Single crystal elasticity of majoritic garnets: Stagnant slabs and thermal anomalies at the base of the transition zone

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The elastic properties of two single crystals of majoritic garnet (Mg2.24Al1.5Si3.22O12 and Mg2.01Fe0.17 Al1.88Si3.15O12), have been measured using simultaneously single-crystal X-ray diffraction and Brillouin spectroscopy in an externally heated diamond anvil cell with Ne as pressure transmitting medium at conditions up to ~30 GPa and ~600 K. This combination of techniques makes it possible to use the bulk modulus and unit-cell volume at each condition to calculate the absolute pressure, independently of secondary pressure calibrants. Substitution of the majorite component into pyrope garnet lowers both the bulk (Ks) and shear modulus (G). The substitution of Fe was found to cause a small but resolvable increase in Ks that was accompanied by a decrease in ∂Ks/∂P, the first pressure derivative of the bulk modulus. Fe substitution had no influence on either the shear modulus or its pressure derivative. The obtained elasticity data were used to derive a thermo-elastic model to describe Vp and Vs of complex garnet solid solutions. Using further elasticity data from the literature and thermodynamic models for mantle phase relations, velocities for mafic, harzburgitic and lherzolitic bulk compositions at the base of Earth’s transition zone were calculated. The results show that Vp predicted by seismic reference models are faster than those calculated for all three types of lithologies along a typical mantle adiabat within the bottom 150 km of the transition zone. The anomalously fast seismic shear velocities might be explained if laterally extensive sections of subducted harzburgite-rich slabs pile up at the base of the transition zone and lower average mantle temperatures within this depth range.

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1. Introduction

Seismic velocity profiles of the Earth’s interior provide essential information for constraining the thermal and chemical state of the mantle (Anderson and Bass, 1986; Irifune and Ringwood, 1987a; Ita and Stixrude, 1992). The correct interpretation of these profiles in terms of mantle mineralogy and chemistry, however, requires laboratory or computational data on the elasticity of candidate minerals at conditions of the Earth’s mantle. In this context, knowledge of the thermo-elastic properties of garnet solid solutions are essential, since they make up a major proportion of both mafic and ultramafic rocks in the upper mantle and transition zone (Irifune and Ringwood, 1987a). Garnets recovered from the Earth’s mantle crystallize in the cubic space group Ia3d forming a series of complex solid solutions that are described using the crystal-structural formula VIII X3 Y2 V4 Z2 O12. Large cations, X = Mg, Ca, Fe2+, occupy the 8-fold coordinated dodecadhedral sites, medium sized cations, Y = Fe3+, Cr, occupy the octahedral sites, whereas the tetrahedral Z site is occupied by Si. At pressures above 5 GPa the coupled substitution of Si and Mg (and Fe) onto the Y site occurs in garnets within mantle assemblages as a result of the breakdown of both orthopyroxene and clinopyroxene. This, so called, majorite substitution increases the proportion of garnet in man-

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tle rocks at the expense of pyroxenes in the Earth’s deep upper mantle and transition zone (Ringwood, 1967). The Al-free garnet end-member is referred to as majorite, Mg3Si2O6 (Mg3Si2O6) and crystallizes with tetragonal symmetry due to ordering of Mg and Si on the octahedral sites. Pure Mg3Mg is stable at pressures between 16 and 23 GPa and temperatures above 1600 °C (Kato and Kumazawa, 1985; Angel et al., 1989). In upper mantle ultramafic rocks garnets are solid solutions that are dominated by the end member pyroxene (Py, Mg3Si2O6) but have sub-equivalent proportions of almandine (Alm, Fe3Al5Si3O12) and pyrope (Py, Ca3Al2Si3O12). With increasing pressure, however, the end member becomes increasingly important and dominates in the transition zone (410–660 km depth). A key issue concerning the structure of the Earth’s interior is the extent and scale at which the mantle can be considered homogeneous. A number of studies have proposed, for example, that the mantle may become richer in mafic material with depth (e.g. Anderson and Bass, 1986). One of the main expressions of such chemical heterogeneity in the mantle would be variation in the chemistry and proportion of garnet. Garnets constitute approximately 40% by volume of ultramafic compositions and 70% of mafic compositions (Anderson and Bass, 1986; Irfune and Ringwood, 1987a; Ito and Stixrude, 1992), but garnets formed from mafic assemblages will have greater Gr and Alm contents and in the transition zone less Mg compared to ultramafic assemblages. Knowledge of how the elastic properties of garnet change as the bulk chemistry changes is, therefore, important.

Several studies have investigated the elastic properties of Py–Mg garnets at room pressure and temperature (Bass and Kanzaki, 1990; O’Neill et al., 1991). Moreover elastic modulus measurements have also been performed at high pressure and room temperature, using ultrasonic techniques on polycrystalline aggregates (Rigden et al., 1994; Gwanmesia et al., 1998; Chen et al., 1999; Wang and Ji, 2001) and through the use of Brillouin spectroscopy on both single crystals (Condron et al., 1999; Sinogeikin and Bass, 2000; Murakami et al., 2008) and powdered samples (Sinogeikin and Bass, 2002). Recent improvements in ultrasonic techniques coupled with synchrotron X-ray radiation have allowed sound velocity measurements on polycrystalline samples along the Py–Mg solid solution to be performed at simultaneous high P and T (Irfune et al., 2008; Gwanmesia et al., 2009; Liu et al., 2015). Furthermore the single-crystal elasticity of an iron-bearing pyrope was recently obtained simultaneously at high-pressures (up to 20 GPa) and high-temperature (750 K) using Brillouin spectroscopy and X-ray diffraction (Lu et al., 2013). While the value of the bulk and shear moduli, K and G, reported by these studies cover a relatively small range, the exact dependence particularly of K on Mg content is unclear, large discrepancies in elastic moduli pressure derivatives exist, the thermal properties are poorly constrained as is the effect of the Alm content. Consequently, the interpretations of seismic velocity gradients in the transition zone remain uncertain.

