

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

3

4 Martha G. Pamato^{1,2}, Alexander Kurnosov¹, Tiziana Boffa Ballaran¹, Daniel J. Frost¹, Luca Ziberna
5 ^{1,3}, Mattia Giannini^{1,4}, Sergio Speziale⁵, Sergey N. Tkachev⁶, Kirill K. Zhuravlev⁶, and Vitali B.
6 Prakapenka⁶

7 ¹ Bayerisches Geoinstitut, Universitaet Bayreuth, D - 95440 Bayreuth, Germany

8 ² Present address: Department of Earth Sciences, University College London, London WC1E 6BT,
9 United Kingdom

10 ³ Present address: School of Earth Sciences, University of Bristol, Bristol BS8 1RJ, United Kingdom

11 ⁴ Present address: University of Picardie Jules Verne, Laboratoire de Réactivité et Chimie des Solides
12 CNRS UMR 7314, 80039 Amiens, France

13 ⁵ Deutsches GeoForschungsZentrum GFZ, Telegrafenberg, 14473 Potsdam, Germany

14 ⁶ GSECARS, University of Chicago, 60637 Chicago, Illinois, USA

15 Corresponding author: M.G. Pamato: Department of Earth Sciences, University College London,
16 London WC1E 6BT, United Kingdom.

17 (m.pamato@ucl.ac.uk)

18

19 **Abstract**

20 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
21 $\text{Mg}_{3.01}\text{Fe}_{0.17}\text{Al}_{1.68}\text{Si}_{3.15}\text{O}_{12}$), have been measured using simultaneously single-crystal X-ray diffraction
22 and Brillouin spectroscopy in an externally heated diamond anvil cell with Ne as pressure transmitting
23 medium at conditions up to ~30 GPa and ~600 K. This combination of techniques makes it possible
24 to use the bulk modulus and unit-cell volume at each condition to calculate the absolute pressure,
25 independently of secondary pressure calibrants.

26

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

39

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

42

43 **1. Introduction**

44 Seismic velocity profiles of the Earth's interior provide essential information for constraining the
45 thermal and chemical state of the mantle (Anderson and Bass, 1986; Irifune and Ringwood, 1987a;
46 Ita and Stixrude, 1992). The correct interpretation of these profiles in terms of mantle mineralogy and
47 chemistry, however, requires laboratory or computational data on the elasticity of candidate minerals
48 at conditions of the Earth's mantle. In this context, knowledge of the thermo-elastic properties of
49 garnet solid solutions are essential, since they make up a major proportion of both mafic and
50 ultramafic rocks in the upper mantle and transition zone (Irifune and Ringwood, 1987a). Garnets
51 recovered from the Earth's mantle crystallize in the cubic space group $Ia\bar{3}d$ forming a series of
52 complex solid solutions that are described using the crystal-structural formula $^{VIII}X_3^{VI}Y_2^{IV}Z_3O_{12}$.

53 Large cations, X = Mg, Ca, Fe²⁺, occupy the 8-fold coordinated dodecahedral sites, medium sized
54 cations, Y= Al, Fe³⁺, Cr, occupy the octahedral sites, whereas the tetrahedral Z site is occupied by Si.
55 At pressures above 5 GPa the coupled substitution of Si and Mg (and Fe) onto the Y site occurs in
56 garnets within mantle assemblages as a result of the breakdown of both orthopyroxene and
57 clinopyroxene. This, so called, majorite substitution increases the proportion of garnet in mantle rocks
58 at the expense of pyroxenes in the Earth's deep upper mantle and transition zone (Ringwood, 1967).
59 The Al-free garnet end-member is referred to as majorite, Mj (Mg₄Si₄O₁₂) and crystallizes with
60 tetragonal symmetry due to ordering of Mg and Si on the octahedral sites. Pure Mj is stable at
61 pressures between 16 and 23 GPa and temperatures above 1600 °C (Kato and Kumazawa, 1985;
62 Angel et al., 1989). In upper mantle ultramafic rocks garnets are solid solutions that are dominated
63 by the end member pyrope (Py, Mg₃Al₂Si₃O₁₂) but have sub-equal proportions of almandine (Alm,
64 Fe₃Al₂Si₃O₁₂) and grossular (Gr, Ca₃Al₂Si₃O₁₂). With increasing pressure, however, the Mj end
65 member becomes increasingly important and dominates in the transition zone (410 – 660 km depth).
66 A key issue concerning the structure of the Earth's interior is the extent and scale at which the mantle
67 can be considered homogeneous. A number of studies have proposed, for example, that the mantle
68 may become richer in mafic material with depth (e.g. Anderson and Bass 1986). One of the main
69 expressions of such chemical heterogeneity in the mantle would be variation in the chemistry and
70 proportion of garnet. Garnets constitute approximately 40 % by volume of ultramafic compositions
71 and 70 % of mafic compositions (Anderson and Bass, 1986; Irifune and Ringwood, 1987a; Ita and
72 Stixrude, 1992), but garnets formed from mafic assemblages will have greater Gr and Alm contents
73 and in the transition zone less Mj compared to ultramafic assemblages. Knowledge of how the elastic
74 properties of garnet change as the bulk chemistry changes is, therefore, important.

75

76 Several studies have investigated the elastic properties of Py–Mj garnets at room pressure and
77 temperature (Bass and Kanzaki, 1990; O'Neill et al., 1991). Moreover elastic moduli measurements
78 have also been performed at high pressure and room temperature, using ultrasonic techniques on

79 polycrystalline aggregates (Rigden et al., 1994; Gwanmesia et al., 1998; Chen et al., 1999; Wang and
80 Ji, 2001) and through the use of Brillouin spectroscopy on both single crystals (Conrad et al., 1999;
81 Sinogeikin and Bass, 2000; Murakami et al., 2008) and powdered samples (Sinogeikin and Bass,
82 2002). Recent improvements in ultrasonic techniques coupled with synchrotron X-ray radiation have
83 allowed sound velocity measurements on polycrystalline samples along the Py–Mj solid solution to
84 be performed at simultaneous high P and T (Irifune et al., 2008; Gwanmesia et al., 2009; Liu et al.,
85 2015). Furthermore the single-crystal elasticity of an iron-bearing pyrope was recently obtained
86 simultaneously at high-pressures (up to 20 GPa) and high-temperature (750 K) using Brillouin
87 spectroscopy and X-ray diffraction (Lu et al., 2013). While the value of the bulk and shear moduli,
88 K_s and G , reported by these studies cover a relatively small range, the exact dependence particularly
89 of K_s on Mj content is unclear, large discrepancies in elastic moduli pressure derivatives exist, the
90 thermal properties are poorly constrained as is the further effect of the Alm content. Consequently,
91 the interpretations of seismic velocity gradients in the transition zone remain uncertain.

92
93 The aim of this study is, therefore, to constrain the elastic properties of majoritic garnets as a function
94 of density, temperature and composition under hydrostatic conditions by employing a combination
95 of single-crystal Brillouin scattering and X-ray diffraction measurements. The simultaneous
96 measurement of elastic properties and density are used to also obtain absolute values of the
97 experimental pressure, avoiding in this way any systematic errors that may be introduced through the
98 use of secondary pressure calibrations. The elasticity data obtained are fitted to a self-consistent
99 thermo-elastic model from which thermodynamic properties of the garnet end-members are
100 estimated. Acoustic velocities of mafic, harzburgitic and lherzolititic assemblages are then calculated
101 along a typical mantle adiabat at conditions of the Earth's transition zone by combining our garnet
102 model with properties for coexisting minerals from the literature. The results are then compared with
103 seismic reference models reported over the same depth interval to constrain the plausible mineralogy
104 and temperature at the base of the Earth's transition zone.

105

106 **2. Experimental methods**107 **2.1. Sample synthesis and characterization**

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

114

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	

115 Note: mixture Py2 = 25 % pyrope glass + 75 % mixture Py1; mixture Py4 = 75 % pyrope glass + 25
 116 % mixture Py3

117

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

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

132

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

144

145 Element concentrations in the recovered samples were measured with a JEOL JXA-8200 electron
146 probe microanalyser (EPMA), operating at 15 kV and 15 nA. The electron beam size was

147 approximately 1-2 μm in diameter and the peak counting times were 20 s. Enstatite or diopside, spinel,
148 forsterite, and metallic iron were used as standards for determining the concentrations of Si, Al, Mg
149 and Fe respectively. The chemical analysis resulted in the following composition: 32.0 (6) % MgO,
150 47.5 (9) % SiO_2 , 19 (2) % Al_2O_3 (in wt.), for the Py-Mj garnet (hereafter named $\text{Py}_{76}\text{Mj}_{24}$) and 29.5(5)
151 % MgO, 46(1) % SiO_2 , 3.3(5) % FeO, 21(2) % Al_2O_3 (in wt.) for the iron bearing sample (hereafter
152 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
153 $\text{Mg}_{3.01}\text{Fe}_{0.17}\text{Al}_{1.68}\text{Si}_{3.15}\text{O}_{12}$, respectively.

