Phase relations in the system $MgSiO_3$–Al_2O_3 up to 2300 K at lower-mantle pressures

Zhaodong Liu [1, 2*], Masayuki Nishi [2], Takayuki Ishii [1], Hongzhan Fei [1], Nobuyoshi Miyajima [1], Tiziana Boffa Ballaran [1], Hiroaki Ohfuji [2], Takeshi Sakai [2], Lin Wang [1], Svyatoslav Shcheka [1], Takeshi Arimoto [2], Yoshinori Tange [3], Yuji Higo [3], Tetsuo Irifune [2], Tomoo Katsura [1]

[1]Bayerisches Geoinstitut, University of Bayreuth, 95440 Bayreuth, Germany

[2]Geodynamics Research Center (GRC), Ehime University

[3]SPring-8, Japan Synchrotron Radiation Institute

* Corresponding author: Zhaodong Liu (bt303897@uni–bayreuth.de)

Bayerisches Geoinstitut, University of Bayreuth, 95440 Bayreuth, Germany

Key Points:

- Phase relations in the system $MgSiO_3$-Al_2O_3 were determined at temperatures up to 2300 K and pressures up to 45 GPa.

- The solubility of Al_2O_3 in bridgmanite and that of $MgSiO_3$ in corundum increase with increasing temperature.

- The Al_2O_3 cannot be fully accommodated in the coldest parts of subducted slabs in the shallow part of the lower mantle.

24   Abstract

25   Phase relations in the system MgSiO$_3$–Al$_2$O$_3$ were investigated at pressures of 27–45 GPa and

26   temperatures of 1700, 2000 and 2300 K using sintered diamond and tungsten carbide anvils in a

27   multi-anvil apparatus. The bulk compositions in the MgSiO$_3$–Al$_2$O$_3$ binary system crystallize a

28   phase assemblage of pyrope and corundum at pressures below 27 GPa and an assemblage of

29   bridgmanite and corundum at pressures above 27 GPa regardless of temperatures. The solubility

30   of Al$_2$O$_3$ in bridgmanite and that of MgSiO$_3$ in corundum increase significantly with increasing

31   temperature. The solubility of Al$_2$O$_3$ in bridgmanite increases from 6.7 mol% at 1700 K to 21.8

32   mol% at 2500 K under a constant pressure of 27 GPa. Bridgmanite becomes more aluminous with

33   increasing pressure from 27 to 45 GPa at a given temperature. The MgSiO$_3$ content in corundum

34   increases with increasing pressure at pressure lower than 27 GPa, while it decrease at pressure

35   higher than 27 GPa. Our results suggest that bridgmanite can incorporate a considerably higher

36   Al$_2$O$_3$ content than that of the pyrope composition (25 mol% Al$_2$O$_3$). The present study further

37   suggests that the entire Al$_2$O$_3$ component is accommodated into bridgmanite in the pyrolite lower

38   mantle. However, Al$_2$O$_3$ cannot be fully accommodated into bridgmanite in the coldest parts of

39   subducted slabs in the shallow part of the lower mantle, and therefore additional phases such as