The aim of this study is, therefore, to constrain the elastic properties of majoritic garnets as a function of density, temperature and composition under hydrostatic conditions by employing a combination of single-crystal Brillouin scattering and X-ray diffraction measurements. The simultaneous measurement of elastic properties and density are used to also obtain absolute values of the experimental pressure, avoiding in this way any systematic errors that may be introduced through the use of secondary pressure calibrations. The elasticity data obtained are fitted to a self-consistent thermo-elastic model from which thermodynamic properties of the garnet end-members are estimated. Acoustic velocities of mafic, harzburgitic and lherzolitic assemblages are then calculated along a typical mantle adiabat at conditions of the Earth’s transition zone by combining our garnet model with properties for coexisting minerals from the literature. The results are then compared with seismic reference models reported over the same depth interval to constrain the plausible mineralogy and temperature at the base of the Earth’s transition zone.

2. Experimental methods

2.1. Sample synthesis and characterization

The growth of large crystals is usually facilitated by adding a flux to the starting material, such as H2O, in order to lower the melting temperature and allow larger crystals to grow from the surrounding melt. The flux to starting material ratio is an important factor in determining the size of the final crystals. In order to assess the optimal H2O content for the growth of large single crystals, four different majoritic garnet starting mixtures were prepared by mixing in a 50/50 proportion an enstatite glass and four pyrope mixtures (Py1, Py2, Py3 and Py4) with different H2O contents (Table 1).

The four pyrope mixtures were then mixed with the enstatite glass to produce hydrous majoritic garnet starting mixtures with differing H2O contents, A’, B’, C’, D’ (Table 1). These were loaded into a multi-chamber capsule fabricated from a 2 mm diameter rhenium rod.

High-pressure experiments aimed at producing majoritic garnets were carried out using a 5000 t multi-anvil apparatus at the Bayerisches Geoinstitut. A 18 mm edge length Cr2O3-doped (5 wt.%) MgO octahedron was used as a pressure medium with tungsten carbide cubes of 52 mm edge length and 11 mm truncation edge length (18/11 assembly). The pressure calibrations for the assembly used in this study are reported in Kepler and Frost (2005). The samples were first pressurized to 17 GPa followed by heating at 1900 °C for 5 min. After heating at high pressure, the experiments were quenched by shutting off the power and the run-products were recovered after decompressing for 18 h. The recovered capsules were embedded in epoxy resin, ground and polished for electron probe microanalysis. Single-crystals of majoritic garnet (up to ∼200 µm in length) were obtained from the starting composition (mixture A) that contained the largest amount of water (Fig. S1, supplementary information).

An iron bearing majoritic garnet with a similar composition to that recovered above was also prepared from a glass starting material that contained H2O added as Mg(OH)2 (Fe-majorite, see Table 1). An oxide mixture of Al2O3, SiO2 and Fe2O3 was initially melted in air at 1600 °C for twenty minutes and then
rapidly quenched in icy water. This glass was then reduced in a 1-atmosphere furnace, at 1000 °C and at an oxygen fugacity (fO2) of 2 logs units below the quartz–fayalite–magnetite oxygen buffer for approximately 12 h. This process was performed twice in order to ensure the complete reduction of the mixture. Mg(OH)2 was then added to the glass to obtain a hydrous composition. The starting material was loaded into a double capsule consisting of a 1.6 mm diameter Re inner capsule and an outer capsule made of a 2 mm diameter platinum tube, welded closed at both ends. The synthesis run was performed using the same procedure and conditions followed for the iron-free samples.

Element concentrations in the recovered samples were measured with a JEOL JXA-8200 electron probe microanalyser (EPMA), operating at 15 kV and 15 nA. The electron beam size was approximately 1–2 μm in diameter and the peak counting times were 20 s. Enstatite or diopside, spinel, forsterite, and metallic iron were used as standards for determining the concentrations of Si, Al, Mg and Fe respectively. The chemical analysis resulted in the following composition: 32.0 (6)% MgO, 47.5 (9)% SiO2, 19 (2)% Al2O3 (in wt.), for the Py-Mj garnet (hereafter named Py76Mj24 and 29.5(5)% MgO, 46(1)% SiO2, 3.3(5)% FeO, 21(2)% Al2O3 (in wt.) for the iron bearing sample (hereafter named Py78Alm6Mj16). The chemical formulas are Mg$_{3.24}$Al$_{1.51}$Si$_{3.23}$O$_{12}$ and Mg$_{3.10}$FeO$_{0.17}$Al$_{1.68}$Si$_{15.15}$O$_{12}$, respectively.

FTIR analyses were performed on crystals of Py76Mj24 produced in the same experiment and show OH absorption bands consistent with approximately 20 ppm wt. H2O. Measurements were carried out at the Laboratoire Magmas et Volcans (LMV) in Clermont-Ferrand, France. The quantitative analyses were performed following the calibration of Paterson (1982). The synthesized majoritic garnets can, therefore, be considered to contain negligible amounts of H2O.

