High-Pressure Experimental Study of

Tetragonal CaSiO$_3$-Pervoskite to 200 GPa

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17 **Abstract**

18 In this study, we have investigated the crystal structure and equation of state of

19 tetragonal $CaSiO_3$-perovskite up to 200 GPa using synchrotron X-ray diffraction in

20 laser-heated diamond anvil cells. X-ray diffraction patterns of the quenched

21 $CaSiO_3$-pervoskite above 148 GPa exhibit much clearer splitting of cubic peaks 200,

22 211, and 220 which are used to characteristically resolve the tetragonal structure from

23 the cubic phase. Together with systematic Rietveld refinement of potential space

24 groups, the observation of a characteristic peak with 2θ around 10.0-10.2° (*d*-spacing

25 of 1.92-1.88 Å) between 148 and 199 GPa at 300 K provides a direct evidence to

26 confirm that tetragonal $CaSiO_3$-perovskite is stable in the *I*4/*mcm* structure. By using

27 the Birch-Murnaghan equations, we have determined the equation of state of

28 tetragonal $CaSiO_3$-perovskite, yielding the bulk modulus K_{0T}= 242(6) GPa with the

29 pressure derivative of the bulk modulus, K_{0T}'=4 (fixed). Using literature results,

30 modeled sound velocities at 580 K and lower-mantle pressures show differences in

31 the compressional (V_P) and shear-wave velocity (V_S) between the cubic and tetragonal

32 phase to be 3.1-3.7(1)% and 3.4-3.9(1)% at 24 GPa, respectively. Elevating pressure

33 to 100 GPa leads to an increase in the differences in V_P and V_S between these two

34 phases. V_S of the cubic phase is 7.8-8.7(2)% greater than the tetragonal

35 $CaSiO_3$-perovskite at 100 GPa, while V_P is 4.5(1)% greater. Since addition of Ti can

36 elevate the transition temperature, the phase transition from the tetragonal to cubic

37 phase may have a seismic signature compatible with the observed mid-lower mantle

38 discontinuity,. Future studies on the Ti effects on the density and velocity profiles of

39 $CaSiO_3$-perovskite are crytically needed to provide tighter constaints on the

40 geophysical consequence of the structural phase transition in the lower mantle.

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42 Key words: tetragonal CaSiO$_3$-perovskite, equation of state, structure, high pressure

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1. Introduction

46 CaSiO$_3$-perovskite is one of the most abundant silicate phases and the dominant host

47 of Ca in the Earth's lower mantle (Anderson, 1989; Kesson et al., 1998; Murakami et

48 al., 2005; Ringwood, 1975). In the lower mantle, the volume percentage of

49 CaSiO$_3$-perovskite is estimated to be 5-8 vol.% but could be up to 22-29 vol.% in the

50 subducting mid-ocean ridge basalts (MORBs) (e.g. Anderson, 1989; Harte, 2010;

51 Hirose et al., 2005; Wood, 2000). Recent high-pressure studies have found that

52 shear-wave velocity of CaSiO$_3$-perovskite is substantially lower than the global

53 seismic model PREM (Dziewonski and Anderson, 1981; Gréaux et al., 2019;

54 Thomson et al., 2019). Enrichment of the recycled MORBs with the low-velocity

55 CaSiO$_3$-perovskite could cause a seismic signature compatible with the large-low

56 shear velocity provinces (Kawai and Tsuchiya, 2014; Thomson et al., 2019).

57 Experimental studies on the structure and elastic properties of CaSiO$_3$ at high

58 pressures are thus important to understand the composition and structure of the lower

59 mantle (e.g. Komabayashi et al., 2007; Kurashina et al., 2004; Mao et al., 1989;

60 Noguchi et al., 2013; Shim et al., 2000; Sun et al., 2016; Wang et al., 1996; Wood,

61 2000; Zhang et al., 2006).

