1 **Single crystal elasticity of majoritic garnets: stagnant slabs and thermal anomalies at the base**
2 **of the transition zone**

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19

20 **Abstract**

21 The elastic properties of two single crystals of majoritic garnet ($\text{Mg}_{3.24}\text{Al}_{1.53}\text{Si}_{3.23}\text{O}_{12}$ and
22 $\text{Mg}_{3.01}\text{Fe}_{0.17}\text{Al}_{1.68}\text{Si}_{3.15}\text{O}_{12}$), have been measured using simultaneously single-crystal X-ray
23 diffraction and Brillouin spectroscopy in an externally heated diamond anvil cell with Ne as
24 pressure transmitting medium at conditions up to ~30 GPa and ~600 K. This combination of
25 techniques makes it possible to use the bulk modulus and unit-cell volume at each condition to
26 calculate the absolute pressure, independently of secondary pressure calibrants.

27

28 Substitution of the majorite component into pyrope garnet lowers both the bulk (K_s) and shear
29 modulus (G). The substitution of Fe was found to cause a small but resolvable increase in K_s that
30 was accompanied by a decrease in $\partial K_s / \partial P$, the first pressure derivative of the bulk modulus. Fe
31 substitution had no influence on either the shear modulus or its pressure derivative. The obtained
32 elasticity data were used to derive a thermo-elastic model to describe V_s and V_p of complex garnet
33 solid solutions. Using further elasticity data from the literature and thermodynamic models for
34 mantle phase relations, velocities for mafic, harzburgitic and lherzolitic bulk compositions at the
35 base of Earth's transition zone were calculated. The results show that V_s predicted by seismic
36 reference models are faster than those calculated for all three types of lithologies along a typical
37 mantle adiabat within the bottom 150 km of the transition zone. The anomalously fast seismic shear
38 velocities might be explained if laterally extensive sections of subducted harzburgite-rich slabs pile
39 up at the base of the transition zone and lower average mantle temperatures within this depth range.

40

41 **Keywords:** elasticity; majoritic garnet; subduction; transition zone; stagnant slabs; thermal
42 anomalies.

43

44 1. Introduction

45 Seismic velocity profiles of the Earth's interior provide essential information for constraining the
46 thermal and chemical state of the mantle (Anderson and Bass, 1986; Irifune and Ringwood, 1987a;
47 Ita and Stixrude, 1992). The correct interpretation of these profiles in terms of mantle mineralogy
48 and chemistry, however, requires laboratory or computational data on the elasticity of candidate
49 minerals at conditions of the Earth's mantle. In this context, knowledge of the thermo-elastic
50 properties of garnet solid solutions are essential, since they make up a major proportion of both
51 mafic and ultramafic rocks in the upper mantle and transition zone (Irifune and Ringwood, 1987a).
52 Garnets recovered from the Earth's mantle crystallize in the cubic space group $1a\bar{3}d$ forming a

53 series of complex solid solutions that are described using the crystal-structural formula
 54 $^{VII}X_3^{VI}Y_2^{IV}Z_3O_{12}$. Large cations, $X = Mg, Ca, Fe^{2+}$, occupy the 8-fold coordinated dodecahedral
 55 sites, medium sized cations, $Y = Al, Fe^{3+}, Cr$, occupy the octahedral sites, whereas the tetrahedral Z
 56 site is occupied by Si. At pressures above 5 GPa the coupled substitution of Si and Mg (and Fe)
 57 onto the Y site occurs in garnets within mantle assemblages as a result of the breakdown of both
 58 orthopyroxene and clinopyroxene. This, so called, majorite substitution increases the proportion of
 59 garnet in mantle rocks at the expense of pyroxenes in the Earth's deep upper mantle and transition
 60 zone (Ringwood, 1967). The Al-free garnet end-member is referred to as majorite, Mj ($Mg_4Si_4O_{12}$)
 61 and crystallizes with tetragonal symmetry due to ordering of Mg and Si on the octahedral sites. Pure
 62 Mj is stable at pressures between 16 and 23 GPa and temperatures above 1600 °C (Kato and
 63 Kumazawa, 1985; Angel et al., 1989). In upper mantle ultramafic rocks garnets are solid solutions
 64 that are dominated by the end member pyrope (Py, $Mg_3Al_2Si_3O_{12}$) but have sub-equal proportions
 65 of almandine (Alm, $Fe_3Al_2Si_3O_{12}$) and grossular (Gr, $Ca_3Al_2Si_3O_{12}$). With increasing pressure,
 66 however, the Mj end member becomes increasingly important and dominates in the transition zone
 67 (410 – 660 km depth). A key issue concerning the structure of the Earth's interior is the extent and
 68 scale at which the mantle can be considered homogeneous. A number of studies have proposed, for
 69 example, that the mantle may become richer in mafic material with depth (e.g. Anderson and Bass
 70 1986). One of the main expressions of such chemical heterogeneity in the mantle would be variation
 71 in the chemistry and proportion of garnet. Garnets constitute approximately 40 % by volume of
 72 ultramafic compositions and 70 % of mafic compositions (Anderson and Bass, 1986; Irifune and
 73 Ringwood, 1987a; Ita and Stixrude, 1992), but garnets formed from mafic assemblages will have
 74 greater Gr and Alm contents and in the transition zone less Mj compared to ultramafic assemblages.
 75 Knowledge of how the elastic properties of garnet change as the bulk chemistry changes is,
 76 therefore, important.

