On the Vp/Vs–Mg# correlation in mantle peridotites: Implications for the identification of thermal and compositional anomalies in the upper mantle

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1. Introduction

The seismological structure of the Earth's upper mantle is known to be highly heterogeneous (Grand, 2002; Li et al., 2008), and much of this heterogeneity is associated with the lithosphere's thermal and compositional structure. Lithospheric discontinuities (i.e. sharp changes in the thermal and/or compositional structure) commonly correlate with the location of seismically active zones, major tectonic boundaries, foci of magma intrusion and major ore deposits (Carlson et al., 2005; Begg et al., 2009). Characterizing and understanding the small-scale (ca 300 km) distribution of thermal and compositional anomalies within the lithosphere is therefore one of the main goals of modern lithospheric modelling.

Seismic tomography provides a unique direct probe of the Earth's three-dimensional thermo-chemical structure. However, owing to resolution limitations and trade-offs between temperature and composition, the seismological detection of small-scale compositional heterogeneities in the upper mantle has proven elusive (Romanowicz, 2008; Afonso et al., 2008). A fundamental problem is the lack of reliable quantitative relationships or indicators (derived from seismic data) that can distinguish between compositional and thermal contributions to variations in seismic velocity. Additionally, uncertainties associated with elastic parameters of some important mantle phases are still significant (see e.g. Table 1 in Stixrude and Lithgow-Bertelloni, 2007). In this context, parameters such as the ratio of compressional to shear wave velocity (Vp/Vs) or the Poisson's ratio \( \nu = 0.5 \frac{(Vp/Vs)^2 - 2}{(Vp/Vs)^2 - 1} \) have been proposed as reliable indicators of compositional variations in peridotites, and have been widely used to infer the thermal and compositional state of the upper mantle (e.g. Lee, 2003; Niu et al., 2004; Speziale et al., 2005;...
systems CFMAS, NCFMAS, and Cr-NCFMAS. To test for any potential computed self-consistently by free-energy minimization within the composition and temperature in upper mantle rocks is lacking. ∼ (Mg# values from Supplementary Table 1). This dataset spans a range of composition spinel peridotite xenoliths from different tectonic settings (see We use the bulk rock compositions of 100 well-studied garnet and clinopyroxene, spinel, feldspars, and garnet were treated as solid solutions using the thermodynamic models summarized by Connolly (2005). For the Cr-NCFMAS system, thermodynamic databases and solution models are identical to those described in Simon and Podladchikov (2008). We also have run parallel computations within the CFMAS system using two different databases and solution models (i.e. Holland and Powell, 1998; Stixrude and Lithgow-Bertelloni, 2005). As shown below, our conclusions apply to all three systems since neither the addition of Na and Cr nor the use of different databases and/or solution models affect our analysis. The physical properties of interest are all outputs of the free-energy minimization scheme. We refer to this method as the energy minimization approach (hereafter EMA; cf. Afonso et al., 2008). The main advantage of EMA is that it maximizes thermodynamic self-consistency, therefore providing a robust description of both phase equilibria and physical properties. However, fourth-order effects in ortho-enstatite and/or orthopyroxene, clinopyroxene, spinel, feldspars, and garnet were treated as solid solutions (i.e. 127 GPa) with that reported inSpeziale et al. (2004; i.e. 136.5 GPa). Although these parameters have been successfully applied at relatively small amounts of Cr (Cr/Cr+Al ≤ 0.2) may have a strong influence on the stability field of spinel (Klemme, 2004), although the exact extent of this effect in natural systems is still not well constrained (Webb and Wood, 1986). Likewise, Na2O can perturb the equilibrium modal proportions of ortho- and clinopyroxene, as well as the location of the Al-rich phase transitions (Stixrude and Lithgow-Bertelloni, 2005; Simon and Podladchikov, 2008). In order to assess whether the addition of these oxides has an effect in our results, we have performed parallel computations on representative samples within the systems NCFMAS and Cr-NCFMAS. In the case of the NCFMAS system, we used the database of Holland and Powell (1998; revised 2002). Olivine, orthopyroxene, clinopyroxene, spinel, feldspars, and garnet were treated as solid solutions in a previous step. Combined methods such as this one are sometimes referred to as hybrid (e.g. Stixrude and Lithgow-Bertelloni, 2005; Afonso et al., 2008), and have been extensively used to study the physical properties of the mantle. This approach permits the inclusion of higher-order effects in the calculations of physical properties, but at the cost of strict self-consistency. Nevertheless, the variation of density and seismic velocities with P, T, and X is identical in both approaches (EMA and ECA) within the range of pressures of interest (1 – 10 GPa), although their absolute values at specific P–T–X conditions can differ by as much as 0.5 and 1%, respectively (see Section 5.2). As a third independent confirmation of our results, we also have used the spreadsheet of Hacker and Abers (2004) for selected samples. Again, the same general behaviour of the system is observed.