62

63 CaSiO$_3$-perovskite has been reported to crystallize in the cubic structure at the

64 expected pressure-temperature conditions of the lower mantle (e.g. Komabayashi et

65 al., 2007; Noguchi et al., 2013; Shim et al., 2000; Sun et al., 2016). However, it can

66 also accommodate a certain amount of minor elements such as Ti (Hirose and Fei,

67   2002; Kesson et al., 1998; Kesson et al., 1994; Nestola et al., 2018; Wood, 2000),

68   which can elevate the phase transition temperature at lower-mantle pressures and may

69   enable the tetragonal phase to exist in the cold subducting slabs (Thomson et al.,

70   2019). The tetragonal to cubic phase transition with the presence of Ti which is likely

71   to happen beyond 1000-km depth may explain the observed seismic reflections in the

72   mid-lower mantle (Kudo et al., 2012; Thomson et al., 2019).

73

74   In contrast to the cubic phase, the crystal structure and equation of state (EoS) of

75   tetragonal CaSiO₃-perovskite were not well constrained. The cubic to tetragonal phase

76   transition was proposed to be caused by a second-order structure distortion, and four

77   space groups, including *P4*/*mmm*, *P4*/*mbm*, *I4*/*mmm* and *I4*/*mcm* were predicted for

78   the tetragonal phase (Shim et al., 2002; Stixrude et al., 2007). Three potential

79   structures (*P4*/*mbm*, *I4*/*mmm* and *I4*/*mcm*) were caused by the octahedral rotations,

80   whereas the tetragonal CaSiO₃ with the *P4*/*mmm* structure could be formed by

81   elongating the *c*-axis of the cubic phase (Shim et al., 2002; Stixrude et al., 2007). In

82   early experimental studies, *P4*/*mmm* was applied to analyze the lattice parameters and

83   unit cell volume of tetragonal CaSiO₃, yielding a modified *c*/*a* ratio (*Z*=1) of

84   0.992-0.998 at 0-100 GPa (Ono et al., 2004; Shim et al., 2002). However, theoretical

85   studies pointed out that the phase transition was second order in nature and should be

86   caused by octahedral rotations (Stixrude et al., 1996; Stixrude et al., 2007). *I4*/*mcm*

87   with the lowest calculated energy is theoretically supported to the structure for the

88   tetragonal CaSiO₃ (Stixrude et al., 2007). In contrast to *P4*/*mmm*, *I4*/*mcm* has a

89   modified *c*/*a* ratio increasing from 1.004 at 20 GPa to 1.023 at ~220 GPa (Jung and

90   Oganov, 2005; Stixrude et al., 2007). *I4*/*mcm* was also preferred in a recent

91   experimental study based on the Rietveld refinement results, which give better fits for

92   the peak positions and intensities than other proposed space groups (Chen et al., 2018).

93   Meanwhile, a few theoretical studies using first-principle calculations also suggested

94   an orthorhombic structure for $CaSiO_3$ at high pressures and low temperatures

95   (Akber-Knutson et al., 2002; Li et al., 2006; Magyari-Kope et al., 2002). In addition,

96   the bulk modulus of tetragonal $CaSiO_3$-perovskite is highly uncertain, ranging from

97   223(6) GPa to 248(8) GPa with a fixed pressure derivative of the bulk modulus to be

98   4 (Chen et al., 2018; Gréaux et al., 2019; Ono et al., 2004; Shim et al., 2002; Thomson

99   et al., 2019). The structure and EoS of tetragonal $CaSiO_3$-perovskite at high pressures

100 thus require further investigation.

101

102 In this study, we have investigated the structure of $CaSiO_3$-perovskite using

103 synchrotron X-ray diffraction in laser-heated diamond anvil cells (DACs). Our study

104 has significantly extended the experimental pressure to 200 GPa. High-resolution

105 XRD data allow us to provide direct constraints on the crystal structure, lattice

106 parameters, and EoS of the tetragonal phase. These results provide a comprehensive

107 understanding on the structure and EoS of tetragonal $CaSiO_3$-perovskite at high

108 pressures.