77

78 Several studies have investigated the elastic properties of Py–Mj garnets at room pressure and
79 temperature (Bass and Kanzaki, 1990; O’Neill et al., 1991). Moreover elastic moduli measurements
80 have also been performed at high pressure and room temperature, using ultrasonic techniques on
81 polycrystalline aggregates (Rigden et al., 1994; Gwanmesia et al., 1998; Chen et al., 1999; Wang
82 and Ji, 2001) and through the use of Brillouin spectroscopy on both single crystals (Conrad et al.,
83 1999; Sinogeikin and Bass, 2000; Murakami et al., 2008) and powdered samples (Sinogeikin and
84 Bass, 2002). Recent improvements in ultrasonic techniques coupled with synchrotron X-ray
85 radiation have allowed sound velocity measurements on polycrystalline samples along the Py–Mj
86 solid solution to be performed at simultaneous high P and T (Irifune et al., 2008; Gwanmesia et al.,
87 2009; Liu et al., 2015). Furthermore the single-crystal elasticity of an iron-bearing pyrope was
88 recently obtained simultaneously at high-pressures (up to 20 GPa) and high-temperature (750 K)
89 using Brillouin spectroscopy and X-ray diffraction (Lu et al., 2013). While the value of the bulk and
90 shear moduli, K_s and G , reported by these studies cover a relatively small range, the exact
91 dependence particularly of K_s on Mj content is unclear, large discrepancies in elastic moduli
92 pressure derivatives exist, the thermal properties are poorly constrained as is the further effect of the
93 Alm content. Consequently, the interpretations of seismic velocity gradients in the transition zone
94 remain uncertain.

95
96 The aim of this study is, therefore, to constrain the elastic properties of majoritic garnets as a
97 function of density, temperature and composition under hydrostatic conditions by employing a
98 combination of single-crystal Brillouin scattering and X-ray diffraction measurements. The
99 simultaneous measurement of elastic properties and density are used to also obtain absolute values
100 of the experimental pressure, avoiding in this way any systematic errors that may be introduced
101 through the use of secondary pressure calibrations. The elasticity data obtained are fitted to a self-
102 consistent thermo-elastic model from which thermodynamic properties of the garnet end-members
103 are estimated. Acoustic velocities of mafic, harzburgitic and lherzolithic assemblages are then

104 calculated along a typical mantle adiabat at conditions of the Earth's transition zone by combining
 105 our garnet model with properties for coexisting minerals from the literature. The results are then
 106 compared with seismic reference models reported over the same depth interval to constrain the
 107 plausible mineralogy and temperature at the base of the Earth's transition zone.

108

109 2. Experimental methods

110 2.1. Sample synthesis and characterization

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

118

Table 1. Starting materials in wt. % of oxides

	pyrope glass	mixture Py1	mixture Py3	enstatite glass	Fe- Majorite	Mixtures A', B', C', D'
Al ₂ O ₃	25.29	19.95	22.3	-	12.91	A': 50 % enstatite glass - 50 % mixture Py1 (10.56 wt. % H ₂ O)
MgO	44.71	23.66	26.45	40.15	26.96	B': 50 % enstatite glass – 50 % mixture Py2 (7.92 wt. % H ₂ O)
SiO ₂	29.99	35.27	39.43	59.85	42.8	C': 50 % enstatite glass – 50 % mixture Py3 (5.91 wt. % H ₂ O)
Fe ₂ O ₃	-	-	-	-	5.28	D': 50 % enstatite glass – 50 % mixture Py4 (1.48 wt. % H ₂ O)
H ₂ O	-	21.12	11.81	-	12.04	
Sum	100	100	100	100	99.99	

119 Note: mixture Py2 = 25 % pyrope glass + 75 % mixture Py1; mixture Py4 = 75 % pyrope glass + 25
 120 % mixture Py3

121

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

125 High-pressure experiments aimed at producing majoritic garnets were carried out using a 5000 t
126 multi-anvil apparatus at the Bayerisches Geoinstitut. A 18 mm edge length Cr₂O₃-doped (5 wt. %)
127 MgO octahedron was used as a pressure medium with tungsten carbide cubes of 52 mm edge length
128 and 11 mm truncation edge length (18/11 assembly). The pressure calibrations for the assembly
129 used in this study are reported in Keppler and Frost (2005). The samples were first pressurized to 17
130 GPa followed by heating at 1900 °C for 5 minutes. After heating at high pressure, the experiments
131 were quenched by shutting off the power and the run-products were recovered after decompressing
132 for 18 hours. The recovered capsules were embedded in epoxy resin, ground and polished for
133 electron probe microanalysis. Single-crystals of majoritic garnet (up to ~200 µm in length) were
134 obtained from the starting composition (mixture A') that contained the largest amount of water (Fig.
135 S1, supplementary information).

136

137 An iron bearing majoritic garnet with a similar composition to that recovered above was also
138 prepared from a glass starting material that contained H₂O added as Mg(OH)₂ (Fe-majorite, see
139 Table 1). An oxide mixture of Al₂O₃, SiO₂ and Fe₂O₃ was initially melted in air at 1600 °C for
140 twenty minutes and then rapidly quenched in icy water. This glass was then reduced in a 1-
141 atmosphere furnace, at 1000 °C and at an oxygen fugacity (*f*O₂) of 2 logs units below the quartz-
142 fayalite-magnetite oxygen buffer for approximately 12 hours. This process was performed twice in
143 order to ensure the complete reduction of the mixture. Mg(OH)₂ was then added to the glass to
144 obtain a hydrous composition. The starting material was loaded into a double capsule consisting of
145 a 1.6 mm diameter Re inner capsule and an outer capsule made of a 2 mm diameter platinum tube,

146 welded closed at both ends. The synthesis run was performed using the same procedure and
147 conditions followed for the iron-free samples.

148

149 Element concentrations in the recovered samples were measured with a JEOL JXA-8200 electron
150 probe microanalyser (EPMA), operating at 15 kV and 15 nA. The electron beam size was
151 approximately 1-2 μm in diameter and the peak counting times were 20 s. Enstatite or diopside,
152 spinel, forsterite, and metallic iron were used as standards for determining the concentrations of Si,
153 Al, Mg and Fe respectively. The chemical analysis resulted in the following composition: 32.0 (6)
154 % MgO, 47.5 (9) % SiO_2 , 19 (2) % Al_2O_3 (in wt.), for the Py-Mj garnet (hereafter named $\text{Py}_{76}\text{Mj}_{24}$)
155 and 29.5(5) % MgO, 46(1) % SiO_2 , 3.3(5) % FeO, 21(2) % Al_2O_3 (in wt.) for the iron bearing
156 sample (hereafter named $\text{Py}_{78}\text{Alm}_6\text{Mj}_{16}$). The chemical formulas are $\text{Mg}_{3.24}\text{Al}_{1.53}\text{Si}_{3.23}\text{O}_{12}$ and
157 $\text{Mg}_{3.01}\text{Fe}_{0.17}\text{Al}_{1.68}\text{Si}_{3.15}\text{O}_{12}$, respectively.