2.2. Simultaneous X-ray diffraction and Brillouin scattering

The P–V–T equations of state and the compressional, V$_p$, and shear, V$_s$, sound velocities of two single-crystals of majoritic garnet (Py76Mj24 and Py78Alm6Mj16) were each determined by means of simultaneous Brillouin spectroscopy and X-ray diffraction. High quality single-crystals, of ~70 μm in size, were selected based on their sharp diffraction profiles. The crystals were parallel polished into platelets with a thickness of 10–18 μm and then loaded into piston cylinder diamond anvils. Boehler–Almax diamonds were employed with 400–350 μm culets in combination with tungsten carbide seats. Rhenium gaskets of 200 μm in thickness were pre-indented to 40–55 μm before drilling 250 μm cylindrical holes. Single-crystals of Sm:YAG (Sm-doped YAlO$_3$ garnet) as well as ruby chips were added as secondary pressure calibrants. A neon gas pressure medium was loaded into the sample chamber using the high pressure gas loading devices at the Bayerisches Geoinstitut (Kurnosov et al., 2008) as well as at GSECARS (Rivers et al., 2008).

The pressure inside the cell was monitored before and after each Brillouin and X-ray measurement using an Acton standard series spectograph from Princeton Instruments, employing the same laser and the same geometry as in the Brillouin experiment. An external resistive heater suitable for the piston cylinder type cells employed in this study was designed and placed around the diamonds for achieving high temperatures (see text S1 supplementary information). An S-type thermocouple located near the diamond surface was used to monitor the temperature inside the cell. However, to constrain the temperature inside the high pressure chamber without relying uniquely on the thermocouple, an alternative approach was used. The fluorescence shifts of Sm:YAG, which are independent of temperature, were used to determine pressure (Troits et al., 2013), whereas temperature was determined using the fluorescence of ruby (Rekhi et al., 1999) by fixing the pressure value obtained from the Sm:YAG measurement. Maximum temperatures reached estimated in this way were 558 K and 470 K for Py76Mj24 and Py78Alm6Mj16, respectively. However, the maximum thermocouple temperature readings were 600 K for Py76Mj24 and 650 K for Py78Alm6Mj16, i.e. larger than the actual temperatures experienced by the majoritic samples.

Simultaneous acquisition of density and sound velocities at room pressure was performed at the Bayerisches Geoinstitut. The lattice parameters of both samples were determined using eight-position centering of 15 Bragg reflections (25° < 2θ < 40°) according to the procedure of King and Finger (1979) on a Huber diffractometer equipped with point detector and driven by the program SINGLE (Angel and Finger, 2011). The resulting unit-cell volumes are 1506.0 (5) Å$^3$ and 1506.8 (1) Å$^3$ for Py76Mj24 and Py78Alm6Mj16 respectively. The unit-cell volumes are practically identical because Alm replaces Mj in the second sample and both components have a qualitatively similar effect on the volume. Typical half-widths of the c0 profiles of different reflections varied between 0.06° and 0.10°. Brillouin scattering measurements were performed in a 80° symmetric/platelet scattering geometry with plate spacing of 4 mm using a coherent Verdi V2 solid state Nd:YVO$_4$ frequency doubled laser (λ = 532.0 nm) at the power of ~150–200 mW. The room pressure Brillouin scattering measurements of Py78Alm6Mj16 were performed at the GeoForschungsZentrum (GFZ) in Potsdam as well as at PETRA III in Hamburg, employing a 60 and 49° forward symmetric scattering geometry with plate spacing of 6 mm and 8 mm respectively. A coherent Verdi V2 solid state Nd:YVO$_4$ frequency doubled laser (λ = 532.0 nm) was used.

Simultaneous measurements of sound velocities and density at different pressures and temperatures were performed at the BM-13-D (GSECARS) beamline at the Advanced Photon Source (APS). The samples were each measured first upon compression up to approximately 20 and 21 GPa at room temperature and then heated to 558 K (Py76Mj24) and 470 K (Py78Alm6Mj16) respectively. During heating the pressure increased to 30 GPa, therefore Brillouin spectra and density were measured along an isotherm (at high temperature) upon decompression. X-ray diffraction measurements were performed using a Perkin Elmer detector, collecting step scans in an omega range of 50° or 70° with a step size of 1° and 5°/step exposure time. Brillouin scattering measurements were performed with a six-pass Sandeck-type tandem Fabry–Pérot interferometer using a coherent Verdi V2 solid state Nd:YVO$_4$ frequency doubled laser (λ = 532.0 nm) as a light source. Measurements were performed in a 50° symmetric/platelet scattering geometry with plate spacing of 6.5–7 mm. Brillouin spectra were collected with a laser power of 400 mW. Acoustic velocities, $V_{acoustic}$, were determined from the frequency shift using the following relationship (Whitfield et al., 1976):

$$V_{acoustic} = \Delta \nu \ast \lambda_0 / 2 \ast \sin(\theta/2)$$

where $\Delta \nu$ is the measured Brillouin shift, $\lambda_0$ is the incident laser wavelength, $\theta$ is the external scattering angle.

3. Results

3.1. Elasticity

The acoustic velocities of the Py76Mj24 and Py78Alm6Mj16 samples measured at ambient conditions in different crystallographic directions as a function of $\gamma$ angle are shown in Fig. 1. Typical Brillouin spectra are also reported in the insets in the same Figure. The elastic anisotropy of the two majoritic-garnets is practically negligible both at ambient conditions and at high pressures and temperatures, as also observed for other
The majoritic single-crystal elastic moduli can then be related to the aggregate moduli through the following equations:

\[
C_{11} = K_s + \frac{4}{3}G = \rho V_p^2 \tag{3}
\]

\[
C_{44} = G = \rho V_S^2 \tag{4}
\]

\[
C_{12} = K_s - \frac{2}{3}G = \rho (V_p^2 - 2V_S^2) \tag{5}
\]

assuming the equality:

\[
2C_{44} = C_{11} - C_{12} \tag{6}
\]

The elastic properties and sound velocities of both samples as a function of density, pressure and temperature are summarized in Table 2.