109

110 ## 2. Experiments

111 The starting material was $CaSiO_3$ wollastonite, purchased from Sigma-Aldrich Co.

112 LLC. The polycrystalline starting material was ground into fine powder and mixed

113 with 5 wt.% Pt as the pressure standard and laser absorber (Fei et al., 2007). The

114 sample mixture was compressed by a DAC into ~10 μm thick pellets. We further cut

115 the sample foil into small pieces. A small sample piece was sandwiched between two

116 NaCl layers, which were pre-loaded to each side of the DAC. NaCl used as the

117   pressure medium and thermal insulator was pre-dried for more than 5 hours at ~105°C

118   to avoid any potential contamination of water in the air. The sample sandwiches were

119   loaded into symmetric DACs with 75/300 μm beveled diamonds anvils. The high

120   pressure and temperature XRD experiments were performed at the

121   GeoSoilEnviroConsortium (GSECARS) of the Advanced Photon Source (APS),

122   Argonne National Laboratory (ANL), with X-ray wavelength of 0.3344 Å. Previous

123   studies have shown that cubic CaSiO₃-perovskite is stable up to 156 GPa and will

124   transform into tetragonal phase after quench (e.g. Noguchi et al., 2013; Shim et al.,

125   2000; Sun et al., 2016). Here we directly compressed the cell to ~160 GPa at 300 K

126   and then performed laser heating. The diffraction patterns were collected at every

127   10-15 GPa from 1400 K to 2600 K up to 203 GPa. Assuming a Graybody radiation,

128   the temperature was determined by fitting the thermal radiation spectrum using Planck

129   radiation function (Prakapenka et al., 2008). Quenched diffraction patterns were

130   collected after each heating cycle at high pressures.

131

132   ## 3. Result

133   The starting CaSiO₃ wollastonite became amorphous at 160 GPa and 300 K. Heating

134   the amorphous material immediately transformed CaSiO₃ to the cubic perovskite

135   structure (Fig. 1). Continuing heating cubic CaSiO₃-perovskite up to 2600 K did not

136   cause any notable change in the XRD patterns. Yet the quenched sample at 300 K and

137   148 GPa has exhibited an obvious splitting of XRD peaks at 12.0º, 14.7º, and 16.9º

138   (wavelength = 0.3344 Å), respectively. In particular, we observed a new peak at

139   ~10.0-10.2º in the quenched patterns, which was not reported or not clear in previous

140   experimental studies (Fig. 2) (Chen et al., 2018; Ono et al., 2004; Shim et al., 2002;

141   Thomson et al., 2019). Further analysis of the obtained XRD patterns revealed that

142 CaSiO$_3$ was stable in the cubic perovskite structure between 158 and 203 GPa at

143 1400-2600 K, but transformed to the tetragonal phase upon quenching. Calculated

144 deviatoric stress at 300 K using collected diffraction patterns of Pt is less than 1.2 GPa

145 at pressures up to 199 GPa (Fig. 1). We further performed the Rietveld refinement on

146 the obtained diffraction patterns for both cubic and tetragonal CaSiO$_3$-perovskite

147 phases (Fig. 2). Cubic CaSiO$_3$-perovskite phase was in the space group $Pm\bar{3}m$. For the

148 tetragonal phase, the $I4/mmm$ structure was firstly excluded because of the absence of

149 two characteristic peaks with d-spacing ~1.42 Å and 1.56 Å at 24-96 GPa (Chen et al.,

150 2018; Shim et al., 2002; Ono et al., 2016). The result of full-profile Rietveld

151 refinement analysis revealed that $I4/mcm$ has the least-fitting residue of 5.4%

152 compared to other two space groups, $P4/mmm$ with a fitting residue of 10.0% and

153 $P4/mbm$ of 11.2% (Fig. 3 and Table 1) (Jung and Oganov, 2005; Shim et al., 2002).

154

155 Here we focused on the lattice parameters and EoS of tetragonal CaSiO$_3$-perovskite

156 (Fig. 4). Experimental data of Sun et al. (2016) between 24 and 124 GPa at 300 K

157 have been re-analyzed to better constrain the lattice parameters and pressure-volume

158 relationship of the tetragonal phase at an extended pressure range. For $I4/mcm$, c-axis

159 is longer than a-axis but is less compressible (Fig. 4). Both a and c-axis of tetragonal

160 CaSiO$_3$-perovskite are more compressible than the lattice parameter of the cubic

161 phase. The pressure-volume data were fitted using the Birch-Murnaghan EoS (Birch,

162 1938) (Fig. 4 and Table 2):

$$P = \frac{3}{2} K_{0T} \left[\left(\frac{V}{V_0} \right)^{-7/3} - \left(\frac{V}{V_0} \right)^{-5/3} \right] \cdot \left\{ 1 + \frac{3}{4} (K' - 4) \left[\left(\frac{V}{V_0} \right)^{-2/3} - 1 \right] \right\},$$

