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1   **Metastable augite at high pressure and temperature conditions and its**

2   **implications for subduction zone dynamics**

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13   **Abstract**

14   (Ca, Mg)-rich clinopyroxenes are abundant in Earth's upper mantle and subduction

15   zones. Experimental studies on the thermoelastic properties of these minerals at

16   simultaneous high pressure and high temperature are important for constraining of the

17   composition and structure of the Earth. Here, we present a synchrotron-based

18   single-crystal X-ray diffraction study of natural diopside-dominated augite

19    $[(Ca_{0.89}Na_{0.05}Mg_{0.06})(Mg_{0.74}Fe_{0.11}Al_{0.14}Ti_{0.01})(Si_{1.88}Al_{0.12})O_{6.00}]$ at $P\&T$ to ~27 GPa

20   and 700 K. The experiment simulates conditions in cold subducting slabs, and results

21   indicate that augite is stable over this pressure and temperature range. A third order

22   high-temperature   Birch–Murnaghan   equation   was   fit   with   the

23 pressure-volume-temperature data, yielding the following thermoelastic parameters:

24 K_{T0} = 111(1) GPa, $K_{T}'_0$ =4.1(1), $(\partial K_0/\partial T)_P$ = −0.008 (5) GPa K^{-1} and α_T = 4(1)×10^{-5}

25 K^{-1} +2(3)×10^{-8} K^{-2}T. A strain analysis shows that the compression along the three

26 principal stress directions is highly anisotropic with $\varepsilon1:\varepsilon2:\varepsilon3$=1.98:2.43:1.00.

27 Additionally, high-pressure structural refinements of room-temperature polyhedral

28 geometry, bond lengths and O3-O3-O3 angle were investigated to ~27 GPa at

29 ambient temperature. Pressure dependences of polyhedral volumes and distortion

30 indicate that the substitution of Al^{3+} for Si^{4+} significantly changes the compressional

31 behavior of the TO$_4$-tetrahedron in augite. Density calculations of this augite along a

32 subducting slab geotherm suggest that augite as well as other common clinopyroxenes

33 would promote slab stagnations at transition zone depths if they are metastably

34 preserved in significant quantities.

35 **Keywords:** pyroxenes, augite, high pressure and temperature, single-crystal X-ray

36 diffraction, subduction zone

37

38 **Introduction**

39 Pyroxenes are among the most important rock-forming minerals and are commonly

40 found in both igneous and metamorphic rocks. Oceanic lithosphere consists of about

41 40% pyroxenes and garnet (Frost, 2008). It was believed that pyroxenes transform

42 into denser majorite garnet while oceanic crust subducts into the mantle (Akaogi and

43 Akimoto, 1977). However, recent studies imply that this reaction is inhibited under

44 cold slab conditions, so pyroxenes may survive in deeper parts of the mantle than was

45 previously thought (Nishi et al., 2008; Nishi et al., 2013; Van Mierlo et al., 2013).

46 Surviving metastable pyroxenes might cause stagnations of some slabs at depths

47 along the 660 km discontinuity, due to their lower densities compared to garnet and

48 broader metastability range compared to the metastable olivine (Agrusta et al., 2014;

49 King et al., 2015; Nishi et al., 2013; Van Mierlo et al., 2013). Therefore, knowledge

50 of the properties of pyroxenes to transition zone pressures ($\geq$ 25 GPa) is very

51 important in modeling the subduction zone environments.

52 Among the pyroxene group minerals, augite is the most common species and occurs

53 in basalts and gabbros, which are major components of the oceanic crust. Augite is

54 also commonly found in andesites, diorites, peridotites and pyroxenites. Augite is

55 monoclinic ($C2/c$ space group) and has relatively complex crystal chemistry.

56 Pyroxenes have a general formula of $M2M1T_2O_6$. In augite, $M1$ sites are usually filled

57 with Mg^{2+}, Fe^{2+}, Ti^{3+} and Al^{3+}, $M2$ are larger polyhedral sites that commonly

58 accommodate Ca^{2+}, Na^+, Fe^{2+}, and Mg^{2+}, while T sites are occupied predominantly by

59 Si^{4+}, but typically contains some Al^{3+} (Clark et al., 1969). In contrast with augite,

60 diopside [$CaMgSi_2O_6$] and hedenbergite [$CaFeSi_2O_6$] are usually Al-free. Although

61 pyroxene minerals have been extensively investigated at high pressures with the

62 discovery of several new polymorphs (Dera et al., 2013a; Finkelstein et al., 2014;

63 Plonka et al., 2012; Zhang et al., 2012), studies of augite at high pressures and

64 temperatures have been limited. Augite is important to the petrology of subducted

65 slabs, therefore it seems urgent to fill the gap in understanding of the compressional

66 behavior of this mineral at simultaneous high pressures and temperatures. In this

67   study, single-crystal X-ray diffraction measurements of natural augite were conducted

68   at 0-26.65(2) GPa at ambient temperature and the crystal structures were refined. The

69   *P-V-T* relations were measured at pressure-temperature conditions to 24.35(2) GPa

70   and 700 K, and thermal equation of state was determined. We discussed the potential

71   effect of metastable augite on subducting slab dynamics in this report.

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73   **Sample and method**

74   Natural augite samples were collected from the Damaping pyroxenite, Zhangjiakou,

75   Hebei Province, China. The crystals were colored light green, and their chemical was

76   estimated as $[(Ca_{0.89}Na_{0.05}Mg_{0.06})(Mg_{0.74}Fe_{0.11}Al_{0.14}Ti_{0.01})(Si_{1.88}Al_{0.12})O_{6.00}]$ based on

77   results of electron microprobe analysis (EMPA). Small chips (size 0.035×0.040 mm)

78   of single-crystal augite with thicknesses less than 0.010 mm were extracted from a

79   larger EMPA sample for this study. A single crystal was first mounted onto a polymer

80   micromesh sample holder (MiTeGen) for ambient-condition X-ray diffraction study.

81   One single crystal was used for each high pressure/temperature experiment. A BX90

82   DAC (Kantor et al., 2012) was used for high-pressure measurements at ambient

83   temperature. This DAC was equipped with two type-I diamond (300 μm culets)

84   mounted on Boehler-Almax-type WC seats, which had ±30 deg. opening angles. A

85   rhenium gasket was used and pre-indented to ~40 μm thickness before a laser drilling

86   of a 190-μm-diameter hole. The augite sample was loaded into the sample chamber

87   with Au powder serving as the pressure calibrant (Fei et al., 2007). At each pressure,

88   Au diffraction patterns were collected before and after sample data collection and the

89   average pressure values were used. A small ruby sphere of ~10 μm was also loaded

90   and used as the pressure indicator for the gas-loading with Ne as the

91   pressure-transmitting medium using the GSECARS gas-loading system (Rivers et al.,

92   2008). An externally heated DAC (EHDAC) was used for high-pressure and

93   high-temperature experiments. Temperatures up to 700 K were generated by

94   resistive-heating and measured with a K-type thermocouple attached to one of the

95   anvils ~500 μm away from the diamond culet. Likewise, Au powder, a ruby sphere

96   and a single-crystal sample were loaded, and Ne was used for pressure-transmitting

97   medium.

98   All of the X-ray diffraction experiments in this study were carried out at experimental

99   station 13-BM-C of the Advanced Photon Source, Argonne National Laboratory. The

100 incident X-ray beam was monochromated to a wavelength of 0.4340 Å, and

101 collimated to a focal spot size of 15×15 μm^2. Diffraction images were acquired on a

102 MAR165 CCD detector. Tilting and rotation of the detector and the

103 sample-to-detector distance were calibrated using ambient LaB_6 as the diffraction

104 standard. To obtain adequate number of diffraction for structure refinements, we

105 collected data at 4 different detector positions achieved by rotating the detector on the

106 6-circle goniometer. At D1 position the detector was perpendicular to the incident

107 X-ray direction, D2 was achieved by rotating the detector about the horizontal axis by

108 20°, whereas D3 and D4 were involved rotating about the vertical axis by 10° and

109 -10°, respectively. Wide and stepped φ exposures were collected for single-crystal

110 samples at each P-T point at D1 position, with an exposure time of 2 s/°. Wide

111 segment exposures with 10° rotation step were collected at each detector position. The

112 φ scan rotation axis was horizontal and perpendicular to the incident X-ray direction.

113 The ATREX/RSV software package (earlier known as GSE_ADA/RSV, (Dera et al.,

114 2013b)), was used to analyze the diffraction images. The lattice parameters and

115 orientation matrix were determined with the RSV software and the reduced reflection

116 data from the four detector positions were merged together. Unit-cell parameters at

117 each P-T condition are reported in Table 1. Crystal structures of augite at high

118 pressures were refined from the intensity data using SHELXL software via the Olex 2

119 user interface (Dolomanov et al., 2009; Sheldrick, 2007), starting from atomic

120 coordinates of Clark et al. (1969). According to the microprobe chemistry and

121 previously reported augite structure model (Clark et al., 1969), the site occupancies

122 were refined without vacancies. The $M2$ sites were fully occupied by Ca^{2+}, Mg^{2+} and

123 Na^+, Fe^{2+}, Mg^{2+}, Ti^{3+} and Al^{3+} occupied the $M1$ sites, while the T sites contained Si^{4+}

124 and Al^{3+}. Cations in the same polyhedral site were set to share the same atomic

125 displacement parameters (ADPs) and the same fractional coordinates. The anisotropic

126 ADPs were only used for cations, due to the limited number of unique observations.

127 At ambient pressure the site-occupancy refinement for the $M2$, $M1$ and T sites led to a

128 mean electron number of 19.2, 13.4 and 14.0 which are very close to the numbers

129 calculated on the basis of the chemical data (19.1, 13.8 and 13.9 for $M2$, $M1$ and T

130 sites, respectively). The refined sum of mean electron number is also in general

131 agreement with the microprobe composition, so the cation contents based on the

132 EMPA composition were used in refinements. We also modeled the site distribution

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133   of Fe between $M2$ and $M1$ sites, and the result indicated that the $M2$ site is free of Fe.

134   Previous studies suggested that Fe^{3+} could be included in $M1$ sites in addition to Fe^{2+},

135   based on Mössbauer measurements and other calculation methods, but only in small

136   quantities (Clark et al., 1969). Clark et al. (1969) proposed a method to infer the

137   Fe^{3+}/Fe^{2+} distribution in augite based on the $M1$-O distance values. In this approach

138    $M1$-O distance in augite is assumed to be a simple linear combination of the average

139    $M1$-O distances observed in various end-member compositions. According to this

140   method and the use of the $M1$-O values of jadeite [$NaAlSi_2O_6$], diopside [$CaMgSi_2O_6$],

141   aegirine [$NaFeSi_2O_6$] (Clark et al., 1969), hedenbergite [$CaFeSi_2O_6$] (Zhang et al.,

142   1997) and [$NaTiSi_2O_6$] (Ullrich et al., 2010) combined with the $M1$-O value in this

143   study, we concluded that our augite sample is free of Fe^{3+}. In high-pressure

144   refinements the site occupancy parameters of the cations were fixed based on the

145   EMPA and ambient-pressure structure refinement. Details of the structural

146   refinements, atomic coordinates, bond lengths and angles are reported in Tables 2, 3

147   and 4. Because of the limited opening angle (±17°) of the EHDAC, the structure

148   refinements were not possible.