2.2. Anelasticity

Viscoelastic relaxation of the elastic moduli in mantle assemblages is the main factor responsible for the intrinsic attenuation of seismic waves (Karato, 1993; Jackson et al., 2002). Assuming Qp = 9/4 Qs (i.e. Song and Helmberger, 2007; Artemieva and Thybo, 2008; Chou et al., 2009). Although these parameters have been successfully applied at crustal P–T–X conditions (X stands for composition) and possibly to locate zones of partial melting in the mantle wedge, we show here that their extension to general upper mantle conditions encounters serious limitations due to the effects of temperature-dependent non-elastic behaviour and phase stability. This implies that for most of the upper mantle compositional effects cannot be unambiguously separated from thermal effects on the basis of seismological studies alone. The ratio of density to shear wave velocity (ρ/Vs) is considered to be superior (e.g. Forte and Perry, 2000; Deschamps et al., 2002; Perry et al., 2003), but a quantitative analysis of its dependence on composition and temperature in upper mantle rocks is lacking. This paper reports a systematic assessment of thermal and compositional effects on densities and seismic velocities in peridotites, applying thermodynamically self-consistent and hybrid methods, the latest mineral physics databases, and experimental results on the non-elastic behaviour of olivine aggregates at seismic frequencies. We use the bulk rock compositions of 100 well-studied garnet and spinel peridotite xenoliths from different tectonic settings (see Supplementary Table 1). This dataset spans a range of composition (Mg# values from ~88 to 95) covering most of the expected variability within the lherzolitic mantle (Pearson et al., 2005). Stable phases, modal proportions, and physical properties are computed self-consistently by free-energy minimization within the systems CFMAS, NCFMAS, and Cr-NCFMAS. To test for any potential bias from the minimization method, we also calculate all physical properties with more standard hybrid methods (Hacker and Abers, 2004; Afonso et al., 2008). We find that neither variations in system components nor the computation method affects our conclusions.

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Anharmonic P–T derivatives for garnet- and spinel-bearing peridotites.</th>
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<tbody>
<tr>
<td>Garnet</td>
<td>∂(Vp/VT)/∂T (km s⁻¹°C⁻¹)</td>
</tr>
<tr>
<td>Spinel</td>
<td>−5.1(±5)×10⁻⁴</td>
</tr>
<tr>
<td>ρ</td>
<td>3.3(±2)×10⁻⁴</td>
</tr>
</tbody>
</table>

Derivatives are averages for the ranges 800–1400 °C and 1.5–P ≤ 8 GPa. Values within brackets indicate the uncertainty in the last digit due to compositional variability. These uncertainties are large enough to preclude reliable estimates of second-order compositional derivatives.

a ∂(Vp/VT)/∂T increases slightly with both pressure and temperature.
b ∂(Vp/Vs)/∂T can be either positive or negative with T depending on the relative amounts of pyroxenes (see text).
in the upper mantle, we compute anelastic effects as a function of grain size \( (d) \), oscillation period \( (T_o) \), temperature \( (T) \), pressure \( (P) \), and empirical parameters \( A, E, \) and \( \alpha \) (Karato, 1993; Afonso et al., 2008)

\[
V_p = V_{p0}(T, P)[1 - (2/9) \cot(\alpha \pi/2) Q_s^{-1}(T_o, T, P, d)]
\]

\[
V_s = V_{s0}(T, P)[1 - (1/2) \cot(\alpha \pi/2) Q_s^{-1}(T_o, T, P, d)]
\]

where \( V_{p0}(T, P) \) and \( V_{s0}(T, P) \) are the unrelaxed high-frequency wave velocities at a given temperature and pressure (i.e. including anharmonic effects) and \( Q_s^{-1}(T_o, T, P, d) = A \{T_o (d^{-1} \exp[-(E + V P)/RT])\}^{\alpha}, \) with 

\[ A = 750 \text{ s}^{-1} \mu \text{m}, \quad \alpha = 0.26, \quad E = 424 \text{ kJ mol}^{-1}, \quad V = 1.3 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}, \]

and \( R \) is the universal gas constant (Jackson et al., 2002). At this stage we cannot account for attenuation effects other than in polycrystalline olivine samples (to which the above parameters apply) due to lack of experimental data on polyphase samples. Additionally, the effect of water on seismic velocities through enhancement of attenuation (e.g. Karato, 2005) is not considered here, so our estimates are likely to represent lower bounds.