Brillouin spectra collected on samples within diamond anvil cells at different pressures, temperatures and orientations typically have different signal to noise ratios that depend on the crystal optical quality and its orientation in addition to the laser focusing, sample alignment and collection time. The resolution of such spectra will influence the uncertainties on the \(V_s\) and \(V_p\) values used to obtain the elastic constants. The uncertainties on the velocities of the garnet crystals were assessed using a set of Brillouin spectra collected for the same sample but with different signal to noise ratios, varied by altering the length of data collection time between one hour to several days. A “calibration curve” was then constructed that describes the standard deviation on the velocity measurements as a function of the signal to noise ratio. Uncertainties of 20 m/s, i.e. 0.2–0.4% can be obtained when the best alignment is achieved, but usually they are larger than this value (see text S2 supplementary information).

### 3.2. Absolute pressure determination

An important advantage in making simultaneous measurements of density and sound velocities for the same sample at the same conditions is that it allows pressure to be determined without having to rely on a secondary pressure scale, such as that of the ruby fluorescence scale. For each experimental point, the absolute pressure (Table 2) was determined according to the equation

\[
P = \int_{0}^{V} \frac{K_T(V)}{V} dV \tag{7}
\]

where the unit-cell volume \(V\) was determined by means of X-ray diffraction, and the isothermal bulk modulus \(K_T\) was derived from the adiabatic bulk modulus \(K_S\) calculated using Brillouin sound velocities, according to the following expression:

\[
K_S = K_T(1 + \alpha \gamma T) \tag{8}
\]

where \(\alpha\) is the volume thermal expansion and \(\gamma\) is the Grüneisen parameter. The values of \(\alpha\) and \(\gamma\) for majoritic garnets were assumed to be equal to those of pyrope and were taken from Ahrens (1995).

The variation of the shear \((V_S)\) and compressional \((V_P)\) wave velocities as a function of absolute pressure obtained in this study at high pressures and temperatures are reported in Fig. 2.

The values of \(V_S\) and \(V_P\) wave velocities of Py76Mj24 and Py78Alm6Mj16 are very similar at room pressure, however, they deviate at high pressures, with Py76Mj24 displaying faster velocities due to the higher pressure derivative of the elastic moduli.

### 3.3. Determination of P–V–T EoS of majoritic garnets

The high-pressure and temperature elastic properties of majoritic garnets are described using the self-consistent thermodynamic formalism described by Stixrude and Lithgow-Bertelloni (2005). This model uses a Mie–Grüneisen equation of state

![Figure 1](image-url)
with a Debye approximation that should describe thermal properties more reliably than the linear or polynomial moduli dependences often employed. In this formalism, the isothermal bulk modulus, \( K_T \), is obtained as the second derivative of the Helmholz free energy with respect to strain \( (f) \) and retains all terms that originate from the truncation to third order in strain of the free energy expansion:

\[
K_T = (1 + 2f)^{5/2} \left[ K_0 + (3K_T K_{T0} - 5K_0)f + \frac{27}{2}(K_0 K'_0 - 4K_0) f^2 \right] \\
+ (\gamma + 1 - q)\gamma \frac{\Delta E_{TH} (V, T)}{V} \\
- \frac{L^2}{V} \left[ TC_V (V, T) - T_0 C_V (V, T_0) \right]
\]

(9)

where

\[
f = \frac{1}{2} \left[ \left( \frac{V_0}{V} \right)^{2/3} - 1 \right] = -\varepsilon
\]

(10)

is the negative of the eulerian strain \( (\varepsilon) \), \( V \) is the molar volume, \( T \) is temperature, \( K_0 \) and \( K'_{T0} \) are the isothermal bulk modulus and its pressure derivative and the subscript zero indicates the reference state set at room conditions, \( q = (\frac{\partial}{\partial P})T = 9(\frac{\partial}{\partial T})P \) and \( \gamma \) is the Grüneisen parameter. \( \Delta E_{TH} \) is the difference in the quasi-harmonic thermal energy between \( T \) and \( T_0 \) and \( C_V \) is the heat capacity at constant volume evaluated in the framework of Debye theory:

\[
C_V = 9N_A k_B \left( \frac{T}{\theta} \right)^3 \int_0^{\frac{\theta}{T}} x^4 e^x \left( e^x - 1 \right) dx
\]

(11)

\[
\theta = \theta_0 \left[ 1 + 6\gamma_0 f + \frac{1}{2}(-12\gamma_0 + 36\gamma_0^2 - 18\gamma_0 q_0) f^2 \right]^{1/2}
\]

(12)

where \( N_A \) is Avogadro's number and \( \theta_0 \) is the room pressure value for the Debye temperature. The isothermal bulk modulus can be converted to the adiabatic bulk modulus \( K_s \) according to equation (8).

The shear modulus of an isotropic material can be calculated from the adiabatic elastic tensor according to the formulation of Stixrude and Lithgow-Bertelloni (2005):

\[
G = (1 + 2f)^{5/2} \left[ \frac{G_0 + (3K_0G_0 - 5G_0)f}{2} \right] \\
+ \frac{6K_0}{V} \left( \frac{C'_0}{2} - 24K_0 - 14G_0 + \frac{9}{2}K_0 K'_0 \right) \right] \right] \\
- \eta_s \Delta E_{TH} (V, T) \\
\]

(13)

where \( G_0 \) and \( G'_0 \) are the shear modulus and its pressure derivative at ambient conditions and \( \eta_s \) is the shear strain derivative of the Grüneisen parameter.