40   MgAl$_2$O$_4$ with calcium ferrite-type structure are necessary to host the excess Al$_2$O$_3$.

41   Keywords: phase relations, bridgmanite, Al$_2$O$_3$, subducted slabs, lower mantle

42

43

44

1. Introduction

Al_2O_3 is the fourth most abundant component in the Earth's mantle [Ringwood, 1975; MacDough and Sun, 1995]. It has been put in the spotlight because of its importance for understanding the mineralogy of the Earth's mantle. Al_2O_3 makes up about 4 wt% in the pyrolite mantle [Sun, 1982] and as much as about 16 wt% in the mid-oceanic ridge basalt (MORB) layers in subducted slabs [Green et al., 1979]. From the upper mantle to the transition zone, Al_2O_3 is primarily accommodated into garnet solid solutions in both pyrolite and MORB compositions [Ringwood, 1967; Irifune, 1987]. Under lower-mantle conditions, the entire Al_2O_3 can be incorporated into bridgmanite, the most abundant mineral in the Earth's mantle, in the pyrolite composition [Irifune, 1994]. On the other hand, bridgmanite cannot accommodate all Al_2O_3 in the MORB composition, and some Al_2O_3 may be accommodated in several Al-rich phases in addition to bridgmanite. [e.g., Irifune and Ringwood, 1993; Ono et al., 2001; Hirose and Fei, 2002]. Moreover, the incorporation of Al_2O_3 can greatly change the crystal chemistry of bridgmanite [e.g., McCammon, 1997]; and thereby significantly affect its physical properties such as elastic properties [Zhang and Weidner, 1999; Brodholt, 2000] and electrical conductivity [Xu et al., 1998]. Therefore, knowledge about the Al_2O_3 effects on the crystal chemistry of bridmanite is of great significance in mineral physics and geophysics, and is seminal for understanding the mineralogy of the lower mantle.

To understand the Al_2O_3 solubility in bridgmanite better, phase relations in the system $MgSiO_3$–Al_2O_3 have been studied extensively at pressure below 27 GPa [Irifune et al., 1996; Kubo and Akaogi, 2000; Hirose et al., 2001; Akaogi et al., 2002]. These studies suggested that bridgmanite coexists with corundum in this system at pressures above 26 GPa. Recently, Liu et al. [2016] demonstrated that the Al_2O_3 solubility in bridgmanite increases from 12 to 29 mol% with

68   increasing pressure from 27 to 52 GPa at a temperature of 2000 K. The pressure dependence at a

69   given temperature, therefore, is now clear, however, the temperature dependence of the Al_2O_3

70   incorporation in bridgmanite is still poorly constrained. Irifune *et al.* [1996] suggested that it

71   increases from 11 mol% at 1760 K to 17 mol% at 2030 K at a pressure of 27 GPa, whereas Kubo

72   and Akaogi [2000] experiments showed an increase from 8 to 13 mol% with increasing

73   temperature from 1670 to 2170 K at almost the same pressure. Therefore, these two studies

74   disagree significantly. Moreover, these studies were conducted only at the lowest pressure

75   conditions for the bridgmanite and corundum coexistence, and no studies have reported the

76   temperature effect on the Al_2O_3 solubility in bridgmanite at higher pressures. Temperatures in the

77   subducted slabs should be significantly lower than in the surrounding mantle, but should approach

78   that of the surrounding mantle due to thermal equilibration [e.g., Ringwood, 1991; Irifune and

79   Ringwood, 1993; Kirby *et al.*, 1996]. Consequently, the temperature effects are vital to constrain

80   the slab dynamics. Nevertheless, our limited knowledge about the temperature dependence of the

81   Al_2O_3 solubility in bridgmanite prevents us from understanding the mineralogy in the deep

82   subducted slabs.

83   The reason for our limited knowledge about the temperature dependence of the Al_2O_3 solubility

84   in bridgmanite is the technical difficulty in high-pressure and high-temperature experiments.

85   Although use of the multi-anvil technique is desired for the determination of phase transitions in

86   multiple-component systems, the pressure ranges of conventional multi-anvil presses are restricted

87   to 27 GPa at high temperatures due to the limited hardness of tungsten carbide (WC) anvils.

88   However, recent development of high-pressure and high-temperature technology using sintered-

89   diamond (SD) anvils in conjunction with *in situ* synchrotron X-ray diffraction observations allows

90   generation of accurate pressures up to 50 GPa routinely at high temperature [Tange *et al.*, 2008;

91   Liu *et al.*, 2016]. By utilizing these techniques, we have investigated phase relations in the system

92    $MgSiO_3$–Al_2O_3 at temperatures up to 2300 K and pressures up to 45 GPa. Based on our new results,

93   the Al_2O_3 solubility in bridgmanite and the host phases of Al_2O_3 in the lower mantle are discussed.