3. Xenolith samples

All thermophysical properties relevant to our study are dependent only on the major-element composition, and not on trace-element abundances. We use the bulk compositions of 100 well-studied spinel and garnet peridotites, including xenoliths from both subcontinental lithospheric mantle (SCLM) and oceanic mantle, as well as samples from selected orogenic massifs (Fig. 1). The Mg# [i.e. atomic ratio=100×MgO/(MgO+FeO)] of these samples ranges from \( \sim 88 \) (in fertile lherzolites) to 95 (in dunites). This wide compositional range includes most of the expected variability in mantle peridotites

![Fig. 1. Plots of major-element oxides versus \( \text{Al}_2\text{O}_3 \) for the samples used in this study. Dashed envelopes include \( \sim 95\% \) of all the peridotites included in the database of Bodinier and Godard (2005); these include orogenic, ophiolitic, and abyssal peridotites. The black square (\( \text{Pm}_1 \)), triangle (\( \text{Pm}_2 \)), and diamond (\( \text{Arc}_9 \)) correspond to: \( \text{Pm}_1 = \) Primitive Upper Mantle (PUM) composition from McDonough and Sun (1995), \( \text{Pm}_2 = \) PUM composition from Jagoutz et al. (1979), \( \text{Arc}_9 = \) “pristine” Archean SCLM from Griffin et al. (2008). Samples for which \( \text{Na}_2\text{O} \) contents were not provided in the original reference or with actual contents <0.01 wt.% are plotted as zero \( \text{Na}_2\text{O} \) wt%.
]
from fertile sublithospheric mantle to highly depleted SCLM harzburgites and dunites (Griffin et al., 1999; Pearson et al., 2005; Griffin et al., 2008; Supplementary Fig. 1). In order to obtain a consistent set of results for the CFMAS database, we select samples with relatively low Cr and Na contents. All samples used in this study have ≤ 0.4 wt.% Cr$_2$O$_3$ and <0.36 wt.% Na$_2$O, and more than 80% of the samples have Cr$_2$O$_3$ and Na$_2$O contents of <0.3 and <0.2 wt.%, respectively. However, as mentioned in the previous section, parallel computations were also carried out within the systems Na$_2$O–CaO–FeO–MgO–Al$_2$O$_3$–SiO$_2$ (NCFMAS) and Cr–NCFMAS. We emphasize that, since our dataset spans a range of major-element composition representative of samples from very different tectonic settings, the restriction on Cr and Na contents does not result in any loss of generality. Samples are listed in Supplementary Table 1, together with their original Al-rich phase and the respective reference.

4. Results

Previous studies on the P–T–X dependence of seismic velocities in peridotites have not considered the effects of anelasticity (Lee, 2003; Hacker and Abers, 2004; Speziale et al., 2005). In order to make a meaningful comparison with these studies, we first discuss our results without consideration of anelastic effects.

4.1. Garnet-bearing assemblages (P≥2 GPa)

Fig. 2a, b and c shows the variation of Vp, Vs, and Vp/Vs in our samples as a function of Mg# within the garnet stability field. There is a good correlation of all three parameters with the bulk Mg#, with Vs and samples as a function of Mg# within the garnet stability field. Linear regression analysis gives the following compositional derivatives: $\delta\ln Vp/\delta Mg# \sim -0.0017$, $\delta\ln Vs/\delta Mg# \sim -0.0033$, and $\delta(Vp/Vs)/\delta Mg# \sim -0.0030$ (Fig. 2a, b, and c). Our value for $\delta\ln Vs/\delta Mg#$ is similar to those reported by Lee (2003) (0.003±2×10$^{-4}$) and Speziale et al. (2005) (0.00345±5×10$^{-5}$). Within uncertainties, our computed $\delta\ln Vp/\delta Mg#$ agrees with that reported by Speziale et al. (2005) (although their value is ~20% greater), but differs from the results of Lee (2003), which show no correlation between Vp and Mg# in garnet-bearing xenoliths. Although the exact cause of this discrepancy is difficult to assess, it is likely related to the facts that (i) Lee’s (2003) database is dominated by xenoliths of the well-studied suites from South Africa, which show anomalous orthopyroxene enrichment and low olivine contents (Lee, pers. commun.), and (ii) Vp decreases with increasing orthopyroxene/olivine ratio (see Section 5.3). This is consistent with the fact that if those samples with Mg#.92 that strongly deviate towards low Vp values are removed from Lee’s (2003) database, a subtle positive correlation between Vp and Mg# emerges (Lee, pers. commun.).

Given these differences, it follows that our value for $\delta(Vp/Vs)/\delta Mg#$ lies between the values reported by Lee (2003) (~0.0041) and Speziale et al. (2005) (~0.00224). The larger scatter associated with lnVp (indicated by its smaller $r^2$, Fig. 2a and d) was also observed in both previous studies. This is not a consequence of a scatter in bulk density (Supplementary Fig. 2), but rather of (i) the intrinsic scatter in the term $K/\rho$ (Supplementary Fig. 3), and (ii) the negative compositional derivative of the bulk modulus (Supplementary Fig. 4).

4.2. Spinel-bearing assemblages (1 GPa≤P≤2 GPa)

Fig. 2d, e, and f illustrates the compositional dependence of Vp, Vs, and Vp/Vs within the spinel stability field. Linear regressions for lnVp
and lnVs result in compositional derivatives ∂lnVp/∂Mg# ∼−0.0041 and ∂lnVs/∂Mg# ∼−0.0049 (Fig. 2d and e). These values are significantly greater than their counterparts for garnet-bearing peridotites (particularly for Vp), which is partly explained by the contrasting behaviour of the bulk modulus in the two stability fields (Supplementary Fig. 4). These ∂lnVp/∂Mg# and ∂lnVs/∂Mg# values suggest a different dependence of seismic parameters on composition in the spinel stability field.

