1 **Revision 1**

2 **Pressure-induced velocity softening in natural orthopyroxene at mantle temperature**

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14 **Abstract**

15 In this study, we have measured the compressional and shear wave velocities of

16 $(Mg_{1.77}Fe_{0.22}Ca_{0.01})Si_2O_6$ natural orthopyroxene up to 13.5 GPa and 873 K using ultrasonic

17 interferometry in conjunction with in-situ synchrotron X-ray diffraction and imaging techniques.

18 Previous acoustic experiments on orthoenstatite (OEn) $MgSiO_3$ indicated that both

19 compressional and shear velocities (V_P and V_S) of OEn undergo continuous velocity softening

20 above 9 GPa at room temperature, which has been attributed to the phase transition from OEn to

21 the metastable, high-pressure clinoenstatite HPCEn2. For the first time, our results suggest that

22 pressure-induced velocity softening can occur in natural orthopyroxene at high temperature

23 conditions relevant to the Earth's cold subduction zones. Estimates of the impedance and

24 velocity contrasts between orthopyroxene (Opx) and high-pressure clinopyroxene (HPCpx) have

25 been calculated, and the possibility of this phase transformation being a plausible candidate for

26 seismic X-discontinuities at depth around 250-350 km is re-evaluated.

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28 **Key words**: Orthopyroxene; Velocity softening; High pressure and high temperature; Ultrasonic

29 interferometry.

Introduction

30

31   Orthopyroxene $(Mg,Fe)SiO_3$ is one of the most abundant minerals in the pyrolite

32   compositional model of Earth's upper mantle (Ringwood 1975). Several polymorphs of pure Mg

33   end-member enstatite $(MgSiO_3)$ are thermodynamically stable under the pressure (P) and

34   temperature (T) conditions of the upper mantle (see Fig. 1), including orthoenstatite [OEn, space

35   group (SG): *Pbca*], protoenstatite (PEn, SG: *Pbcn*), low-pressure clinoenstatite (LPCEn, SG:

36    $P2_1/c$), and high-pressure clinoenstatite (HPCEn, SG: *C2/c*) (Gasparik 1990; Pacalo and

37   Gasparik 1990). Recently, a metastable, high-pressure monoclinic polymorph with space group

38    $P2_1/c$ (designated as HPCEn2) has been discovered and reported to be persistent at least up to

39   673 K (J. Zhang et al. 2012; J. Zhang et al. 2014). Given the abundance of pyroxene in the

40   Earth's upper mantle, investigating the phase transformation behavior and physical properties of

41   pyroxene-structured groups has attracted the attention of many research groups (e.g., Angel and

42   Hugh-Jones 1994; Angel and Jackson 2002; Finkelstein et al. 2015; Frisillo and Barsch 1972;

43   Hugh-Jones and Angel 1997; Jackson et al. 2004; Jahn 2008; Kung et al. 2006; Lin 2003; Xu et

44   al. 2018; J. Zhang et al. 2012; Zhao et al. 1995).

45   Kung et al. (2004) observed a substantial softening of both the compressional and shear

46   velocities (V_P and V_S) in OEn above 9 GPa at room temperature. Subsequent experimental and

47   computational investigations (Li et al. 2014; J. Zhang et al. 2014) suggest that the softening

48   behavior may be related to the phase transformation from OEn to the newly discovered

49   monoclinic phase HPCEn2 with space group $P2_1/c$. At room temperature or moderate high

50   temperature, due to the reconstructive nature of the phase transition from OEn to HPCEn [which

51   requires reorientation of the stacked layers], the phase transformation is always kinetically

52   inhibited by energy barriers (Dera et al. 2013; J. Zhang et al. 2014); see black dotted line below

53   700K in Fig. 1. Thus, OEn would transform to the metastable phase HPCEn2. A recent study has

54   shown this metastable phase transition could occur at high temperatures up to 700 K (Xu et al.

55   2018). The velocity softening observed in MgSiO$_3$, at around 9 GPa, has also been observed in

56   FeSiO$_3$-orthoferrosilite at room temperature at ~5 GPa (see Kung and Li 2014). However, prior

57   to the current study, no attempt has ever been made to experimentally investigate if this pressure-

58   induced velocity softening can persist at high temperature. Li et al. (2014) speculate that if such a

59   softening behavior occurs at high temperatures in natural orthopyroxene compositions, the

60   velocity and impedance contrasts between Opx and HPCpx at mantle depths would be enhanced,

61   which could, in turn, increase their detectability in seismic studies.

62   The phase transition from Opx to HPCpx has been proposed to explain the seismic X-

63   discontinuity (e.g., Revenaugh and Jordan 1991; Woodland and Angel 1997) for a long time

64   because the transition pressure from Opx to HPCpx is well consistent with the depth of the

65   seismic discontinuity (Angel et al. 1992) and the phase transition boundary is sharp enough to

66   generate the discontinuity (Woodland 1998). Previous acoustic studies on Opx have been

67   conducted at high temperature and ambient pressure (e.g., Jackson et al. 2007; Kung et al. 2011)

68   or at room temperature and high pressure (e.g., Chai et al. 1997; Flesch et al. 1998; Kung et al.