158 FTIR analyses were performed on crystals of $\text{Py}_{76}\text{Mj}_{24}$ produced in the same experiment and show
159 OH absorption bands consistent with approximately 20 ppm wt. H_2O . Measurements were carried
160 out at the Laboratoire Magmas et Volcans (LMV) in Clermont-Ferrand, France. The quantitative
161 analyses were performed following the calibration of Paterson (1982). The synthesized majoritic
162 garnets can, therefore, be considered to contain negligible amounts of H_2O .

163

164 **2.2. Simultaneous X-ray diffraction and Brillouin scattering**

165 The P - V - T equations of state and the compressional, V_p , and shear, V_s , sound velocities of two
166 single-crystals of majoritic garnet ($\text{Py}_{76}\text{Mj}_{24}$ and $\text{Py}_{78}\text{Alm}_6\text{Mj}_{16}$) were each determined by means of
167 simultaneous Brillouin spectroscopy and X-ray diffraction. High quality single-crystals, of $\sim 70 \mu\text{m}$
168 in size, were selected based on their sharp diffraction profiles. The crystals were parallel polished
169 into platelets with a thickness of 10-18 μm and then loaded into piston cylinder diamond anvil cells.
170 Boehler-Almax diamonds were employed with 400-350 μm culets in combination with tungsten
171 carbide seats. Rhenium gaskets of 200 μm in thickness were pre-indented to 40-55 μm before

172 drilling 250 μm cylindrical holes. Single-crystals of Sm:YAG (Sm-doped YAlO_3 garnet) as well as
173 ruby chips were added as secondary pressure calibrants. A neon gas pressure medium was loaded
174 into the sample chamber using the high pressure gas loading devices at the Bayerisches Geoinstitut
175 (Kurnosov et al., 2008) as well as at GSECARS (Rivers et al., 2008).

176

177 The pressure inside the cell was monitored before and after each Brillouin and X-ray measurement
178 using an Acton standard series spectrograph from Princeton Instruments, employing the same laser
179 and the same geometry as in the Brillouin experiment. An external resistive heater suitable for the
180 piston cylinder type cells employed in this study was designed and placed around the diamonds for
181 achieving high temperatures (see text S1 supplementary information). An S-type thermocouple
182 located near the diamond surface was used to monitor the temperature inside the cell. However, to
183 constrain the temperature inside the high pressure chamber without relying uniquely on the
184 thermocouple, an alternative approach was used. The fluorescence shifts of Sm:YAG, which are
185 independent of temperature, were used to determine pressure (Trots et al., 2013), whereas
186 temperature was determined using the fluorescence of ruby (Rekhi et al., 1999) by fixing the
187 pressure value obtained from the Sm:YAG measurement. Maximum temperatures reached
188 estimated in this way were 558 K and 470 K for $\text{Py}_{76}\text{Mj}_{24}$ and $\text{Py}_{78}\text{Alm}_6\text{Mj}_{16}$ respectively. However,
189 the maximum thermocouple temperature readings were 600 K for $\text{Py}_{76}\text{Mj}_{24}$ and 650 K for
190 $\text{Py}_{78}\text{Alm}_6\text{Mj}_{16}$, i.e. larger than the actual temperatures experienced by the majoritic samples.

191

192 Simultaneous acquisition of density and sound velocities at room pressure was performed at the
193 Bayerisches Geoinstitut. The lattice parameters of both samples were determined using eight-
194 position centring of 15 Bragg reflections ($25^\circ < 2\theta < 40^\circ$) according to the procedure of King and
195 Finger (1979) on a Huber diffractometer equipped with point detector and driven by the program
196 SINGLE (Angel and Finger, 2011). The resulting unit-cell volumes are 1506.6 (5) $\text{\AA}^3$ and 1506.8
197 (1) $\text{\AA}^3$ for $\text{Py}_{76}\text{Mj}_{24}$ and $\text{Py}_{78}\text{Alm}_6\text{Mj}_{16}$ respectively. The unit-cell volumes are practically identical

198 because Alm replaces Mj in the second sample and both components have a qualitatively similar
 199 effect on the volume. Typical half-widths of the ω profiles of different reflections varied between
 200 0.060° and 0.100° . Brillouin scattering measurements were performed in a 80° symmetric/platelet
 201 scattering geometry with plate spacing of 4 mm using a coherent Verdi V2 solid state Nd:YVO₄
 202 frequency doubled laser ($\lambda = 532.0$ nm) at the power of ~ 150 -200 mW. The room pressure
 203 Brillouin scattering measurements of Py₇₈Alm₆Mj₁₆ were performed at the GeoForschungsZentrum
 204 (GFZ) in Potsdam as well as at PETRA III in Hamburg, employing a 60 and 49 degree forward
 205 symmetric scattering geometry with plate spacing of 6 mm and 8 mm respectively. A coherent
 206 Verdi V2 solid state Nd:YVO₄ frequency doubled laser ($\lambda = 532.0$ nm) was used.
 207 Simultaneous measurements of sound velocities and density at different pressures and temperatures
 208 were performed at the BM-13-D (GSECARS) beamline at the Advanced Photon Source (APS). The
 209 samples were each measured first upon compression up to approximately 20 and 21 GPa at room
 210 temperature and then heated to 558 K (Py₇₆Mj₂₄) and 470 K (Py₇₈Alm₆Mj₁₆) respectively. During
 211 heating the pressure increased to 30 GPa, therefore Brillouin spectra and density were measured
 212 along an isotherm (at high temperature) upon decompression. X-ray diffraction measurements were
 213 performed using a Perkin Elmer detector, collecting step scans in an omega range of 50° or 70° with
 214 a step size of 1° and 5 s/step exposure time. Brillouin scattering measurements were performed with
 215 a six-pass Sandercock-type tandem Fabry-Pérot interferometer using a coherent Verdi V2 solid state
 216 Nd:YVO₄ frequency doubled laser ($\lambda = 532.0$ nm) as a light source. Measurements were performed
 217 in a 50° symmetric/platelet scattering geometry with plate spacing of 6.5-7 mm. Brillouin spectra
 218 were collected with a laser power of 400 mW. Acoustic velocities, V_{acoustic} , were determined from
 219 the frequency shift using the following relationship (Whitfield et al., 1976):

$$220 \quad V_{\text{acoustic}} = \Delta\nu * \lambda_0 / 2 * \sin(\theta/2) \quad (1)$$

221 where $\Delta\nu$ is the measured Brillouin shift, λ_0 is the incident laser wavelength, θ is the external
 222 scattering angle.