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

159

160 **2.2. Simultaneous X-ray diffraction and Brillouin scattering**

161 The P - V - T equations of state and the compressional, V_p , and shear, V_s , sound velocities of two single-
162 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
163 simultaneous Brillouin spectroscopy and X-ray diffraction. High quality single-crystals, of $\sim 70 \mu\text{m}$
164 in size, were selected based on their sharp diffraction profiles. The crystals were parallel polished
165 into platelets with a thickness of 10-18 μm and then loaded into piston cylinder diamond anvil cells.
166 Bohler-Almax diamonds were employed with 400-350 μm culets in combination with tungsten
167 carbide seats. Rhenium gaskets of 200 μm in thickness were pre-indented to 40-55 μm before drilling
168 250 μm cylindrical holes. Single-crystals of Sm:YAG (Sm-doped YAlO_3 garnet) as well as ruby chips
169 were added as secondary pressure calibrants. A neon gas pressure medium was loaded into the sample
170 chamber using the high pressure gas loading devices at the Bayerisches Geoinstitut (Kurnosov et al.,
171 2008) as well as at GSECARS (Rivers et al., 2008).

172

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

187
188 Simultaneous acquisition of density and sound velocities at room pressure was performed at the
189 Bayerisches Geoinstitut. The lattice parameters of both samples were determined using eight-position
190 centring of 15 Bragg reflections ($25^\circ < 2\theta < 40^\circ$) according to the procedure of King and Finger (1979)
191 on a Huber diffractometer equipped with point detector and driven by the program SINGLE (Angel
192 and Finger, 2011). The resulting unit-cell volumes are $1506.6(5) \text{ \AA}^3$ and $1506.8(1) \text{ \AA}^3$ for $\text{Py}_{76}\text{Mj}_{24}$
193 and $\text{Py}_{78}\text{Alm}_6\text{Mj}_{16}$ respectively. The unit-cell volumes are practically identical because Alm replaces
194 Mj in the second sample and both components have a qualitatively similar effect on the volume.
195 Typical half-widths of the ω profiles of different reflections varied between 0.060° and 0.100° .
196 Brillouin scattering measurements were performed in a 80° symmetric/platelet scattering geometry
197 with plate spacing of 4 mm using a coherent Verdi V2 solid state Nd:YVO₄ frequency doubled laser
198 ($\lambda = 532.0 \text{ nm}$) at the power of $\sim 150\text{-}200 \text{ mW}$. The room pressure Brillouin scattering measurements

199 of $\text{Py}_{78}\text{Alm}_6\text{Mj}_{16}$ were performed at the GeoForschungsZentrum (GFZ) in Potsdam as well as at
200 PETRA III in Hamburg, employing a 60 and 49 degree forward symmetric scattering geometry with
201 plate spacing of 6 mm and 8 mm respectively. A coherent Verdi V2 solid state Nd:YVO₄ frequency
202 doubled laser ($\lambda = 532.0$ nm) was used.

203 Simultaneous measurements of sound velocities and density at different pressures and temperatures
204 were performed at the BM-13-D (GSECARS) beamline at the Advanced Photon Source (APS). The
205 samples were each measured first upon compression up to approximately 20 and 21 GPa at room
206 temperature and then heated to 558 K ($\text{Py}_{76}\text{Mj}_{24}$) and 470 K ($\text{Py}_{78}\text{Alm}_6\text{Mj}_{16}$) respectively. During
207 heating the pressure increased to 30 GPa, therefore Brillouin spectra and density were measured along
208 an isotherm (at high temperature) upon decompression. X-ray diffraction measurements were
209 performed using a Perkin Elmer detector, collecting step scans in an omega range of 50° or 70° with
210 a step size of 1° and 5 s/step exposure time. Brillouin scattering measurements were performed with
211 a six-pass Sandercock-type tandem Fabry-Pérot interferometer using a coherent Verdi V2 solid state
212 Nd:YVO₄ frequency doubled laser ($\lambda = 532.0$ nm) as a light source. Measurements were performed
213 in a 50° symmetric/platelet scattering geometry with plate spacing of 6.5-7 mm. Brillouin spectra
214 were collected with a laser power of 400 mW. Acoustic velocities, V_{acoustic} , were determined from the
215 frequency shift using the following relationship (Whitfield et al., 1976):

$$216 \quad V_{\text{acoustic}} = \Delta\nu * \lambda_0 / 2 * \sin(\theta/2) \quad (1)$$

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

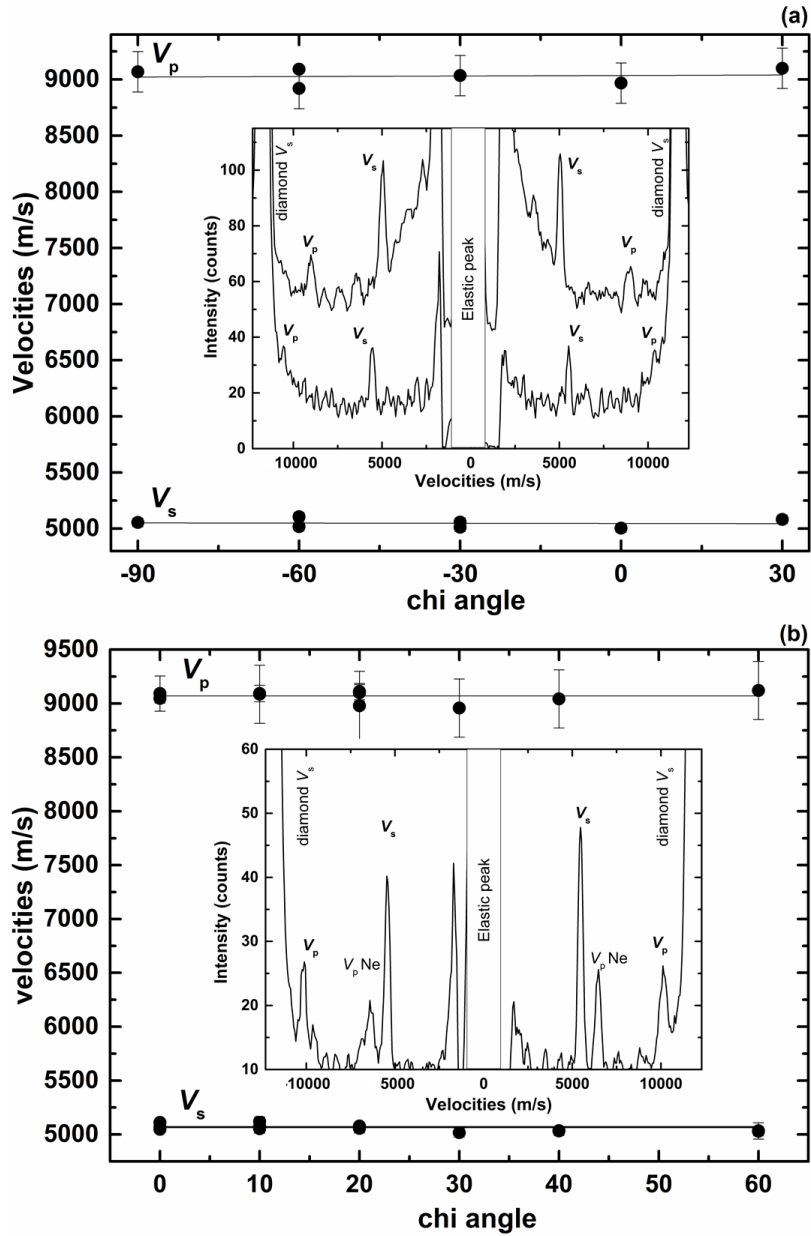
219

220 **3. Results**

221 **3.1. Elasticity**

222 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
223 in different crystallographic directions as a function of χ angle are shown in Fig. 1.

224



225

226 **Fig. 1.** (a) Compressional and shear wave velocities of $\text{Py}_{76}\text{Mj}_{24}$ as a function of crystallographic
 227 direction at room pressure and temperature. Inset: Brillouin spectra collected for a given
 228 crystallographic orientation at room pressure and temperature (top) and at 28.04 GPa and 558 K
 229 (bottom). (b) Compressional and shear wave velocities of $\text{Py}_{78}\text{Alm}_6\text{Mj}_{16}$ as a function of
 230 crystallographic direction at room pressure and temperature. The Brillouin spectrum reported in the
 231 inset was collected at 21.10 GPa.