149

150   **Results and discussion**

151   **Equation of state of augite at 298 K**

152   Figures 1 and 2 present the unit-cell parameters of augite as a function of pressure. V,

153   a, b, c and β angle undergo nonlinear decrease to 26.65(2) GPa with no discontinuity

154   in the compression curves. A third-order Birch–Murnaghan equation of state (BM3

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155   EoS) was fit with the *P-V* data using the EosFit7c program (Angel et al., 2014). The

156   isothermal bulk modulus (K_{T0}) and its pressure derivative (K'_{T0}) were calculated to be

157   111(1) GPa and 4.1(2). The Eulerian finite strain ($f_E = [(V_0/V)^{2/3}-1]/2$) versus

158   "normalized pressure" ($F_E = P/[3f_E(2f_E+1)^{5/2}]$) plot (Angel, 2000) was also used to

159   analyze the *P-V* data, and a weighted linear fit yielded an intercept value of 111(1)

160   GPa which is in good agreement with the results indicated by BM3 EoS (Figure 3).

161   The linear moduli of *a*, *b* and *c* were also calculated using the linear BM3 equation

162   (Figure 1) and EosFit7c program. The compressibilities (β) (Angel, 2000) of each axis

163   were calculated (Table 5) yielding $\beta_a:\beta_b:\beta_c$=1:1.44:1.11, which shows that *b* has the

164   highest compressibility and *c* is more compressible than *a*.

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Strain analysis

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167   Strain tensor analysis was performed to assess the degree of anisotropy between

168   principal stress directions, because the *a*- and *c*-axis are not the principal strain axes

169   while *b*-axis is coincident with one of them. Unit-cell parameters of augite were used

170   to analyze unit strain ellipsoid with win_STRAIN (Angel 2015), modified after

171   Ohashi (1982). Table 6 shows the strain values and directions of the three major

172   compression axes at each pressure. In order to visualize the orientation of the strain

173   tensor, we calculated the representation quadratic surface of augite using the method

174   suggested by Knight (2010). As shown in Figure 4, the softest major axis is parallel to

175   the *b*-axis, and the stiffest direction is oriented in the *a-c* plane.

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Polyhedral compression and distortion

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178   The evolutions of the volume of the $M2O_8$-polyhedron, $M1O_6$-octahedron and

179   TO_4-tetrahedron with increasing pressure were investigated and shown in Figures 5

180   and 6. The eight coordinated $M2O_8$-polyhedron is the most compressible while the

181   TO_4-tetrahedron is the least. Likewise, the compression of the $M2O_8$-polyhedron is

182   the smoothest, and the TO_4-tetrahedron is the least smooth. The distortions of these

183   polyhedra were also analyzed (Robinson et al., 1971). As shown in Figure 7 the

184   distortion index of the $M2O_8$-polyhedron decreases quickly with increasing pressure

185   up to ~15 GPa, where it becomes less responsive to pressure. This change can be

186   explained by examining evolutions of the bond lengths with pressure. As shown in

187   Figure 8 the longest bonds $M2$-O3(C2, D2) becomes comparable to other bonds at

188   about 15 GPa. The $M1O_6$-octahedron has the smallest distortion index, which

189   decreases to the minimum at ~20 GPa, and then increases again to a value comparable

190   to the ambient distortion (Figures 7 and 9).

191   Pyroxenes are characterized by single chains of tetrahedra that extend parallel to the

192   c-axis. These chains have significant rotation freedoms at high pressures, which can

193   be described by the reduction of the O3-O3-O3 angle (Figures 10 and 11). The $\angle$

194   O3-O3-O3 of augite shows a linear decrease of approximately $-0.47°$/GPa in the

195   pressure range of 0-8.30(4) GPa, then experiences a minor increase with increasing

196   pressure between 8.30(4) and 11.40(3) GPa (Table 4 and Figure 11). This is similar to

197   what was reported for kosmochlor [$NaCrSi_2O_6$] (Posner et al., 2014), in which the

198   inflection occurs at 31.3 GPa. In augite this "hardening" of rotation of tetrahedral

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199   chains is accompanied by a volume drop of TO_4-tetrahedra in augite (Figure 6), which

200   was also observed in kosmochlor (Posner et al., 2014). Above 11.40(3) GPa the $\angle$

201   O3-O3-O3 decreases again, this time at an approximate rate of (0.37°/GPa), as the

202   TO_4-tetrahedra become more incompressible (Figure 6). However, the

203   pressure-dependencies of the unit-cell volume and lattice parameters do not exhibit

204   any distinct discontinuities correlated with this curious behavior of the O3-O3-O3

205   angle (Figures 1 and 2).

206

207   **Thermal equation of state**

208   The unit-cell parameters of augite at various P-T conditions are given in Table 1, and

209   were used for subsequent calculations. Figure 12 shows the volume data measured at

210   298, 500 and 700 K. The high-temperature Birch-Murnaghan (HTBM) equation was

211   fit with the P-V-T data. The equation is given by the following form:

212    $$P=(3/2)\,K_{T0}\,[(V_{T0}/V)^{7/3}-(V_{T0}/V)^{5/3}]\times\{1+(3/4)(K'_{T0}-4)[\,(V_{T0}/V)^{2/3}-1]\} \tag{1}$$

213   where K_{T0}, $K_{T}'_0$ and V_{T0} are bulk modulus, its pressure derivative and the unit cell

214   volume at ambient pressure and temperature (in Kelvin), respectively. The effects of

215   temperature on K_{T0} and V_{T0} are expressed by the follows:

216    $$V_{T0} = V_0\,\exp\!\int_{300}^{T}\alpha_{\mathrm{T}}\,dT \tag{2}$$

217    $$K_{T0}=K_0+(\partial K_0/\partial T)_P\times(T-298) \tag{3}$$

218    $$\alpha_T=\alpha_0+\alpha_1 T \tag{4}$$

219   where $(\partial K_0/\partial_T)_P$ and α_T are the temperature derivative of the bulk modulus and the

220   volumetric thermal expansion at ambient pressure.

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221   Fitting the P-V-T data to the HTBM (1) yielded K_{T0} = 111(1) GPa, $K_{T}'_0$ =4.1(1),

222     $(\partial K_0/\partial T)_P$ = −0.008 (5) GPa K^{-1} and $\alpha_T(K^{-1})$ = 4(1)×10^{-5} +2(3)×10^{-8}T. In view of the

223   relatively low temperature range (298-700 K in this study) and limited

224   high-temperature data, α_T is often assumed to be constant over the temperature range

225   i.e. $\alpha_T = \alpha_0$ (e.g., Nishihara et al., 2003; Xu et al., 2016). Therefore, the P-V-T data

226   were also fitted by constraining $\alpha_T = \alpha_0$, which yielded K_{T0} = 111(1) GPa, $K_{T}'_0$ =

227   4.1(1), $(\partial K_0/\partial T)_P$ = −0.008 (5) GPa K^{-1} and $\alpha_T(K^{-1})$= 5.1(3)×10^{-5}. The K_{T0} values

228   derived from high-temperature and pressure data are in excellent agreement with that

229   from EoS fit at ambient temperature (K_{T0} = 111(1) GPa).

230

231   **Comparison with previous studies**

232   Due to the compositional complexity of augite, it is necessary to evaluate the effects

233   of cation substitutions on polyhedral compressions. Here we compared the polyhedral

234   compressions of augite and other important clinopyroxene end-members including

235   jadeite [NaAlSi$_2$O$_6$], diopside [CaMgSi$_2$O$_6$], hedenbergite [CaFe^{2+}Si$_2$O$_6$] and aegirine

236   [NaFe^{3+}Si$_2$O$_6$], all of which have $C2/c$ symmetry. In these pyroxenes the M2 site is

237   normally occupied by Ca^{2+} (eight coordinated) and Na$^+$ (six coordinated) (Downs,

238   2003), and the Ca^{2+}- and Na$^+$-polyhedra exhibit about comparable compression below

239   ~8 GPa, above which the Ca^{2+}-polyhedra are more incompressible than Na-polyhedra.

240   Our augite has minor Na and Mg contents in addition to Ca^{2+} occupying the M2 Site,

241   but this substitution does not distinctly change the compression behavior of the

242   Ca^{2+}-dominated polyhedral, as shown in Figure 13(a). In comparison with the M2 site,

243   different cations occupying the $M1$ site have distinct effects on the compression of the

244     $M1$-octahedon (Figure 13(b)). The $M1$ site fully occupied by Al^{3+} is the most

245   incompressible among these clinopyroxenes, while the Mg-octahedron is the most

246   compressible. Fe^{2+}- and Fe^{3+}-octahedra have distinctly different compression trends,

247   with the latter being stiffer (McCarthy et al., 2008b), and comparable to the

248   Al^{3+}-octahedron, while Fe^{2+}- is nearer to the Mg^{2+}-octahedron. The $M1$ site of augite

249   in this study is mainly Mg^{2+}-occupied, but has significant contents of Fe^{2+} and Al^{3+},

250   and below ~11 GPa the compression of the octahedron is similar to that of

251   Mg^{2+}-octahedron in diopside. Above ~11 GPa, it becomes stiffer and closer to the

252   trend of the Fe^{2+}-octahedron in hedenbergite. The T site is almost fully filled by Si^{4+}

253   in most pyroxene minerals, but can contain small amount of Al^{3+} in augite (e.g., Bindi

254   et al., 2003; Hazen and Finger, 1977). In this study we investigated the effect of the

255   incorporation of Al^{3+} into the T site on the tetrahedral compression. As shown in

256   Figure 13(c), the Al-free end-member $C2/c$ pyroxenes display very similar tetrahedral

257   compression trends, while the compression of the T-tetrahedron augite is notably

258   different, below ~13 GPa it also results in the compression trend, however, after that

259   it has a distinct volume drop at ~14 GPa as indicated by the pressure dependences of

260   the O3-O3-O3 angle and the T-O bond lengths (Figures 11 and 14). We also used a

261   second-order BM EOS to calculate the zero-pressure bulk modulus (K_{T0}) values of

262   these T-tetrahedra, and the results suggest that augite has a larger tetrahedral K_{T0}

263   (345(30) GPa) than aegirine (328(22) GPa), hedenbergite (306(16) GPa) and diopside

264   (321(15) GPa), but smaller than jadeite (386(10) GPa). Therefore, the tetrahedral K_{T0}

265   values of clinopyroxenes depend not only on cations occupying the T sites. To

266   summarize, the incorporation of Na^+ and Mg^{2+} does not significantly change the

267     $M2$-polyhedral compression in augite. The substitutions of Fe^{2+} and Al^{3+} in the $M1$

268   site, however, cause a distinct $M1$-octahedral compression change after ~11 GPa. The

269   most significant effect of the cation substitution occurs in the T site, with an evident

270   tetrahedral volume drop during the compression.

271   The K_{T0} value of augite (whole crystal) obtained in this work was also compared with

272   previous investigations of jadeite, diopside, hedenbergite and aegirine. It is clear that

273   the polyhedral compression is not the only factor that constrains the K_{T0} values of

274   these pyroxenes. Among these C2/c pyroxenes jadeite has the most incompressible

275     $M1$-octahedron and the largest K_{T0} value that ranges from 124.5(4) to 136.5(14) GPa

276   (McCarthy et al., 2008a; Nestola et al., 2006; Posner et al., 2014; Zhao et al., 1997),

277   and hedenbergite [$CaFe^{2+}Si_2O_6$] and aegirine [$NaFe^{3+}Si_2O_6$] have nearly identical K_{T0}

278   values (116.1(5)-117(1) GPa) (Downs and Singh, 2006; McCarthy et al., 2008b;

279   Nestola et al., 2006; Zhang et al., 1997; Zhao et al., 1998), even though the

280   Fe^{2+}-octahedron is much more compressible than the Fe^{3+}-octahedron. Previous

281   studies on diopside give a relatively large range of K_{T0} values (104.1(9)-118(1) GPa)

282   (Aleksandrov and Ryzhova, 1961; Levien and Prewitt, 1981; Thompson and Downs,

283   2008; Zhang et al., 1997). In this study, the K_{T0} value (111(1) GPa) of a

284   diopside-dominant augite derived from a BM3 Eos fitting of the P-V data is also

285   within the value range of the pure diopside, although significant Al^{3+} and Fe^{2+} were

286   incorporated in the $M1$ and T sites.