Although the general behaviour of both Vp and Vs with Mg# is similar to that observed within the garnet stability field, Vp/Vs shows no apparent correlation. To exclude the possibility of spurious effects due to the mixing of compositions from natural garnet-bearing and spinel-bearing peridotites within one stability field, we have included 20 extra samples of natural spinel peridotites (mainly from the Erro–Tobbio unit and the Pannonian Basin) in the database. We find the same lack of Vp/Vs-Mg# correlation in these samples regardless of the method used to calculate bulk properties (see Discussion). We are not aware of any similar analysis for spinel-bearing peridotites, and thus any independent validation is at present not possible. However, we note that a visual inspection of fig. 12 of Lee (2003) suggests little or no correlation between Vp/Vs and Mg# for the “spinel-facies” peridotites. Since spinel is stable in peridotitic rocks to depths of ~50–60 km under most circumstances, and possibly down to ~100 km in strongly depleted rocks (Klemme, 2004), the application of correlations derived for garnet-bearing peridotites in seismic studies of the uppermost mantle is probably not justified. As shown below, consideration of anelastic attenuation further complicates the matter.

4.3. Compositional and temperature derivatives

All calculations were performed within a wide T–P range (500 ≤ T ≤ 1500 °C and 0.06 ≤ P ≤ 13 GPa). With these data we have calculated the pressure and temperature (anharmonic) derivatives of Vp, Vs, and Vp/Vs within the two stability fields. Results are given in Table 1. Note that although Vp/Vs increases with temperature within the garnet field, it can either increase or decrease within the spinel field, depending on the relative amounts of orthopyroxene vs olivine in the sample. This is because the bulk modulus of orthopyroxene is more dependent on temperature than that of olivine (e.g. Table 3 of Afonso et al., 2008), and because of the stronger correlation between olivine and orthopyroxene contents when spinel is the stable Al-rich phase in the assemblage (Section 5.3). Consequently, spinel-bearing rocks with more (less) than ~15 vol.% orthopyroxene exhibit a decrease (increase) of Vp/Vs with temperature. This intrinsic oscillation of Vp/Vs prevents any meaningful estimation of its bulk anharmonic derivative.

Previous studies have suggested that ∂lnρ/∂lnVs can be used as a diagnostic for compositional variations in the mantle (Forte and Perry, 2000; Karato and Karki, 2001; Forte and Mitrovica, 2001; Deschamps et al., 2002; Perry et al., 2003; Trampert et al., 2004; Simmons et al., 2008). However, only a few studies have focused on the uppermost mantle (Forte and Perry, 2000; Deschamps et al., 2002; Perry et al., 2003; Godey et al., 2004), and they are based on simplified empirical (not self-consistent) parameterizations between density and Vs anomalies. We have analyzed different anomaly ratios from our data set and find that lnVs displays the best correlation with Mg# (Fig. 3a and b). Furthermore, the ratio between the compositional and temperature (anharmonic) derivatives of Vp/Vs is similar to, but more reliable than (i.e. less scatter), the Vp/Vs case. Although lnρ also correlates well with composition (particularly in the case of garnet-bearing assemblages; Fig. 3c and d), our results reveal several hitherto unrecognized advantages of using lnρ/Vs rather than lnρ/Vp as a general indicator of compositional anomalies. Foremost among these are (i) the greater sensitivity of lnρ to temperature variations (Karato, 1993; Jackson et al., 2002); (ii) the larger compositional derivative of lnρ/Vs; (iii) the smaller scatter of lnρ/Vs in the spinel field; and (iv) the similarity in the anharmonic derivatives ∂(lnρ/Vs)/∂Mg# (~−5.85 ± 0.15 × 10−2 kg m−4 s−1 Mγ−1, Fig. 3) and ∂(ρ/Vs)/∂T (3.1 ± 0.3 × 10−5 kg m−4 s−1 °C−1, not shown here) of both spinel- and garnet-bearing assemblages. While the first two factors ensure a better response to temperature and compositional variations, respectively, the last two eliminate the problem of phase stability. Also, a preliminary assessment based on isobaric partial melting experiments on peridotites (Herzberg, 2004) indicates that the general behaviour of Vp/Vs as a function of bulk Mg# (or degree of melt extraction) varies substantially with pressure, but the ρ/Vs ratio does not (Afonso et al., manuscript in preparation). This implies that if two different mantle parcels that experienced the same degree of partial melting at different depths (i.e. pressures) are brought to a common depth by tectonic processes, their Vp/Vs–Mg# relations can be substantially different. Assuming an average Vp/Vs–Mg# correlation could therefore result in a serious over- or underestimation of the true Mg# variation. The ρ/Vs–Mg# correlation, on the other hand, remains comparable throughout a wide range of pressures and therefore is more likely to reflect the “true” Mg# variation. Despite these advantages, the indicator ∂lnρ/∂lnVs is also affected by attenuation, although considerably less than Vp/Vs, as discussed below.