232

233 Typical Brillouin spectra are also reported in the insets in the same Figure. The elastic anisotropy of
 234 the two majoritic-garnets is practically negligible both at ambient conditions and at high pressures
 235 and temperatures, as also observed for other garnets (e.g. Sinogeikin and Bass, 2000; Murakami et
 236 al., 2008; Lu et al., 2013).

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

$$240 \quad |C_{rism}q_lq_m - \rho V_{acoustic}^2 \delta_{rs}| = 0 \quad (2)$$

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

$$251 \quad C_{11} = K_s + \frac{4}{3} G = \rho V_p^2 \quad (3)$$

$$252 \quad C_{44} = G = \rho V_s^2 \quad (4)$$

$$253 \quad C_{12} = K_s - \frac{2}{3} G = \rho(V_p^2 - 2V_s^2) \quad (5)$$

254 assuming the equality:

$$255 \quad 2C_{44} = C_{11} - C_{12} \quad (6)$$

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

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)

259

260 Brillouin spectra collected on samples within diamond anvil cells at different pressures, temperatures
261 and orientations typically have different signal to noise ratios that depend on the crystal optical quality
262 and its orientation in addition to the laser focusing, sample alignment and collection time. The
263 resolution of such spectra will influence the uncertainties on the V_s and V_p values used to obtain the
264 elastic constants. The uncertainties on the velocities of the garnet crystals were assessed using a set
265 of Brillouin spectra collected for the same sample but with different signal to noise ratios, varied by
266 adjusting the length of data collection time between one hour to several days. A "calibration curve"
267 was then constructed that describes the standard deviation on the velocity measurements as a function

268 of the signal to noise ratio. Uncertainties of 20 m/s, i.e. 0.2-0.4 % can be obtained when the best
269 alignment is achieved, but usually they are larger than this value (see text S2 supplementary
270 information).

271

272 **3.2. Absolute pressure determination**

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

$$277 \quad P = \int_{V_0}^V \frac{K_T(V)}{V} dV \quad (7)$$

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

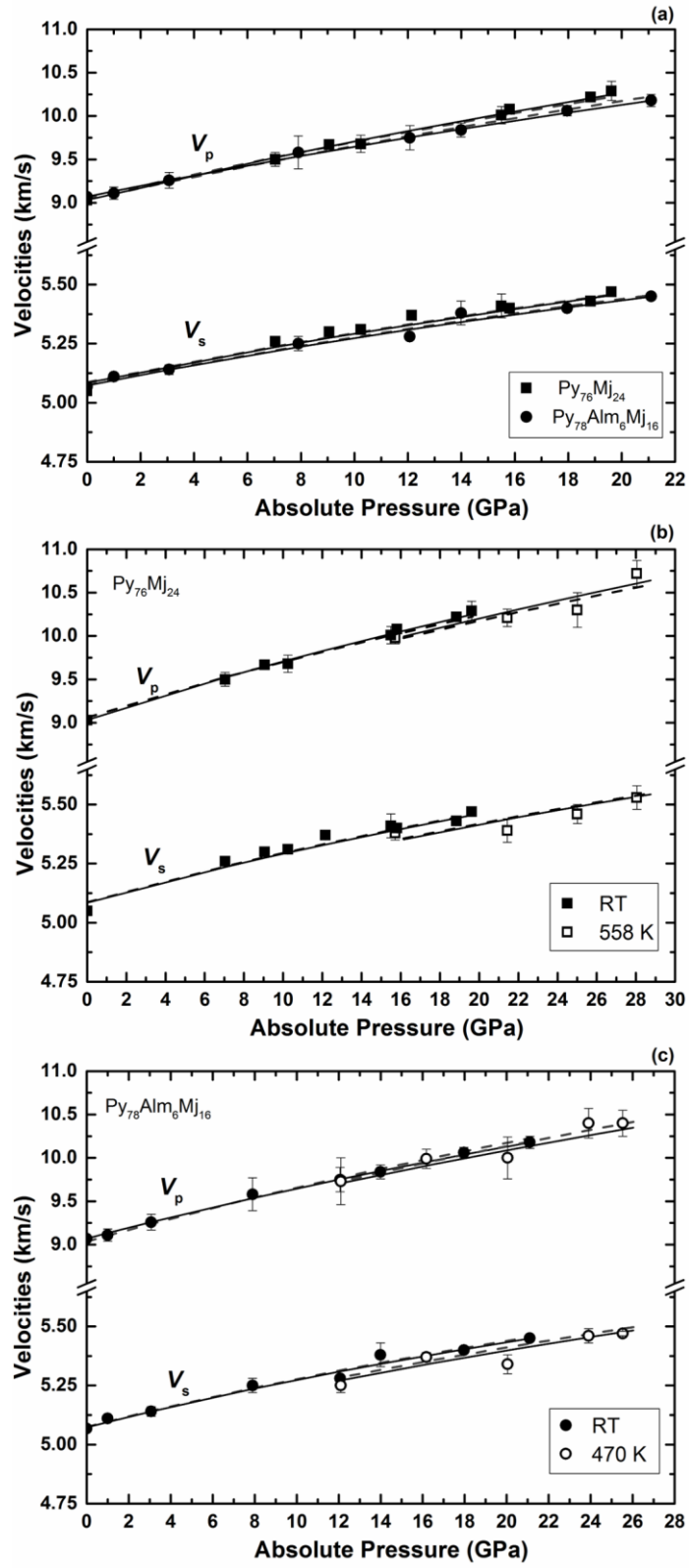
$$281 \quad K_S = K_T(1 + \alpha\gamma T) \quad (8)$$

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

284

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

287



288

289 **Fig. 2.** Variation of the shear (V_s) and compressional (V_p) wave velocities as a function of absolute
 290 pressure of (a) $\text{Py}_{76}\text{Mj}_{24}$ and $\text{Py}_{78}\text{Alm}_6\text{Mj}_{16}$ at room temperature, (b) of $\text{Py}_{76}\text{Mj}_{24}$ at room temperature
 291 and at 558 K and (c) of $\text{Py}_{78}\text{Alm}_6\text{Mj}_{16}$ at room temperature and at 470 K. Solid curves are calculated

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

294

295 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
 296 pressure, however, they deviate at high pressures, with $\text{Py}_{76}\text{Mj}_{24}$ displaying faster velocities due to
 297 the higher pressure derivative of the elastic moduli.

298

299 **3.3. Determination of P - V - T Eos of majoritic garnets**

300 The high-pressure and temperature elastic properties of majoritic garnets are described using the self-
 301 consistent thermodynamic formalism described by Stixrude and Lithgow-Bertelloni (2005). This
 302 model employs a Mie-Grüneisen equation of state with a Debye approximation that should describe
 303 thermal properties more reliably than the linear or polynomial moduli dependences often employed.
 304 In this formalism, the isothermal bulk modulus, K_T , is obtained as the second derivative of the
 305 Helmholtz free energy with respect to strain (f) and retains all terms that originate from the truncation
 306 to third order in strain of the free energy expansion:

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

309 where

$$310 \quad f = \frac{1}{2} \left[\left(\frac{V_0}{V} \right)^{2/3} - 1 \right] = -\varepsilon \tag{10}$$

311 is the negative of the eulerian strain (ε), V is the molar volume, T is temperature, K_{T_0} and K'_{T_0} are the
 312 isothermal bulk modulus and its pressure derivative and the subscript zero indicates the reference
 313 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
 314 the quasi-harmonic thermal energy between T and T_0 and C_V is the heat capacity at constant volume
 315 evaluated in the framework of Debye theory:

316 $C_V = 9nN_A k_B \left(\frac{\theta}{T}\right)^{-3} \int_0^{\theta/T} \frac{x^4 e^x}{(e^x - 1)^2} dx$ (11)

317 $\theta = \theta_0 \left[1 + 6\gamma_0 f + \frac{1}{2}(-12\gamma_0 + 36\gamma_0^2 - 18\gamma_0 q_0) f^2\right]^{\frac{1}{2}}$ (12)

318 where N_A is Avogadro's number and θ_0 is the room pressure value for the Debye temperature. The
 319 isothermal bulk modulus can be converted to the adiabatic bulk modulus K_S according to equation
 320 (8).

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

323 $G = (1 + 2f)^{5/2} \left[G_0 + (3K_0 G'_0 - 5G_0) f + \left(6K_0 G'_0 - 24K_0 - 14G_0 + \frac{9}{2} K_0 K'_0 \right) f^2 \right] - \eta_S \frac{\Delta E_{TH}(V,T)}{V}$
 324 (13)

325 where G_0 and G'_0 are the shear modulus and its pressure derivative at ambient conditions and η_S is the
 326 shear strain derivative of the Grüneisen parameter.