69   2004; D. Zhang et al. 2013; J. Zhang and Bass 2016). The high P-T experiments on Opx have all

70   been focused on the investigation of the phase relationships and equation of state (EOS) of

71   orthopyroxene (e.g., Akashi et al. 2009; Xu et al. 2018; J. Zhang et al. 2014; Zhao et al. 1995).

72   To our knowledge, no direct experimental measurements of the acoustic velocities of

73   orthopyroxene at simultaneous high P-T conditions have been reported. To help us better

74   understand the cause of X-discontinuity, such acoustic velocity data at high pressure and high

75   temperature are needed.

76   In this study, we have conducted sound velocity and density measurements on a natural

77 orthopyroxene sample at simultaneous high P-T conditions using ultrasonic interferometry in

78 conjunction with in-situ synchrotron X-ray diffraction and imaging techniques. The elastic bulk

79 and shear properties as a function of pressure along a 673 K isotherm were determined directly,

80 thereby allowing an investigation of pressure induced velocity softening in orthopyroxene at

81 temperatures relevant to the Earth's subduction zones.

Experimental Methods

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83   The polycrystalline sample of orthopyroxene used in the ultrasonic experiment was hot-

84 pressed at 5 GPa and 1273 K for 1 hour in a 1000-ton uniaxial split-cylinder apparatus (USCA-

85 1000) in the High Pressure Laboratory at Stony Brook University using natural pyroxene powder

86 (purchased from Ward's Scientific Establishment) as the starting material. The hot-pressing

87 experiment followed a specific P-T path designed to obtain a crack-free, fine-grained, and

88 homogeneous pyroxene sample (more details in Gwanmesia and Liebermann 1992).

89   High-pressure ultrasonic interferometric experiments were performed up to 13.5 GPa and

90 873 K in a 1000-ton Kawai-type, multi-anvil apparatus (T-25) in conjunction with synchrotron

91 X-radiation at beamline 13-ID-D of GSECARS of the Advanced Photon Source, Argonne

92 National Laboratory. Details of the experimental setup can be found elsewhere (Li and

93 Liebermann 2014) and a sketch up of the cell assembly is shown in Figure S1 in the

94 supplementary material. A dual mode $LiNbO_3$ transducer was used to generate and receive both

95 the compressional (P) wave and shear (S) wave simultaneously (50 MHz resonant frequency for

96 P wave and 30 MHz for S wave). The temperature was measured using W/Re3%-W/Re25%

97 thermocouple wires, with the junction immediately next to the sample near the center of the cell.

98 A dense alumina rod was placed on the top of the sample and served as the acoustic buffer rod.

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99   Two thin pieces of gold foil (2 μm thickness) were put at the top and bottom of the sample

100   respectively to enhance the mechanical coupling and signal propagation, as well as serving as a

101   delineation of the sample's boundaries in X-radiography images. A disk of NaCl placed at the

102   back of the sample provided pseudo-hydrostatic environment for the sample, which also used as

103   an internal pressure marker using the equation of state from Decker (1971).

104   The experimental P-T path for the acoustic experiment is shown in Figure 1. X-ray

105   diffraction patterns of NaCl and the Opx sample, as well as the P and S wave travel times and

106   images of the sample were collected at a series of pressure and temperature conditions along the

107   designated P-T path. The initial compression to 3 GPa was performed at room temperature,

108   followed by heating to 473 K and further compression to 5 GPa. After heating the sample to 673

109   K at 5 GPa, pressure was increased up to 13.5 GPa along the 673 K isotherm, during which the

110   X-ray diffraction data of the sample were monitored closely by comparing with the standard

111   spectra of orthopyroxene (Opx, SG: *Pbca*) phase. At the peak pressure, the temperature was

112   increased to 873 K while the ram load was kept constant. Due to the relaxation of the pressure

113   medium, the pressure was found to have slightly decreased to 13.1 GPa and the sample was

114   transforming to high-pressure clinopyroxene (HPCpx, SG: *C2/c*, solid circles in Fig. 1, more

115   details in Results). An isothermal decompression along 873 K was then performed and data for

116   HPCpx were collected as pressure was slowly decreased to 9.9 GPa.

117   X-ray diffraction patterns were collected in energy dispersive mode at fixed 2θ (6.10°). The

118   recorded diffraction patterns from the sample were analyzed using the Le Bail method with the

119   GSAS/EXPGUI program (Larson and Von Dreele 1994; Toby 2001) to derive the lattice

120   parameters and thus densities (see Figure S2 in supplementary material). The measured cell

121   parameters of NaCl were used to determine the cell pressures using the equation of state of

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122   Decker's implemented in PDindexer software (Seto et al. 2010). The maximum uncertainty in

123   the calculated pressure is ~0.4 GPa (Decker 1965, 1971). P and S wave travel times were

124   obtained by the pulse echo overlap (PEO) method, which has been described elsewhere (Li et al.