223

224 3. Results

225 3.1. Elasticity

226 The acoustic velocities of the $\text{Py}_{76}\text{Mj}_{24}$ and $\text{Py}_{78}\text{Alm}_6\text{Mj}_{16}$ samples measured at ambient conditions
 227 in different crystallographic directions as a function of χ angle are shown in Fig. 1.

230 **Fig. 1.** (a) Compressional and shear wave velocities of $\text{Py}_{76}\text{Mj}_{24}$ as a function of crystallographic
 231 direction at room pressure and temperature. Inset: Brillouin spectra collected for a given
 232 crystallographic orientation at room pressure and temperature (top) and at 28.04 GPa and 558 K

(bottom). (b) Compressional and shear wave velocities of $\text{Py}_{78}\text{Alm}_6\text{Mj}_{16}$ as a function of crystallographic direction at room pressure and temperature. The Brillouin spectrum reported in the inset was collected at 21.10 GPa.

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 garnets (e.g. Sinogeikin and Bass, 2000; Murakami et al., 2008; Lu et al., 2013).

The measured sound velocities are a function of the wave propagation direction and polarization q_i (referred to the crystal reference system), the elastic moduli C_{ijkl} and the density ρ of a given material, according to the Christoffel equation:

$$|C_{rlsm}q_lq_m - \rho V_{acoustic}^2 \delta_{rs}| = 0 \quad (2)$$

where δ_{rs} is the Kronecker delta. Elastic constants can thus be obtained by fitting the solutions of the equation of motion to the measured sound velocities. However, as reported in previous studies (Murakami et al., 2008), the elastic constants of majoritic garnet can also be calculated by averaging the measured acoustic velocities over several non-symmetric directions given the negligible anisotropy. The aggregate values so obtained are indistinguishable, within experimental uncertainties, from those derived from least-squares fitting to Christoffel's equation. In this study, aggregate V_p and V_s wave velocities were obtained as the average of all longitudinal and transverse velocity measurements (for up to three orientations) at each pressure and temperature. The aggregate elastic moduli were then calculated from these aggregate velocities. The majoritic single-crystal elastic moduli can then be related to the aggregate moduli through the following equations:

$$C_{11} = K_s + \frac{4}{3} G = \rho V_p^2 \quad (3)$$

$$C_{44} = G = \rho V_s^2 \quad (4)$$

$$C_{12} = K_s - \frac{2}{3} G = \rho (V_p^2 - 2V_s^2) \quad (5)$$

258 assuming the equality:

259 $2C_{44} = C_{11} - C_{12}$ (6)

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

262

Table 2. Single-crystal and aggregate elastic properties, aggregate sound velocities as a function of absolute pressure, temperature and density of majoritic garnets.

ρ (g/cm ³)	P_{abs} (GPa)	T (K)	C_{11} (GPa)	C_{12} (GPa)	C_{44} (GPa)	V_s (km/s)	V_p (km/s)	K_s (GPa)	G (GPa)
<i>Py₇₆Mj₂₄</i>									
3.552(3)	0.00010(1)	298	290(3)	109(2)	91(1)	5.05(1)	9.03 (3)	169(3)	91(1)
3.692(3)	7.1(2)	298	333(6)	128(6)	102(1)	5.26(2)	9.50 (8)	197(6)	102(1)
3.729(3)	9.10(11)	298	349(4)	139(3)	105(1)	5.30(2)	9.67 (2)	209(3)	105(1)
3.750(3)	10.2(4)	298	351(8)	140(8)	106(1)	5.31(2)	9.68(10)	210(8)	106(1)
3.783(3)	12.2(7)	298			109(1)	5.37(2)			109(1)
3.844(3)	15.9(5)	298	390(4)	166(2)	112(1)	5.40(2)	10.080(8)	241(3)	112(1)
3.840(3)	15.6(7)	298	385(9)	161(9)	112(1)	5.41(5)	10.01(10)	235(9)	112(1)
3.892(3)	18.9(4)	298	406(4)	176(2)	115(1)	5.436(7)	10.22 (2)	253(3)	115(1)
3.904(3)	19.7(9)	298	414(10)	180(9)	117(2)	5.47(2)	10.29(11)	258(9)	117(2)
4.024(4)	28.8(1.8)	558	463(14)	216(14)	123(3)	5.53(5)	10.72(15)	298(14)	123(3)
3.980(4)	25(2)	558	422(17)	185(17)	119(3)	5.46(4)	10.30(20)	264(14)	119(3)
3.926(4)	22.0(1.0)	558	409(9)	181(9)	114(2)	5.39(5)	10.21(10)	257(9)	114(2)
3.834(4)	16.2(5)	558	382(6)	160(6)	111(2)	5.38(3)	9.98 (7)	234(6)	111(2)
<i>Py₇₈Alm₆Mj₁₆</i>									
3.601(3)	0.00010(1)	298	296(4)	111(2)	92(1)	5.068(8)	9.07(3)	173(3)	92(1)
3.622(3)	1.00(6)	298	301(5)	111(5)	95(1)	5.11(1)	9.11(7)	174(5)	95(1)
3.664(3)	3.10(12)	298	314(7)	120(7)	97(1)	5.14(2)	9.26(9)	185(7)	97(1)
3.757(3)	7.9(6)	298	345(14)	138(14)	104(2)	5.25 (3)	9.58(19)	207(14)	104(2)
3.832(3)	12.1(7)	298	364(11)	150(11)	107(1)	5.28(1)	9.75(14)	222(11)	107(1)
3.874(3)	14.5(5)	298	374(7)	150(8)	112(2)	5.38(5)	9.84(8)	225(7)	112(2)
3.931(3)	18.0(4)	298	398(6)	168(5)	115(1)	5.40(1)	10.06(6)	245(5)	115(1)
3.981(3)	21.1(6)	298	412(7)	176(7)	118(1)	5.45(1)	10.18(7)	255(6)	118(1)
4.047(4)	26.0(1.6)	470	438(13)	195(12)	121(1)	5.47(1)	10.40(15)	276(13)	121(1)
4.022(4)	24.4(1.7)	470	435(9)	195(9)	120(2)	5.46(3)	10.40(17)	275(15)	120(2)
3.961(4)	20.4(1.9)	470	396(20)	170(20)	113(2)	5.34(4)	10.00(24)	245(20)	113(2)
3.897(4)	16.5(7)	470	389(9)	164(9)	113(1)	5.37(2)	9.99(11)	239(9)	113(1)
3.826(4)	12.4(1.3)	470	362(20)	151(20)	106(1)	5.25(3)	9.73(27)	221(20)	106(1)