327 The formalism described above was used to fit the aggregate wave velocities V_P and V_S of Py₇₆Mj₂₄
 328 and Py₇₈Alm₆Mj₁₆. The values of the EoS parameters (Table 3), K_{T0} , K'_{T0} , G_0 , G'_0 and η_{S0} were
 329 obtained through a least square minimization of the differences between observed and calculated
 330 aggregate wave velocities. In the refinement the ambient volume V_0 was fixed to the value obtained
 331 from X-ray diffraction, the Grüneisen parameter γ_0 and the logarithmic volume derivative of the
 332 effective Debye temperature, q_0 , were kept at values previously determined for garnets (Xu et al.,
 333 2008). The room pressure value of the Debye temperature was calculated from the experimental
 334 sound velocities according to the equations from Robie and Edwards (1966):

335 $\theta_0 = \frac{h}{k} \left(3 \frac{n}{4\pi V_0} \right)^{\frac{1}{3}} \left[3^{\frac{1}{3}} \left(\frac{1}{V_{P0}^3} + \frac{2}{V_{S0}^3} \right)^{-\frac{1}{3}} \right]$ (14)

336 where h is the Plank constant, k is the Boltzmann constant, $n = 160$ is the number of atoms in the
 337 garnet unit cell, and V_{P0} and V_{S0} are the experimental longitudinal and transverse velocities at ambient
 338 conditions.

339

Table 3. EoS parameters 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}
$\text{Mg}_{3.24}\text{Al}_{1.53}\text{Si}_{3.23}\text{O}_{12}$ (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
$\text{Mg}_{3.01}\text{Fe}_{0.17}\text{Al}_{1.68}\text{Si}_{3.15}\text{O}_{12}$ (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)

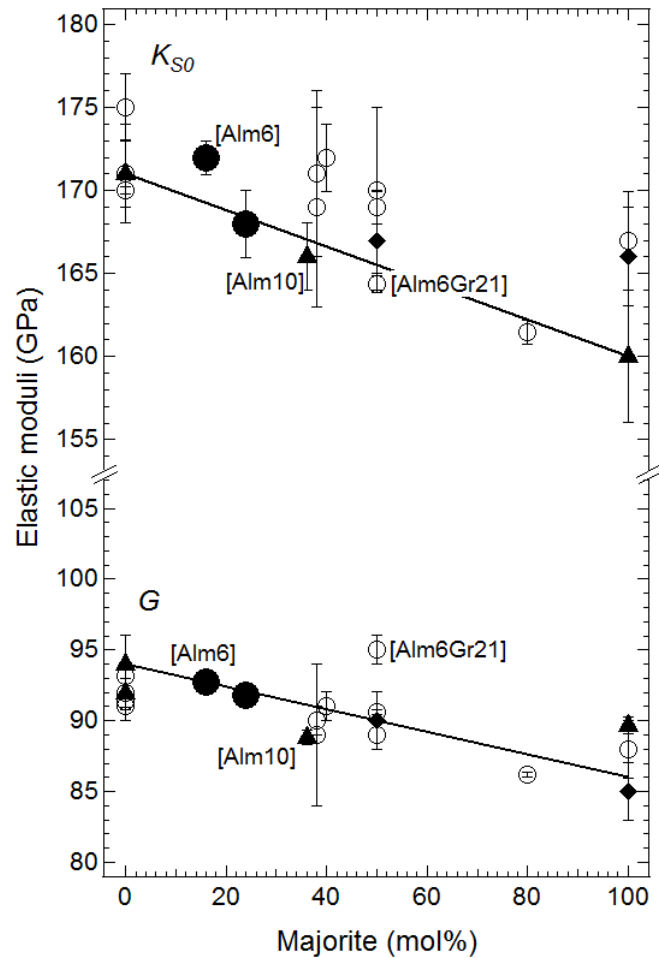
341

342

343 4. Discussion

344 4.1. Comparison with literature data

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



360

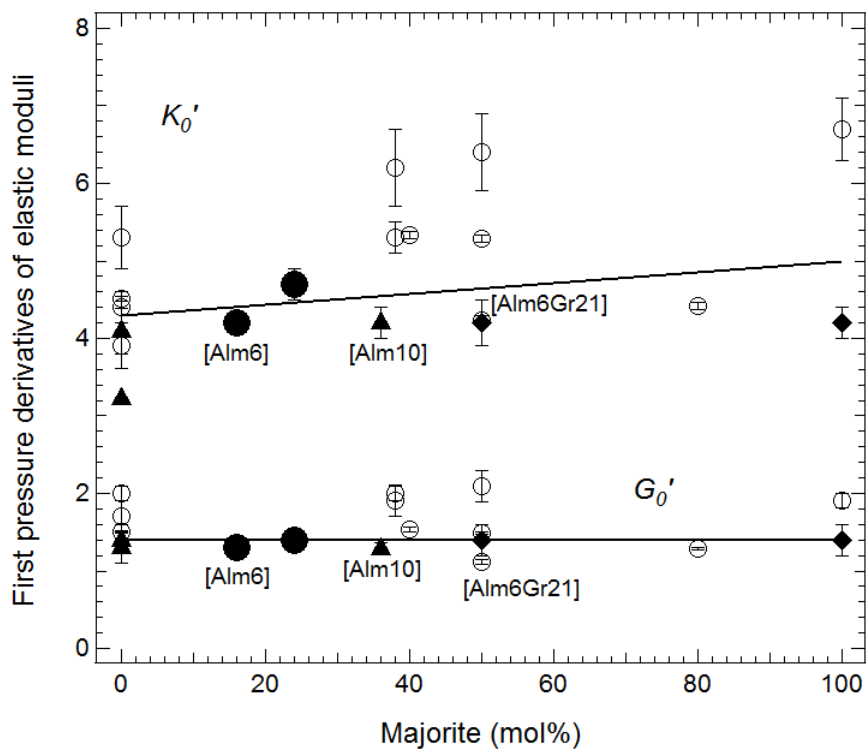
361 **Fig. 3.** Ambient elastic moduli (K_{S0} and G_0) as a function of majorite content along the binary
 362 majorite–pyrope join. Filled circles: this study; open circles: ultrasonic measurements from Ridgen
 363 et al. (1994), Chen et al. (1999), Liu et al. (2000), Gwanmesia et al. (1998; 2006; 2009), Irifune et al.
 364 (2008), Zhou et al. (2012), Liu et al. (2015); filled triangles and diamonds: Brillouin spectroscopy
 365 measurements on single-crystal and polycrystalline samples, respectively, by Pacalo and Weidner
 366 (1997), Sinogeikin and Bass (2000; 2002), Murakami et al. (2008). Three measurements made on
 367 more complex compositions have the proportions of almandine [Alm] and grossular [Gr] in the
 368 garnets indicated. The solid lines show a linear dependence of K_{S0} and G_0 with composition calculated
 369 using the end-member data reported in Table 4.

370

371 In Fig. 4 the moduli pressure derivatives K'_{S0} and G'_0 are plotted as a function of Mj content. There is
 372 very little variation in G'_0 even for Alm and Gr bearing samples but K'_{S0} covers a significant range

373 with many ultrasonic measurements indicating relatively high values. As it can be seen in Fig. 2a
 374 there are clearly resolvable differences in the pressure derivatives between the $\text{Py}_{76}\text{Mj}_{24}$ and
 375 $\text{Py}_{78}\text{Alm}_6\text{Mj}_{16}$ samples. The combination of absolute pressure determinations and the use of a Ne
 376 pressure medium should ensure that these derivatives are of the highest precision measured for garnet
 377 samples to date. The lower values of K'_{50} determined for the Alm bearing sample is consistent with
 378 the studies of Murakami et al. (2008) and Irifune et al. (2008).