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287   Numerous thermal expansion studies have been conducted on pyroxene minerals, and

288   the values of α_T show a large variation range (1.84-9.26$\times10^{-5}$ K^{-1}) with various

289   compositions and structures (see summarizations in Yang and Prewitt (2000) and

290   Tribaudino and Mantovani (2014)). Augite in this study is diopside-rich and has a α_T

291   value of 5.1(3)$\times10^{-5}$ K^{-1}, which is higher than that of previous studies of diopside end

292   member [CaMgSi$_2$O$_6$] (3.41-3.44$\times10^{-5}$ K^{-1}) (Finger and Ohashi, 1976; Richet et al.,

293   1998). The discrepancy is likely due to the compositional difference. Augite in this

294   study has significant contents of Al in the M1 and T sites, compared to the end

295   member-diopside. Incorporation of Al was previously regarded as a reason for

296   decrease in the thermal expansion (Tribaudino and Mantovani, 2014).

297

298   **Implications**

299   Clinopyroxenes are major components of Earth's upper mantle. The (Ca, Mg)-rich

300   clinopyroxenes provide important constraints when modeling the mineralogy of the

301   upper mantle (Frost, 2008). At normal mantle temperature condition clinopyroxes

302   would disappear at transition zone depth because they are dissolved into majorite

303   garnet (Ringwood, 1982). However, clinopyroxenes could survive in subducting slabs

304   to greater depths because the pyroxene-garnet transition would be inhibited at

305   relatively low slab temperatures (Bina, 2013; Nishi et al., 2013; Van Mierlo et al.,

306   2013). On the other hand, high-pressure experimental studies demonstrate that

307   common Ca and Na-rich clinopyroxenes (with $C2/c$ space group) like diopside

308   [CaMgSi$_2$O$_6$], hedenbergite [CaFeSi$_2$O$_6$] and jadeite [NaAlSi$_2$O$_6$] are stable even at

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309   very high pressures. Diopside retains its $C2/c$ symmetry to ~50 GPa at room

310   temperature and transforms to the β-CaMgSi$_2$O$_6$ phase at ~56 GPa (Chopelas and

311   Serghiou, 2002; Plonka et al., 2012). High pressure diffraction and Mössbauer studies

312   of hedenbergite also show that it is stable over 50 GPa until two discontinuities take

313   place at 53 and 68 GPa (Hu et al., 2015; Zhang et al., 1999). Jadeite is also stable at

314   high pressures to 30 GPa (Posner et al., 2014), and the jadeite-diopside solid solution

315   has no phase transition within pressure range of 0-47 GPa (Zhang et al., 2016).

316   Aegirine [NaFe^{3+}Si$_2$O$_6$] also retains its symmetry to ~60 GPa, even though a

317   Na-coordination change induced isosymmetric phase transition takes place at ~24

318   GPa (Xu et al., 2016). Based on these studies one can expect that Ca and Na-rich

319   clinopyroxenes within the CaO-Na$_2$O-MgO-Fe$^{(2+/3+)}$O-Al$_2$O$_3$-SiO$_2$ system which are

320   important to the upper mantle and subduction zones, have large pressure ranges of

321   metastabilities (possibly 0-50 GPa at ambient temperature), however extensive studies

322   of the temperature effects are required (e.g., Nishihara et al., 2003; Zhao et al., 1998;

323   Zhao et al., 1997). Among the $C2/c$ clinopyroxenes augite is the most common and

324   occurs in various igneous rocks like basalt, gabbro and peridotite, and also in

325   metamorphic rocks like gneiss, schist and granulite (Banno, 1959; O'Har, 1961; Otten

326   and Buseck, 1987; Rooney et al., 2005; Schlinger and Veblen, 1989; Schorn and

327   Diener, 2016; Takeda et al., 1997; Tracy and Robinson, 1977). In this study the

328   diopside-rich augite was found to be metastable at simultaneously high pressure and

329   temperature to ~27 GPa and 700 K. Recently, the topic of metastable preservation of

330   pyroxenes to significant depths in cold slabs has attracted increasing attention, and is

15

331 treated as one of the explanations of the stagnations of some subducting slabs near the

332 base of the mantle transition zone (Agrusta et al., 2014; Bina, 2013; King et al., 2015;

333 Nishi et al., 2013; Van Mierlo et al., 2013). The main reason is that pyroxene is the

334 least dense mineral in the pyrolitic assemblage, and the density difference between the

335 slabs and surrounding mantle is a key factor that controls buoyancy, however, other

336 factors like viscosity also need to be considered (Agrusta et al., 2014; Nishi et al.,

337 2013). Pyroxenes can survive even at high temperatures, while in contrast, metastable

338 olivine can only persist under very cold conditions (Nishi et al., 2008; Nishi et al.,

339 2009). Even so, deciphering the effects of metastable pyroxenes on slab dynamics still

340 requires a lot of further measurements, including density and elasticity of relevant

341 minerals at simultaneous high-pressure and temperature conditions. However, such

342 work on pyroxenes is limited (e.g., Akashi et al., 2009; Nishihara et al., 2003; Zhao et

343 al., 1998; Zhao et al., 1997), and the pressure range is relatively low compared to

344 transition zone depth. In this study we conducted single-crystal X-ray diffraction

345 measurements on natural augite at simultaneously high-pressure and temperature to

346 ~27 GPa and 700 K, simulating conditions within the coldest part of a subducting slab.

347 The diffraction data reveal that augite is metastable within this range of *P-T* condition,

348 and the *P-V-T* data were used to calculate related thermoelastic parameters.

349 To date, numerous seismic studies on subducting slab morphology show that most

350 slabs are denser than the mantle before they sink into the transition zone depths,

351 where the densities of slabs and surrounding mantle become comparable (Figure 15).

352 However, depending on the slab geometry and thermal structure become different,

353   some subducted slabs sink into the lower mantle (e.g., Centre America), while others

354   stagnate (e.g., Tonga) (Fukao and Obayashi, 2013; Fukao et al., 2001; Grand, 2002;

355   Kawakatsu and Yoshioka, 2011; Li et al., 2008; Van der Hilst et al., 1997). Density is

356   the principle factor controlling buoyancy, and the metastable pyroxene is a candidate

357   contributor for slab stagnations (Agrusta et al., 2014; Bina, 2013; King et al., 2015;

358   Nishi et al., 2013; Van Mierlo et al., 2013). To better understand the effect of

359   metastable pyroxenes on the slab dynamics we calculated the density profiles of

360   augite and other common mantle pyroxene minerals along a geotherm that is typical

361   for cold subduction (Ganguly et al., 2009). The third order HTBM equation (formula

362   (1)-(4)) was used, and the minerals and related themoelastic parameters are shown in

363   Table 7. The results comparing the PREM model (Dziewonski and Anderson, 1981)

364   and a Tonga-type slab (Ganguly et al., 2009) are presented in Figure 15. In this Figure

365   augite $[(Ca_{0.89}Na_{0.05}Mg_{0.06})(Mg_{0.74}Fe_{0.11}Al_{0.14}Ti_{0.01})(Si_{1.88}Al_{0.12})O_{6.00}]$ and   aegirine

366    $[NaFe^{3+}Si_2O_6]$ are notably denser than other pyroxenes (jadeite $[NaAlSi_2O_6]$, diopside

367    $[CaMgSi_2O_6]$, omphacite $[Di_{63}Jd_{37}]$ and clinoenstatite $[Mg_2Si_2O_6]$) because of their

368   higher Fe contents. At depth above the transition zone these Fe-free pyroxenes have

369   densities closer to PREM pyrolite, while in the transition zone densities of augite and

370   aegirine are more comparable to the PREM. On the other hand, the Tonga-type slab is

371   significantly denser than all of these pyroxenes at depth below ~425 km. One could

372   conclude that the presence of the Fe-rich pyroxenes like augite and aegirine would

373   promote the sinking of slabs into the transition zone at the 410 km discontinuity. At

374   the 660 km boundary as the ringwoodite decomposes into much denser Mg-perovskite

17

375 and ferropericlase (Green and Ringwood, 1967; Ito and Takahashi, 1989; Liu, 1976),

376 the slab and surrounding mantle densities become comparable, based on our

377 calculations all of these pyroxenes would contribute to the stagnation of the slab if

378 they are preserved in significant quantities.

379

380 **Acknowledgements**

397   Energy Sciences, under Contract No.DE-AC02-06CH11357. J. Xu acknowledges

398   supports from Graduate Student Joint Training Program of the Institute of

399   Geochemistry, Chinese Academy of Sciences.

400

401   **References**

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624

625

626   **Figure 1** Normalized unit cell volume and lattice parameters (*a*, *b* and *c*) of augite as

627   a function of pressure at room temperature. The error bars of the data points are

628   smaller than the symbols.

629   **Figure 2** Pressure dependence of β angle at ambient temperature. The error bars of

630   the data points are smaller than the symbols.

631   **Figure 3** Eulerian strain-normalized pressure (F_E-f_E) plot of unit cell volume.

632   **Figure 4** The orientation of the representation quadric for the isothermal

633   compressibility tensor of augite at 26.65 GPa, viewd down *b*.

634   **Figure 5** Pressure dependences of $M1O_6$, $M2O_8$ and TO_4 polyhedral volumes. The

635   error bars of the data points are smaller than the symbols.

636   **Figure 6** Pressure dependences of the polyhedral and unit-cell volumes. The error

637   bars of the data points are smaller than the symbols.

638   **Figure 7** Pressure dependences of distortion indices of different polyhedral.

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639 **Figure 8** Pressure dependences of the $M2$-O bond lengths in $M2O_8$ polyhedron.

640 **Figure 9** Pressure dependences of the $M1$-O bond lengths in $M1O_6$ polyhedron

641 **Figure 10** An illustration of the O3-O3-O3 angle.

642 **Figure 11** Tetrahedral chains kinking as described by O3-O3-O3 angle as a function

643 of pressure.

644 **Figure 12** The unit-cell volume as a function of pressure and temperature.

645 **Figure 13** Polyhedral volumes as a function of pressure in jadeite (Posner et al., 2014),

646 aegirine (McCarthy et al., 2008b), hedenbergite (Zhang et al., 1997), diopside

647 (Thompson and Downs, 2008) and augite (This study). (a), (b) and (c) are

648 $M2$-polyhedron, $M1$-octahedron and T-tetrahedron, respectively.

649 **Figure 14** Pressure dependences of the T-O bond lengths in TO_4 polyhedron.