263

264 Brillouin spectra collected on samples within diamond anvil cells at different pressures,
 265 temperatures and orientations typically have different signal to noise ratios that depend on the
 266 crystal optical quality and its orientation in addition to the laser focusing, sample alignment and
 267 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 adjusting 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).

275

276 **3.2. Absolute pressure determination**

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

$$281 \quad P = \int_{V_0}^V \frac{K_T(V)}{V} dV \quad (7)$$

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

$$285 \quad K_S = K_T(1 + \alpha\gamma T) \quad (8)$$

286 where α is the volume thermal expansion and γ is the Grüneisen parameter. The values of α and γ
287 for majoritic garnets were assumed to be equal to those of pyrope and were taken from Ahrens
288 (1995).

289

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

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Fig. 2. Variation of the shear (V_s) and compressional (V_p) wave velocities as a function of absolute pressure of (a) $Py_{76}Mj_{24}$ and $Py_{78}Alm_6Mj_{16}$ at room temperature, (b) of $Py_{76}Mj_{24}$ at room temperature and at 558 K and (c) of $Py_{78}Alm_6Mj_{16}$ at room temperature and at 470 K. Solid curves

are calculated from the parameters given in Table 3, whereas dashed curves are calculated from the thermo-elastic model parameters for garnet end members reported in Table 4.

The values of V_S and V_P wave velocities of $\text{Py}_{76}\text{Mj}_{24}$ and $\text{Py}_{78}\text{Alm}_6\text{Mj}_{16}$ are very similar at room pressure, however, they deviate at high pressures, with $\text{Py}_{76}\text{Mj}_{24}$ 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 employs a Mie-Grüneisen equation of state 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 Helmholtz 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:

$$K_T = (1 + 2f)^{5/2} \left[K_0 + (3K_{T0}K'_{T0} - 5K_0)f + \frac{27}{2}(K_0K'_0 - 4K_0)f^2 \right] + (\gamma + 1 - q)\gamma \frac{\Delta E_{TH}(V,T)}{V} - \frac{\gamma^2}{V} [TC_V(V,T) - T_0C_V(V,T_0)] \quad (9)$$

where

$$f = \frac{1}{2} \left[\left(\frac{V_0}{V} \right)^{2/3} - 1 \right] = -\epsilon \quad (10)$$

is the negative of the eulerian strain (ϵ), V is the molar volume, T is temperature, K_{T0} and K'_{T0} are the isothermal bulk modulus and its pressure derivative and the subscript zero indicates the reference state set at room conditions, $q = \left(\frac{\partial \ln \gamma}{\partial \ln V} \right)$ and γ is the Grüneisen parameter. ΔE_{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:

$$C_V = 9nN_A k_B \left(\frac{\theta}{T}\right)^{-3} \int_0^{\theta/T} \frac{x^4 e^x}{(e^x - 1)^2} dx \quad (11)$$

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

where N_A is Avogadro's number and θ 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):

$$G = (1 + 2f)^{5/2} \left[G_0 + (3K_0 G'_0 - 5G_0) f + \left(6K_0 G'_0 - 24K_0 - 14G_0 + \frac{9}{2} K_0 K'_0 \right) f^2 \right] - \eta_s \frac{\Delta E_{TH}(V, T)}{V} \quad (13)$$

where G_0 and G'_0 are the shear modulus and its pressure derivative at ambient conditions and η_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 , G'_0 and η_{s0} 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 γ_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):

$$\theta_0 = \frac{h}{k} \left(3 \frac{n}{4\pi V_0} \right)^{\frac{1}{3}} \left[3^{\frac{1}{3}} \left(\frac{1}{V_{P0}^3} + \frac{2}{V_{S0}^3} \right)^{-\frac{1}{3}} \right] \quad (14)$$

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_{P0} and V_{S0} are the experimental longitudinal and transverse velocities at ambient conditions.