5. Discussion

5.1. The effects of NaO and Cr2O3

Although the system CFMAS is commonly considered a good starting basis for modelling the physical properties of mantle rocks (Palme and O’Neill, 2005), it is pertinent to ask whether the addition of other major elements to our chemical system would affect our conclusions. Na and Cr are of particular relevance here because they are known to perturb the equilibrium modal proportions of ortho- and clinopyroxene, as well as the location of the spinel–garnet transition (Sithrude and Lithgow-Bertelloni; 2005; Simon and Podladchikov, 2008). To assess this we have run parallel computations within the systems NCFMAS and Cr-CFMAS on selected samples. Supplementary Figs. 5–8 summarize the results for both spinel- and garnet-bearing assemblages. As expected, the absolute values of physical properties vary considerably when using different databases, thermodynamic formalisms and system components. This is not surprising since the inclusion of Cr in thermodynamic databases as well as the elastic parameters for Cr-rich end-members are still incomplete (e.g. Lee, 2003; Klemme et al., 2009). However, the general trends and correlations between parameters (or the lack of it) discussed in this work are similar in all three systems regardless of the database employed.

In the system Cr-CFMAS, chromium is strongly partitioned into spinel, thus expanding the pressure range at which spinel can coexist with garnet (e.g. O’Neill, 1981; Klemme, 2004). However, our results indicate that the main factor controlling the validity of Vp/Vs correlations (obtained in garnet-bearing peridotites) is whether or not garnet is present in the assemblage rather than spinel. In other words, the depth at which garnet first appears is the relevant factor to consider rather than the extension of the divariant field in which spinel and garnet coexist. Unfortunately, the effect of Cr, Fe3+, and Na on the pressure at which garnet first appears in natural peridotites remains poorly known, but evidence from experimental and thermodynamic modelling indicate that it is small (Webb and Wood, 1986; Klemme and O’Neill, 2000; Klemme, 2004; Klemme et al., 2009, and references therein).

5.2. Hybrid methods

Thermodynamic equilibrium typically is not imposed in studies of the physical properties of mantle rocks. In these, properties are computed either as functions of prescribed phase volume fractions, or by estimating the amount of end-members and phases in the rock using its bulk composition and a least-squares analysis (Lee, 2003;
An important drawback with these methods is that they cannot model self-consistently the redistribution of components (i.e. Al\textsubscript{2}O\textsubscript{3}) between phases (i.e. pyroxene and garnet) with varying T–P conditions; this redistribution in turn controls the relative abundances of the end-members in the phases and their physical properties. On the other hand, these methods allow the use of more realistic equations of state and higher-order derivatives (e.g. for K or G) that are not included in available thermodynamic databases. A compromise can be obtained by supplementing phase equilibria calculations with higher-order property derivatives (e.g. Ita and Stixrude, 1992; Afonso et al., 2008). However, since the P–T dependences of physical parameters used to calculate the final bulk properties are typically different from those used in the phase equilibria computation, the method is not self-consistent. This approach has been widely used in the literature and is sometimes referred to as the hybrid approach (e.g. Stixrude and Lithgow-Bertelloni, 2005; Afonso et al., 2008). Given its popularity, and to provide an additional check on our results, we have also computed bulk properties of our samples with the hybrid method described by Afonso et al. (2008) and summarized in the Methods section. Furthermore, bulk properties of representative samples were also computed using the popular method of Hacker and Abers (2004). Similarly to what is described in the previous section, we find that although the absolute values of certain properties can vary considerably from one method to another, the general trends and correlations analyzed in the paper are similar in all cases (Fig. 4).

5.3. Modal effects

Previous studies have highlighted some correlations between seismic wave velocities and modal contents of orthopyroxene and olivine in continental peridotites (e.g. Lee, 2003; Matsukage et al., 2005). This is of particular relevance since mantle metasomatism by fluids rich in silica but poor in Fe, Ca, and Al could in principle increase the orthopyroxene/olivine modal ratio of peridotites without changing their bulk Mg\# to any significant extent (e.g. Kelemen et al., 1998). However,
it is now generally accepted that the enrichment in orthopyroxene (or silica) is typical of xenoliths from the SW Kaapvaal Craton, and not a general feature of all cratonic domains (e.g. Griffin et al., 2008). Indeed, although our dataset includes cratonic samples from South Africa, Norway, Greenland, and Canada, the only samples exhibiting an obvious enrichment in orthopyroxene are those from South Africa.