125   2002; Li et al. 2004). The error for travel times is about 0.2 ns. The bond perturbations

126   contributed by the gold foils to travel time for Opx (0.7 ns for P waves and -0.7 ns for S waves)

127   and HPCpx (0.8 ns for P waves and -1.0 ns for S waves) were corrected following the procedures

128   of Niesler and Jackson (1989). Sample lengths were obtained from the X-radiography images

129   recorded by the CCD camera, with a precision within 0.25%. The length of the recovered sample

130   measured after high pressure run is $L_0 = 0.987(1)$ mm.

131   Scanning Electron Microscope (SEM) analysis was conducted on the recovered sample at

132   Geodynamic Research Center, Ehime University, Japan. The results (Fig. 2) indicate that the

133   sample is homogenous with average grain size less than 10 microns. Part of the final recovered

134   sample was used for chemical analysis by using a 5-spectrometer Cameca SX-100 electron

135   microprobe at American Museum of Natural History. All elemental analyses were performed at

136   an accelerating voltage of 15 kV, a beam current of 20 nA, and using a beam size of 1 μm. We

137   measured Si (calibrated on diopside), Fe (fayalite), Mg (diopside), Ca (diopside). The counting

138   time was 20 s for all elements. The composition of this natural sample was determined to be

139   $(Mg_{1.77}Fe_{0.22}Ca_{0.01})Si_2O_6$.

140   **Results**

141   Travel times in the current sample were measured as a function of pressure along both 673 K

142   and 873 K isotherms. As shown in Fig. 3a, P wave travel times decreased monotonically with

143   increasing pressure, with a rapid reduction in the rate of change with pressure from $~5 \times 10^{-2}$

144   s/GPa at 5 GPa to $~5 \times 10^{-3}$ s/GPa at 13.5 GPa. While for S waves shown in Fig. 3b, the travel

145   times decreased with increasing pressure up to ~11 GPa and then became independent of

146   pressure within 11-11.8 GPa; above 11.8 GPa, the S wave travel times begin to increase as

147   pressure was increased to 13.5 GPa. In their study of $MgSiO_3$, Kung et al. (2004) reported that

148   both P and S wave travel times decreased up to 9 GPa, then started to increase up to ~13 GPa.

149   Similar anomalies have also been observed within 5-7 GPa in a the study on $FeSiO_3$ ferrosilite

150   (see Fig. 4 in Kung and Li 2014). These anomalies have been interpreted as precursors to the

151   transition to the metastable HPCEn2 phase (Kung and Li 2014; Li et al. 2014). Taking into

152   account the different composition as well as temperature [$(Mg_{1.77}Fe_{0.22}Ca_{0.01})Si_2O_6$ and 673 K]

153   compared with those at room temperature for $MgSiO_3$ and $FeSiO_3$, the observed travel times in

154   this study, especially for S waves, are consistent with those in previous studies, suggesting that

155   the anomalous travel time-pressure behavior can be sustained at 673 K in Opx with magnesium-

156   rich compositions. Fig. 3c shows the length changes of the sample as a function of pressure and

157   temperature obtained using X-radiography images. The lengths of the Opx sample decreased

158   with increasing pressure up to 13.5 GPa in a nearly linear manner; no anomalous behavior was

159   observed. Thus, the anomalous behavior of the acoustic travel times in Fig. 3 a and b is solely

160   due to changes in the intrinsic elastic properties of orthopyroxene.

161   X-ray diffraction patterns are shown in Fig. 4. After cold compression to 5.0 GPa and heating

162   to 673 K, orthopyroxene (Opx, SG: *Pbca*) remains the single phase of the sample (Fig. 4 a and b).

163   During the subsequent compression along 673 K, although the travel times exhibit anomalous

164   behavior after 11.0 GPa, the X-ray diffraction patterns collected from 11.0 GPa to 13.5 GPa (Fig.

165   4c) did not change dramatically nor exhibit extra peaks, continuing to exhibit the strong

166   fingerprint of Opx. The values of χ^2 (a measure of the goodness of fit) from fitting to single Opx

167   (SG: *Pbca*) phase remain in a low level ($\chi^2 < 4$). According to a previous study by J. Zhang et al.

168   (2012) on a natural Fe-bearing orthopyroxene $(Mg_{1.74}Fe_{0.16}Al_{0.05}Ca_{0.04}Cr_{0.01})(Si_{1.94}Al_{0.06})O_6$, the

169   phase transition from Opx to HPCpx2 occurred at 14.26 GPa on compression at room

170   temperature. J. Zhang et al. (2014) also reported two transition pressures for natural samples

171   (14.5 GPa for near end-member Mg Opx; 13.3 GPa for Al + Fe-bearing Opx) at high temperature

172   of 673 K. It is likely that in the current experiments the Opx (SG: *Pbca*) phase did not transform

173   to HPCpx (SG: *P2₁/c*) at the maximum pressure of 13.5 GPa.