The formalism described above was used to fit the aggregate wave velocities \( V_P \) and \( V_S \) of \( Py76Mj24 \) and \( Py78Alm6Mj16 \). The values of the EoS parameters (Table 3), \( K_{T0}, K'_{T0}, G_0 \) and \( \eta_s \) were obtained through a least square minimization of the differences between observed and calculated aggregate wave velocities. In the refinement the ambient volume \( V_0 \) was fixed to the value obtained from X-ray diffraction, the Grüneisen parameter \( \gamma_0 \) and the logarithmic volume derivative of the effective Debye temperature, \( q_0 \), were kept at values previously determined for garnets (Xu et al., 2008). The room pressure value of the Debye temperature was calculated from the experimental sound velocities according to the equations from Robie and Edwards (1966):

\[
\theta_0 = \frac{h}{k} \left( \frac{3}{4\pi V_0} \right) \left[ \frac{3}{2} \left( \frac{1}{V_{pq}} + \frac{2}{V_{ps}} \right) \right]^{-\frac{1}{2}}
\]

(14)

where \( h \) is the Plank constant, \( k \) is the Boltzmann constant, \( n = 160 \) is the number of atoms in the garnet unit cell, and \( V_{pq} \),
Table 3, whereas for garnet of dashed 470 K. end shear temperature members of (a) curves are reported in Table 4. and of the Py–Mj join made in this and previous studies, plotted as a function of Mj concentration. The Py78Alm6Mj16 sample is also plotted in addition to two other Alm and Alm and Gr bearing samples from Murakami et al. (2008) and Irifune et al. (2008) respectively. There seems to be a very good agreement between the several studies suggesting that \( G_0 \) decreases slightly with Mj content. Furthermore, Py78Alm6Mj16 lies on the same trend, in excellent agreement with studies on the end-member Alm (Jiang et al., 2004), which has an almost identical \( G_0 \) to Py. The sample studied by Murakami et al. (2008) with 10% Alm plots slightly below the Py–Mj trend, on the other hand, although the difference is relatively small. The Alm and Gr bearing sample of Irifune et al. (2008) plots well above the trend, this is also consistent with measurements on the pure Gr end-member (Jiang et al., 2004), which shows a significantly greater \( G_0 \) (109 GPa) compared to Py. A little more scatter exists in the Py–Mj trend for \( K_{S0} \) with a number of relatively high estimates being made by ultrasonic studies at Mj contents \( \sim 40–50\% \). Many of the Brillouin scattering studies are in good agreement, however. That \( K_{S0} \) for Py78Alm6Mj16 is higher than Py76Mj24 is in qualitative agreement with measurements made on pure Alm, which are higher than the Py end member (Jiang et al., 2004).

In Fig. 4 the moduli pressure derivatives \( K'_{S0} \) and \( G'_0 \) are plotted as a function of Mj content. There is very little variation in \( G'_0 \) even for Alm and Gr bearing samples but \( K'_{S0} \) covers a significant range with many ultrasonic measurements indicating relatively high values. As it can be seen in Fig. 2(a) there are clearly resolvable differences in the pressure derivatives between the Py76Mj24 and Py78Alm6Mj16 samples. The combination of absolute pressure determinations and the use of a Ne pressure medium should ensure that these derivatives are of the highest precision measured for garnet samples to date. The lower values of \( K'_{S0} \) determined for the Alm bearing sample is consistent with the studies of Murakami et al. (2008) and Irifune et al. (2008).

Using the equation of state parameters obtained for Py76Mj24 and Py78Alm6Mj16 (Table 3) sound velocities for these two compositions have been calculated at 20 GPa as a function of temperature up to 2000 K (Fig. 5). These are compared with the trend determined for a polycrystalline Py23Alm8Mj50Gr21 sample by Irifune et al. (2008) up to 1673 K and \( \sim 18 \) GPa.

Irifune et al. (2008) reported that the observed behavior was very different from that normally obtained by extrapolating linear dependences of elastic moduli with temperature, as commonly performed in literature studies (see for example Lu et al., 2013). Note, however, that the thermo-elastic model for the for Py76Mj24 and Py76Alm8Mj16 samples reproduces the non-linear temperature behavior of the velocities.

4.2. Calculation of elastic properties for majoritic garnets from end member compositions

Garnet compositions are likely to vary within the upper mantle and transition zone as a result of pressure and temperature dependent changes in chemical partitioning between coexisting minerals in addition to variations in the mantle’s bulk composition. In order to model the effects of these changes in chemistry on seismic velocities, elastic properties for complex garnet compositions need to be calculated from those of the major end-members, i.e. Py,
Table 3
EoS parameters of majoritic garnets.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$V_0$ (cm$^3$ mol$^{-1}$)</th>
<th>$K_0$ (GPa)</th>
<th>$K'_{T0}$</th>
<th>$\theta_0$ (K)</th>
<th>$\gamma_0$</th>
<th>$\eta_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg$<em>{12.84}$Al$</em>{13.5}$Si$<em>{23}$O$</em>{42}$ (Py$<em>{76}$Mj$</em>{24}$)</td>
<td>113.4</td>
<td>167(2)</td>
<td>166(2)</td>
<td>4.7(2)</td>
<td>791</td>
<td>1</td>
</tr>
<tr>
<td>Mg$<em>{8.01}$Fe$</em>{17}$Al$<em>{15.8}$Si$</em>{22}$O$<em>{42}$ (Py$</em>{98}$Alm$<em>{6}$Mj$</em>{6}$)</td>
<td>113.4</td>
<td>173(1)</td>
<td>172(1)</td>
<td>4.1(1)</td>
<td>795</td>
<td>1.06</td>
</tr>
</tbody>
</table>

$^a$ Calculated via equation (14).
$^b$ Fixed to previously determined values (Xu et al., 2008).