650 **Figure 15** Calculated density profiles of augite as well as other common

651 clinopyroxenes to ~800 km, and the PREM (Dziewonski and Anderson, 1981) model

652 and the density profile of a Tonga-type slab (Ganguly et al., 2009) are also showed.
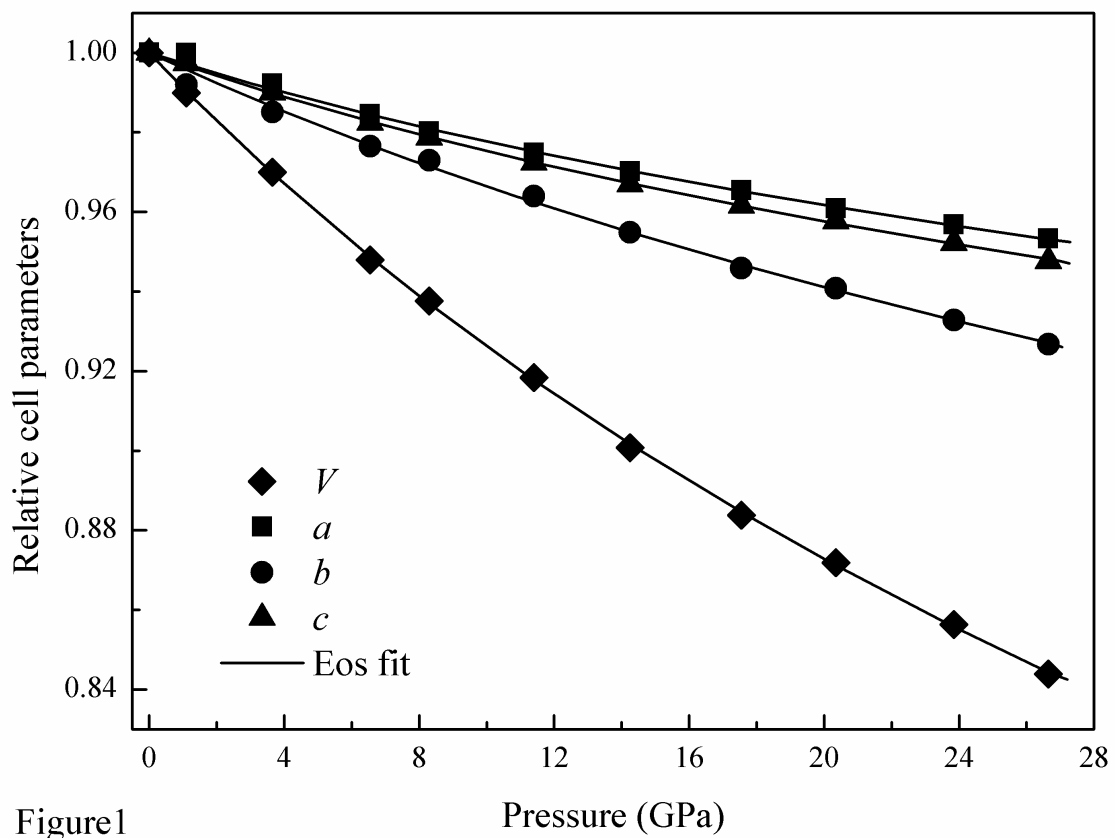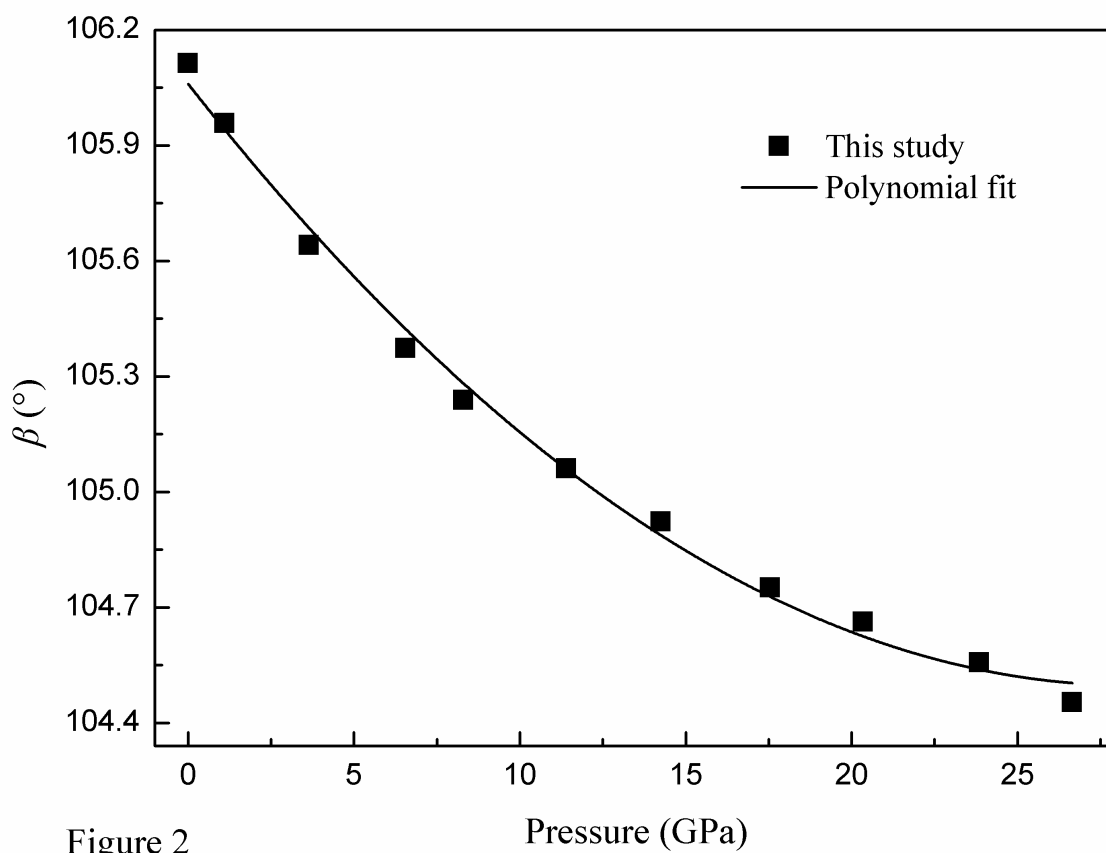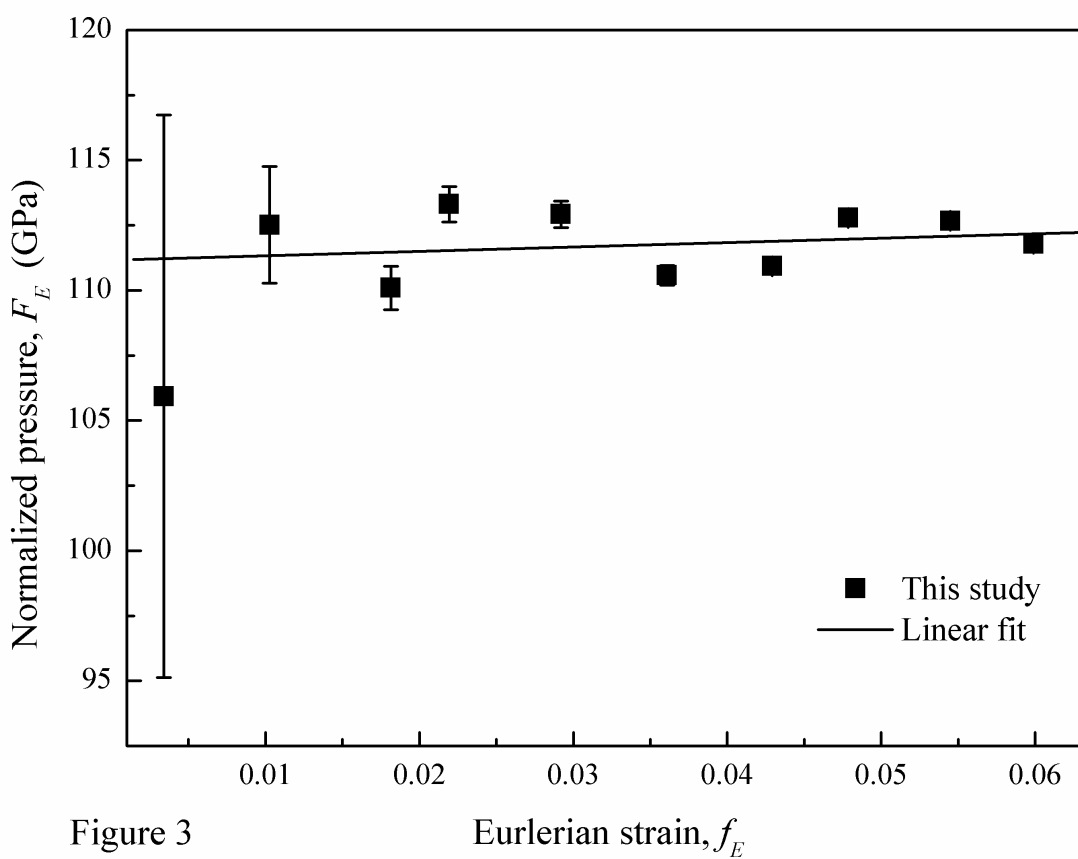
653 (*Color online*).

Figure1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8   Pressure (GPa)

Legend:
■ M2-O3(C2,D2)
● M2-O3(C1,D1)
▲ M2-O2(C2,D2)
▼ M2-O1(A1,B1)
◆ Mean bondlength