164 where K_{0T} and V_0 are the isothermal bulk modulus and unit cell volume at the ambient

165 conditions, respectively. K' is the pressure derivative of the bulk modulus. To have a

166 better comparison with previous experimental and theoretical results, we normalized

167 the Z number of the tetragonal phase to 1. In the normalized unit cell, c equals that of

168 the tetragonal CaSiO$_3$-perovskite with Z=4 divided by 2, while a equals the initial a

169 divided by $\sqrt{2}$ (Chen et al., 2018; Jung and Oganov, 2005; Ono et al., 2004; Shim et

170 al., 2002). With a fixed K' of 4, we obtained the modified V_0 = 45.1(3) Å^3 (Z=1) and

171 K_{0T} = 242(6) GPa.

172

4. Discussion

174 Due to the similarity in the XRD patterns between the cubic and tetragonal CaSiO$_3$,

175 the stable structure of CaSiO$_3$ at high pressure-temperature conditions has been under

176 debate for years (e.g. Chen et al., 2018; Jung and Oganov, 2005; Ono et al., 2004;

177 Shim et al., 2002; Stixrude et al., 2007). Splitting of the cubic 200 peak was applied to

178 determine the occurrence of the phase transition at high pressures (Chen et al., 2018;

179 Komabayashi et al., 2007; Kurashina et al., 2004; Noguchi et al., 2013; Ono et al.,

180 2004; Shim et al., 2002; Sun et al., 2016). Here, our obtained XRD patterns above 148

181 GPa showed a well-resolved splitting of the cubic 211 and 220 peaks after quench

182 than patterns collected at relatively lower pressures in previous studies (Chen et al.,

183 2018; Ono et al., 2004; Shim et al., 2002). Using the refined space groups and lattice

184 parameters, we also calculated the full width at half maximum (FWHM) of the

185 tetragonal 004+220, 204+312, and 224+400 peak pairs at high pressure and 300 K

186 (Fig. 5). Across the cubic-tetragonal transition, the 200, 211, and 220 peaks of the

187 cubic phase split into 004+220, 204+312, and 224+400 peaks, respectively, in the

188 tetragonal structure. The FWHM of tetragonal peak pairs exhibit a substantial increase

189 with pressure up to 200 GPa. It is thus easier to identify the presence of tetragonal

190 CaSiO$_3$-perovskite from the XRD patterns above 148 GPa. Previous studies

191   mentioned that the observed splitting may be a result of the increased deviatoric stress

192   inside the DAC, and a deviatoric stress of ~7 GPa is enough to induce the peak

193   splitting at temperatures as high as 1550 K (Chen et al., 2018; Shim et al., 2002). Here

194   we showed that the quenched patterns have a deviatoric stress less than 1.2 GPa up to

195   199 GPa (Singh, 1993; Sun et al., 2016) (Figure 1b). The peak splitting in the

196   quenched pattern only can be caused by the phase transition but not the deviatoric

197   stress (Chen et al., 2018; Shim et al., 2002).

198

199   More importantly, we have observed the presence of an additional peak with 2θ at

200   ~10.0-10.2° from 148 to 199 GPa at 300 K (d-spacing of 1.92-1.88 Å) (Fig. 2).

201   Although Sun et al. (2016) did observe the 211 peak, their motivation is to determine

202   the thermal EoS of cubic CaSiO₃-perovskite. The XRD data of the tetragonal phase

203   were not carefully analyzed, and the 211 peak in Sun et al. (2016) was completely

204   ignored. In this work, we carefully analyzed the XRD patterns of the tetragonal phase

205   and performed the Rietveld refinement for potential structures. Based on the Rietveld

206   refinement results, only $I4/mcm$ can yield reasonable fit to this peak which was

207   indexed as peak 211 and has the least full-profile refinement residue of 5.4%

208   compared to $P4/mmm$ and $P4/mbm$ (Fig. 3). We also examined the XRD patterns of

209   tetragonal CaSiO₃-perovskite in Sun et al. (2016) between 24 and 124 GPa at 300 K

210   which also recorded the tetragonal 211 peak as a continuous ring (Fig. 2). Missing this