379



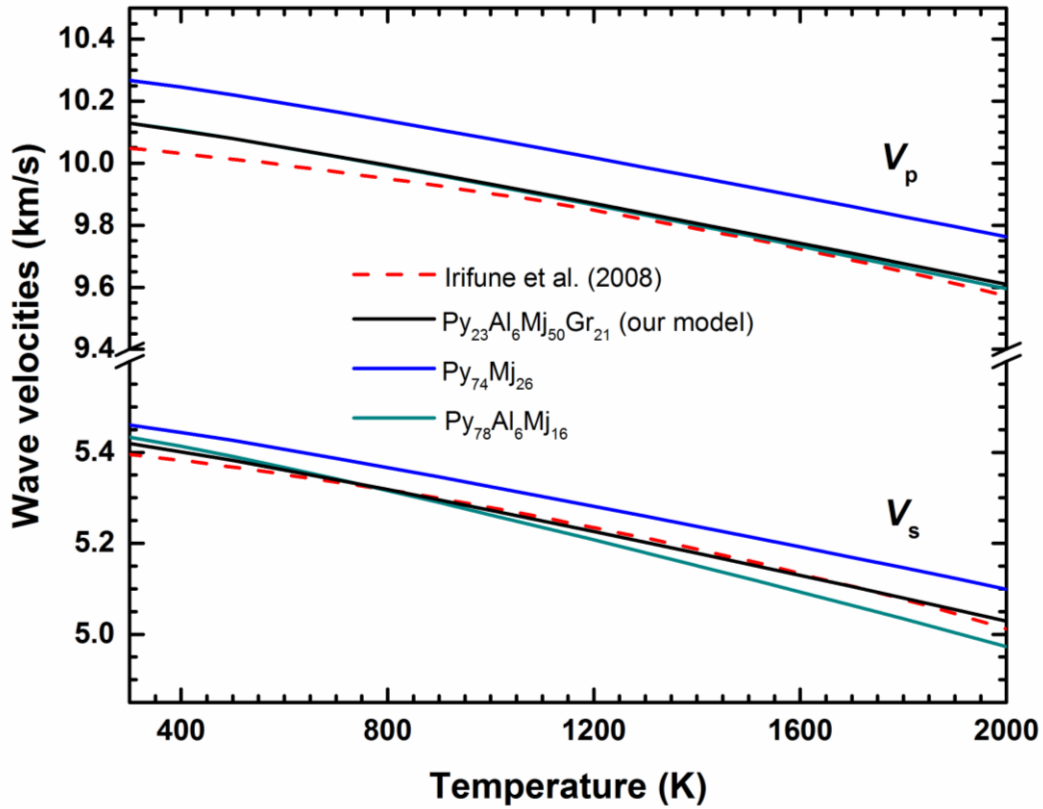
380

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

385

386 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
 387 velocities for these two compositions have been calculated at 20 GPa as a function of temperature up

388 to 2000 K (Fig. 5). These are compared with the trend determined for a polycrystalline
 389 $\text{Py}_{23}\text{Alm}_6\text{Mj}_{50}\text{Gr}_{21}$ sample by Irifune et al. (2008) up to 1673 K and ~ 18 GPa.
 390



391
 392 **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,
 393 extrapolated as a function of temperature using the EoS parameters reported in Table 3. The velocities
 394 of a complex garnet composition, $\text{Py}_{23}\text{Alm}_6\text{Mj}_{50}\text{Gr}_{21}$ (black), have been calculated using an end-
 395 member model based on the experimental data (Table 4). The dashed curves (red) show fits to
 396 ultrasonic measurements performed on a similar $\text{Py}_{23}\text{Alm}_6\text{Mj}_{50}\text{Gr}_{21}$ garnet composition by Irifune et
 397 al. (2008).

398
 399 Irifune et al. (2008) reported that the observed behavior was very different from that normally
 400 obtained by extrapolating linear dependences of elastic moduli with temperature, as commonly
 401 performed in literature studies (see for example Lu et al., 2013). Note, however, that the thermo-

402 elastic model for the for Py₇₆Mj₂₄ and Py₇₆Alm₈Mj₁₆ samples reproduces the non-linear temperature
403 behavior of the velocities.

404

405 **4.2. Calculation of elastic properties for majoritic garnets from end member compositions**

406 Garnet compositions are likely to vary within the upper mantle and transition zone as a result of
407 pressure and temperature dependent changes in chemical partitioning between coexisting minerals in
408 addition to variations in the mantle's bulk composition. In order to model the effects of these changes
409 in chemistry on seismic velocities, elastic properties for complex garnet compositions need to be
410 calculated from those of the major end-members, i.e. Py, Mj, Alm and Gr. The elastic properties of a
411 phase consisting of a solid solution of n end-members in a single mineral phase can be derived through
412 a weighted summation of the individual elastic properties of the corresponding end-members:

$$413 \psi_{ss} = \frac{1}{\sum_{i=1}^n \frac{1}{m_i V_i} \sum_{i=1}^n \frac{m_i V_i}{\psi_i}} \quad (15)$$

414 where ψ_{ss} is the bulk elastic property of interest, ψ_i is the elastic property of component i and V_i and
415 m_i are the volume and mole fraction of component i . This summation assumes that the property in
416 question varies as a linear function of the end-member properties. Recent determinations of K'_{T_0} for
417 solid solutions along the Gr-Py binary suggest that this may not always be an accurate assumption
418 (Du et al., 2015). Due to potential non-linear effects it is possible that fictive end-member properties,
419 determined using data on garnets that have intermediate compositions (and that may, therefore, be
420 closer to those in the mantle), may reproduce the experimental velocities better than using data
421 obtained for end-member compositions.

422

423 Using the equation of state model described in Section 3.3, velocities for the Py₇₆Mj₂₄ and
424 Py₇₈Alm₆Mj₁₆ samples were calculated through a summation of the elastic properties of the
425 appropriate end-members, as in equation (15). The initial values of V_0 , K'_{T_0} , θ_0 , γ_0 , q_0 , G_0 , G'_0 , and
426 η_{s0} for the Py, Mj and Alm end-members were initially taken from Xu et al. (2008) (Table 4), although

427 Debye temperatures for Py and Mj were recalculated in accordance with equation (14). The resulting
428 velocities were then compared with the high pressure and temperature experimental values, and the
429 properties for Py, Mj and Alm were refined to minimize the calculated and observed differences.
430 Values which differ from those reported in the compilation of Xu et al. (2008) are reported in bold in
431 Table 4. The lines in Figures 3 and 4 show how the moduli and their derivatives change across the
432 Py-Mj join according to the resulting model.

433

434 Using data for Gr from the literature (Xu et al., 2008), the model has been used to calculate acoustic
435 velocities for the $\text{Py}_{23}\text{Alm}_6\text{Mj}_{50}\text{Gr}_{21}$ composition examined by Irifune et al. (2008). The model
436 calculations, performed at 20 GPa as a function of temperature, are compared with the experimental
437 curves of Irifune et al. (2008) in Fig. 5. The shear velocity curve reported by Irifune et al. (2008) is
438 extremely well reproduced by the resulting model, both in terms of the absolute values and the
439 velocity gradient with temperature. The calculated longitudinal velocities are higher by $\sim 1 \text{ km s}^{-1}$ than
440 the experimental values at room temperature but converge to be in excellent agreement at mantle
441 temperatures. Although the agreement should be in principal good at all temperatures, it is possible
442 that in the multianvil measurements deviatoric stresses at low temperatures cause this difference,
443 which decreases with temperature (Gwamnesia et al., 2006).

444

445 **4.3. Implication for the Earth's transition zone**

446 The elastic properties of garnets determined in this study were used along with additional literature
447 data (summarized in Table 4) to calculate seismic velocities for pyrolite, harzburgite and MORB bulk
448 compositions at the base of the transition zone, in the depth range between 480 and 660 km.
449 Calculations were not performed at lower pressures due to the absence of sufficient data on the
450 clinopyroxene mineral properties. The calculations were performed along an adiabat with a potential
451 temperature of 1673 K employing thermodynamic models to describe variations in the proportion and
452 chemistry of the mineral phases. A Voigt-Reuss-Hill averaging scheme was used to extract the

453 aggregate elastic properties from those of the individual minerals. Phase relations at the base of the
 454 transition zone are relatively simple and can be described using models that have been derived within
 455 a number of experimental studies (Frost, 2003; Frost and Dolejs, 2007; Saikia et al., 2008).

456

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.

457

458 At 480 km a pyrope composition will be comprised of only wadsleyite and majoritic garnet (Irifune
 459 and Isshiki, 1998). Based on the bulk composition and using Fe-Mg partitioning data from Irifune
 460 and Isshiki (1998) it is then straight forward to calculate the compositions of both phases, which
 461 results in 42 vol. % garnet with the composition Py₁₄Alm₈Mj₅₆Gr₂₁. At approximately 540 km,
 462 wadsleyite undergoes a phase transition to ringwoodite over a depth interval of approximately 20 km,
 463 which can be described using thermodynamic models that have been fit to experimental data (Frost,
 464 2003; Frost and Dolejs, 2007). Between 480 and 620 km the garnet composition and proportion
 465 remain constant apart from small changes in Fe-Mg partitioning between wadsleyite and ringwoodite.
 466 However, at 620 km CaSiO₃ perovskite (Ca-Pv) starts to exsolve from garnet, with the volume

467 proportion of Ca-Pv gradually increasing with depth at the expense of the grossular component of
468 garnet (Saikia et al., 2008). As a consequence, the garnet composition loses Ca but also becomes less
469 majoritic. The gradual increase of Ca-Pv and the consequent compositional variations in garnet can
470 be described using the thermodynamic model of Saikia et al. (2008). At the base of the transition zone
471 the pyrolite mineralogy comprises 58 vol. % ringwoodite, $(Mg_{0.9}Fe_{0.1})_2SiO_4$, 36 vol. % garnet
472 $(Py_{34}Alm_9Mj_{51}Gr_4)$ and 6 vol % $CaSiO_3$ perovskite.