Figure 9

Figure 10

Figure 11

Figure 12

Figure 13(a)   Pressure (GPa)
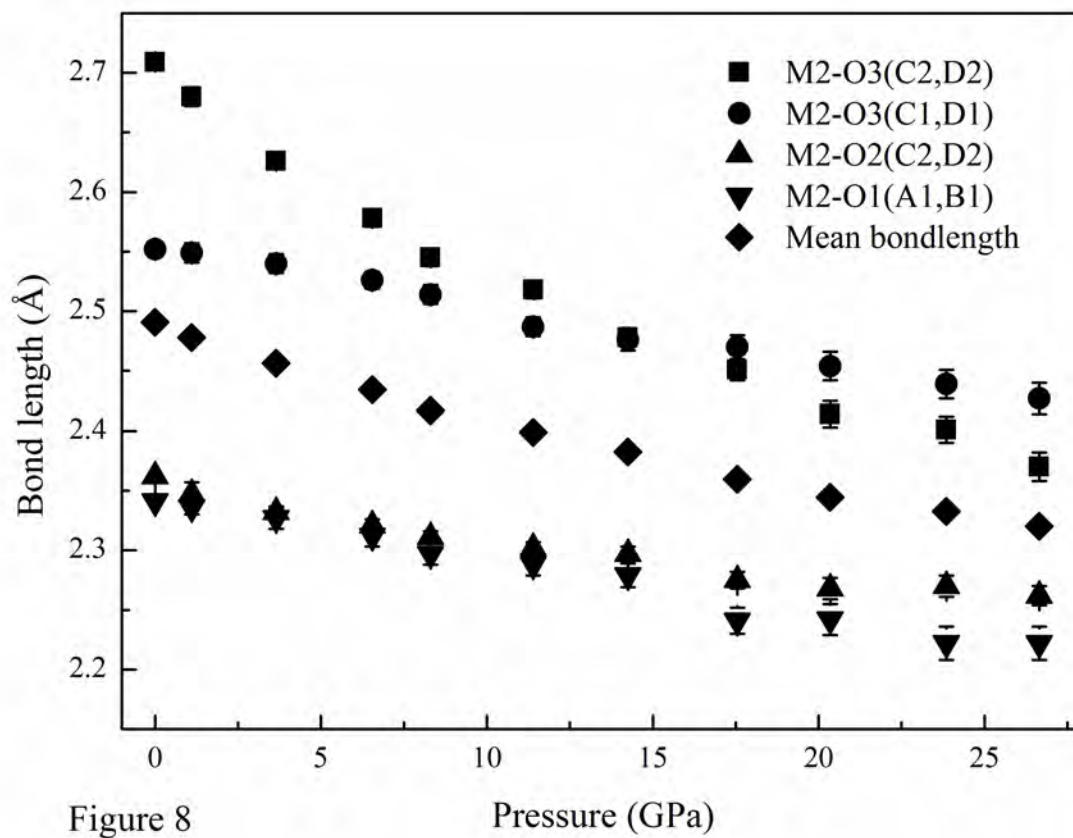
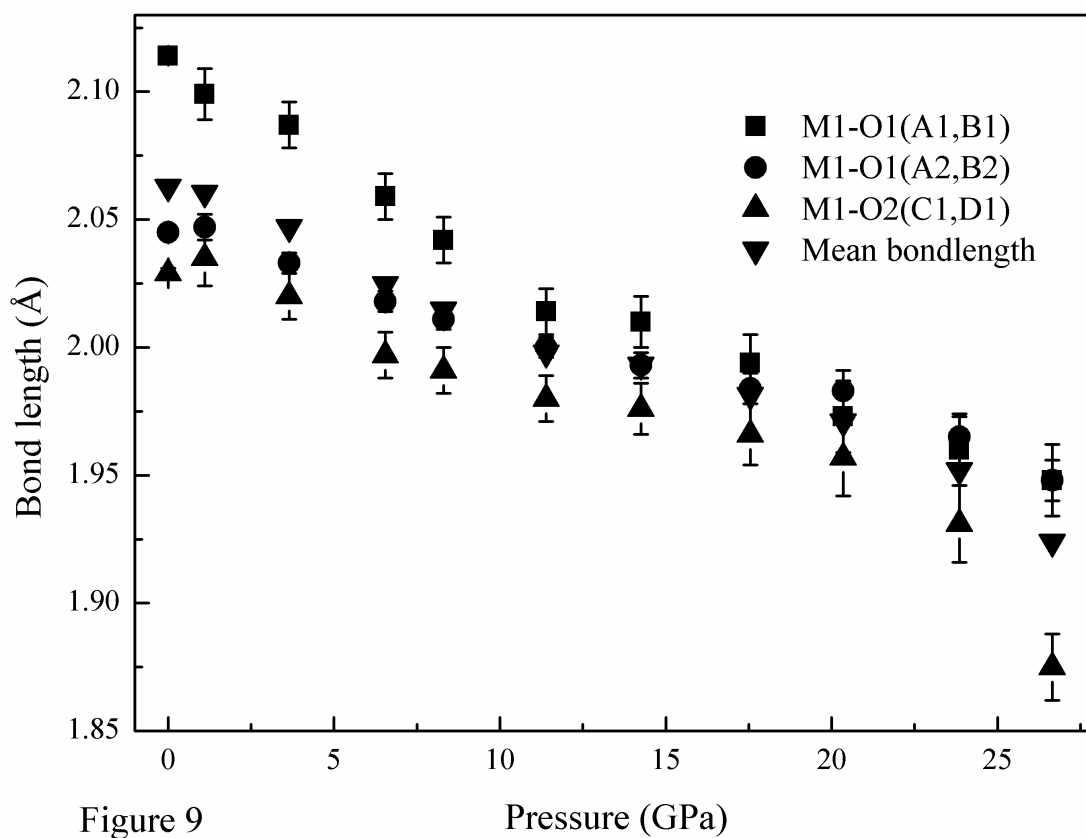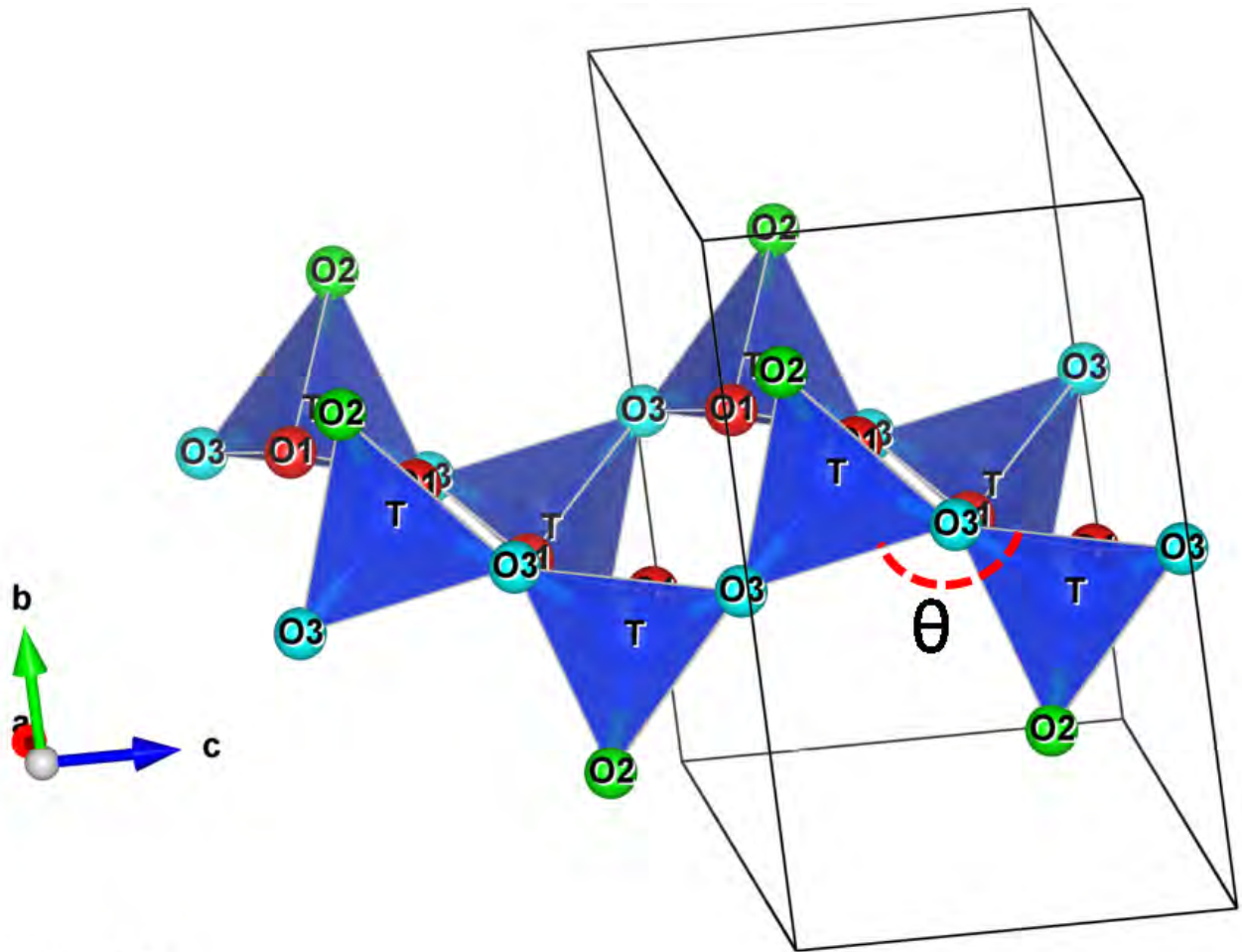Figure 13(b)   Pressure (GPa)
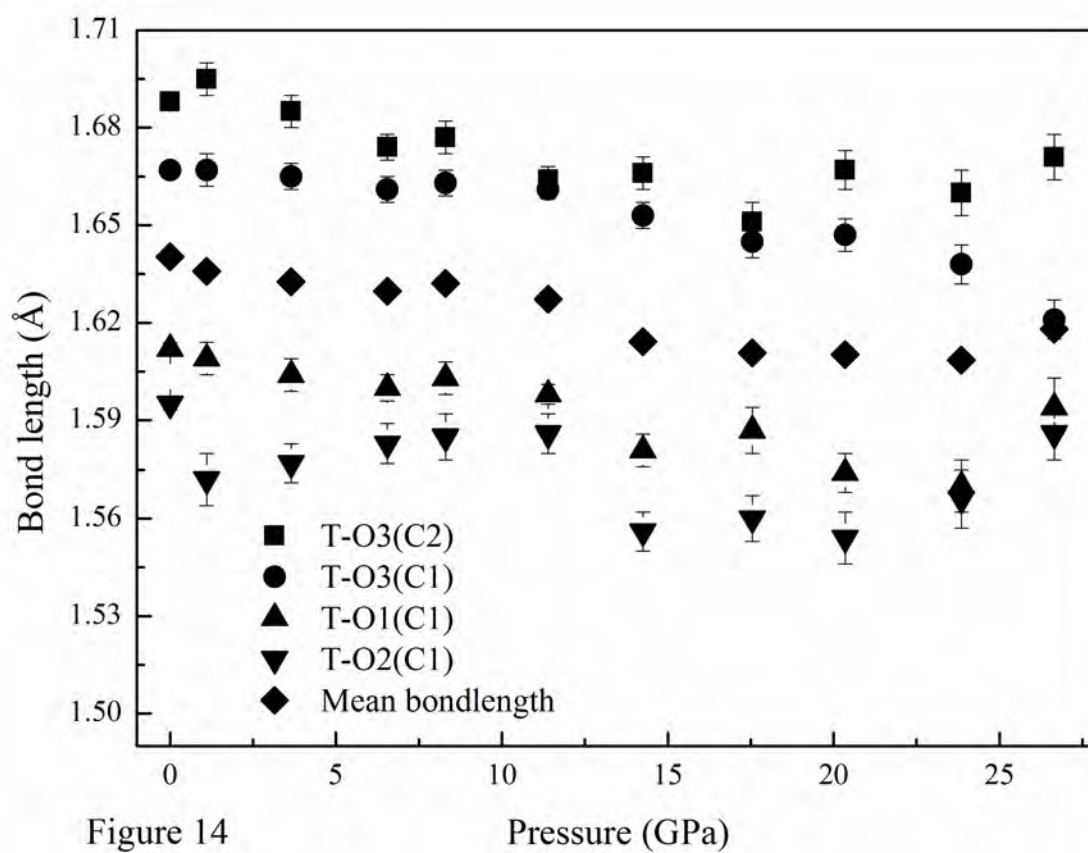
Figure 13(c)