Table 4
Thermo-elastic parameters of mantle components used for calculating the sound wave velocities and densities as a function of pressure and temperature in the transition zone.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Formula</th>
<th>$V_0$ (cm$^3$ mol$^{-1}$)</th>
<th>$K_0$ (GPa)</th>
<th>$K'_{T0}$ (GPa)</th>
<th>$\theta_0$ (K)</th>
<th>$\gamma_0$</th>
<th>$G_0$ (GPa)</th>
<th>$G'_0$ (GPa)</th>
<th>$\eta_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyrope</td>
<td>Mg$_6$Al$_2$Si$<em>3$O$</em>{12}$</td>
<td>113.08</td>
<td>171</td>
<td>4.3</td>
<td>804$^a$</td>
<td>1.4</td>
<td>94</td>
<td>1.4</td>
<td>1.2</td>
</tr>
<tr>
<td>Majorite</td>
<td>Mg$_5$Si$<em>2$O$</em>{12}$</td>
<td>113.97</td>
<td>160</td>
<td>5.0</td>
<td>779$^a$</td>
<td>1.5</td>
<td>86</td>
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</tr>
<tr>
<td>Almandine</td>
<td>Fe$_2$Al$_2$Si$<em>3$O$</em>{12}$</td>
<td>115.43</td>
<td>175</td>
<td>3.7</td>
<td>741</td>
<td>1.4</td>
<td>96</td>
<td>1.1</td>
<td>2.1</td>
</tr>
<tr>
<td>Grossular</td>
<td>Ca$_2$Al$_2$Si$<em>3$O$</em>{12}$</td>
<td>125.12</td>
<td>167</td>
<td>3.9</td>
<td>823</td>
<td>1.5</td>
<td>109</td>
<td>1.2</td>
<td>2.4</td>
</tr>
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<td>Wadsleyite</td>
<td>Mg$_5$Si$<em>2$O$</em>{4}$</td>
<td>40.49</td>
<td>169</td>
<td>4.3</td>
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<td>1.2</td>
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<td>1.4</td>
<td>2.6</td>
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<td>Ringwoodite</td>
<td>Fe$_2$Si$<em>2$O$</em>{4}$</td>
<td>42.80</td>
<td>169</td>
<td>4.3</td>
<td>719</td>
<td>1.2</td>
<td>72</td>
<td>1.4</td>
<td>1.1</td>
</tr>
<tr>
<td>Stishovite</td>
<td>SiO$_{2}$</td>
<td>27.45</td>
<td>236</td>
<td>3.9</td>
<td>802</td>
<td>1.89</td>
<td>157</td>
<td>2.2</td>
<td>1.3</td>
</tr>
</tbody>
</table>

$^a$ Calculated via equation (14); values in italics are taken from Xu et al. (2008) and are in good agreement with recent experimental measurements, whereas values that differ from those reported in the compilation of Xu et al. (2008) are reported in bold.

Fig. 3. Ambient elastic moduli ($K_{SO}$ and $G_0$) as a function of majorite content along the binary majorite–pyrope join. Filled circles: this study; open circles: ultrasonic measurements from Ridgen et al. (1994), Chen et al. (1999), Liu et al. (2000), Gwanmesia et al. (1998, 2006, 2009), Irfune et al. (2008), Zhou et al. (2012), Liu et al. (2015); filled triangles and diamonds: Brillouin spectroscopy measurements on single-crystal and polycrystalline samples, respectively, by Pacalo and Weidner (1997), Sinogeikin and Bass (2000, 2002), Murakami et al. (2008). Three measurements made on more complex compositions have the proportions of almandine [Alm] and grossular [Gr] in the garnets indicated. The solid lines show a linear dependence of $K_{SO}$ and $G_0$ with composition calculated using the end-member data reported in Table 4.

Fig. 4. Ambient first pressure derivatives of the elastic moduli ($K'_{T0}$ and $G'_0$) as a function of majorite content along the binary majorite–pyrope system. Symbols are the same as in Fig. 3. The solid lines show a linear dependence of $K'_{T0}$ and $G'_0$ with composition calculated using the end-member data reported in Table 4.

Mj, Alm and Gr. The elastic properties of a phase consisting of a solid solution of $n$ end-members in a single mineral phase can be derived through a weighted summation of the individual elastic properties of the corresponding end-members:

$$\psi_{SS} = \frac{1}{\sum_{i=1}^{n} \frac{m_i \psi_i}{\psi_i}}$$

where $\psi_{SS}$ is the bulk elastic property of interest, $\psi_i$ is the elastic property of component $i$ and $V_i$ and $m_i$ are the volume and mole fraction of component $i$. This summation assumes that the property in question varies as a linear function of the end-member properties. Recent determinations of $K'_{T0}$ for solid solutions along
the Gr–Py binary suggest that this may not always be an accurate assumption (Du et al., 2015). Due to potential non-linear effects it is possible that fictive end-member properties, determined using data on garnets that have intermediate compositions (and that may, therefore, be closer to those in the mantle), may reproduce the experimental velocities better than using data obtained for end-member compositions.