Our results (Fig. 5) indicate that when spinel is the only Al-rich phase $V_p$ correlates well with olivine content and to a lesser extent with orthopyroxene content. This is not surprising, however, since olivine content correlates well with orthopyroxene content within the spinel stability field (not shown here). Together with the derivatives in Table 1, this suggests that when garnet is absent, a change of ~13 vol.% in olivine mode is equivalent to a temperature change of 100 °C (as long as the temperature is below the limit of 900 °C, see next section). On the other hand, $V_p/V_s$ correlates better with orthopyroxene than with olivine content (Fig. 5). Unfortunately, the dependence of $\partial (V_p/V_s)/\partial T$ on orthopyroxene content (Table 1) limits somewhat the use of $V_p/V_s$ as a robust indicator of opx/ol ratio in

$\textbf{Fig. 5.}$ Orthopyroxene and olivine modal effects on $V_p$, $V_s$, and $V_p/V_s$. Panels in the left column are for spinel-bearing assemblages; panels in the right column are for garnet-bearing assemblages. Reference $T_o$ and $P_o$ as in Fig. 2. Thin dashed line represents the best linear regression (in a least-squares sense) to all data points. Associated scatter is indicated by the values of $r^2$. 
peridotites. In the case of Vs, there is a poorer correlation with olivine content, but a good one with bulk Mg#, suggesting that melt depletion/enrichment effects (i.e. extraction/addition of Ca, Fe, Al) are the dominant factor controlling the bulk Vs. Indeed, using the derivatives in Table 1 one obtains that a change of 100 °C is equivalent to a change of −18 vol.% in olivine.

Within the garnet stability field we find that the best correlations are Vp versus Mg# and Vs versus Mg#, which is consistent with the results in Fig. 2 and supports the use of this parameter over other possible options (e.g. orthopyroxene mode). In this case, using the derivatives in Table 1 we obtain that a temperature change of 100 °C is equivalent to a change in olivine content of −36 and 23 vol.% for Vp and Vs, respectively, reflecting the poor modal control on seismic velocities. Due to the small associated $r^2$ values, however, these figures are subject to significant uncertainties. Similarly, Vp/Vs exhibits no significant correlation with orthopyroxene content, and only weak with olivine content. We also find, as hypothesised by Lee (2003), that the weak correlation between Vp and olivine content tends to decrease with pressure due to the anomalously high pressure derivative of orthopyroxene (see tables in Stixrude and Lithgow-Bertelloni, 2005; Afonso et al., 2008).

5.4. Anelasticity

The anelastic behaviour responsible for seismic wave attenuation becomes important in olivine-rich rocks at temperatures $\gtrsim$900 °C (Jackson et al., 2002). Since all of the sublithospheric upper mantle and up to 40% of the subcontinental lithospheric mantle have temperatures higher than this limit (Afonso et al., 2008; Fig. 7b), any attempt at constraining either mantle composition or temperatures from seismic data must include attenuation effects. Shear waves are more strongly affected by anelasticity than compressional waves, and therefore both Vp/Vs and Poisson’s ratio become strongly dependent on temperature at $T \gtrsim$900 °C. The variation of Vp/Vs with temperature within the garnet stability field is shown in Fig. 6a for two representative samples. For the computation of attenuation effects (Section 2) we chose a reference period $T_0 = 50$ s (20 mHz) and varied the average grain size between 1

Fig. 6. a) Vp/Vs versus temperature for two representative samples with Mg# = 88.9 (red colour) and 93.3 (green colour) within the garnet stability field. Reference pressure is $P_o = 4$ GPa. Anelastic attenuation is calculated as explained in the text. The envelopes enclose Vp/Vs values for grain sizes between 1 and 10 mm. The anharmonic approximation is shown with dashed lines; red and green lines are from this study; black line is from Lee (2003). The black circles denote Vp/Vs values for the same sample (i.e. no change in composition) separated by $\Delta T = 300$ °C (1300 °C–1000 °C) and 100 °C (1400 °C–1300 °C) within the anelastic regime. Note that if relations based on anharmonic approximations (e.g. $\partial (Vp/Vs)/\partial Mg# = -0.003$, Fig 2C) are used to make the conversion from $\Delta Vp/Vs$ to $\Delta Mg#$, unrealistically large values of 6–7 units for the latter are recovered. b) $\rho / V_s$ [kg m$^{-3}$] versus temperature for the same samples shown in a). The anharmonic behaviour is shown with dashed lines. For $\rho / V_s$, the compositional dependence is large enough to produce no overlapping of the envelopes at $T \gtrsim$1250 °C. The error associated with the conversion from $\Delta \rho / V_s$ to $\Delta Mg#$ using the anharmonic approximation is considerably smaller than in the Vp/Vs case.
and 10 mm. Fig. 6a shows that a change in temperature of 300 °C in the anelastic regime (between 1000 and 1300 °C) translates into a fictitious change of ∼7 units in Mg# if anharmonic estimates are used for the conversion; this variation is large enough to cover the entire range of common peridotitic compositions in the upper mantle. In other words, a lateral temperature difference of 300 °C within or at the base of the lithosphere could be mistaken for a large difference in composition when using Vp/Vs–Mg# correlations without accounting for anelasticity. At temperatures >1300 °C, the error is increased approximately by a factor of two (ΔT~100 °C translates into ΔMg# ~ 5.7; Fig. 6a). Therefore, the common practice of interpreting observed variations of Vp, Vs, and/or Vp/Vs in the upper mantle in terms of either compositional (e.g. Artemieva and Thybo, 2008) or temperature (e.g. Chou et al., 2009) variations with no consideration of anelasticity and phase stability is...
likely to produce erroneous conclusions. We illustrate this in more detail in the next section.