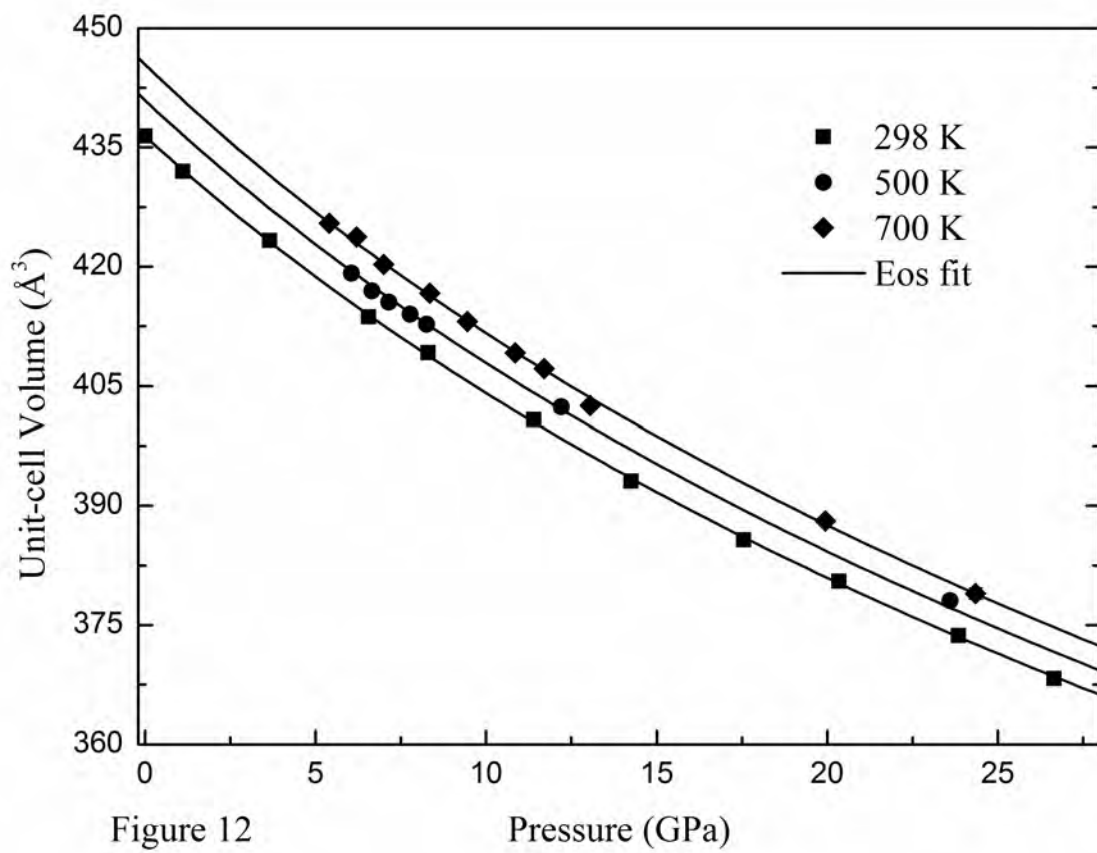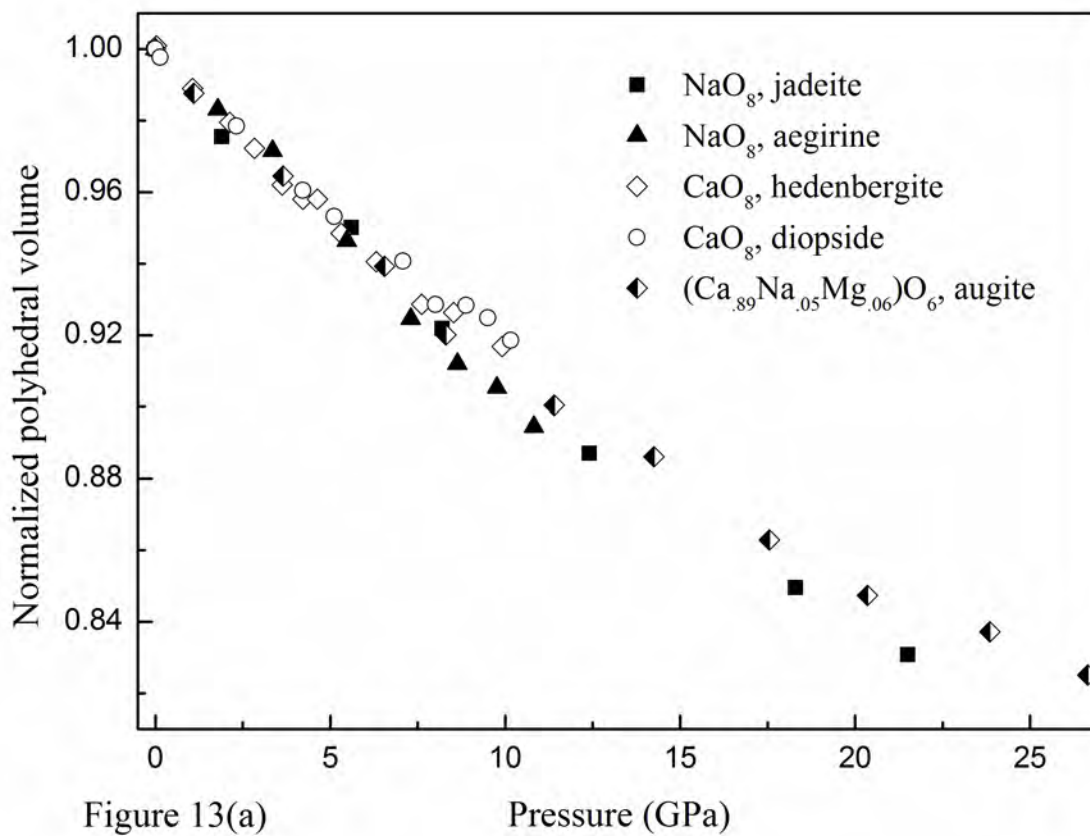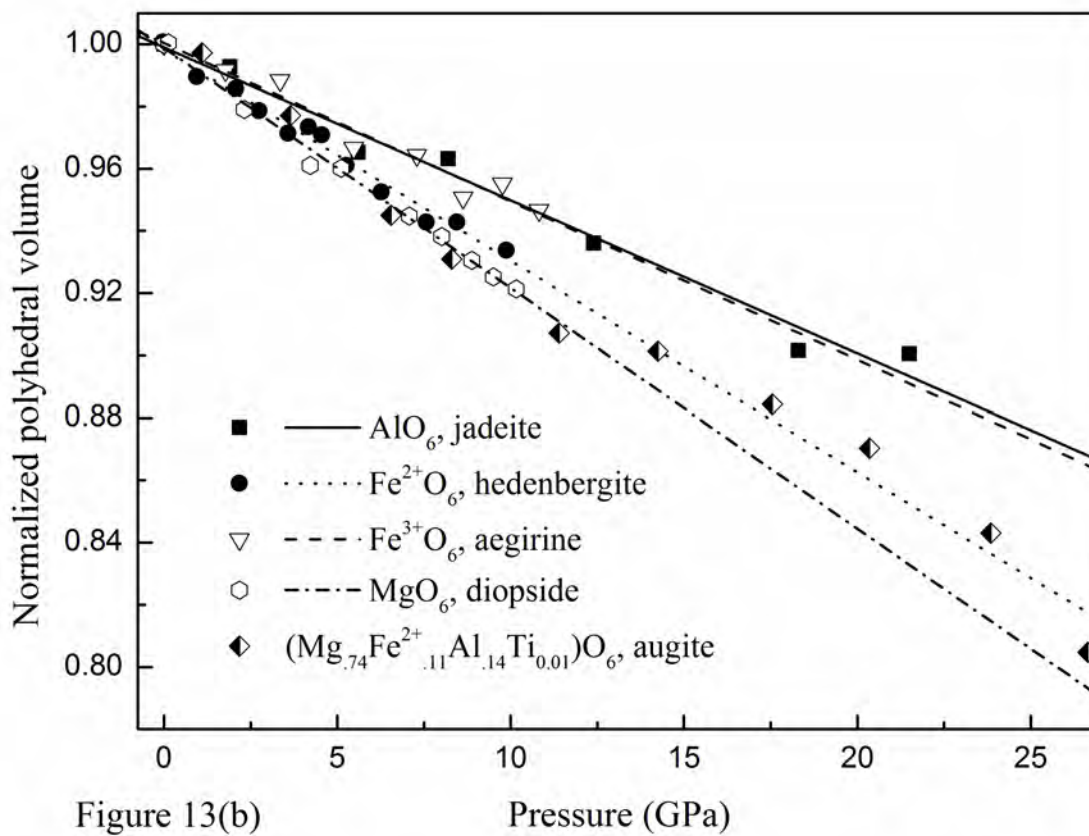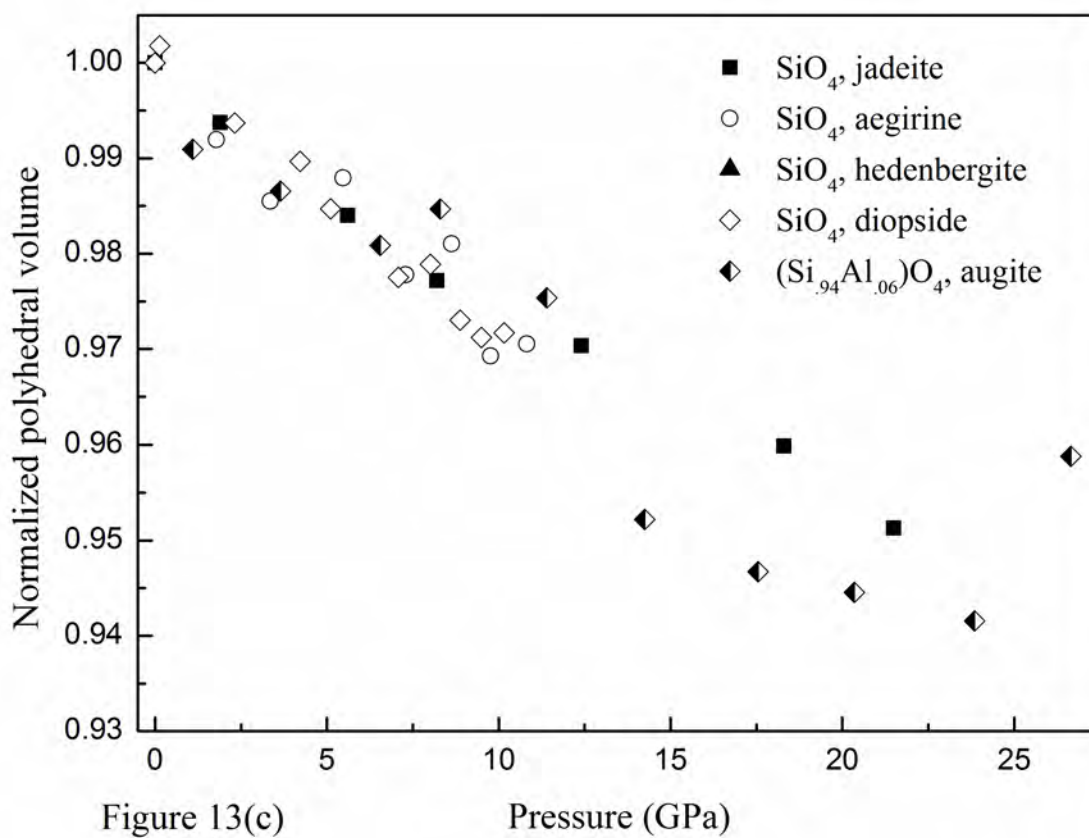Figure 14   Pressure (GPa)
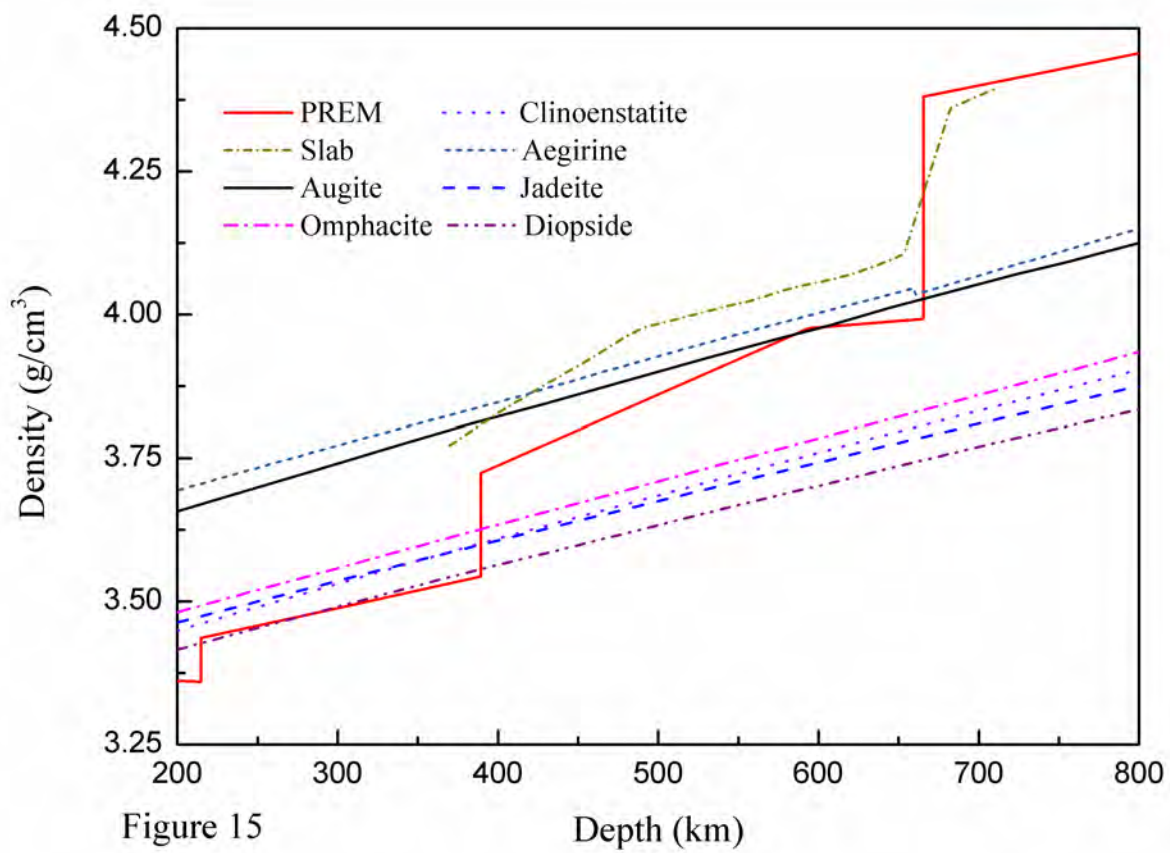
Figure 15