94

2. Experimental methods

96   A fine-grained oxide mixture of composition $En_{50}Cor_{50}$ (En: $MgSiO_3$, Cor: Al_2O_3; the number

97   represents mol%, oxide grain size: 50 nm) and $En_{75}Cor_{25}$ glass (pyrope composition, hereafter

98   denoted as pyropic glass) along the $MgSiO_3$–Al_2O_3 join are used as starting materials. Detailed

99   chemical compositions of those two starting materials were reported in Liu *et al.* [2016] and also

100   examined using an electron probe microanalyzer in the present study (see Table S1 in supporting

101   information). The starting materials were put into graphite or platinum capsules and then heated at

102   800 K for one hour to purge water, and finally put into the cell assembly for the high-pressure and

103   high-temperature experiments.

104   *In situ* X-ray diffraction (XRD) experiments were performed at pressures of 32–49 GPa at

105   temperatures of 1700 and 2000 K using SD anvils with 1.5 mm truncation as second-stage anvils

106   in a DIA-type multi-anvil apparatus at the synchrotron radiation facility, SPring-8 (SPEED-*Mk.*

107   *II*). The experimental facility for *in situ* XRD measurements was described by Katsura *et al.*

108   [2004], and the ultrahigh pressure cell assembly was identical to that of Tange *et al.* [2009], as

109   also shown in **Figure 1**. Pressures were determined based on the *P–V–T* equation of state of Au

110   proposed by Tsuchiya [2003]. General relations between the generated pressure and the press load

111   at temperatures of 300, 1700 and 2000 K are shown in **Figure 2a**. Uncertainties in pressure

112   determination in these *in situ* experiments are approximately ± 0.2 GPa. Sample temperatures were

113   measured with a $W_{97}Re_3$–$W_{75}Re_{25}$ thermocouple, whose hot junction was placed on the bottom of

114   the sample capsule. The sample was compressed to the target pressure and then heated at the target

115   temperature for 3–5 hours. *In situ* XRD patterns were collected for 3–5 hours at the target pressure

116   and temperature. Then, the run was quenched by turning off the electronic power, and the pressure

117   was released slowly over several hours. Finally, *in situ* XRD patterns of the quenched samples

118   were collected under ambient conditions for one hour.

119   We also conducted high-pressure quench experiments at the Bayerisches Geoinstitut,

120   University of Bayreuth, Germany. Runs at pressures below 25 GPa were conducted using WC

121   anvils with a 10.0 mm octahedral pressure medium and 4.0 mm anvil truncation in a 12-MN multi-

122   anvil press with a split-sphere guide block (Sumitomo 1200-ton) [Keppler and Frost, 2005]. One

123   run conducted at a pressure of 35 GPa and a temperature of 2300 K was also performed using WC

124   anvils with 1.5 mm truncation with this press. This pressure at 2300 K was estimated from the FeO

125   content in bridgmanite [Tange *et al.*, 2009], in equilibrium with magnesiowüstite and stishovite,

126   using synthetic $(Mg_{0.7}Fe_{0.3})SiO_3$ pyroxene as a starting material (see Text S1 and Figure S1 in

127   supporting information for pressure calibration details). Runs at pressures above 25 GPa were

128   performed using a 7 and 5.7 mm pressure medium and 3 and 1.5 mm truncation, respectively, in a

129   15-MN press with a DIA-type guide block system (IRIS-15) [Ishii *et al.*, 2016]. **Figure 2b** shows

130   the relationships between pressures and press loads at temperatures of 1700 and 2000 K for IRIS-

131   15, which were calibrated using decomposition of pyrope into aluminous bridgmanite and

132   corundum [Hirose *et al.*, 2001] and the Al_2O_3 solubility in bridgmanite [Liu *et al.*, 2016]. Pressure

133   uncertainties of these quench experiments were on the order of $\pm$ 0.5 GPa.

134   Recovered samples were mounted in epoxy resin, ground to expose the central portion, and

135   then polished using 0.25 μm diamond paste. Phases present in the quench runs were identified

136   using a micro-focused X-ray diffractometer (XRD, Bruker, D8 DISCOVER) equipped with a two-

137   dimensional solid state detector (VANTEC500) and a micro-focus source (IμS) with Co-Kα

138   radiation operated at 40 kV and 500 μA. The X-ray beams were focused to 50 μm using a IFG

139   polycapillary X-ray mini-lens. Textural observation was performed using a LEO1530 scanning

140   electron microscope (SEM) operating at an acceleration voltage of 15–20 kV and a beam current

141   of 10 nA. Chemical compositions of each phase present in the quench runs were determined using

142   a JEOL JXA-8200 electron probe microanalyzer (EPMA) operating at acceleration voltages of 10

143   or 15 kV and a beam current of 5 nA with standards of enstatite for Mg and Si, and pyrope for Al.

