strongly correlated and anticorrelated with temperature. The values are taken in the mid-mantle when the a priori model M1, pyrolite composition and Brown & Shankland (1981) geotherm, is inverted. A similar matrix holds throughout the mantle.
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Figure 7. Influence of fixed temperature profile (d) on inverted mineralogy (a, b, c) using pyrolite as an *a priori* composition. In order to study effect of hot and cold geotherms, Brown & Shankland’s geotherm (*T*₁, solid line) is plotted with error-bars of ±400 K (shaded area). An example of geotherm from convection modelling is taken from Bunge et al. 2001 (*T*₂, dot-dashed line). Fixing temperature implies significant modifications of all compositional parameters. A hot lower mantle is associated with high values of *X*ₚᵥ, *X*₈₀ and *X*₇₀. A pure perovskitic lower mantle (*i.e.* *X*ₚᵥ+*X*₈₀=1) would call for a geotherm hotter by ~900 K compared to profile *T*₁. This would lead to the existence of a thermal and chemical boundary layer between the upper mantle and the lower mantle. In all cases, the composition is uniform throughout the lower mantle, except the peculiar behavior of *X*₇₀ down to ~1300 km depth. A non-uniform composition would be obtained if the lower mantle were either isothermal or superadiabatic.
Figure 8. Influence of elastic data of MgPv and AlPv on inverted parameters. Uncertainties on bulk modulus $K_{0,T}$ of MgPv are considered, using values of 246, 250 and 261 GPa, with associated correlated parameters $(\partial K_{0,T}/\partial T)_P$ and $\alpha_0$ within the three ellipses of Fig. 1 (corresponding results with shading area). $X_{Fe}$ and temperature are the most sensitive parameters. Equation of state parameters given by Zhang & Weidner (1999) are taken as an alternative extreme set for AlPv (dot-dashed line). This leads to unusual values of $X_{Pv}$, decreasing from the top, where $X_{Fe}$<~75% of the pyrolite value, to the bottom of the lower mantle, where $X_{Fe}$ reaches surprising low value of ~0.04. The temperature remains within the area resulting of uncertainties on MgPv. Alternative sets for MgMw (Dewaele et al. 2000) and for CaPv (Shim et al. 2000) give very similar results as those obtained with preferred elasticity datasets. Despite the fact that considerable attention has been given to experiments on MgPv, the uncertainties still significantly impact our conclusions.
Figure 9. Profiles of density ($\rho$) and bulk sound velocity ($V_\phi$) before and after inversion. These properties are plotted as residuals relative to the seismic models PREM (Dziewonski & Anderson 1981) and ak135 (Kennett et al. 1995). As required by our inversion, the inverted parameters match both PREM and ak135 models, within 0.5% for density and within 0.1% for bulk sound velocity. All the inversions discussed in this paper lead to similar a posteriori fits.
Figure 10. Computed Bullen parameter $\eta$ associated with the inverted lower mantle model IM1 (pyrolite composition and Brown & Shankland’s geotherm as an a priori model). Below 1300 km, $\eta$ is close to 1, in agreement with a homogeneous and adiabatic lower mantle as discussed in the text. From 800 km to 1300 km, it is significantly lower than 1, ranging from 0.95 to 0.99. Since in this region the associated temperature profile is subadiabatic, this is due to the iron depletion. Its contribution to $\eta$ is negative and large enough to counterbalance the positive subadiabatic contribution. Similar Bullen parameters are computed in all the numerical experiment performed in this study.
APPENDIX A: BULK PROPERTIES OF AN ASSEMBLAGE AT HIGH P AND HIGH T

Birch Murnaghan equation of state

We use the Birch-Murnaghan equation of state (3rd order) to relate pressure $P$, temperature $T$ and volume $V$ (Bullen 1975):

$$P = \frac{3}{2} K_T \left[ \left( \frac{V_{T,0}}{V} \right)^{\frac{7}{3}} - \left( \frac{V_{T,0}}{V} \right)^{\frac{5}{3}} \right] \times \left\{ 1 - \frac{3}{4} (4 - K'_{0,T}) \left[ \left( \frac{V_{T,0}}{V} \right)^{\frac{4}{3}} - 1 \right] \right\} \quad (A1)$$

where $K_T$, $K'_{0,T}$ and $V_{T,0}$ are the isothermal bulk modulus, its pressure derivative and the volume at ambient pressure and temperature $T$ (in K). $K'_{0,T}$ is assumed to be a constant. $K_T$ and $V_{T,0}$ are obtained from parameters at ambient conditions as follows:

$$K_T = K_{0,T} + \left( \frac{\partial K_{0,T}}{\partial T} \right)_P (T - 298) \quad (A2)$$

$$V_{T,0} = V_0 \exp \left( \int_{298}^{T} \alpha(T')dT' \right) \quad (A3)$$

where $K_{0,T}$ and $V_0$ are the values at ambient conditions ($P = 1$ bar, $T = 298$ K), and $(\partial K_{0,T}/\partial T)_P$ is assumed to be a constant, $\alpha(T)$ is the thermal expansion at ambient pressure and at temperature $T$.