Table 1 Unit cell parameters and densities of augite at various temperatures and pressures

T (K)	P (GPa)	a (Å)	b (Å)	c (Å)	β (°)	V (Å^3)	ρ (g/cm^3)
298	0.0001	9.719(1)	8.880(1)	5.2636(4)	106.11(1)	436.4(1)	3.327
298	1.05(5)	9.718(3)	8.808(4)	5.2497(7)	105.96(1)	432.0(3)	3.361
298	3.65(7)	9.644(3)	8.747(4)	5.2108(7)	105.64(1)	423.3(2)	3.430
298	6.55(4)	9.569(3)	8.671(4)	5.1712(7)	105.37(1)	413.7(2)	3.510
298	8.30(4)	9.527(3)	8.640(4)	5.1516(7)	105.24(1)	409.2(2)	3.549
298	11.40(3)	9.474(3)	8.560(4)	5.1184(7)	105.06(1)	400.8(2)	3.623
298	14.25(2)	9.429(3)	8.479(4)	5.0894(7)	104.92(1)	393.1(2)	3.694
298	17.55(1)	9.383(3)	8.399(4)	5.0615(7)	104.75(1)	385.7(2)	3.765
298	20.35(2)	9.339(3)	8.354(4)	5.0409(7)	104.66(1)	380.5(2)	3.816
298	23.85(1)	9.300(3)	8.283(4)	5.0120(7)	104.56(1)	373.7(2)	3.886
298	26.65(2)	9.265(3)	8.229(4)	4.9882(7)	104.45(1)	368.3(2)	3.943
500	6.05(2)	9.613(4)	8.740(8)	5.1876(23)	105.88(5)	419.2(5)	3.464
500	6.65(2)	9.600(4)	8.720(7)	5.1809(21)	105.96(5)	417.0(4)	3.482
500	7.15(1)	9.596(4)	8.710(4)	5.1725(19)	106.01(4)	415.5(4)	3.495
500	7.78(2)	9.550(4)	8.697(6)	5.1679(15)	105.30(3)	414.0(4)	3.508
500	8.25(1)	9.577(4)	8.688(9)	5.1612(20)	106.04(5)	412.7(5)	3.519
500	12.20(2)	9.460(3)	8.638(13)	5.1204(13)	105.22(2)	402.4(6)	3.609
500	23.60(1)	9.326(5)	8.453(23)	5.0101(18)	106.82(3)	378.1(4)	3.841
700	5.40(1)	9.615(3)	8.816(6)	5.2162(7)	105.79(1)	425.5(3)	3.413
700	6.20(3)	9.578(3)	8.825(6)	5.2064(8)	105.67(1)	423.7(3)	3.427
700	7.00(3)	9.592(3)	8.770(6)	5.1947(6)	105.90(1)	420.3(3)	3.455
700	8.35(4)	9.568(3)	8.749(6)	5.1782(6)	106.00(1)	416.7(3)	3.485
700	9.45(5)	9.520(4)	8.710(6)	5.1664(7)	105.33(1)	413.1(3)	3.515

700	10.85(3)	9.495(3)	8.675(4)	5.1484(6)	105.24(1)	409.2(2)	3.549
700	11.70(3)	9.525(4)	8.659(5)	5.1407(7)	106.17(1)	407.2(3)	3.566
700	13.05(1)	9.471(4)	8.594(7)	5.121(16)	105.03(3)	402.5(4)	3.608
700	19.95(2)	9.432(3)	8.485(10)	5.0558(14)	106.42(2)	388.1(5)	3.742
700	24.35(1)	9.302(4)	8.386(16)	5.0217(18)	104.67(3)	379.0(7)	3.831

Table 2 Structural refinement details of augite at different pressures to 26.65 GPa

Pressure (GPa)	0.0001	1.05(5)	3.65(7)	6.55(4)	8.30(4)	11.40(3)
R_{int} (%)	5.19	7.21	6.24	5.57	5.75	5.56
R_1 (all reflections, %)	3.69	3.77	3.82	3.40	2.93	2.61
R_1 (Fo>4sig(Fo), %)	3.69	3.77	3.82	3.40	2.93	2.61
wR_2 (all reflections, %)	9.35	10.31	9.45	8.92	7.52	6.69
Goodness of fit	1.052	1.073	0.996	1.061	1.067	1.047
No. of total reflections	3196	564	625	592	556	537
No. of reflections (Fo> 4sig(Fo))	749	181	197	182	154	145
No. of fitting parameters	32	32	32	32	32	32
Pressure (GPa)	14.25(2)	17.55(1)	20.35(2)	23.85(1)	26.65(2)	
R_{int} (%)	5.50	6.31	5.85	5.34	7.20	
R_1 (all reflections, %)	3.46	4.26	3.23	4.02	4.23	
R_1 (Fo> 4sig (Fo), %)	3.46	4.22	3.23	4.02	4.23	
wR_2 (all reflections, %)	8.22	9.98	7.61	9.96	10.51	
Goodness of fit	1.091	1.062	1.077	1.032	1.030	
No. of total reflections	534	509	487	501	488	
No. of reflections (Fo> 4sig (Fo))	142	128	113	117	105	
No. of fitting parameters	32	32	32	32	32	

Table 3 Fractional coordinates and displacement parameters of atoms in augite at different pressures

Pressure (GPa)	0.0001	1.05(5)	3.65(7)	6.55(4)	8.30(4)	11.40(3)	14.25(2)	17.55(1)	20.35(2)	23.85(1)	26.65(2)
M2											
x	0	0	0	0	0	0	0	0	0	0	0
y	0.30145(8)	0.3018(3)	0.3028(3)	0.3038(3)	0.3049(3)	0.3056(2)	0.3070(3)	0.3076(4)	0.3085(3)	0.3093(4)	0.3105(4)
z	0.2500	0.2500	0.2500	0.2500	0.2500	0.2500	0.2500	0.2500	0.2500	0.2500	0.2500
Uiso	0.0102(2)	0.0134(8)	0.0129(7)	0.0123(6)	0.0123(8)	0.0132(8)	0.0085(7)	0.0093(9)	0.0090(7)	0.0118(8)	0.0110(11)
M1											
x	0	0	0	0	0	0	0	0	0	0	0
y	0.9074(1)	0.9079(5)	0.9083(4)	0.9091(4)	0.9105(4)	0.9111(3)	0.9109(4)	0.9117(6)	0.9121(5)	0.9117(5)	0.9107(7)
z	0.2500	0.2500	0.2500	0.2500	0.2500	0.2500	0.2500	0.2500	0.2500	0.2500	0.2500
Uiso	0.0090(2)	0.0143(11)	0.0134(9)	0.0127(9)	0.0154(11)	0.0163(10)	0.0104(8)	0.0119(10)	0.0112(10)	0.0108(10)	0.0129(13)
T											
x	0.28717(7)	0.2867(2)	0.2869(2)	0.2869(2)	0.2868(2)	0.2867(1)	0.2865(2)	0.2866(3)	0.2860(2)	0.2848(3)	0.2863(3)
y	0.09319(6)	0.0944(3)	0.0944(2)	0.0947(2)	0.0953(3)	0.0958(2)	0.0965(3)	0.0966(3)	0.0975(3)	0.0980(3)	0.0989(4)
z	0.2290(1)	0.2281(2)	0.2278(2)	0.2270(2)	0.2273(2)	0.2273(2)	0.2277(2)	0.2287(3)	0.2285(3)	0.2287(3)	0.2303(4)
Uiso	0.0066(1)	0.0097(7)	0.0102(6)	0.0103(7)	0.0121(8)	0.0095(7)	0.0081(6)	0.0093(8)	0.0097(7)	0.0096(10)	0.0100(10)
O1											
x	0.1147(2)	0.1146(5)	0.1143(5)	0.1135(4)	0.1125(5)	0.1122(3)	0.1132(5)	0.1118(7)	0.1120(5)	0.1106(7)	0.1098(8)
y	0.0865(2)	0.0868(8)	0.0880(7)	0.0878(6)	0.0889(8)	0.0879(6)	0.0887(6)	0.0909(7)	0.0898(6)	0.0904(8)	0.0895(9)
z	0.1397(3)	0.1405(7)	0.1398(5)	0.1393(6)	0.1394(5)	0.1393(4)	0.1391(7)	0.1396(9)	0.1408(7)	0.1396(8)	0.1379(10)
Uiso	0.0095(3)	0.0094(9)	0.0093(7)	0.0100(7)	0.0095(7)	0.0091(6)	0.0084(8)	0.0093(11)	0.0108(11)	0.0115(14)	0.0082(16)
O2											
x	0.3619(2)	0.3610(7)	0.3592(5)	0.3591(5)	0.3592(6)	0.3577(4)	0.3568(5)	0.3567(7)	0.3564(6)	0.3554(6)	0.3577(7)
y	0.2517(2)	0.2512(8)	0.2539(7)	0.2563(6)	0.2576(8)	0.2602(7)	0.2591(6)	0.2609(7)	0.2618(7)	0.2654(9)	0.2710(11)
z	0.3192(4)	0.3203(8)	0.3216(6)	0.3230(6)	0.3249(6)	0.3273(4)	0.3269(6)	0.3314(8)	0.3324(7)	0.3327(8)	0.3346(10)
Uiso	0.0113(3)	0.0138(11)	0.0125(8)	0.0117(8)	0.0125(8)	0.0117(6)	0.0103(9)	0.0109(11)	0.0152(12)	0.0145(13)	0.0092(17)
O3											
x	0.3516(2)	0.3522(6)	0.3533(5)	0.3540(4)	0.3553(5)	0.3559(4)	0.3562(5)	0.3553(6)	0.3576(6)	0.3565(7)	0.3576(8)
y	0.0183(2)	0.0198(7)	0.0214(6)	0.0224(6)	0.0235(7)	0.0227(5)	0.0254(7)	0.0263(7)	0.0281(6)	0.0283(8)	0.0309(10)
z	0.9952(3)	0.9938(6)	0.9906(6)	0.9877(5)	0.9872(5)	0.9859(4)	0.9854(7)	0.9838(9)	0.9846(8)	0.9847(9)	0.9867(10)
Uiso	0.0101(3)	0.0101(9)	0.0106(7)	0.0106(7)	0.0085(7)	0.0090(6)	0.0094(8)	0.0083(11)	0.0087(11)	0.0095(11)	0.0048(14)

Table 4 Selected bond lengths (Å) and angles (°), polyhedral volume (Å^3) and distortion parameters of augite at ambient and high pressures to 26.65 GPa. Note: Nomenclature after Zhang et al., (1997).