211   important peak in previous experimental studies may be caused by a relatively

212   low-resolution of the XRD patterns or over masking of the cake patterns (Chen et al.,

213   2018; Ono et al., 2004; Shim et al., 2002). Rotation of the sample when collecting the

214   XRD patterns also helps to reveal the 211 peak. We thus present the direct

215   experimental evidence to confirm that CaSiO₃ is stable in the tetragonal $I4/mcm$

216   structure at high pressures and 300 K, consistent with theoretical predictions (Jung

217   and Oganov, 2005; Stixrude et al., 2007). Compared to the peak splitting, the presence

218   of peak 211 is a better indicator for the cubic to tetragonal phase transition.

219

220   Detailed comparison between the cubic and tetragonal phases has shown that, the

221   phase transition affects the bond length of the Si-O octahedra and leads to the

222   distortion of the nearby octahedra inside the X-Y plane (Jung and Oganov, 2005).

223   Angles between two Si-O bonds within the X-Y plane decrease from 180° in the cubic

224   structure to 153° in the tetragonal structure at 163 GPa and 300 K, and exhibit a weak

225   increase with pressure due to the enhanced distortion at higher pressures (Jung and

226   Oganov, 2005). Cubic CaSiO₃-perovskite has six equal Si-O bonds in length in an

227   octahedron (Fig. 6). Increasing temperature can cause a weak increase in the Si-O

228   bond length of the cubic phase. Tetragonal CaSiO₃-perovskite has two different Si-O

229   bonds. The Si-O1 bond in the tetragonal structure is 1.9(1)% shorter than the Si-O2

230   bond but has a length similar to the cubic phase. Meanwhile, a-axis of the tetragonal

231    $I4/mcm$ phase is ~2.5% shorter than that of the cubic phase because of the distortion

232   in structure. With Z=1, previous experimental studies reported a modified c/a value

233   less than 1 for the $P4/mmm$ phase (Fig. 7) (Chen et al., 2018; Jung and Oganov, 2005;

234   Ono et al., 2004; Shim et al., 2002; Stixrude et al., 2007). For the $I4/mcm$ structure,

235   c-axis is longer than a-axis, leading to a modified c/a ratio greater than 1. The

236   modified c/a ratio of the tetragonal CaSiO₃-perovskite increases from ~1.003 at 24

237   GPa to ~1.012 at 199 GPa (Fig. 7). The modified c/a ratio showing here between 24

238   and 199 GPa is in general agreement with a recent experimental study and follows a

239   similar trend with pressure as the theoretical predictions (Chen et al., 2018; Stixrude

240   et al., 2007).

241

242   The unit cell volume of the $I4/mcm$ phase at a given pressure shown here is slightly

243   smaller than that reported in previous studies using the $P4/mmm$ structure (Ono et al.,

244   2004; Shim et al., 2002). The difference is caused by using different sequence of

245   peaks in two space groups to analyze the XRD pattern. If we also apply the $P4/mmm$

246   structure for tetragonal CaSiO₃ by ignoring the 211 peak, the calculated unit cell

247   volume is similar to that shown in previous studies (Fig. 4) (Ono et al., 2004; Shim et

248   al., 2002). Above 45 GPa, the unit cell volume of the $P4/mmm$ structure in Ono et al.,

249   (2004) are greater than other results, potentially due to large deviatoric stress with no

250   pressure medium in the high-pressure experiments (Chen et al., 2018; Shim et al.,

251   2002; Thomson et al., 2019). K_{0T} of the tetragonal CaSiO₃-perovskite with a fixed

252   K_{0T}'=4 is highly uncertain, ranging from 223(6) GPa to 248(8) GPa in previous

253   experimental studies (Chen et al., 2018; Gréaux et al., 2019; Ono et al., 2004; Shim et

254   al., 2002; Thomson et al., 2019). Here, fitting the P-V data at a much larger pressure

255   range up to 200 GPa yielded K_{0T} of 242(6) with a fixed K_{0T}'=4. For a better

256   comparison, we re-analyzed the previous experimental P-V data using a

257   self-consistent pressure scale of Fei et al., (2007) for a better comparison (Table 3)