473

474 In contrast to pyrolite, an average MORB composition in the mantle transition zone is composed
475 almost entirely of garnet (89 vol. %) with additional stishovite (11 vol %) (Irifune et al., 1986). As
476 for the pyrolite composition, in the lower transition zone Ca-Pv starts to exsolve from majoritic
477 garnet, the phase relations of which can also be described using the thermodynamic model of (Saikia
478 et al., 2008). Because the Ca content of subducted oceanic crust (MORB) is higher than that of
479 pyrolite, garnets should become saturated in $CaSiO_3$ at lower pressures. However, the saturation
480 pressure is also a function of the garnet majorite component (Saikia et al., 2008), which is lower in
481 MORB with respect to a pyrolite composition. These two effects act in opposite directions and ensure
482 that the exsolution of $CaSiO_3$ perovskite from garnet occurs at approximately the same depth as
483 observed for the pyrolite composition. With increasing pressure, as $CaSiO_3$ perovskite exsolves, the
484 garnet becomes more Al-rich. At the base of the transition zone the MORB mineralogy comprises 72
485 vol. % garnet $(Py_{58}Alm_{20}Mj_3Gr_{19})$, 11 vol, % SiO_2 and 17 vol. % $CaSiO_3$ perovskite.

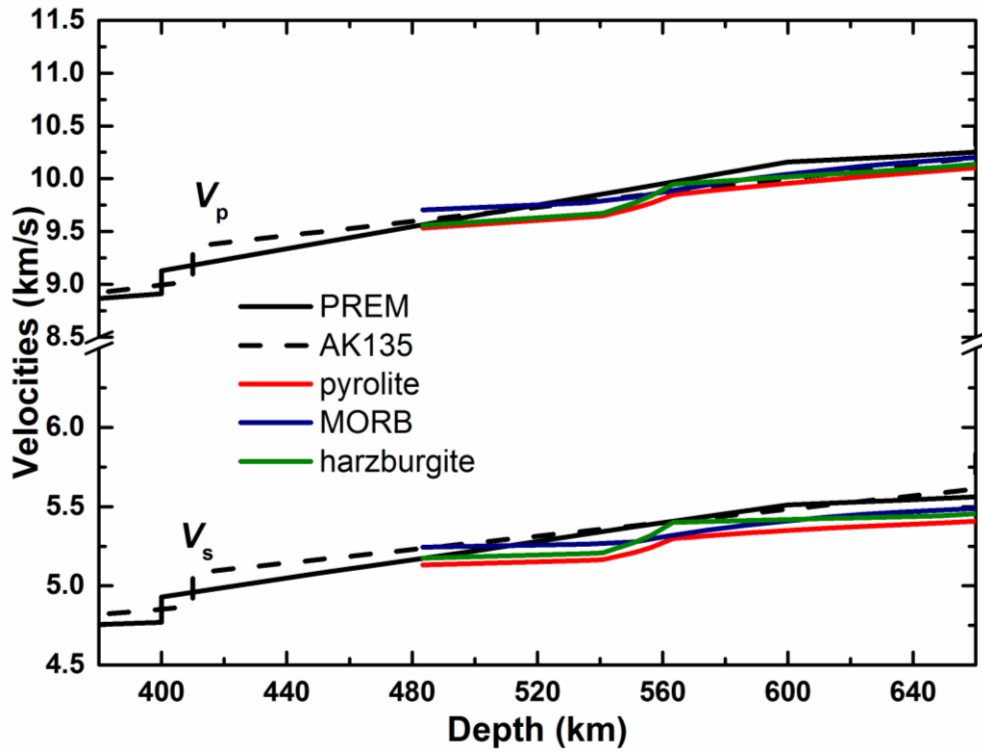
486

487 Harzburgite phase relations are similar to those of pyrolite over the same depth interval, with the main
488 difference being a higher proportion of $(Fe,Mg)_2SiO_4$. At 480 km the average harzburgite composition
489 employed (Irifune and Ringwood, 1987b) is calculated to comprise 81.5 vol. % wadsleyite and 18.5
490 vol. % of majoritic garnet with the composition $Alm_{12}Mj_{80}Gr_8$. Phase transformations are similar to
491 those in pyrolite, although due to the low Ca content the exsolution of $CaSiO_3$ is almost insignificant
492 and the low Al content results in a more majorite rich garnet.

493

494 The sound velocities V_S and V_P calculated for the three bulk compositions described above are
495 compared with the seismic reference models PREM and AK135 in Fig. 6.

496



497

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

503

504 Although the pyrolite model is in agreement at least with AK135 in terms of V_P , there is a consistent
505 negative deviation for V_S , by ~ 0.2 km/s, between pyrolite and both reference models over the 150 km
506 of the base of the transition zone. Garnet elastic properties are the main reason for this deviation as
507 both ringwoodite and CaSiO_3 -perovskite have velocities that are above both reference models at these
508 conditions. Reference models are globally averaged velocity structures and it should, in principal, be

509 possible to approximate this structure using an average mantle composition, mineralogy and
510 temperature. Reference models are unlikely to capture the detail of the velocity structure, however,
511 particularly in the transition zone, due to the overly simplified polynomial functions upon which they
512 are based (Cammarano et al., 2005). Trade-offs between the magnitude of seismic discontinuities and
513 the velocity gradient, for example, are likely to cause inaccuracies in the determinations of both. On
514 average, however, negative deviations from the real mantle velocity structure would be expected to
515 be balanced by near-by positive deviations. This would appear not to be the case in the transition
516 zone, however, if a pyrolite model along a 1600 K adiabat is assumed to resemble the real mantle.

517

518 Irifune et al. (2008) also reported that estimated velocities for pyrolite are lower than the reference
519 models at approximately 575 km, but suggested that the subsequent exsolution of CaSiO₃ perovskite
520 from garnet would decrease the discrepancy towards the base of the transition zone. Sinogeikin and
521 Bass (2002) similarly argued that CaSiO₃ perovskite exsolution would raise the velocity gradient.
522 Note, however, that in this study, the gradual formation of CaSiO₃-rich perovskite and the resulting
523 compositional variations in garnet have been taken into account. A very slight increase in the velocity
524 gradient for the pyrolite model occurs above 570 km due to CaSiO₃ exsolution. Without this
525 exsolution the pyrolite velocities would have the same gradient as the harzburgite model. Although
526 shear wave properties of CaSiO₃ perovskite are poorly constrained, the G_0 used in the current model
527 (Xu et al., 2008) is at the very high limit of recent theoretical studies (Kawai and Tsuchiya, 2015) and
528 is higher than experimental estimates (Kudo et al., 2012). Therefore, it seems unlikely that the V_s for
529 CaSiO₃ perovskite is significantly underestimated, in fact the contrary seems more likely. It appears,
530 therefore, that pyrolite along a 1673 K adiabat provides a poor match to seismic reference models at
531 the base of the transition zone.

532 Other bulk compositions have been proposed for the transition zone, such as piclogite (Bass and
533 Anderson, 1984; Anderson and Bass, 1986), however from Fig. 6 it appears that increasing the
534 basaltic component of a mineralogical assemblage does not result in an increase of V_s values to levels

535 compatible with the reference models. For the MORB composition, the exsolution of CaSiO_3
536 perovskite can be clearly seen to cause an increase in gradient above 550 km. Although the resulting
537 gradient is closer to the reference models, the absolute values remain 0.1 km/s below both reference
538 models throughout the base of the transition zone.