Table 3. EoS paramaters of majoritic garnets

Sample	V_0 ($\text{cm}^3\text{mol}^{-1}$)	K_{s0} (GPa)	K_{T0} (GPa)	K'_{T0}	θ_0 (K) ^a	γ_0^b	q_0^b	G_0 (GPa)	G_0'	η_{s0}
Mg _{3.24} Al _{1.53} Si _{3.23} O ₁₂ (Py ₇₆ Mj ₂₄)	113.4	167(2)	166(2)	4.7(2)	791	1	1.4	91.8(7)	1.40(5)	1.3
Mg _{3.01} Fe _{0.17} Al _{1.68} Si _{3.15} O ₁₂ (Py ₇₈ Alm ₆ Mj ₁₆)	113.4	173(1)	172(1)	4.1(1)	795	1.06	1.4	92.7(6)	1.37(5)	1.9

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

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347

348 **4. Discussion**

349 **4.1. Comparison with literature data**

350 Fig. 3 shows determinations of the adiabatic bulk (K_{S0}) and shear (G_0) moduli for garnets along the
351 Py-Mj join made in this and previous studies, plotted as a function of Mj content. The
352 Py₇₈Alm₆Mj₁₆ sample is also plotted in addition to two other Alm and Alm and Gr bearing samples
353 from Murakami et al. (2008) and Irifune et al. (2008) respectively. There seems to be a very good
354 agreement between the several studies suggesting that G_0 decreases slightly with Mj content.
355 Furthermore, Py₇₈Alm₆Mj₁₆ lies on the same trend, in excellent agreement with studies on the end-
356 member Alm (Jiang et al., 2004), which has an almost identical G_0 to Py. The sample studied by
357 Murakami et al. (2008) with 10 % Alm plots slightly below the Py-Mj trend, on the other hand,
358 although the difference is relatively small. The Alm and Gr bearing sample of Irifune et al. (2008)
359 plots well above the trend, this is also consistent with measurements on the pure Gr end-member
360 (Jiang et al., 2004), which shows a significantly greater G_0 (109 GPa) compared to Py. A little more
361 scatter exists in the Py-Mj trend for K_{S0} with a number of relatively high estimates being made by
362 ultrasonic studies at Mj contents ~ 40-50 %. Many of the Brillouin scattering studies are in good
363 agreement, however. That K_{S0} for Py₇₈Alm₆Mj₁₆ is higher than Py₇₆Mj₂₄ is in qualitative agreement

364 with measurements made on pure Alm, which are higher than the Py end member (Jiang et al.,
 365 2004).

366
 367 **Fig. 3.** Ambient elastic moduli (K_{so} and G_o) as a function of majorite content along the binary
 368 majorite–pyrope join. Filled circles: this study; open circles: ultrasonic measurements from Ridgen
 369 et al. (1994), Chen et al. (1999), Liu et al. (2000), Gwanmesia et al. (1998; 2006; 2009), Irifune et
 370 al. (2008), Zhou et al. (2012), Liu et al. (2015); filled triangles and diamonds: Brillouin
 371 spectroscopy measurements on single-crystal and polycrystalline samples, respectively, by Pacalo
 372 and Weidner (1997), Sinogeikin and Bass (2000; 2002), Murakami et al. (2008). Three
 373 measurements made on more complex compositions have the proportions of almandine [Alm] and
 374 grossular [Gr] in the garnets indicated. The solid lines show a linear dependence of K_{so} and G_o with
 375 composition calculated using the end-member data reported in Table 4.

377 In Fig. 4 the moduli pressure derivatives K'_{S0} and G'_0 are plotted as a function of Mj content. There is
 378 very little variation in G'_0 even for Alm and Gr bearing samples but K'_{S0} covers a significant range
 379 with many ultrasonic measurements indicating relatively high values. As it can be seen in Fig. 2a
 380 there are clearly resolvable differences in the pressure derivatives between the $\text{Py}_{76}\text{Mj}_{24}$ and
 381 $\text{Py}_{78}\text{Alm}_6\text{Mj}_{16}$ samples. The combination of absolute pressure determinations and the use of a Ne
 382 pressure medium should ensure that these derivatives are of the highest precision measured for
 383 garnet samples to date. The lower values of K'_{S0} determined for the Alm bearing sample is
 384 consistent with the studies of Murakami et al. (2008) and Irifune et al. (2008).
 385

386
 387 **Fig. 4.** Ambient first pressure derivatives of the elastic moduli (K'_0 and G'_0) as a function of majorite
 388 content along the binary majorite–pyrope system. Symbols are the same as in Fig. 3. The solid lines
 389 show a linear dependence of K'_0 and G'_0 with composition calculated using the end-member data
 390 reported in Table 4.

391

392 Using the equation of state parameters obtained for $\text{Py}_{76}\text{Mj}_{24}$ and $\text{Py}_{76}\text{Alm}_8\text{Mj}_{16}$ (Table 3) sound
 393 velocities for these two compositions have been calculated at 20 GPa as a function of temperature
 394 up to 2000 K (Fig. 5). These are compared with the trend determined for a polycrystalline
 395 $\text{Py}_{23}\text{Alm}_6\text{Mj}_{50}\text{Gr}_{21}$ sample by Irifune et al. (2008) up to 1673 K and ~ 18 GPa.
 396

397
 398 **Fig. 5.** The variation in acoustic velocities of $\text{Py}_{76}\text{Mj}_{24}$ (blue) and $\text{Py}_{76}\text{Alm}_8\text{Mj}_{16}$ (green) at 20 GPa,
 399 extrapolated as a function of temperature using the EoS parameters reported in Table 3. The
 400 velocities of a complex garnet composition, $\text{Py}_{23}\text{Alm}_6\text{Mj}_{50}\text{Gr}_{21}$ (black), have been calculated using
 401 an end-member model based on the experimental data (Table 4). The dashed curves (red) show fits
 402 to ultrasonic measurements performed on a similar $\text{Py}_{23}\text{Alm}_6\text{Mj}_{50}\text{Gr}_{21}$ garnet composition by Irifune
 403 et al. (2008).
 404

405 Irifune et al. (2008) reported that the observed behavior was very different from that normally
 406 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.

410

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, 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:

$$\psi_{ss} = \frac{1}{\sum_{i=1}^n \frac{1}{m_i V_i} \sum_{i=1}^n \frac{m_i V_i}{\psi_i}} \quad (15)$$

where ψ_{ss} is the bulk elastic property of interest, ψ_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.

429

Using the equation of state model described in Section 3.3, velocities for the Py₇₆Mj₂₄ and Py₇₈Alm₆Mj₁₆ 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'_{T0} , θ_0 , γ_0 , q_0 , G_0 , G'_0 , and η_{s0} 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 Figures 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 $\text{Py}_{23}\text{Alm}_6\text{Mj}_{50}\text{Gr}_{21}$ 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 $\sim 1 \text{ km s}^{-1}$ 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).