258   (Shim et al., 2002; Ono et al., 2004; Chen et al., 2018; Thomson et al., 2019; Jung and

259   Oganov, 2005; Stixrude et al., 2007; Caracas et al., 2005). Previous experimental

260   studies with a much lower K_{0T} could be caused by limited experimental pressure

261   range at 300 K or the untransformed lower-pressure materials (Chen et al., 2018; Ono

262   et al., et al., 2004; Thomson et al., 2019; Gréaux et al., 2019). K_{0T} of the tetragonal

263   phase in Shim et al. (2002) is much greater than our and other literature results,

264   potentially due to their limited experimental data points and narrow pressure range

265   (Chen et al., 2018; Ono et al., et al., 2004). In addition, tetragonal CaSiO₃-perovskite

266 has a slightly lower K_{0T} than the cubic phase, although a few experimental studies

267 reported a low K_{0T} of 208-237 GPa for the cubic phase (Gréaux et al., 2019; Kawai

268 and Tsuchiya, 2014; Noguchi et al., 2013; Ricolleau et al., 2009; Shim et al., 2000;

269 Shim et al., 2002; Wang et al., 1996; Zhang et al., 2006).

270

5. Geophysical implications

272 A recent experimental study showed that addition of Ti in CaSiO₃-perovskite could

273 elevate the phase transition temperature from the tetragonal to the cubic phase

274 (Thomson et al., 2019). Ti-bearing tetragonal CaSiO₃-perovskite may exist in the cold

275 subducting slabs in the Earth's lower mantle (Ono et al., 2004; Thomson et al., 2019).

276 Here we modeled the sound velocity of tetragonal and cubic endmember

277 CaSiO₃-perovskite using our obtained EoS and literature results (Fig. 8) (Gréaux et al.,

278 2019; Thomson et al., 2019). The modeling was performed at 580 K between 24 and

279 136 GPa following the phase boundary constrained by Kurashina et al. (2004). For the

280 cubic phase, Thomson et al. (2019) and Gréaux et al. (2019) reported different bulk

281 and shear modulus as well as their pressure and temperature derivatives. Both of their

282 results were used to calculate the sound velocities of the cubic phase. Due to lack of

283 experimental constraints, some thermal parameters of tetragonal CaSiO₃, such as

284 dK/dT and dG/dT, were assumed to be the same as the cubic phase (Thomson et al.,

285 2019; Gréaux et al., 2019). Uncertainties of the calculated sound velocities because of

286 using different literature elastic parameters were shown in shading in Fig. 8 (Gréaux

287 et al., 2019; Thomson et al., 2019). There is no density change across the phase

288 transition. The compressional (V_P) and shear-wave velocities (V_S) of tetragonal

289 CaSiO₃-perovskite are 3.1-3.7(1)% and 3.4-3.9(1)% lower than the cubic phase at the

290 top of the lower mantle, respectively (Fig. 8). Yet the difference in V_P and V_S between

291 the cubic and tetragonal phase increases to 4.5(1)% and 7.8-8.7(2)% at 100 GPa,

292 respectively. Due to lack of experimental constraints on the influence of Ti on the

293 phase boundary and thermal elastic properties of the tetragonal and cubic phases, our

294 modeling can only provide a preliminary estimation on the influence of the phase

295 transition of $CaSiO_3$ on the velocity profiles of the lower mantle. With the presence of

296 Ti, the tetragonal to cubic phase transition may be seismically detectable in the

297 mid-lower mantle.

298

299 In summary, the structure of $CaSiO_3$ has been studied up to 200 GPa by synchrotron

300 XRD in laser-heated DACs. Quenching to 300 K leads to the transition of $CaSiO_3$

301 from the cubic to tetragonal structure. Compared to previous experimental results,

302 here we have observed more distinct splitting of the cubic 200, 211, and 220 peaks

303 after temperature quench between 148 and 199 GPa. More importantly, the

304 observation of a characteristic peak 211 with 2θ around 10.0-10.2°allows us to

305 confirm that $CaSiO_3$ at high pressures and 300 K is in the *I4/mcm* structure. We note

306 that the *I4/mcm* tetragonal phase has a modified c/a ratio (Z=1) greater than 1, which

307 increases from 1.002 at ~20 GPa to 1.012 at ~200 GPa. The obtained K_{0T} of the

308 *I4/mcm* phase is smaller than that of the cubic $CaSiO_3$-perovskite. The comparison

309 between tetragonal and cubic $CaSiO_3$-perovskite at 580 K is useful to estimate the

310 influence of the phase transition on the sound velocity of the lower mantle, indicating

311 the phase transition can cause substantial increase in the sound velocity. Future studies

312 are expected to determine the effect of Ti on the thermoelastic parameters of

313 tetragonal $CaSiO_3$-perovskite and provide new insights in understanding the

314 composition and structure of the lower mantle.