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

545

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

550

551 One of the few remaining plausible explanations for the deviation between mineral and seismic
552 models at the base of the transition zone would be if the average mantle temperature over this depth
553 interval is below the 1673 K adiabat. While mantle adiabatic temperatures determined from erupted
554 basalt melt compositions vary by approximately $\pm 150^\circ$, (Lee et al., 2009), the estimated temperature
555 needed for the pyrolite model to match the seismic model at the base of the transition zone is ~ 500
556 K lower than 1673 K. This would place mantle temperatures far outside of the range of adiabatic
557 temperature estimates from the surface or from temperature estimates based on the depth of the 410
558 km discontinuity (Frost, 2008). Saikia et al. (2008) noted that to associate the 520 km seismic
559 discontinuity with the wadsleyite to ringwoodite transformation requires lower than expected average
560 mantle temperatures. This can be seen in Fig. 6, where the wadsleyite to ringwoodite transformation

561 along a 1673 K adiabat occurs at 550 km, and only if temperatures were ~300 K lower would the
562 transition occur at 520 km. Saikia et al. (2008) suggested that a possible cause of lower mantle
563 temperatures may be the presence of subducting slabs stagnating at the base of the transition zone
564 and flattening out to form significant lateral cold heterogeneities. Some tomographic models (e.g.
565 Káráson and van der Hilst, 2000) appear to clearly indicate that such heterogeneities exist. As
566 temperatures in the centre of such slabs could be easily 600 K below the average mantle, then they
567 could drag down average mantle temperatures at these depths, assuming that the lateral anomalies
568 were large enough. Furthermore it is possible that a significant proportion of this material will be of
569 near harzburgite composition. It can be estimated that temperatures would have to be only 200 K
570 below the 1673 K adiabat for harzburgite mineral model velocities to match seismic reference models
571 at the base of the transition zone. If such global horizontal anomalies exist, this average reduction in
572 temperature may be plausible and would be also consistent with the 520 km seismic discontinuity
573 being caused by the wadsleyite to ringwoodite transformation.

574

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

580

581 **Acknowledgements**

582 We thank S. Linhardt, H. Schulze, R. Njũl, D. Krauße, U. Trentz, S. Übelhack and H. Fischer for
583 their technical assistance. We also thank D. Novella and N. Bolfan-Casanova for measuring the water
584 content of the samples. Support provided by ERC advanced Grant no. 227893 “DEEP” funded
585 through the EU 7th Framework Programme. This research used resources of the Advanced Photon
586 Source, a U.S. Department of Energy (DOE) Office of Science User Facility operated for the DOE

587 Office of Science by Argonne National Laboratory under Contract No. DE-AC02-06CH11357. We
588 acknowledge the support of GeoSoilEnviroCARS (Sector 13), which is supported by the National
589 Science Foundation - Earth Sciences (EAR-1128799), and the Department of Energy, Geosciences
590 (DE-FG02-94ER14466).

591

592 **References**

593 Ahrens, T.J., 1995. Mineral Physics and Crystallography, a handbook of physical constants, AGU
594 Publications, Washington DC., pp. 64-97.

595 Anderson, D.L., and Bass, J.D., 1986. Transition region of the Earth's upper mantle. *Nature*. 320,
596 321-328, doi:10.1038/320321a0.

597 Angel, R.J., Finger, L.W., Hazen, R.M., Kanzaki, M., Weidner, D.J., Liebermann, R.C., and Veblen
598 D.R., 1989. Structure and twinning of single - crystal MgSiO₃ garnet synthesised at 17 GPa
599 and 1800 °C. *Am. Mineral*. 74, 509-512.

600 Angel, R.J., and Finger, L.W., 2011. SINGLE: a program to control single-crystal diffractometers. *J.*
601 *Appl Cryst*. 44, 247-251, doi:10.1107/S0021889810042305.

602 Bass, J.D., and Anderson, D.L., 1984. Composition of the upper mantle-geophysical tests of two
603 petrological models. *Geophys. Res. Lett*. 11, 237-240, doi:10.1029/GL011i003p00229

604 Bass, J.D., and Kanzaki, M., 1990. Elasticity of a majorite-pyrope solid solution. *Geophys. Res. Lett*.
605 17, doi:10.1029/GL017i011p01989.

606 Cammarano, F., Deuss, A., Goes, S., and Giardini, D., 2005. One-dimensional physical reference
607 models for the upper mantle and transition zone: combining seismic and mineral physics
608 constraints. *J. Geophys. Res.* 110, B01306, doi:10.1029/2004JB003272.

609 Chen, G., Cooke, J.A., Gwanmesia, G.D., and Liebermann, R.C., 1999. Elastic wave velocities of
610 Mg₃Al₂Si₃O₁₂-pyrope garnet to 10 GPa. *Am. Mineral*. 84, 384-388.

611 Conrad, P.G., Zha, C.-S, Mao, H.-K, and Hemley, R.J., 1999. The high-pressure, single crystal
612 elasticity of pyrope, grossular and andradite. *Am. Mineral*. 84, 374-383.

613 Du, W., Clark, S.M., and Walker, D., 2015. Thermo-compression of pyrope-grossular garnet solid
614 solutions: Non-linear compositional dependence. *Am. Mineral.* 100, 215-222, doi:
615 <http://dx.doi.org/10.2138/am-2015-4752>.

616 Frost, D.J., 2003. The structure and sharpness of $(\text{Mg,Fe})_2\text{SiO}_4$ phase transformations in the transition
617 zone. *Earth Planet. Sci. Lett.* 216, 313-318, doi:10.1016/S0012-821X(03)00533-8.

618 Frost, D.J., 2008. The upper mantle and transition zone. *Elements.* 4(3), 171-176,
619 doi:10.2113/GSELEMENTS.4.3.171.

620 Frost, D.J., and Dolejš, D., 2007. Experimental determination of the effect of H_2O on the 410 km
621 discontinuity. *Earth Planet. Sci. Lett.* 256(1-2), 182-195, doi:10.1016/j.epsl.2007.01.023.

622 Gwanmesia, G.D., Chen, G., and Liebermann, R.C., 1998. Sound velocities in MgSiO_3 -garnet to 9
623 GPa at room temperature. *Geophys. Res. Lett.* 25, 4553-4556, doi:10.1029/1998GL900189.

624 Gwanmesia, G.D., Zhang, J., Darling, K., Kung, J., Li, B., Wang, L., Neuville, D., and Liebermann,
625 R.C., 2006. Elasticity of polycrystalline pyrope ($\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$) to 9 GPa and 1000 °C. *Phys.*
626 *Earth Planet. In.* 155, 179-190, doi:10.1016/j.pepi.2005.10.008.

627 Gwanmesia, G.D., Wang, L., Triplett, R., and Liebermann, R.C., 2009. Pressure and temperature
628 dependence of the elasticity of pyrope-majorite [$\text{Py}_{60}\text{Mj}_{40}$ and $\text{Py}_{50}\text{Mj}_{50}$] garnets solid
629 solution measured by ultrasonic interferometry technique. *Phys. Earth Planet. In.* 174, 105-
630 112, doi:10.1016/j.pepi.2008.07.029.

631 Irifune, T., Sekine, T., Ringwood, A.E., and Hibberson, W.O., 1986. The eclogite-garnetite
632 transformation at high pressure and some geophysical implications. *Earth Planet Sci Lett.* 77,
633 245–256.

634 Irifune, T., and Ringwood, A.E., 1987a. Phase transformations in primitive MORB and pyrolite
635 compositions to 25 GPa and some geophysical implications. In: Manghnani, M.H., Syono, Y.
636 (Eds.), *High pressure research in mineral physics*. Terra Scientific, Tokyo, pp 231–242.

637 Irifune, T., and Ringwood, A.E., 1987b. Phase transformations in a harzburgite composition to 26
638 GPa: implications for dynamical behaviour of the subducting slab. *Earth Planet. Sci. Lett.* 86,
639 365-376, doi:10.1016/0012-821X(87)90233-0.

640 Irifune, T., and Isshiki, M., 1998. Iron partitioning in a pyrolite mantle and the nature of the 410-km
641 seismic discontinuity. *Nature.* 392, 702-705, doi:10.1038/33663.

642 Irifune, T., Higo, Y., Inoue, T., Kono, Y., Ohfuji, H., and Funakoshi, K., 2008. Sound velocities of
643 majorite garnet and the composition of the mantle transition region. *Nature.* 451, 814-817,
644 doi:10.1038/nature06551.

645 Ita, J., and Stixrude, L., 1992. Petrology, elasticity, and composition of the mantle transition zone. *J.*
646 *Geophys. Res.* 97(B5), 6849-6866, doi:10.1029/92JB00068.

647 Jacobsen, S.D., 2006. Effect of water on the equation of state of nominally anhydrous minerals, in:
648 Keppler, H., and Smyth, J.R. (Eds.), *Water in nominally anhydrous minerals, Reviews in*
649 *Mineralogy and Geochemistry, Geochemical Society Mineralogical Society of America, vol.*
650 *62, pp. 321-342.*

651 Jiang, F.M., Speziale, S., and Duffy, T.S., 2004. Single-crystal elasticity of grossular- and almandine-
652 rich garnets to 11 GPa by Brillouin scattering. *J. Geophys. Res.* 109 (B10), B10210,
653 doi:10.1029/2004JB003081.

654 Kárason, H., and Van der Hilst, R.D., 2000. Constraints on mantle convection from seismic
655 tomography, in: Richards, M.R., Gordon, R.G., and Van der Hilst, R.D. (Eds.), *The History*
656 *and Dynamics of Global Plate Motion, Geophys. Monog. Ser., 121, AGU, Washington, D.C.,*
657 *pp. 277-288, doi:10.1029/GM121p0277.*

658 Kato, T., and Kumazawa, M., 1985. Garnet phase of MgSiO₃ filling the pyroxene–ilmenite gap at
659 very high temperature. *Nature,* 316, 803-805, doi:10.1038/316803a0.