174   After heating to 873 K, clear changes were identified in the X-ray diffraction pattern (Fig.

175   4d), indicative of the phase transformation from Opx (*Pbca*) to HPCpx (*C2/c*). However, based

176   on the travel times and the X-ray diffraction pattern at 13.1 GPa 873 K, it is hard to evaluate

177   whether a complete transformation occurred or not because many peaks of HPCpx overlap with

178   those of Opx. Thus, it is likely that the sample at 13.1 GPa, 873 K consists mostly HPCpx with a

179   small amount of Opx. Due to the resolution limit of the current energy dispersive data, however,

180   the proportions of Opx (*Pbca*) and HPCpx (*C2/c*) could not be determined. On further

181   decompression below 9.9 GPa, the acoustic signal was lost. The recovered phase was low-

182   pressure clinopyroxene LPCpx (*P2₁/c*), which was not observed during compression, confirming

183   the full conversion to the HPCpx (*C2/c*) phase at 873 K before it was quenched to ambient

184   condition.

185   **Discussion**

186   P and S wave velocities of the natural pyroxene are calculated by $V_{(P, S)} = 2L/T_{(P, S)}$ and

187   plotted as a function of pressure in Figure 5. The results are compared to published P and S wave

188   velocities measured in Mg end-member orthoenstatite and Fe end-member orthoferrosilite by

189   using ultrasonic interferometry at room temperature, as well as to published data for synthetic

190   Fe-bearing Opx $(Mg_{0.87}Fe_{0.13})_2Si_2O_6$ derived from nuclear resonant inelastic X-ray scattering,

191   NRIXS (Kung and Li 2014; Kung et al. 2004; D. Zhang et al. 2013). At room temperature,

192   pressure-induced velocity softening has been observed for the Mg end-member, the Fe end-

193   member, and the synthetic $Mg_2Si_2O_6$-$Fe_2Si_2O_6$ solid solution. The P wave velocity of Opx in this

194   study increases steadily with pressure and decreases slightly at ~13 GPa, while the S wave

195   velocity exhibits a pronounced velocity softening above 11 GPa, reaching ~ 1.6% at ~13.5 GPa.

196   Stronger S wave softening than P wave was also observed in the Fe end-member ferrosilite

197   experiment (see orange pentagons in Fig. 5, in which the solid pentagons are for compression

198   while open pentagons are for decompression). These data for ferrosilite indicate that this could

199   be due to the presence of iron in the structure, which greatly reduces the shear elastic stiffness

200   coefficients under pressure, especially C_{44}, C_{55}, and C_{66} (Kung and Li 2014; D. Zhang et al.

201   2013). Similar behavior was observed in synthetic Fe-bearing Opx using NRIXS (D. Zhang et al.

202   2013). In that study, only the Debye sound velocity was obtained directly, and then V_P and V_S

203   were calculated using density and bulk modulus data from a separate P-V-T experiment. In their

204   experiment, D. Zhang et al. (2013) used the Opx (SG: *Pbca*) EOS to fit the data up to 10.5 GPa

205   and the HPCpx2 (SG: *P2₁/c*) EOS to fit the data at 12.3 GPa and 17 GPa. Thus, the velocity

206   softening is caused by the structure changes in two different phases. But from our XRD results,

207   the velocity softening occurs within a single phase with the *Pbca* symmetry. Therefore, the

208   elastic softening of enstatite-rich pyroxene cannot be properly evaluated unless simultaneous

209   measurements of acoustic velocity and X-ray diffraction for phase characterization are available.

210   The compression mechanism of Opx may be described by the rotation and kinking of SiO_4

211   tetrahedral chains and distortions of MgO_6 octahedra (see Fig. 3 in Li et al. 2014). Both the Si-O

212   and Mg-O bond lengths show monotonic decreases as a function of pressure, while the A-site

213   SiO_4 tetrahedral chain angles θ_A, which was reported to be highly correlated with C_{55}, do not

214   exhibit monotonic behavior with pressure (Li et al. 2014). The trend change in O3A-O3A-O3A

215   chain angle suggests a weakening restoring force which may be due to the increased kinking of

216   silicon tetrahedral chains. As shown in Fig. 5, larger velocity softening for S waves than that for

217   P waves has been observed in all three cases with different compositions and/or at different

218   temperatures, which could be interpreted using the relationship between elastic moduli (K_S, G)

219   and velocities ($V_P = \sqrt{(K_S + \frac{4}{3}G)/\rho}$, $V_S = \sqrt{G/\rho}$). Thus, the decrease of both P and S wave

220   velocities in Opx could be largely due to the softening in shear modulus G, which is

221   predominantly caused by the softening of the shear elastic constant C_{55} with increasing pressure

222   as reported by previous density functional theory calculations of Li et al. (2014) and Qian et al.

223   (2018).

224   Compared to pure Mg-end member and Fe-end member studies, the softening behavior of the

225   natural sample at high temperature starts at a higher pressure, which may indicate a positive

226   dP/dT slope of the phase boundary between Opx and HPCpx2. At higher temperature, the phase

227   transition of Opx to HPCpx2 would occur at higher pressure. The elastic moduli K_S and G as a

228   function of pressure at 673 K are plotted in Fig. 6. The propagated uncertainties in the bulk and

229   shear moduli are approximately 0.5%. The shear modulus increases to about 11 GPa, then

230   decreases slightly, which also serves as a precursor to the pressure-induced phase transition from

231   *Pbca* into *P2₁/c* structure from 12 to 14 GPa as observed in Raman data for Opx (J. Zhang et al.