315

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454

455

456   Table 1. Atomic position of tetragonal CaSiO$_3$-perovskite (Z=4) at 163 GPa and 300

457   K

Tetragonal *I4/mcm*			
Cell (Å) (4.471/4.471/6.384)			
Ca	0.5	0	0.25
Si	0	0	0
O	0	0	0.25
O	0.310	0.190	0

458

459   Table 2. Pressure-volume data of tetragonal CaSiO$_3$-perovskite at high pressures and
460   300 K

461

P (GPa)	*a* (Å)	*c* (Å)	*V* (Å³)
21.5(4)*	4.904(2)	6.947(3)	167.0(2)
24.9(6)*	4.882(3)	6.926(4)	165.1(3)
30.2(5)*	4.875(2)	6.920(3)	164.4(2)
38.4(7)*	4.837(1)	6.868(3)	160.7(1)
43.6(11)*	4.822(3)	6.823(5)	158.7(3)
52.0(13)*	4.776(2)	6.796(3)	155.0(2)
57.0(15)*	4.753(4)	6.747(5)	152.4(4)
59.9(15)*	4.743(2)	6.741(3)	151.7(2)
63.4(16)*	4.741(2)	6.731(3)	151.3(2)
69.9(17)*	4.717(3)	6.701(4)	149.1(3)
84.4(21)*	4.673(1)	6.651(2)	145.2(1)
93.4(24)*	4.643(2)	6.621(3)	142.7(2)
98.1(26)*	4.621(4)	6.585(5)	140.6(4)
124.0(30)*	4.565(3)	6.503(5)	135.5(3)
148.3(36)	4.502(3)	6.433(5)	130.4(3)
148.4(36)	4.500(3)	6.430(5)	130.2(3)
159.2(38)	4.481(2)	6.400(4)	128.5(2)
163.3(40)	4.471(2)	6.384(3)	127.6(2)
171.4(41)	4.460(2)	6.374(3)	126.8(2)
172.6(41)	4.461(1)	6.378(2)	126.9(1)
179.2(43)	4.449(3)	6.356(2)	125.8(2)
193.1(48)	4.428(3)	6.333(5)	124.2(3)
199.2(47)	4.415(2)	6.315(4)	123.1(2)

*Sun et al. (2016)

462

463

464

465 Table 3. EoS of the tetragonal CaSiO$_3$-perovskite under self-consistent pressure scales

	This study	Shim 2002	Ono 2004	Chen 2018	Thomson 2019	Jung 2005[*]	Stixrude 2007[*]	Caracas 2005[*]
K_{0T} (GPa)	242 (5)	259 (5)	235 (9)	228(6)	224(4)	219.04	252	249
K'	4[#]	4[#]	4[#]	4[#]	4[#]	4.08	4.1	4.09
V_0 (Å^3)	45.1(3)	45.58[f]	45.9 (4)	46.2(1)	46.10(6)	46.89	44.00	44.537

466 [#]fixed
467 [*]theoretical results, under 0 K
468

469 **Figure caption**

470 Figure 1. (a) Experimental pressure-temperature conditions of CaSiO$_3$-perovskite.

471 Blue: cubic CaSiO$_3$-perovskite; red: tetragonal CaSiO$_3$-perovskite; solid circles: this

472 study; open circles: Sun et al. (2016); diamonds: Noguchi et al. (2013); squares:

473 Kurashina et al. (2004); grey lines: typical lower mantle geotherm and a

474 representative cold slab geotherm, respectively (Brown and Shankland, 1981; Kirby et

475 al., 1996); dashed black lines: phase boundary between the cubic and tetragonal

476 phases based on previous experimental results (Kurashina et al., 2004; Noguchi et al.,

477 2013; Sun et al., 2016); (b) potential deviatoric stress (absolute value) under 300 K.