Using the equation of state model described in Section 3.3, velocities for the Py76Alm24 and Py34Alm9Mj51Gr4 samples were calculated through a summation of the elastic properties of the appropriate end-members, as in equation (15). The initial values of $V_0$, $K'_0$, $\gamma_0$, $\beta_0$, $G_0$, $C'_0$, and $\rho_0$ for the Py, Mj and Alm end-members were initially taken from Xu et al. (2008) (Table 4), although Debye temperatures for Py and Mj were recalculated in accordance with equation (14). The resulting velocities were then compared with the high pressure and temperature experimental values, and the properties for Py, Mj and Alm were refined to minimize the calculated and observed differences. Values which differ from those reported in the compilation of Xu et al. (2008) are reported in bold in Table 4. The lines in Figs. 3 and 4 show how the moduli and their derivatives change across the Py–Mj join according to the resulting model.

Using data for Gr from the literature (Xu et al., 2008), the model has been used to calculate acoustic velocities for the Py76Alm24Mj24Gr21 composition examined by Irifune et al. (2008). The model calculations, performed at 20 GPa as a function of temperature, are compared with the experimental curves of Irifune et al. (2008) in Fig. 5. The shear velocity curve reported by Irifune et al. (2008) is extremely well reproduced by the resulting model, both in terms of the absolute values and the velocity gradient with temperature. The calculated longitudinal velocities are higher by ~1 km s$^{-1}$ than the experimental values at room temperature but converge to be in excellent agreement at mantle temperatures. Although the agreement should be in principal good at all temperatures, it is possible that in the multianvil measurements deviatoric stresses at low temperatures cause this difference, which decreases with temperature (Gwamnesia et al., 2006).

4.3. Implication for the Earth’s transition zone

The elastic properties of garnets determined in this study were used along with additional literature data (summarized in Table 4) to calculate seismic velocities for pyrolite, harzburgite and MORB bulk compositions at the base of the transition zone, in the depth range between 480 and 660 km. Calculations were not performed at lower pressures due to the absence of sufficient data on the clinopyroxene mineral properties. The calculations were performed along an adiabat with a potential temperature of 1673 K employing thermodynamic models to describe variations in the proportion and chemistry of the mineral phases. A Voigt–Reuss–Hill averaging scheme was used to extract the aggregate elastic properties from those of the individual minerals. Phase relations at the base of the transition zone are relatively simple and can be described using models that have been derived within a number of experimental studies (Frost, 2003; Frost and Dolejs, 2007; Saikia et al., 2008).

At 480 km a pyrolite composition will be comprised of only wadsleyite and majoritic garnet (Irifune and Isshiki, 1998). Based on the bulk composition and using Fe–Mg partitioning data from Irifune and Isshiki (1998) it is then straightforward to calculate the compositions of both phases, which results in 42 vol.% garnet with the composition Py14Alm6Mj36Gr0. At approximately 540 km, wadsleyite undergoes a phase transition to ringwoodite over a depth interval of approximately 20 km, which can be described using thermodynamic models that have been fit to experimental data (Frost, 2003; Frost and Dolejs, 2007). Between 480 and 620 km the garnet composition and proportion remain constant apart from small changes in Fe–Mg partitioning between wadsleyite and ringwoodite. However, at 620 km CaSiO$_3$ perovskite (Ca-Pv) starts to exsolve from garnet, with the volume proportion of Ca-Pv gradually increasing with depth at the expense of the grossular component of garnet (Saikia et al., 2008). As a consequence, the garnet composition loses Ca but also becomes less majoritic. The gradual increase of Ca-Pv and the consequent compositional variations in garnet can be described using the thermodynamic model of Saikia et al. (2008). At the base of the transition zone the pyrolytic mineralogy comprises 58 vol.% ringwoodite, (MgSi$_2$FeO$_{1.75}$SiO$_3$, 36 vol.% garnet (Py$_{14}$Al$_{6}$Mj$_{36}$Gr$_{0}$) and 6 vol.% CaSiO$_3$ perovskite.

In contrast to pyrolite, an average MORB composition in the mantle transition zone is composed almost entirely of garnet (89 vol.%) with additional stishovite (11 vol.%) (Irifune et al., 1986). As for the pyrolyte composition, in the lower transition zone Ca-Pv starts to exsolve from majoritic garnet, the phase relations of which can also be described using the thermodynamic model of Saikia et al. (2008). Because the Ca content of subducted oceanic crust (MORB) is higher than that of pyrolite, garnets should become saturated in CaSiO$_3$ at lower pressures. However, the saturation pressure is also a function of the garnet majorite component (Saikia et al., 2008), which is lower in MORB with respect to a pyrolite composition. These two effects act in opposite directions and ensure that the exsolution of CaSiO$_3$ perovskite from garnet occurs at approximately the same depth as observed for the pyrolytic composition. With increasing pressure, as CaSiO$_3$ perovskite exsolves, the garnet becomes more Al-rich. At the base of the transition zone the MORB mineralogy comprises 72 vol.% garnet (Py$_{11}$Al$_{5}$Mj$_{36}$Gr$_{11}$), 11 vol. % SiO$_2$ and 17 vol.% CaSiO$_3$ perovskite.

Harzburgite phase relations are similar to those of pyrolite over the same depth interval, with the main difference being a higher proportion of (Fe,Mg)$_2$SiO$_4$. At 480 km the average harzburgite composition employed (Irifune and Ringwood, 1987b) is calculated to comprise 81.5 vol.% wadsleyite and 18.5 vol.% of majoritic garnet with the composition Al$_2$Mg$_{10}$Gr$_8$. Phase transformations are similar to those in pyrolyte, although due to the low Ca content the exsolution of CaSiO$_3$ is almost insignificant and the low Al content results in a more majoritic rich garnet.
The sound velocities $V_S$ and $V_P$ calculated for the three bulk compositions described above are compared with the seismic reference models PREM and AK135 in Fig. 6.