We assume a linear dependence of $\alpha$ with temperature: $\alpha(T) = \alpha_0 + \alpha_1 T$.

Bulk properties of an assemblage

From the molar abundances $n_i$ of each end-member $i$, the molar volume of a lower mantle assemblage is deduced from

$$V = \sum_i n_i V_i, \quad (A4)$$

where $V_i$ is the partial molar volume of the end-member $i$. The other bulk properties are obtained as follows:

a) density $\rho$ from

$$\rho = \frac{1}{V} \sum_i n_i M_i, \quad (A5)$$

where $M_i$ is the molar weight,

b) adiabatic incompressibility $K_S$ by using its thermodynamical definition, i.e. an incompressibility corresponding to the Reuss average for an assemblage (Watt et al. 1976) from

$$K_S = -V \left( \frac{\partial P}{\partial V} \right)_S = V \left( \sum_i n_i \frac{V_i}{K_{S_i}} \right)^{-1}, \quad (A6)$$

where $K_{S_i}$ is

$$K_{S_i} = K_{T_i} \left( 1 + \frac{\alpha_i^2 V_i K_{T_i} T}{C_{V_i}} \right), \quad (A7)$$

where $C_{V_i}$ is the heat capacity at constant volume (see below),
Table A1. Heat capacity at standard pressure $P = 1$ bar.

\begin{align*}
\text{\textit{C}_P^*} & \quad \text{Jmol}^{-1}\text{K}^{-1} \\
& \quad a_1 \quad a_2 \quad a_3 \quad a_4 \quad a_5 \quad a_6 \quad a_7 \\
& \quad 10^2 \quad 10^{-2} \quad 10^7 \quad 10^{-6} \quad 10^9 \quad 10^4 \quad 10^4 \\
\text{MgPv} & \quad 0.361^1 \quad 1.576 \quad 0.415 \quad 0.870 \quad -0.072 \quad 0.476 \quad -8.284 \\
\text{FePv} & \quad 1.422^2 \quad 0.154 \quad -0.119 \quad 0.000 \quad 0.274 \quad 0.000 \quad -1.454 \\
\text{AlPv} & \quad 1.166^3 \quad 0.155 \quad -0.590 \quad 1.624 \quad 0.676 \quad 0.043 \quad -0.607 \\
\text{MgMw} & \quad 0.334^1 \quad 0.430 \quad 0.006 \quad 0.402 \quad 0.040 \quad 0.092 \quad -1.596 \\
\text{FeMw} & \quad 0.684^2 \quad 0.119 \quad 0.170 \quad 0.000 \quad 0.135 \quad 0.000 \quad -1.188 \\
\text{CaPv} & \quad 0.970^3 \quad 0.811 \quad -0.221 \quad 1.845 \quad 0.355 \quad 0.167 \quad -3.100 \\
\end{align*}

\* $C_P(T) = a_1 + a_2 T + a_3 T^{-2} + a_4 T^2 + a_5 T^{-3} + a_6 T^{-1/2} + a_7 T^{-1}$

\begin{enumerate}
\item Vibrational approach after Gillet et al. (2000);  \textsuperscript{2} Fei et al. (1991);  \textsuperscript{3} Debye model.
\end{enumerate}

c) bulk sound velocity $V_\phi$ from

$$V_\phi = \sqrt{\frac{K_S}{\rho}}. \quad \text{(A8)}$$

**Heat capacity**

The thermodynamical equilibrium at pressure $P$ and temperature $T$ between the perovskite and magnesiowüstite phases is defined by the equation 7 reported in the section 4.1. It requires the computation of the standard chemical potentials $\mu_i^0(P, T)$ at pressure $P$ and temperature $T$ of each end-member $i$. The heat capacity of each end-member is needed to compute each $\mu_i^0$ at $P$ and $T$. It is also used to compute the heat capacities at constant volume $C_V$ via the expression $C_V = C_P - \alpha^2 VT$. 