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.

Phase	Formula	V_0 (cm ³ /mol)	K_{T0} (GPa)	K'_{T0}	θ_0 (K)	γ_0	q_0	G_0 (GPa)	G_0'	η_{s0}
Pyrope	Mg ₃ Al ₂ Si ₃ O ₁₂	<i>113.08</i>	<i>171</i>	4.3	804^a	<i>1.01</i>	<i>1.4</i>	<i>94</i>	<i>1.4</i>	1.2
Majorite	Mg ₄ Si ₄ O ₁₂	113.97	160	5.0	779^a	<i>0.98</i>	<i>1.5</i>	86	<i>1.4</i>	1.4
Almandine	Fe ₃ Al ₂ Si ₃ O ₁₂	<i>115.43</i>	175	3.7	<i>741</i>	<i>1.06</i>	<i>1.4</i>	<i>96</i>	1.1	<i>2.1</i>
Grossular	Ca ₃ Al ₂ Si ₃ O ₁₂	<i>125.12</i>	<i>167</i>	<i>3.9</i>	<i>823</i>	<i>1.05</i>	<i>1.9</i>	<i>109</i>	<i>1.2</i>	<i>2.4</i>
Wadsleyite	Mg ₂ SiO ₄	<i>40.52</i>	<i>169</i>	<i>4.3</i>	<i>853</i>	<i>1.21</i>	<i>2</i>	<i>112</i>	<i>1.4</i>	<i>2.6</i>
Wadsleyite	Fe ₂ SiO ₄	<i>42.80</i>	<i>169</i>	<i>4.3</i>	<i>719</i>	<i>1.21</i>	<i>2</i>	<i>72</i>	<i>1.4</i>	<i>1.1</i>
Ringwoodite	Mg ₂ SiO ₄	<i>39.49</i>	<i>185</i>	<i>4.2</i>	<i>891</i>	<i>1.11</i>	<i>2.4</i>	<i>123</i>	<i>1.4</i>	<i>2.3</i>
Ringwoodite	Fe ₂ SiO ₄	<i>41.86</i>	<i>213</i>	<i>4.2</i>	<i>652</i>	<i>1.26</i>	<i>2.4</i>	<i>92</i>	<i>1.4</i>	<i>1.8</i>
Ca-Perovskite	CaSiO ₃	<i>27.45</i>	<i>236</i>	<i>3.9</i>	<i>802</i>	<i>1.89</i>	<i>0.9</i>	<i>157</i>	<i>2.2</i>	<i>1.3</i>
Stishovite	SiO ₂	<i>14.02</i>	<i>314</i>	<i>3.8</i>	<i>1055</i>	<i>1.35</i>	<i>2.9</i>	<i>220</i>	<i>1.9</i>	<i>4.6</i>

^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.

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 straight forward to calculate the compositions of both phases, which results in 42 vol. % garnet with the composition Py₁₄Alm₈Mj₅₆Gr₂₁. 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

472 (Frost, 2003; Frost and Dolejs, 2007). Between 480 and 620 km the garnet composition and
473 proportion remain constant apart from small changes in Fe-Mg partitioning between wadsleyite and
474 ringwoodite. However, at 620 km CaSiO_3 perovskite (Ca-Pv) starts to exsolve from garnet, with the
475 volume proportion of Ca-Pv gradually increasing with depth at the expense of the grossular
476 component of garnet (Saikia et al., 2008). As a consequence, the garnet composition loses Ca but
477 also becomes less majoritic. The gradual increase of Ca-Pv and the consequent compositional
478 variations in garnet can be described using the thermodynamic model of Saikia et al. (2008). At the
479 base of the transition zone the pyrolite mineralogy comprises 58 vol. % ringwoodite,
480 $(\text{Mg}_{0.9}\text{Fe}_{0.1})_2\text{SiO}_4$, 36 vol. % garnet ($\text{Py}_{34}\text{Alm}_9\text{Mj}_{51}\text{Gr}_4$) and 6 vol % CaSiO_3 perovskite.

481

482 In contrast to pyrolite, an average MORB composition in the mantle transition zone is composed
483 almost entirely of garnet (89 vol. %) with additional stishovite (11 vol %) (Irifune et al., 1986). As
484 for the pyrolite composition, in the lower transition zone Ca-Pv starts to exsolve from majoritic
485 garnet, the phase relations of which can also be described using the thermodynamic model of
486 (Saikia et al., 2008). Because the Ca content of subducted oceanic crust (MORB) is higher than that
487 of pyrolite, garnets should become saturated in CaSiO_3 at lower pressures. However, the saturation
488 pressure is also a function of the garnet majorite component (Saikia et al., 2008), which is lower in
489 MORB with respect to a pyrolite composition. These two effects act in opposite directions and
490 ensure that the exsolution of CaSiO_3 perovskite from garnet occurs at approximately the same depth
491 as observed for the pyrolite composition. With increasing pressure, as CaSiO_3 perovskite exsolves,
492 the garnet becomes more Al-rich. At the base of the transition zone the MORB mineralogy
493 comprises 72 vol. % garnet ($\text{Py}_{58}\text{Alm}_{20}\text{Mj}_3\text{Gr}_{19}$), 11 vol, % SiO_2 and 17 vol. % CaSiO_3 perovskite.

494

495 Harzburgite phase relations are similar to those of pyrolite over the same depth interval, with the
496 main difference being a higher proportion of $(\text{Fe,Mg})_2\text{SiO}_4$. At 480 km the average harzburgite
497 composition employed (Irifune and Ringwood, 1987b) is calculated to comprise 81.5 vol. %

498 wadsleyite and 18.5 vol. % of majoritic garnet with the composition $\text{Alm}_{12}\text{Mj}_{80}\text{Gr}_8$. Phase
 499 transformations are similar to those in pyrolite, although due to the low Ca content the exsolution of
 500 CaSiO_3 is almost insignificant and the low Al content results in a more majorite rich garnet.