(a) $M2O_8$ polyhedron

Pressure (GPa)	0.0001	1.05(5)	3.65(7)	6.55(4)	8.30(4)	11.40(3)	14.25(2)	17.55(1)	20.35(2)	23.85(1)	26.65(2)
M2-O1(A1, B1)	2.341(2)	2.336(4)	2.327(6)	2.312(6)	2.297(6)	2.288(5)	2.279(6)	2.241(7)	2.242(7)	2.222(9)	2.222(7)
M2-O2(C2, D2)	2.362(2)	2.347(6)	2.332(4)	2.321(3)	2.311(4)	2.302(3)	2.297(3)	2.275(4)	2.268(4)	2.270(5)	2.262(5)
M2-O3(C1, D1)	2.552(2)	2.549(6)	2.540(5)	2.526(5)	2.514(6)	2.487(4)	2.476(6)	2.470(7)	2.454(7)	2.439(8)	2.427(7)
M2-O3(C2, D2)	2.709(2)	2.680(6)	2.626(5)	2.578(5)	2.545(5)	2.518(4)	2.478(5)	2.451(6)	2.414(6)	2.401(7)	2.370(7)
Mean bond length	2.4909	2.4779	2.4564	2.4342	2.4169	2.3988	2.3825	2.3595	2.3446	2.3328	2.3203
Volume	25.5418	25.2239	24.6351	23.9899	23.5001	22.9983	22.6351	22.0410	21.6447	21.3856	21.0754
Distortion index	0.05605	0.05503	0.05158	0.04835	0.04658	0.04317	0.03964	0.04286	0.03814	0.03725	0.03362

(b) $M1O_6$ octahedron

Pressure (GPa)	0.0001	1.05(5)	3.65(7)	6.55(4)	8.30(4)	11.40(3)	14.25(2)	17.55(1)	20.35(2)	23.85(1)	26.65(2)
M1-O1(A1, B1)	2.114(2)	2.099(7)	2.087(6)	2.059(6)	2.042(6)	2.014(5)	2.010(6)	1.994(8)	1.973(4)	1.960(5)	1.948(5)
M1-O1(A2, B2)	2.045(2)	2.047(3)	2.033(3)	2.018(3)	2.011(3)	2.000(2)	1.993(3)	1.984(4)	1.983(7)	1.965(9)	1.948(8)
M1-O2(C1, D1)	2.029(2)	2.035(8)	2.020(6)	1.997(6)	1.991(7)	1.980(6)	1.976(6)	1.966(8)	1.957(8)	1.931(8)	1.875(8)
Mean bond length	2.0627	2.0604	2.0469	2.0246	2.0147	1.9978	1.9931	1.9813	1.9709	1.9520	1.9239
Volume	11.6003	11.5679	11.3341	10.9632	10.7989	10.5231	10.4555	10.2593	10.0957	9.7793	9.3356
Distortion index	0.01649	0.01248	0.01317	0.01126	0.00907	0.00598	0.00571	0.00524	0.00473	0.00716	0.01696
Quadratic elongation λ	1.0062	1.0056	1.0061	1.0063	1.0066	1.0070	1.0065	1.0075	1.0074	1.0094	1.0117
Bond angle variance σ^2	19.6504	18.5428	19.9639	20.9821	21.9413	23.3730	22.2517	25.7723	25.4550	32.2050	39.1661

(c) TO_4 tetrahedron

Pressure (GPa)	0.0001	1.05(5)	3.65(7)	6.55(4)	8.30(4)	11.40(3)	14.25(2)	17.55(1)	20.35(2)	23.85(1)	26.65(2)
T-O1(C1)	1.612(2)	1.609(5)	1.604(5)	1.600(4)	1.603(5)	1.598(3)	1.581(5)	1.587(7)	1.574(6)	1.570(8)	1.594(9)
T-O2(C1)	1.595(2)	1.572(8)	1.577(6)	1.583(6)	1.585(7)	1.586(6)	1.556(6)	1.560(7)	1.554(8)	1.566(9)	1.586(8)
T-O3(C1)	1.667(1)	1.667(5)	1.665(4)	1.661(4)	1.663(4)	1.661(3)	1.653(4)	1.645(5)	1.647(5)	1.638(6)	1.621(6)
T-O3(C2)	1.688(2)	1.695(5)	1.685(5)	1.674(4)	1.677(5)	1.664(4)	1.666(5)	1.651(6)	1.667(6)	1.660(7)	1.671(7)
Mean bond length	1.6403	1.6359	1.6327	1.6297	1.6321	1.6273	1.6142	1.6107	1.6103	1.6085	1.6180
Volume	2.2457	2.2253	2.2155	2.2027	2.2113	2.1904	2.1384	2.1261	2.1212	2.1145	2.1532
Distortion index	0.02248	0.02779	0.02582	0.02331	0.02326	0.02165	0.02826	0.02314	0.02873	0.02516	0.01711
Quadratic elongation λ	1.0062	1.0074	1.0062	1.0062	1.0065	1.0070	1.0071	1.0064	1.0077	1.0074	1.0068
Bond angle variance σ^2	26.4038	30.2510	25.6264	26.1053	27.2935	28.7848	28.8200	25.9136	31.4456	30.9482	28.9754

| O3-O3-O3 | 166.0(1) | 164.9(3) | 163.6(3) | 162.9(3) | 162.1(4) | 162.7(3) | 160.8(4) | 160.2(4) | 158.9(4) | 158.8(4) | 157.0(4) |

Table 5 Linear BM3 fitting parameters and axial compressibilities of the lattice

parameters *a, b* and *c*

	a	*b*	*c*
M_0(GPa)	362(24)	250(12)	327(6)
M'	18(4)	9(1)	16(1)
β_0(GPa^{-1})	0.0028(2)	0.0040(2)	0.00306(6)

Table 6 Eulerian Strain tensor at different pressures

Pressure (GPa)	Eulerian finite strain along each major axis (Negative values indicate compression)			Directions of the major axes represented by their angles with a-, b- and c-axes of the unit cell lattice								
	"Soft" axis in a-c plane($\varepsilon1$)	b-axis($\varepsilon2$)	"Hard" axis in a-c plane($\varepsilon3$)	"Soft" axis in a-c plane($\varepsilon1$)				b-axis($\varepsilon2$)		"Hard" axis in a-c plane($\varepsilon3$)		
0.0001	-0.0029(2)	-0.0081(5)	0.0009(3)	58.5(0.0)	90.0(0.0)	164.5(0.0)	90.0(0.0)	0.0(0.0)	90.0(0.0)	148.5(0.0)	90.0(0.0)	105.5(0.0)
1.05(5)	-0.0122(2)	-0.0151(5)	-0.0033(3)	45.3(0.0)	90.0(0.0)	150.9(0.0)	90.0(0.0)	0.0(0.0)	90.0(0.0)	135.3(0.0)	90.0(0.0)	119.1(0.0)
3.65(7)	-0.0216(2)	-0.0238(5)	-0.0080(3)	42.4(0.0)	90.0(0.0)	147.8(0.0)	90.0(0.0)	0.0(0.0)	90.0(0.0)	132.4(0.0)	90.0(0.0)	122.2(0.0)
6.55(4)	-0.0265(2)	-0.0274(5)	-0.0106(3)	40.7(0.0)	90.0(0.0)	145.9(0.0)	90.0(0.0)	0.0(0.0)	90.0(0.0)	130.7(0.0)	90.0(0.0)	124.1(0.0)
8.30(4)	-0.0337(2)	-0.0367(5)	-0.0145(3)	41.8(0.0)	90.0(0.0)	146.8(0.0)	90.0(0.0)	0.0(0.0)	90.0(0.0)	131.8(0.0)	90.0(0.0)	123.2(0.0)
11.40(3)	-0.0399(2)	-0.0461(5)	-0.0181(3)	42.7(0.0)	90.0(0.0)	147.6(0.0)	90.0(0.0)	0.0(0.0)	90.0(0.0)	132.7(0.0)	90.0(0.0)	122.4(0.0)
14.25(2)	-0.0462(2)	-0.0556(5)	-0.0213(3)	43.0(0.0)	90.0(0.0)	147.8(0.0)	90.0(0.0)	0.0(0.0)	90.0(0.0)	133.0(0.0)	90.0(0.0)	122.2(0.0)
17.55(1)	-0.0511(2)	-0.0609(5)	-0.0247(3)	42.2(0.0)	90.0(0.0)	146.8(0.0)	90.0(0.0)	0.0(0.0)	90.0(0.0)	132.2(0.0)	90.0(0.0)	123.2(0.0)
20.35(2)	-0.0569(2)	-0.0694(5)	-0.0283(3)	43.6(0.0)	90.0(0.0)	148.2(0.0)	90.0(0.0)	0.0(0.0)	90.0(0.0)	133.6(0.0)	90.0(0.0)	121.8(0.0)
23.85(1)	-0.0619(2)	-0.0760(5)	-0.0313(3)	44.4(0.0)	90.0(0.0)	148.8(0.0)	90.0(0.0)	0.0(0.0)	90.0(0.0)	134.4(0.0)	90.0(0.0)	121.2(0.0)

Table 7 Thermoelastic properties of high pressure minerals used for density calculations.

Mineral	V_0 (Å^3)	K_{T0} (GPa)	K_{T0}'	$\partial K_0/\partial T$	$\alpha_0 \times 10^{-5}$	$\alpha_1 \times 10\text{-}8$ (K^{-1})
Jadeite[a]	403.32(8)	124.5(4.0)	5.0(fixed)	-0.016(5)	2.56(22)	0.26(18)
Aegirine[b]	431.5(1)	118(3)	4.2(3)	-0.016(5)	2.64(13)	0
Diopside[c]	438.67(6)	109(4)	4.8(6)	-0.021(4)	2.32(5)	1.88(7)
Omphacite[d]	424.7(7)	126(1)	4.0(fixed)	-0.015(4)	2.2(1)	0
Clinoenstatite[e]	405.0(2.6)	106.9(25.9)	5.3(3.9)	-0.021(10)	2.01(44)	2.1(1.1)

References: a-Zhao et al. (1997); b-Tribaudino et al. (2008) and Xu et al. (2016), note that $\partial K_0/\partial T$ was assumed to be the same as in jadeite (no data of $\partial K_0/\partial T$ for aegirine is currently available); c-Zhao et al. (1998); d-Nishihara et al. (2003); e-Shinmei et al. (1999)