Although the pyrolite model is in agreement at least with AK135 in terms of $V_P$, there is a consistent negative deviation for $V_S$, by $\sim 0.2$ km/s, between pyrolite and both reference models over the 150 km of the base of the transition zone. Garnet elastic properties are the main reason for this deviation as both ringwoodite and CaSiO$_3$-perovskite have velocities that are above both reference models at these conditions. Reference models are generally averaged velocity structures and it should, in principal, be possible to approximate this structure using an average mantle composition, mineralogy and temperature. Reference models are unlikely to capture the detail of the velocity structure, however, particularly in the transition zone, due to the overly simplified polynomial functions upon which they are based (Cammarano et al., 2005). Trade-offs between the magnitude of seismic discontinuities and the velocity gradient, for example, are likely to cause inaccuracies in the determinations of both. On average, however, negative deviations from the real mantle velocity structure would be expected to be balanced by near-by positive deviations. This would appear not to be the case in the transition zone, however, if a pyrolite model along a 1600 K adiabat is assumed to resemble the real mantle.

Irfune et al. (2008) also reported that estimated velocities for pyrolite are lower than the reference models at approximately 575 km, but suggested that the subsequent exsolution of CaSiO$_3$ perovskite from garnet would decrease the discrepancy toward the base of the transition zone. Sinogeikin and Bass (2002) similarly argued that CaSiO$_3$ perovskite exsolution would raise the velocity gradient. Note, however, that in this study, the gradual formation of CaSiO$_3$-rich perovskite and the resulting compositional variations in garnet have been taken into account. A very slight increase in the velocity gradient for the pyrolite model occurs above 570 km due to CaSiO$_3$ exsolution. Without this exsolution the pyrolite velocities would have the same gradient as the harzburgite model. Although shear wave properties of CaSiO$_3$ perovskite are poorly constrained, the $G_S$ used in the current model (Xu et al., 2008) is at the very high limit of recent theoretical studies (Kawai and Tsuchiya, 2015) and is higher than experimental estimates (Kudo et al., 2012). Therefore, it seems unlikely that the $V_S$ for CaSiO$_3$ perovskite is significantly underestimated, in fact the contrary seems more likely. It appears, therefore, that pyrolite along a 1673 K adiabat provides a poor match to seismic reference models at the base of the transition zone.

Other bulk compositions have been proposed for the transition zone, such as picrolite (Bass and Anderson, 1984; Anderson and Bass, 1986), however from Fig. 6 it appears that increasing the basaltic component of a mineralogical assemblage does not result in an increase of $V_S$ values to levels compatible with the reference models. For the MORB composition, the exsolution of CaSiO$_3$ perovskite can be clearly seen to cause an increase in gradient above 550 km. Although the resulting gradient is closer to the reference models, the absolute values remain 0.1 km/s below both reference models throughout the base of the transition zone.

A number of other effects that could, in principal, cause differences between mineral and seismic models are also likely to further lower the calculated mineral velocities. For example, anelastic effects that cause dispersion and variations of mineral velocities as a function of acoustic wavelength are likely to lower the velocities of mineral models that account for them. Similarly, the presence of minor defects such as those caused by the presence of dissolved OH$^-$ in minerals also will only lower velocities (Jacobsen, 2006).

If subducted material accumulates at the base of the transition zone it is possible that a significant portion of the material in this regions is composed of melt depleted harzburgite. As shown in Fig. 6, although melt depletion increases the proportion of (Fe,Mg)$_2$SiO$_4$ phase which raises velocities, they still fall below the reference models.

One of the few remaining plausible explanations for the deviation between mineral and seismic models at the base of the transition zone would be if the average mantle temperature over this depth interval is below the 1673 K adiabat. While mantle adiabatic temperatures determined from erupted basalt melt compositions vary by approximately $\pm 15^\circ$ (Lee et al., 2009), the estimated temperature needed for the pyrolite model to match the seismic model at the base of the transition zone is $\sim 500$ K lower than 1673 K. This would place mantle temperatures far outside of the range of adiabatic temperature estimates from the surface or from temperature estimates based on the depth of the 410 km discontinuity (Frost, 2008). Salkia et al. (2008) noted that to associate the 520 km seismic discontinuity with the wadsleyite to ringwoodite transformation requires lower than expected average mantle temperatures. This can be seen in Fig. 6, where the wadsleyite to ringwoodite transformation along a 1673 K adiabat occurs at 550 km, and only if temperatures were $\sim 300$ K lower would the transition occur at 520 km. Salkia et al. (2008) suggested that a possible cause of lower mantle temperatures may be the presence of subducting slabs stagnating at the base of the transition zone and flattening out to form significant lateral cold heterogeneities. Some tomographic models (e.g. Káraón and Van der Hilst, 2000) appear to clearly indicate that such heterogeneities exist. As temperatures in the center of such slabs could be easily 600 K below the average mantle, they could drag down average mantle temperatures at these depths, assuming that the lateral anomalies were large enough. Furthermore it is possible that a significant proportion of this material will be of near harzburgite composition. It can be estimated that temperatures would have to be only 200 K below the 1673 K adiabat for harzburgite mineral model velocities to match seismic reference models at the base of the transition zone. If such global horizontal anomalies exist, this average reduction in temperature may be plausible and would be also consistent with the 520 km seismic discontinuity being caused by the wadsleyite to ringwoodite transformation.
Appendix A. Supplementary material

Supplementary material related to this article can be found online at http://dx.doi.org/10.1016/j.epsl.2016.07.019.

References