232   2012; J. Zhang et al. 2014).

233   **Implications**

234   Based on the current study, Opx (SG: *Pbca*) with Mg-rich composition transforms into

235   HPCpx (SG: *C2/c*) when the temperature is increased from 673 to 873 K at ~13 GPa, providing

236   an upper bound in temperature at which Opx can be preserved at high pressures. Considering the

237   geotherm of cold slabs shown in Fig. 1, when T < 873 K the Opx may experience softening

238   before its transformation to HPCpx, lowering the seismic velocity of the subducting slab as well

239   as increasing the seismic velocity contrast at the phase transition to HPCpx. In addition, previous

240   studies on the compositional effects on the phase transition of Opx (*Pbca*) to HPCpx2 (*P2$_1$/c*)

241   show that 10 mol% Fe content could decrease the onset pressure of the initial formation of

242   HPCpx2 by ~1 GPa while a small amount of Al and Ca (0.212 pfu and 0.032 pfu, respectively)

243   would increase the pressure by over 3 GPa (J. Zhang et al. 2013). Thus, in regions where the

244   composition of Opx is the Al-free, Ca-free and Fe-rich, there is a possibility the velocity

245   softening behavior of Opx can occur at shallower depth in the subduction zones.

246   Seismic X-discontinuities at 250-350 km depths with a positive shear impedance (ρV_S)

247   contrast (3-8%) in the upper mantle have been observed in many seismic studies (e.g., Deuss and

248   Woodhouse 2002; Deuss and Woodhouse 2004; Revenaugh and Jordan 1991; Schmerr et al.

249   2013; Zhang and Lay 1993). The phase transformation of Opx (*Pbca*) to HPCpx (*C2/c*) has been

250   proposed to be one of the plausible candidates for the cause of X-discontinuity. The shear

251   impedance contrast caused by this phase transition has been estimated to be only around 1% (e.g.,

252   Woodland 1998; Woodland and Angel 1997; D. Zhang et al. 2013), which is relatively small

253   compared to seismological observations. However, based on extant studies (this study; Kung and

254   Li 2014; Kung et al. 2004), the pressure-induced velocity softening behavior is a characteristic

255   property of the Opx (*Pbca*) phase at least up to 673K, regardless of whether the transformation is

256   to HPCpx (*C2/c*) or the metastable phase HPCpx2 (*P2$_1$/c*). Thus, the shear impedance contrast of

257   Opx-HPCpx would be enhanced in the pressure range where the softening behavior occurs. Here,

258   we provide the direct information of the elasticity of both Opx and HPCpx phases at high

259   temperatures in a same experiment. Thermal effects of K_S and G were corrected from the data at

260   3.1 GPa in this experiment for Opx and the results from Kung et al. (2005) for HPCpx. Along the

261   cold subduction slab geotherm shown in Fig. 1, the density jumps at a pressure range of ~10-12

262   GPa is about 2.4%, associating with the shear velocity jumps of 5.7-6.3% and shear impedance

263   contrasts   of   8.0-8.4%.   The   impedance   contrasts   here   are   defined   by:

264    $C = \frac{\rho_{HPCpx}V_{HPCpx} - \rho_{Opx}V_{Opx}}{\frac{1}{2}(\rho_{HPCpx}V_{HPCpx} + \rho_{Opx}V_{Opx})} \times 100\%$. Considering the abundance of Opx in the Earth's

265   interior, the estimation of shear impedance contrast is about 0.8-1.7% in the pyrolitic

266   composition and up to 3.4% in some pyroxene-enriched regions (Irifune and Ringwood 1987;

267   Ringwood 1975, 1991), comparable to those seismic observations for the X-discontinuity. In Fe-

268   rich subduction zones where the softening behavior should occur at shallower depth, the

269   impedance contrast caused by the phase transition of Opx (*Pbca*) to HPCpx (*C2/c*) would be

270   even larger than previously estimated. Therefore, the Opx-HPCpx phase transition could still be

271   one of the contributing factors for the seismic X-discontinuity, especially in the pyroxene rich

272   area along the cold subducted slabs.

Acknowledgements

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423

424 **Table 1.** Elasticity properties of Fe-bearing natural orthopyroxene at high temperature and

425 pressure.