3. Results

145   Experimental conditions and phases present in the recovered samples are listed in **Table 1**. At

146   pressures below 25 GPa under temperatures of 1700 and 2300 K, the starting material of $En_{50}Cor_{50}$

147   transforms into pyrope and corundum (see Figure S2 in supporting information), and these

148   corundum can contain significant amounts of the $MgSiO_3$ component (see Table S2 in supporting

149   information). The $MgSiO_3$ solubility in corundum increases with increasing pressure and

150   temperature, e.g., 7.9 ± 0.4 mol% at 20 GPa to 12.6 ± 0.6 mol% at 25 GPa under a temperature of

151   1700 K and 12.6 ± 0.6 mol% at 1700 K to 26.7 ± 0.7 mol% at 2300 K under a pressure of 25 GPa.

152   **Figure 3a** shows representative back-scattered electron images of the quenched samples for

153   $En_{50}Cor_{50}$ oxide mixture and pyropic glass at a pressure of 27 GPa and at temperatures of 1700

154   and 2500 K, respectively. The corresponding XRD profiles in **Figure 3b** and Figure S2 (see

155   supporting information) of these run products are consistent with the presence of a mixture of

156   bridgmanite and corundum. As shown in **Table 2**, the chemical compositions of phases in the

157 recovered samples using these two different starting materials are identical within analytical

158 uncertainties, implying that chemical equilibrium was achieved under these conditions.

159 **Figure 4** illustrates the solubility of Al_2O_3 in bridgmanite and that of $MgSiO_3$ in corundum,

160 respectively, as a function of temperatures at a constant pressure of 27 GPa as determined in the

161 present and previous studies [Irifune *et al.*, 1996; Kubo and Akaogi, 2000; Akaogi *et al.*, 2002;

162 Liu *et al.*, 2016]. The Al_2O_3 solubility in bridgmanite apparently increases linearly with

163 temperature (**Figure 4a**), and this tendency is similar to that for FeO in bridgmanite reported by

164 Fei *et al.* [1996]. In the present study, the Al_2O_3 solubility in bridgmanite reaches 21.7 ± 0.6 mol%

165 at 2500 K. The best fit of all the experimental data to a linear function yields the relation of

166 $X_{Al_2O_3} = -0.19 \ (2) + 1.60 \ (1) \cdot 10^{-5} \cdot T$, where $X_{Al_2O_3}$ is the Al_2O_3 solubility in mole percent

167 in bridgmanite at a pressure of 27 GPa, T is the temperature in Kelvin and the number in

168 parentheses represents standard deviations for the last digit. This equation suggests that

169 bridgmanite with a pyrope composition, i.e., with 25 mol% Al_2O_3, could form at a temperature of

170 approximately 2750 K at this pressure. **Figure 4b** demonstrates that the $MgSiO_3$ solubility in

171 corundum also increases with increasing temperature at 27 GPa, and reaches as much as $38.0 \pm$

172 0.5 mol% at 2500 K in the present study. The values for corundum reported by Irifune *et al.* [1996]

173 and Kubo and Akaogi [2000] are, however, larger than those in the present study at given the same

174 temperature. One possible reason for this discrepancy may be related to the low resolution of the

175 EPMA due to the small grain sizes of corundum and bridgmanite obtained in earlier studies. The

176 grain size of phases in the runs at 27 GPa in our study is considerably larger than 3 μm in **Figure**

177 **3**, the composition is thus accurate due to the grain size is larger than the resolution of the EPMA.