The ratio \( \rho/V_s \) is appreciably less sensitive to anelastic effects and therefore a similar temperature variation results in a smaller fictitious Mg# change (2.5–4 units; Fig. 6b) than for the \( V_p/V_s \) case. Nevertheless, due to the non-linear effects of temperature on shear modulus the curves for both \( V_p/V_s \) and \( \rho/V_s \) steepen with increasing temperature within the anelastic regime. Although the slope \( \Delta(\rho/V_s)/\Delta T \) of the anharmonic lines in Fig. 6 seems to be greater than for \( V_p/V_s \), which at first glance may be interpreted as a stronger \( T \)-vs-\( X \)-dependence, this is not the case. While a unit change in Mg# represents a temperature change of \( \sim 220 \) °C in the \( V_p/V_s \) case, the same \( \Delta \text{Mg#} \) translates into a temperature change of \( \sim 190 \) °C in the \( \rho/V_s \) case (i.e. the anharmonic temperature dependence of \( \rho/V_s \) is \( \sim 14\% \) smaller than that of \( V_p/V_s \)). In addition, \( \rho/V_s \) is much more robust (i.e. greater \( r^2 \), cf. Figs. 2 and 3).

6. A synthetic example

To highlight some of the advantages and limitations of using \( \rho/V_s \) over \( V_p/V_s \) we have constructed two synthetic lithospheric models using the finite-element code LitMod (Afonso et al., 2008). We emphasize that these models are for illustration purposes only and thus deliberately oversimplified. In the following discussion, we use the classification of Griffin et al. (1999; modified from Janse, 1994) to identify mantle domains of specific age and composition (see Table S2 in supplementary material). The first synthetic model (hereafter model MT) is made up of a compositionally homogeneous lithospheric mantle with a typical Tecton composition (Mg# = 89.9) over a homogeneous sublithospheric upper mantle (Mg# = 89.3; Fig. 7a). The second model (hereafter model MC) is composed of three distinct lithospheric domains with different, but realistic, compositions (Tecton Mg# = 89.9, Proton Mg# = 90.4, Archon...
Mg# = 92.1, Pristine Archon Mg# = 93.1; Fig. 8a). The thermal structure of the two models is identical (Fig. 7b) and has been chosen to be representative of Tecton, Proton, and Archon domains, in correspondence with the average mantle compositions of model MC.

Fig. 7d shows the resulting Vp/Vs pattern predicted by the model MT (no compositional variations) when anelasticity effects are neglected. Under these circumstances, the Vp/Vs pattern is relatively insensitive to temperature variations, as shown by the poor correlation between Vp/Vs contours and the temperature field. This simply reflects the fact that the slope of the anharmonic temperature derivatives of the Vp/Vs ratio is small (Fig. 6a). A constant-depth slice of Vp/Vs (e.g. at 150 km depth) therefore would show only slight variations, in agreement with the absence of compositional anomalies. However, when seismic velocities are corrected for anelasticity, the Vp/Vs pattern becomes strongly dependent on the temperature structure at temperatures ≥900 °C, where Vp/Vs contours essentially mimic the temperature field (Fig. 7e). In this case, a constant-depth slice of Vp/Vs at 150 km depth would reveal a strong variation, not in response to a strong lateral gradient in bulk composition but to a strong temperature gradient. Therefore, the actual depth interval in which anharmonic Vp/Vs–Mg# correlations would apply is strictly limited to the region between the spinel–garnet transition and the 900 °C isotherm (e.g. the region between the 1.74 contour line and the thick dotted line in Fig. 7e). According to petrological–geophysical models of the lithosphere (Afonso et al., 2008; Figs. 7e and 8d), the thickness of this depth interval varies between ~0 km in thin (e.g. Phanerozoic) lithospheric domains to about 50% of the thermal lithospheric thickness in thick (e.g. Archean) domains.

Fig. 8c shows the Vp/Vs pattern predicted by model MC including anelasticity effects. It is evident from this figure that isolating the compositional signature from the purely thermal signature (Fig. 7e) at mid- to lower lithospheric levels would be extremely difficult (i.e. the Vp/Vs variation patterns are almost identical). To isolate the compositional signature we subtract the field in Fig. 7e (temperature only) from that in Fig. 8c (temperature and compositional effects); the result is plotted in Fig. 8d. This exercise reveals that the maximum differences (in absolute values) amount to ∼0.016 for most of the model, which is close to or even smaller than the resolution limit of current seismological methods (e.g. Trampert and Spetzler, 2006; Schutt et al., 2008). Furthermore, the regions where anharmonic correlations would apply (shaded green area) are characterized by even smaller ΔVp/Vs values (∼0.01). The unavoidable conclusion is that even with high-resolution methods, compositional differences <4–5 Mg# within a peridotitic mantle cannot be resolved with confidence using seismic data only. On the other hand, significant lithological variations such as a shallow (i.e. cold) eclogitic body within a peridotitic lithospheric mantle could still be recovered due to the large Vp/Vs contrasts between these two lithologies (∼0.02–0.03), assuming that the size of the body is larger than the resolution of the seismic model.