	Pressure	T	Length	2tp	2ts	V_P	V_S	K_S	G	Volume	ρ
	(GPa)	(K)	(mm)	(μs)	(μs)	(km/s)	(km/s)	(GPa)	(GPa)	(Å^3)	(g/cm^3)
Opx	0	300								838.45(10)	3.295
Opx	0.9	300	0.993	0.2497	0.4175	7.96(2)	4.76(1)	109.9	75.2	831.87(9)	3.321
Opx	3.1	300	0.982	0.2335	0.4031	8.42(2)	4.87(1)	132.7	80.5	814.88(9)	3.390
Opx	3.1	473	0.984	0.2363	0.4083	8.33(2)	4.82(1)	129.6	78.5	817.54(11)	3.379
Opx	5.0	673	0.978	0.2269	0.3989	8.62(2)	4.90(1)	143.8	81.8	811.62(11)	3.404
Opx	6.5	673	0.973	0.2205	0.3918	8.82(2)	4.97(1)	154.4	84.7	804.71(11)	3.433
Opx	7.0	673	0.971	0.2187	0.3903	8.88(2)	4.98(1)	158.0	85.3	801.30(11)	3.447
Opx	8.1	673	0.967	0.2155	0.3873	8.98(2)	4.99(1)	164.5	86.7	794.65(10)	3.476
Opx	9.2	673	0.964	0.2131	0.3849	9.05(2)	5.01(1)	169.6	87.9	789.40(8)	3.499
Opx	10.0	673	0.963	0.2111	0.3835	9.12(2)	5.02(1)	174.7	88.8	784.09(8)	3.523
Opx	11.0	673	0.961	0.2095	0.3829	9.17(2)	5.02(1)	179.2	89.3	779.33(7)	3.545
Opx	11.8	673	0.959	0.2087	0.3829	9.19(2)	5.01(1)	181.6	89.3	775.59(8)	3.562
Opx	12.6	673	0.957	0.2081	0.3845	9.20(2)	4.98(1)	184.6	88.7	771.46(9)	3.581
Opx	13.5	673	0.954	0.2077	0.3871	9.19(2)	4.93(1)	187.2	87.5	767.94(9)	3.597
HPCpx*	13.1	873	0.945	0.2000	0.3662	9.45(2)	5.16(1)				
HPCpx	11.9	873	0.947	0.1986	0.3604	9.54(2)	5.26(1)	196.7	100.4	380.32(4)	3.632
HPCpx	9.9	873	0.951	0.2028	0.3630	9.38(2)	5.24(1)	184.7	98.8	384.04(4)	3.597
LPCpx	0	300	0.987								

426   Note*: a mixture phase of HPCpx and Opx

427

428   **FIG. 1.** Topology of the phase diagram for $(Mg,Fe)SiO_3$ and the pressure-temperature path in

429   the ultrasonic experiments presented in the study (lines with arrows and circles). Open circles:

430   orthopyroxene (Opx); Solid circles: high-pressure clinopyroxene (HPCpx). Solid lines: Phase

431   boundaries for $MgSiO_3$ (black, Gasparik 1990) and $FeSiO_3$ (blue, Woodland and Angel 1997).

432   Black dotted lines: Extrapolated phase boundaries below 700 K. Gray dash line: Cold slab

433   geotherm (Kirby et al. 1996). OEn = orthoenstatite; HPCEn = high-pressure clinoenstatite;

434   LPCEn = low-pressure clinoenstatite; PEn = protoenstatite; OFs = orthoferrosilite; HPCFs =

435   high-pressure clinoferrosilite; LPCFs = low-pressure clinoferrosilite; Wad = Wadsleyite; St =

436   stishovite; Rwd = ringwoodite.

437

438   **FIG. 2.** Scanning Electron Microscope (SEM) image of the recovered sample.

439

440   **FIG. 3.** (a) P wave and (b) S wave travel times of $(Mg,Fe)SiO_3$ as a function of pressure. The

441   error for travel times is about 0.2ns. (c) Length changes (L/L_0) in sample. The error for sample

442   length is about ±0.1%.

443

444   **FIG. 4.** X-ray diffraction patterns. (a) starting material with orthopyroxene structure (Pbca) at

445   ambient conditions; (b) after cold compression to 5.0 GPa, the sample was heated to 673 K; (c)

446   Opx after compressed to 13.5 GPa along 673 K; (d) HPCpx at 13.1 GPa after transforming from

447   orthopyroxene by heating to 873 K with minor amount of Opx (not indexed); (e) the final

448   recovered phase identified as low-pressure clinopyroxene ($P2_1/c$). Tickmarks in red indicate peak

449   positions for the NaCl pressure medium.

20

450

451 **FIG. 5.** P and S wave velocities of pyroxene as a function of pressure up to 13.5 GPa

452 determined by ultrasonic measurements in this study compared with previous results (see

453 Legend). UI: ultrasonic interferometry; NRIXS: nuclear resonant inelastic X-ray scattering.

454

455 **FIG. 6.** Adiabatic bulk (K_S) and shear (G) modulus for orthopyroxene as a function of pressure