178 **Figure 5** shows selected back-scattered electron images of the quenched samples for the

179 $En_{50}Cor_{50}$ oxide mixture and pyropic glass at pressures higher than 27 GPa. Aluminous

180   bridgmanite, corundum, and Au pressure markers are found in these *in situ* runs. **Figure 6a** shows

181   *in situ* synchrotron XRD patterns for $En_{50}Cor_{50}$ under 31.9–48.5 GPa at 1700 K. In all XRD

182   patterns, the major peaks are assigned to bridgmanite, corundum, and Au, while the other minor

183   ones can be assigned to stishovite, surrounding diamond capsules, and MgO disks. For the product

184   recovered from the run at 48.5 GPa and 1700 K for two hours, the element mapping by means of

185   analytical transmission electron microscopy (ATEM) reported in Figure S3 further confirms that

186   bridgmanite, corundum and trace amount of stishovite coexist in this sample. However, the TEM

187   mapping combined with energy dispersive X-ray spectroscopy (EDXS) suggest the compositions

188   of these phases are not homogeneous, which may be caused by the unreached chemical equilibrium

189   due to the short heating time as a result of the instability of the heater in this run (Text S2). **Figure**

190   **6b** shows the XRD pattern of the S6615 run. It is found that perovskite with a $LiNbO_3$ structure

191   with a rhombohedral symmetry coexists with corundum at 35 GPa and 2300 K. EPMA analysis

192   on this $LiNbO_3$ structure demonstrate that it contains 27.3 ± 0.3 mol% of Al_2O_3. Its lattice

193   parameters (a = b = 4.849 (1); c = 12.712 (10)) are slightly higher than those (a = b = 4.783 (2); c

194   = 12.680 (11)) for the same phase with the pyrope composition obtained by Liu *et al.* [2016],

195   which can be explained by a higher Al_2O_3 content in the present study than that of the latter study.

196   The present result further confirms that bridgmanite with the Al_2O_3 content higher than 25 mol%

197   would transform into the $LiNbO_3$ structure upon releasing pressure, which is consistent with the

198   result of earlier works [Funamori *et al.*, 1997; Miyajima *et al.*, 1999; Liu *et al.*, 2016; Ishii *et al.*,

199   2017]. However, Liu *et al.* [2016] also found that the bridgmanite phase containing 29.5 mol%

200   exists in the M1677 run, and this difference may be caused by the effect of nanoscale grain size

201   with a higher surface energy as suggested by Liu et al. [2016].

202   Two experiments were performed using the pyropic glass as the starting material at pressures

203   of 42.3 and 44.5 GPa and at temperatures of 2000 and 1700 K, respectively (**Figure 6c**). *In situ*

204   XRD observations suggest that the phases present in these runs are bridgmanite and corundum. In

205   particular, a trace amount of corundum coexists with bridgmanite at 42.3 GPa and 2000 K, which

206   is also confirmed by the back-scattered electron observations in **Figure 5d**. Composition analysis

207   on several large grains (3 μm) suggests that bridgmanite in this recovered sample contains $21.9 \pm$

208   0.6 mol% Al_2O_3. These results suggest that bridgmanite with the pyrope composition should form

209   at a slightly higher pressure than 42.3 GPa, providing more convincing evidence that the Al_2O_3

210   solubility exceeds 25 mol% above 45 GPa at 2000 K [Liu *et al.*, 2016]. The composition of

211   bridgmanite in M1677 run (51.8 GPa and 2000 K) in Liu *et al.* [2016] was estimated based on

212   relations between unit-lattice parameters and Al_2O_3 contents. Here, instead, we determined the

213   accurate compositions of the phases in M1677 run by adjusting the EPMA analytical beam-size to

214   1 μm, and found that the Al_2O_3 content in bridgmanite is 29.5 ± 0.7 mol%, in excellent agreement

215   with that (29 ± 5 mol%) estimated from its unit-cell lattice parameters. Therefore, for the sample

216   at 44.5 GPa and 1700 K, since the grain size of this run product is smaller than 1 μm, the Al_2O_3

217   content in bridgmanite has been estimated to be approximately 16 ± 3 mol% from its unit-cell

218   lattice parameters (see Table S3 in supporting information) [Liu *et al.*, 2016].