In Fig. 9 we plot the horizontal derivatives (i.e. lateral heterogeneities) of shear wave velocities (∂lnVs/∂x) and bulk density (∂lnρ/∂x) as predicted by model MC. Since the temperature derivatives of both Vs and ρ have the same sign (i.e. they both decrease with temperature), ∂lnVs/∂x and ∂lnρ/∂x also have the same (positive) sign when temperature is the cause of a change in these properties. On the other hand, the compositional derivatives of Vs and ρ have opposite signs (i.e., Vs increases while ρ decreases with Mg#; Fig. 2 and Supplementary Fig. 2), and therefore the derivatives ∂lnVs/∂x and ∂lnρ/∂x have opposite signs in regions where changes in composition are the cause of changes in Vs and ρ. Consequently, the sign of the ratio ∂lnVs/∂lnρ (or ∂lnVs/∂lnρ) becomes a robust indicator of compositional (negative sign) and thermal (positive sign) anomalies in a peridotitic mantle. In addition, parallel computations indicate that it is also highly sensitive to lithological variations (e.g. eclogites and/or pyroxenites within peridotites).

As expected, vertical changes in composition are not well resolved by the horizontal derivatives (Fig. 9). In this case, the vertical derivatives

![Fig. 9](image-url)
∂lnP/∂y and ∂lnVs/∂y need to be used in combination with an appropriate depth-dependent reference model (i.e. to remove the “background” change in Vs and ρ with depth).

7. Conclusions

In the light of the above considerations, can we distinguish small-scale thermal from compositional anomalies in the upper mantle? The results presented here show that previous methods based only on seismic parameters may produce results that are not meaningful for spinel-bearing peridotites or for olivine-rich assemblages at T>900 °C. On the other hand, the ratio ρ/Vs is a more robust compositional indicator, but requires bulk density as an independent input. Since both density and elastic moduli depend on bulk composition, any model (inverse or forward) of these properties requires a framework that ensures an internally consistent coupling among P, T, and composition (bulk and phase). Current joint inversion methods are not well suited because they rely on long-period normal-mode observations (e.g. Kuo and Romanowicz, 2002; Trampert et al., 2004), while studies based on the combination of short-period body waves and gravity anomalies model these two geophysical fields through scaling factors (e.g. Forte and Perry, 2000; Deschamps et al., 2002; Perry et al., 2003; Godey et al., 2004; Simmons et al., 2009), and therefore are not strictly self-consistent (i.e. ∂Vp and ∂Vs are not coupled through thermodynamic constraints). Recently developed techniques that combine geophysical and petrological modelling within a consistent thermodynamic framework (Khan et al., 2008; Afonso et al., 2008; Ritsema et al., 2005; Fullea et al., 2009) are particularly promising and open new possibilities for joint inversion-forward methods to model the density and seismic and thermal structure of the upper mantle in a self-consistent manner. Nevertheless, a robust methodology will still need more detailed studies on the effects of intrinsic attenuation, fluid content, and thermodynamic modelling of mantle assemblages.

The main conclusions of this study can be summarized as follows:

1) There is a good correlation between the anharmonic Vp/Vs ratio (or Poisson’s ratio) and bulk Mg# in peridotites (∂ln(Vp/Vs)/∂Mg# = –0.0030) only when garnet is present in the assemblage. There is no correlation between the anharmonic Vp/Vs ratio and bulk Mg# when spinel is the only Al-rich phase in the assemblage. In this case, however, Vp correlates well with olivine content.

2) Anelastic attenuation of seismic waves strongly affects Vp/Vs, and thus precludes the use of anharmonic Vp/Vs–Mg# correlations at T>900 °C. This in combination with 1) limit the usage of anharmonic Vp/Vs–Mg# correlations to a depth interval between the spinel–garnet transition and the 900 °C isotherm. The thickness of this interval ranges from ~0 km in Phanerozoic lithospheric domains to ~50% of the lithospheric mantle in Archean domains. However, these regions are characterized by Δ(Vp/Vs) values smaller than the resolution of current seismological methods.

3) The ratio ρ/Vs is a robust indicator of compositional heterogeneities within the upper mantle. However, its reliability in distinguishing thermal from compositional anomalies relies heavily on whether ρ and Vs are determined self-consistently and on an appropriate inclusion of seismic attenuation effects.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found in the online version, at doi: 10.1016/j.epsl.2009.12.005.

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