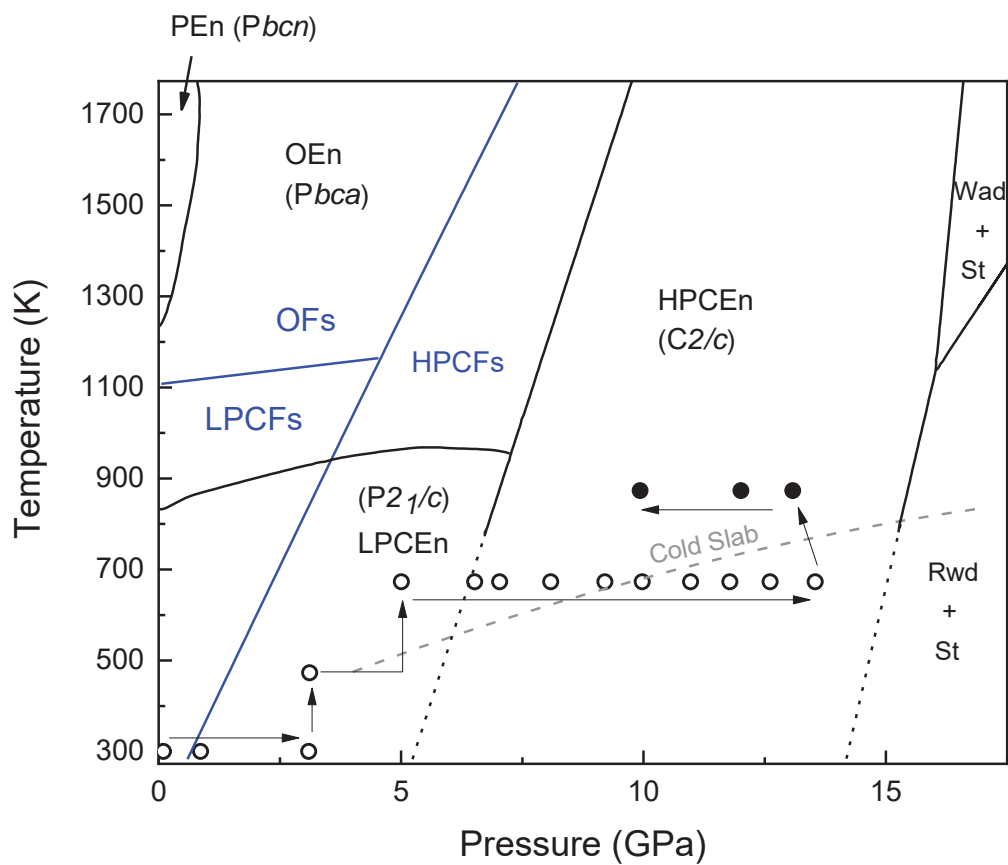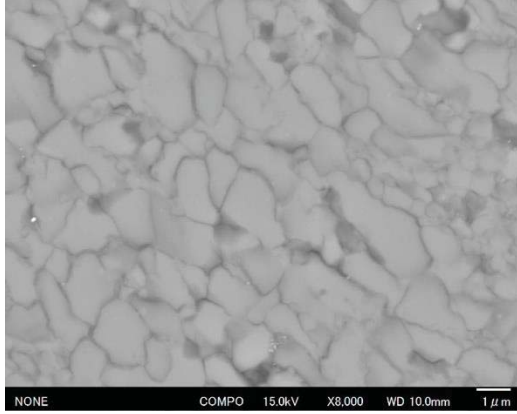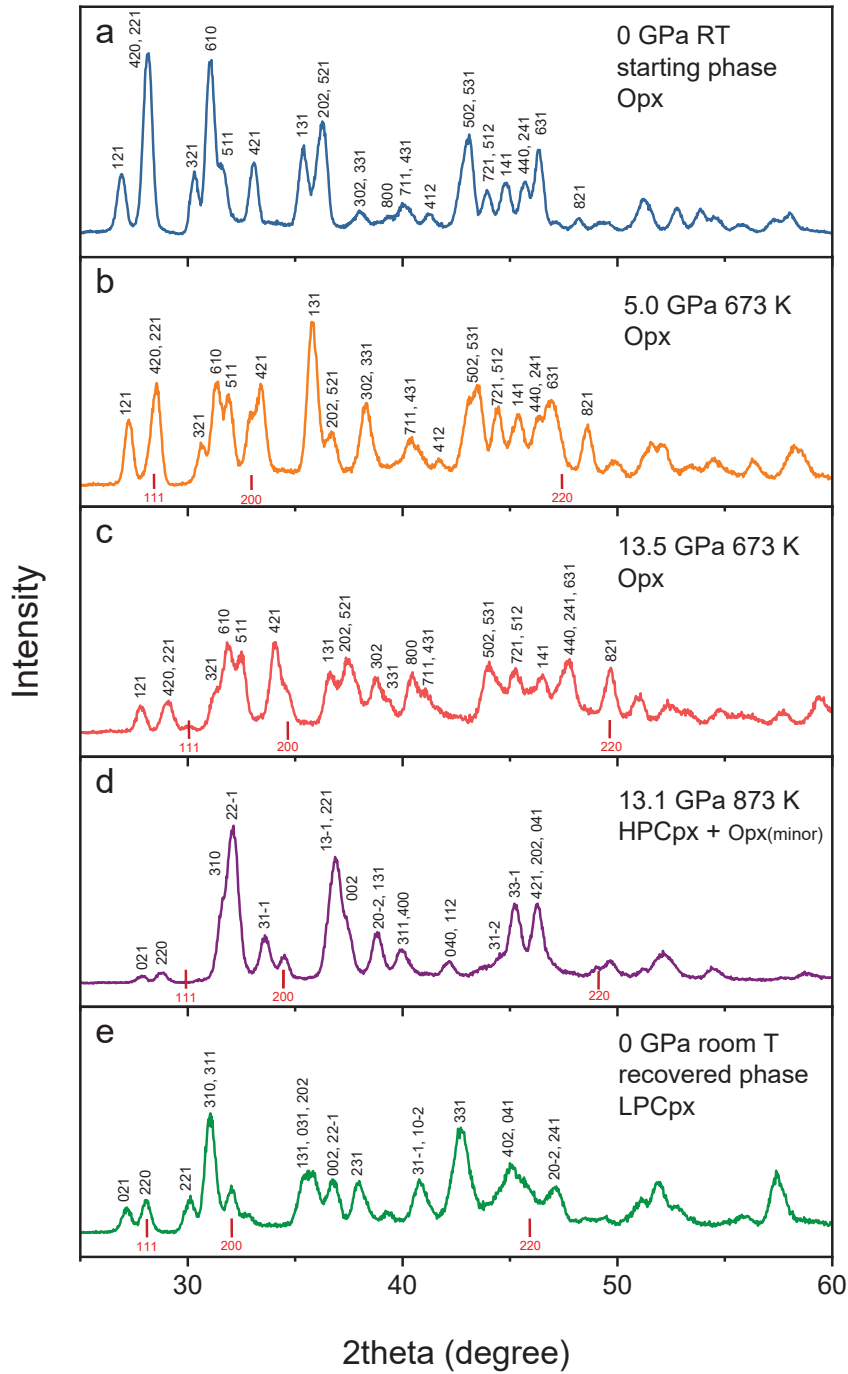456 up to 13.5 GPa at 673 K determined from the ultrasonic measurements (this study).