501

502 The sound velocities V_s and V_p calculated for the three bulk compositions described above are
 503 compared with the seismic reference models PREM and AK135 in Fig. 6.

504

505

506 **Fig. 6.** Sound velocities for pyrolite (red) harzburgite (green) and MORB (blue) compositions
 507 obtained from the parameters reported in Table 4 along a mantle adiabat of 1673 K at pressures
 508 corresponding to the transition zone. The solid and dashed black curves show PREM and AK135
 509 seismic reference models, respectively. Voigt and Reuss bounds for each lithology can be found in
 510 Figure S4 in the supplementary information.

511

512 Although the pyrolite model is in agreement at least with AK135 in terms of V_p , there is a
 513 consistent negative deviation for V_s , by ~ 0.2 km/s, between pyrolite and both reference models over

514 the 150 km of the base of the transition zone. Garnet elastic properties are the main reason for this
515 deviation as both ringwoodite and CaSiO_3 -perovskite have velocities that are above both reference
516 models at these conditions. Reference models are globally averaged velocity structures and it
517 should, in principal, be possible to approximate this structure using an average mantle composition,
518 mineralogy and temperature. Reference models are unlikely to capture the detail of the velocity
519 structure, however, particularly in the transition zone, due to the overly simplified polynomial
520 functions upon which they are based (Cammarano et al., 2005). Trade-offs between the magnitude
521 of seismic discontinuities and the velocity gradient, for example, are likely to cause inaccuracies in
522 the determinations of both. On average, however, negative deviations from the real mantle velocity
523 structure would be expected to be balanced by near-by positive deviations. This would appear not to
524 be the case in the transition zone, however, if a pyrolite model along a 1600 K adiabat is assumed to
525 resemble the real mantle.

526

527 Irifune et al. (2008) also reported that estimated velocities for pyrolite are lower than the reference
528 models at approximately 575 km, but suggested that the subsequent exsolution of CaSiO_3
529 perovskite from garnet would decrease the discrepancy towards the base of the transition zone.
530 Sinogeikin and Bass (2002) similarly argued that CaSiO_3 perovskite exsolution would raise the
531 velocity gradient. Note, however, that in this study, the gradual formation of CaSiO_3 -rich perovskite
532 and the resulting compositional variations in garnet have been taken into account. A very slight
533 increase in the velocity gradient for the pyrolite model occurs above 570 km due to CaSiO_3
534 exsolution. Without this exsolution the pyrolite velocities would have the same gradient as the
535 harzburgite model. Although shear wave properties of CaSiO_3 perovskite are poorly constrained,
536 the G_0 used in the current model (Xu et al., 2008) is at the very high limit of recent theoretical
537 studies (Kawai and Tsuchiya, 2015) and is higher than experimental estimates (Kudo et al., 2012).
538 Therefore, it seems unlikely that the V_s for CaSiO_3 perovskite is significantly underestimated, in

539 fact the contrary seems more likely. It appears, therefore, that pyrolite along a 1673 K adiabat
540 provides a poor match to seismic reference models at the base of the transition zone.

541 Other bulk compositions have been proposed for the transition zone, such as piclogite (Bass and
542 Anderson, 1984; Anderson and Bass, 1986), however from Fig. 6 it appears that increasing the
543 basaltic component of a mineralogical assemblage does not result in an increase of V_s values to
544 levels compatible with the reference models. For the MORB composition, the exsolution of CaSiO_3
545 perovskite can be clearly seen to cause an increase in gradient above 550 km. Although the
546 resulting gradient is closer to the reference models, the absolute values remain 0.1 km/s below both
547 reference models throughout the base of the transition zone.

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

554

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

559

560 One of the few remaining plausible explanations for the deviation between mineral and seismic
561 models at the base of the transition zone would be if the average mantle temperature over this depth
562 interval is below the 1673 K adiabat. While mantle adiabatic temperatures determined from erupted
563 basalt melt compositions vary by approximately $\pm 150^\circ$, (Lee et al., 2009), the estimated temperature
564 needed for the pyrolite model to match the seismic model at the base of the transition zone is ~ 500

565 K lower than 1673 K. This would place mantle temperatures far outside of the range of adiabatic
566 temperature estimates from the surface or from temperature estimates based on the depth of the 410
567 km discontinuity (Frost, 2008). Saikia et al. (2008) noted that to associate the 520 km seismic
568 discontinuity with the wadsleyite to ringwoodite transformation requires lower than expected
569 average mantle temperatures. This can be seen in Fig. 6, where the wadsleyite to ringwoodite
570 transformation along a 1673 K adiabat occurs at 550 km, and only if temperatures were ~300 K
571 lower would the transition occur at 520 km. Saikia et al. (2008) suggested that a possible cause of
572 lower mantle temperatures may be the presence of subducting slabs stagnating at the base of the
573 transition zone and flattening out to form significant lateral cold heterogeneities. Some tomographic
574 models (e.g. Kárason and van der Hilst, 2000) appear to clearly indicate that such heterogeneities
575 exist. As temperatures in the centre of such slabs could be easily 600 K below the average mantle,
576 then they could drag down average mantle temperatures at these depths, assuming that the lateral
577 anomalies were large enough. Furthermore it is possible that a significant proportion of this material
578 will be of near harzburgite composition. It can be estimated that temperatures would have to be only
579 200 K below the 1673 K adiabat for harzburgite mineral model velocities to match seismic
580 reference models at the base of the transition zone. If such global horizontal anomalies exist, this
581 average reduction in temperature may be plausible and would be also consistent with the 520 km
582 seismic discontinuity being caused by the wadsleyite to ringwoodite transformation.

583

584 A further issue that needs to be investigated is the effect of the mineral akimotoite which is
585 expected to form in both harzburgite and pyrolite compositions if temperatures at the base of the
586 transition zone were several hundred degrees lower than the 1673 K adiabat. The elastic properties
587 of akimotoite are poorly explored, however in a recent experimental study the presence of
588 akimotoite has been proposed to raise seismic velocities at the base of the transition zone (Zhou et
589 al., 2014).

590

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