660 Kawai, K., and Tsuchiya, T., 2015. Small shear modulus of cubic CaSiO₃ perovskite. *Geophys. Res.*
661 *Lett.* 42, 2718–2726, doi:10.1002/2015GL063446.

662 Keppler, H., and Frost, D.J., 2005. Introduction to minerals under extreme conditions, in: Miletich,
663 R. (Ed.), Mineral behaviour at extreme conditions, EMU Notes in Mineralogy, vol.7, pp. 1-
664 30.

665 King, H.E., and Finger, L., 1979. Diffracted beam crystal centering and its application to high
666 pressure crystallography. *J. of Appl. Crystallogr.* 12, 374-378.
667 doi:10.1107/S0021889879012723.

668 Kudo, Y., Hirose, K., Murakami, M., Asahara, Y., Ozawa, H., Ohishi, Y., and Hirao, N., 2012. Sound
669 velocities measurements of CaSiO₃ perovskite to 133 GPa and implications for lowermost
670 mantle seismic anomalies. *Earth Planet. Sci. Lett.* 1-7, 349-350,
671 doi:10.1016/j.epsl.2012.06.040.

672 Kurnosov, A., Kantor, I., Boffa Ballaran, T., Lindhardt, S., Dubrovinsky, L., Kuznetsov, A., and
673 Zehnder, B.H., 2008. A novel gas-loading system for mechanically closing of various types
674 of diamond anvil cells. *Rev. Sci. Instrum.* 79, 045110, doi:10.10163/1.2902506.

675 Lee, C.T.A., Luffi, P., Plank, T., Dalton, H.A., and Leeman, W.P., 2009. Constraints on the depths
676 and temperatures of basaltic magma generation on Earth and other terrestrial planets. *Earth
677 Planet. Sci. Lett.* 279, 20-33, doi:10.1016/j.epsl.2008.12.020.

678 Liu, J., Chen, G., Gwanmesia, G.D., and Liebermann, R.C., 2000. Elastic wave velocities of pyrope-
679 majorite garnets (Py₆₂Mj₃₈ and Py₅₀Mj₅₀) to 9 GPa. *Phys. Earth Planet. In.* 120, 153-163,
680 doi:10.1016/S0031-9201(00)00152-7.

681 Liu, Z., Irifune, T., Gréaux, S., Arimoto, T., Shinmei, T., and Higo, Y., 2015. Elastic wave velocity
682 of polycrystalline Mj₈₀Py₂₀ garnet to 21 GPa and 2000 K. *Phys. Chem. Minerals.* 42, 213-222,
683 doi:10.1007/s00269-014-0712-y.

684 Lu, C., Mao, Z., Lin, J.-F., Zhuravlev, K.K., Tkachev, S.N., and Prakapenka, V.B., 2013. Elasticity
685 of single-crystal iron-bearing pyrope up to 20 GPa and 750 K. *Earth Planet. Sci. Lett.* 361,
686 134-142, doi:10.1016/j.epsl.2012.11.041.

687 Murakami, M., Sinogeikin, S.V., Litasov, K., Ohtani, E., and Bass, J.D., 2008. Single-crystal
688 elasticity of iron-bearing majorite to 26 GPa: Implications for seismic velocity structure of
689 the mantle transition zone. *Earth Planet. Sci. Lett.* 274, 339-345,
690 doi:10.1016/j.epsl.2008.07.045.

691 O'Neill, B., Bass, J.D., Rossman, G.R., Geiger, C.A., and Langer, K., 1991. Elastic properties of
692 pyrope. *Phys. Chem. Mineral.* 17, 617-621, doi:10.1007/BF00203841.

693 Pacalo, R.E.G., and Weidner, D.J., 1997. Elasticity of majorite, MgSiO₃ tetragonal garnet. *Phys.*
694 *Earth Planet. Int.* 99, 145–154, doi:10.1016/S0031-9201(96)03158-5.

695 Paterson, M.S., 1982. The determination of hydroxyl by infrared absorption in quartz, silicate glasses
696 and similar materials. *Bulletin de Mineralogie.* 105, 20-29.

697 Rekhi, S., Dubrovinsky, L., and Saxena, S.K., 1999. Temperature-induced ruby fluorescence shifts
698 up to a pressure of 15 GPa in an externally heated diamond anvil cell. *High Temp.- High*
699 *Pressures.* 31, 299-305, doi:10.1068/htrt161.

700 Rigden, S.M., Gwanmesia, G.D., and Liebermann, R.C., 1994. Elastic wave velocities of a pyrope-
701 majorite garnet to 3 GPa. *Phys. Earth Planet. In.* 86, 35-44, doi:10.1016/0031-9201(94)05060-
702 0.

703 Ringwood, A.E., 1967. Pyroxene-garnet transition in the Earth's mantle. *Earth Planet. Sci. Lett.* 2,
704 255-263.

705 Rivers, M., Prakapenka, V.B., Kubo, A., Pullins, C., Holl, C.M., and Jacobsen, S.D., 2008. The
706 COMPRES/GSECARS gas-loading system for diamond anvil cells at the Advanced Photon
707 Source. *High Pressure Res.* 28(3), 273–292, doi:10.1080/08957950802333593.

708 Robie, R.A., and Edwards, J.L., 1966. Some Debye temperatures from single crystal elastic constant
709 data. *J. Appl. Phys.* 37, 2659–2663, dx.doi.org/10.1063/1.1782100.

710 Saikia, A., Frost, D.J., and Rubie, D.C., 2008. Splitting of the 520-kilometer seismic discontinuity
711 and chemical heterogeneity in the mantle. *Science.* 319(5869), 1515-1518,
712 doi:10.1126/science.1152818.

713 Sinogeikin, S.V., and Bass, J.D., 2000. Single-crystal elasticity of pyrope and MgO to 20 GPa by
714 Brillouin scattering in the diamond anvil cell. *Phys. Earth Planet. In.* 120, 43-62,
715 doi:10.1016/S0031-9201(00)00143-6.

716 Sinogeikin, S.V., and Bass, J.D., 2002. Elasticity of Majorite and a Majorite-Pyrope solid solution to
717 high pressure: implications for the transition zone. *Geophys. Res. Lett.* 29(2), 1017,
718 doi:10.1029/2001GL013937.

719 Stixrude, L., and Lithgow-Bertelloni, C., 2005. Thermodynamics of mantle minerals – I. Physical
720 properties. *Geophys. J. Int.* 162, 610-632, doi: 10.1111/j.1365-246X.2005.02642.x.

721 Trots, D.M., Kurnosov, A., Boffa Ballaran, T., Tkachev, S., Zhuravlev, K., Prakapenka, V.,
722 Berkowski, M., and Frost, D.J., 2013. The Sm:YAG primary fluorescence pressure scale. *J.*
723 *Geophys. Res. Solid Earth.* 118, doi:10.1002/2013JB010519.

724 Wang, Z., and Ji, S., 2001. Elasticity of six polycrystalline silicate garnets at pressure up to 3.0 GPa.
725 *Am. Mineral.* 86, 1209-1218, doi: 10.2138/am-2001-1009.

726 Whitfield, C.H., Brody, E.M., and Bassett, W.A., 1976. Elastic moduli of NaCl by Brillouin scattering
727 at high pressure in a diamond anvil cell. *Rev. Sci. Instrum.* 47, 942, doi:10.1063/1.1134778.

728 Xu, W., Lithgow-Bertelloni, C., Stixrude, L., and Ritsema, J., 2008. The effect of bulk composition
729 and temperature on mantle seismic structure. *Earth Planet. Sci. Lett.*, 275, 70-79.
730 doi:10.1016/j.epsl.2008.08.012.

731 Zhou, C., Irifune, T., Gréaux, S., Whitaker, M.L., Shinmei, T., Ohfuji, H., Negishi, R., and Higo, Y.,
732 2012. Elasticity and sound velocities of polycrystalline $Mg_3Al_2(SiO_4)_3$ garnet up to 20 GPa
733 and 1700 K. *J. Appl. Phys.* 112, 014910. doi:10.1063/1.4736407.

734 Zhou, C., Gréaux, S., Nishiyama, N., Irifune, T., and Higo, Y., 2014. Sound velocities measurement
735 on $MgSiO_3$ akimotoite at high pressures and high temperatures with simultaneous in situ X-
736 ray diffraction and ultrasonic study. *Phys. Earth Planet. In.* 228, 97-105,
737 doi:10.1016/j.pepi.2013.06.005.