219   The lattice parameters and molar volume of aluminous bridgmanite and corundum in the

220   present and previous studies [D'Amour *et al.*, 1978; Weng *et al.*, 1981; Ito *et al.*, 1978, 1998;

221   Irifune *et al.*, 1996; Kubo and Akaogi, 2000; Yagi *et al.*, 2004; Walter *et al.*, 2004; Liu *et al.*, 2016]

222   are shown as a function of the Al_2O_3 and $MgSiO_3$ content, respectively, in **Figure 7**. It is clearly

223   seen that the value of a, b, and c-axis of aluminous bridgmanite increases almost linearly with

224   increasing Al_2O_3 content within analytical uncertainties in **Figure 7a**. A linear function is adapted

225   to the present data and those of Liu et al. [2016], and got the following equations:

226                         $a = 4.777 (\pm 0.001) + 0.014 (\pm 0.007) \times \chi_{Al2O3}$

227                         $b = 4.928 (\pm 0.002) + 0.109 (\pm 0.011) \times \chi_{Al2O3}$

228                         $c = 6.900 (\pm 0.002) + 0.236 (\pm 0.012) \times \chi_{Al2O3}$

229   where χ_{Al2O3} represents the mole fraction of the Al_2O_3 in bridgmanite ($0 \leq \chi_{Al2O3} < 0.30$). These

230   equations agree well with those obtained in Irifune *et al.* [1996] except that the slope for the change

231   in lattice parameters with the Al_2O_3 content is slightly smaller than that obtained in the latter study.

232   The same equation to corundum produces following results (**Figure 7b**):

233                         $a = b = 4.764 (2) + 0.023(9) \times \chi_{MgSiO3}$

234                         $c = 12.991 (6) + 0.136 (3) \times \chi_{MgSiO3}$

235   where χ_{MgSiO3} represents the mole fraction of the $MgSiO_3$ in bridgmanite ($0 \leq \chi_{MgSiO3} < 0.4$). The

236   molar volume of bridgmanite increases almost linearly with increasing Al_2O_3 contents (**Figure 7c**),

237   and can be best expressed as $V(x) = 1.35 (8) \cdot x + 24.468 (12)$, where x is the mole

238   fraction of Al_2O_3 ($0 \leq x < 0.3$), and the number in parentheses represents standard deviations for

239   the last digit. It can be also seen in **Figure 7d** that the molar volume of corundum increases slightly

240   with increasing $MgSiO_3$ contents, expressed as $V(x) = 0.42 (7) \cdot x + 25.64 (1)$, where

241   x is the mole fraction of $MgSiO_3$ ($0 \leq x < 0.4$). The effect of $MgSiO_3$ contents on the volume of

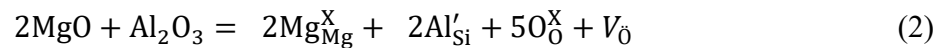242   corundum is significantly smaller than that of Al_2O_3 for bridgmanite.

243   **Discussion**

11

4.1 Al substitution mechanism in bridgmanite

It is thought that Al is incorporated into the crystal structure of bridgmanite through two types of possible substitution mechanisms [Hirsch and Shankland, 1991; Richmond and Brodholt, 1998; Navrotsky *et al.*, 1999, 2003; Andrault *et al.*, 2007]: (1) the charge-coupled substitution: substituting of Mg and Si by Al,

$$Al_2O_3 = Al_{Mg}^{\cdot} + Al_{Si}' + 3O_O^X \tag{1}$$

(2) the oxygen vacancy substitution: substitution of Al into the Si site and creating an oxygen vacancy,