Figure 1

Figure 2
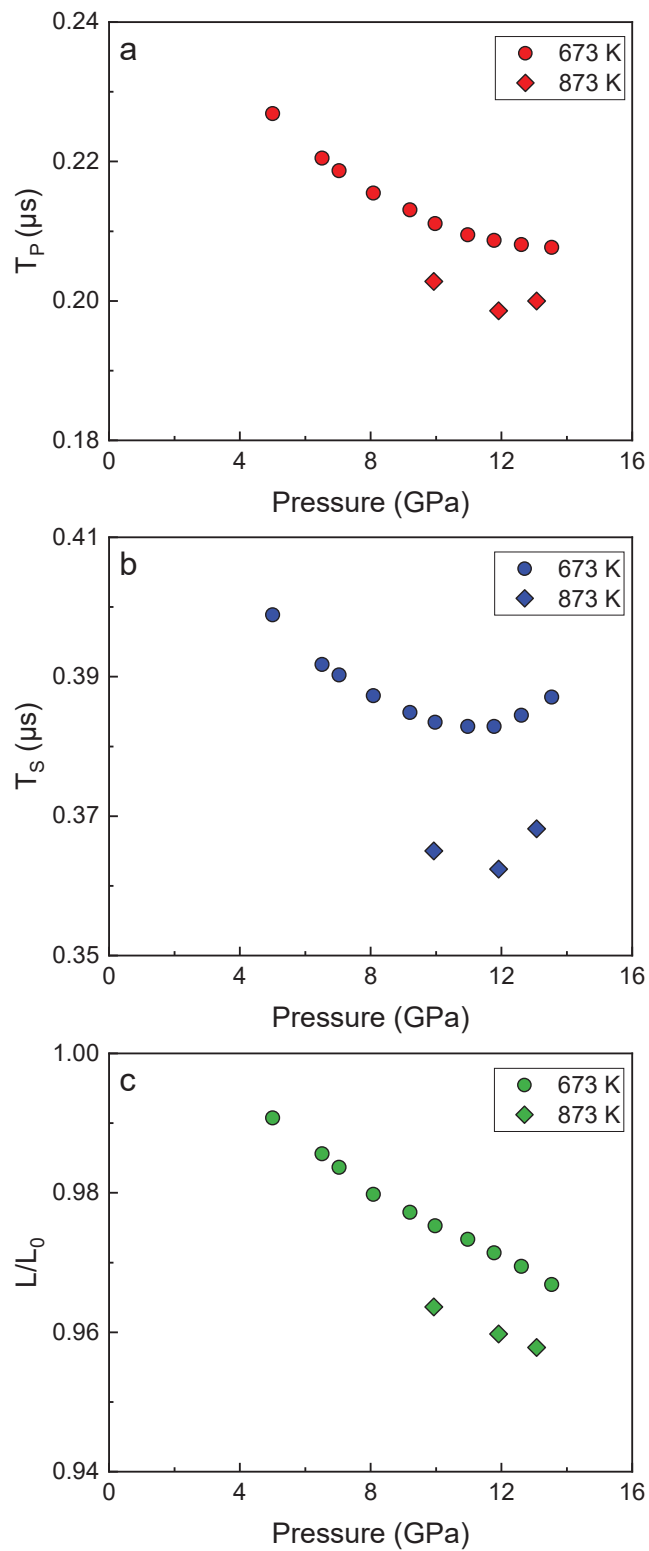
Figure 3

Figure 4

Figure 5

Figure 6