478

479 Figure 2. XRD and Rietveld refinement results of CaSiO$_3$-perovskite at high pressures.

480 (a) Representative XRD patterns of CaSiO$_3$-perovskite at high pressures and

481 temperatures. Red line: cubic CaSiO$_3$-perovskite at 170 GPa and 2500 K; blue line:

482 tetragonal CaSiO$_3$-perovskite at 163 GPa and 300 K; (b) Cake patterns of tetragonal

483 CaSiO$_3$-perovskite at 163 GPa and 300 K, respectively. The characteristic 211 peak at

484 2θ around 10° in the $I4/mcm$ tetragonal phase is shown as a continuous ring; (c) Full

485 profile Rietveld refinement results of tetragonal and cubic CaSiO$_3$-perovskite. Cross:

486 experimental XRD pattern; black line: refined results; red: tetragonal phase; blue:

487 cubic phase; vertical ticks: peaks of tetragonal CaSiO$_3$-perovskite, Pt and NaCl,

488 respectively. X-ray wavelength is 0.3344 Å.

489

490   Figure 3. Rietveld refinement analysis of tetragonal CaSiO$_3$-perovskite. Crosses:

491   experimental XRD pattern; red line: refinement results of $I4/mcm$ with a residue of

492   5.4%; blue line: refinement results of $P4/mbm$ with a residue of 11.2%; purple line:

493   refinement results of $P4/mmm$ with a residue of 10.0%; black lines: refinement

494   residue; vertical ticks: peak positions of Pt, NaCl, and tetragonal CaSiO$_3$, respectively.

495

496   Figure 4. Pressure-volume relationship of tetragonal CaSiO$_3$-perovskite at high

497   pressures and 300 K. Red circles and line: the $I4/mcm$ phase in this study; green: the

498     $P4/mmm$ phase (Shim et al., 2002); blue: the $P4/mmm$ phase (Ono et al., 2004);

499   orange: the $I4/mcm$ phase in Chen et al. (2018); grey: this study assuming a $P4/mmm$

500   tetragonal phase; black: calculated volume of the cubic CaSiO$_3$-perovskite at 300 K

501   (Sun et al., 2016)

502

503   Figure 5. Modeled peak widths of the tetragonal phase at high pressures. Orange:

504   tetragonal peak 004+220 from splitting of the cubic 200 peak after quenched; red:

505   tetragonal peak 204+312 from splitting of the cubic 211 peak after quenched; blue:

506   tetragonal peak 224+400 from splitting of the cubic 220 peak after quenched.

507

508   Figure 6. Bond length of CaSiO$_3$-perovskite. Grey cicles: length of the Si-O1 bond of

509   the tetragonal phase; grey diamonds: length of the Si-O2 bond of the tetragonal phase;

510   brown, orange, purple, blue, and red circles: Si-O bond length of the cubic phase at

511   1400 K, 1600 K, 1800 K, 2100 K, and 2500 K, respectively.

512

513

514

515   Figure 7. Lattice parameters of tetragonal CaSiO$_3$-perovskite. (a) Variation of a and c

516   axis of tetragonal CaSiO$_3$-perovskite with pressure at 300 K. Blue: c-axis; red: a-axis;

517   (b) The modified c/a ratio of tetragonal CaSiO$_3$-perovskite at high pressures and 300

518   K. Red: this study; green: Shim et al. (2002); blue: Ono et al. (2004); orange: Chen et

519   al. (2018); purple: Stixrude et al. (2007).

520

521   Figure 8. Modeled compressional (V_P) and shear-wave velocities (V_S) of

522   CaSiO$_3$-perovskite at high pressures and 580 K. Solid lines: tetragonal phase; dashed

523   lines: cubic phase; red: V_P; blue: V_S; bold dashed and solid lines: calculated using the

524   elastic parameters from this work and Gréaux et al. (2019); thin dashed and solid lines:

525   calculated using the elastic parameters from this work and Thomson et al.

526   (2019).Density was assumed to be the same for both phases due to the second-order

527   phase transition. Vertical ticks represent the calculation errors using standard error

528   propagation from the used parameters.

529

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532