$$2MgO + Al_2O_3 = 2Mg_{Mg}^X + 2Al_{Si}' + 5O_O^X + V_{\ddot{O}} \tag{2}$$

where subscripts indicate the site and superscripts indicate the charge (X) for neutral, ($'$) for negative charge, ($\cdot$) for a positive charge (point defect notation from Kröger and Vink [1956]). **Figure 8a** shows the cation ratio between Mg and Si (Mg/Si) as a function of the Al pfu in aluminous bridgmanite in the present study and previous works [Irifune et al., 1996; Kubo and Akaogi, 2000; Liu et al., 2016]. This ratio is mainly along the trend line for the charge-coupled substitution within the analytical uncertainties, while it is far below the trend line of the oxygen vacancy substitution, suggesting the charge-coupled substitution dominates in the aluminous bridgmanite. This result is well consistent with some earlier experimental works on aluminous bridgmanite [Stebbins *et al.*, 2001; Walter *et al.*, 2006]. **Figure 8b** further supports this idea due to the value of Si cation in the bridgmanite is almost along the trend line for the charge-coupled substitution. However, XRD patterns in such as **Figure 3** and **6** demonstrate that trace stishovite

264 coexisted with bridgmanite in some runs, suggesting that trace amounts of the oxygen vacancy

265 substitution may also occurs in the aluminous bridgmanite.

4.2 Phase diagram in the MgSiO$_3$–Al$_2$O$_3$ system

267   **Figure 9** shows the phase diagram of the garnet-corundum-bridgmanite transition in the

268 system MgSiO$_3$–Al$_2$O$_3$ at pressures of 20–45 GPa and at temperatures of 1700, 2000 and 2300 K.

269 The pressure of the disproportionation of pyrope at various temperatures is estimated from the runs

270 at 1700 and 2000 K in **Figure 2b** together with the study by Hirose *et al.* [2001]. At pressures

271 lower than 25 GPa at these three temperatures, En$_{50}$Cor$_{50}$ crystallizes an assemblage of pyrope

272 plus corundum. Depending on temperatures, pyrope would decompose into bridgmanite and

273 corundum at 25.5–27 GPa. At a pressure of 27 GPa at these temperatures, the two-phase field of

274 bridgmanite and corundum is thus stabilized. At this pressure, the Al$_2$O$_3$ solubility in bridgmanite

275 increases from 6.7 ± 0.5 to 21.7 ± 0.6 mol% with increasing temperature from 1700 to 2500 K. In

276 the same temperature range, the MgSiO$_3$ solubility in corundum also increases from 16.3 ± 0.8 to

277 38.0 ± 0.5 mol%. Therefore, the two-phase region of bridgmanite and corundum becomes narrower

278 with increasing temperature. The shrinkage of the two-phase region also occurs at higher pressures

279 with increasing temperature. These shrinkages are related to the mixing entropy and enthalpy

280 [Panero *et al.*, 2006].

281   At a constant temperature, bridgmanite becomes more aluminous with increasing pressure. The

282 Al$_2$O$_3$ solubility in bridgmanite increases from 6.7 ± 0.5 to 16 ± 3 mol% with increasing pressure

283 from 27 to 44.5 GPa at 1700 K, from 12.2 ± 0.3 to 21.9 ± 0.6 mol% for pressures from 27 to 42.3

284 GPa at 2000 K, and from 19.2 ± 0.4 to 27.3 ± 0.3 mol% for pressures from 27 to 35 GPa at 2300

285 K. In contrast, the MgSiO$_3$ content in corundum decreases with increasing pressure, e.g., $16.4 \pm$

13

286   0.8 to 7 $\pm$ 4.0 mol% at 1700 K and 32.2 $\pm$ 0.4 to 21.7 $\pm$ 0.5 mol% at 2300 K. Both Al_2O_3 and

287    $MgSiO_3$ enrichment in bridgmanite and corundum, respectively, can be explained by the cation

288   substitution in the crystal structure of bridgmanite and corundum [e.g., Brodholt, 2000; Kubo and

289   Akaogi, 2000; Walter *et al.*, 2004; Liu *et al.*, 2016].

290   Increasing proportions of the Al_2O_3 and $MgSiO_3$ components in bridgmanite and corundum,

291   respectively, increases the lattice parameters of each of the phases (**Figure 7a and 7b**). The lower

292   molar volume of bridgmanite (about 64% of the corundum volume), results in the partitioning of

293   alumina into bridgmanite coexisting with increasingly alumina-rich corundum as pressure

294   increases, accompanied by an increased ratio of bridgmanite to corundum. A simple lever rule

295   analysis of the phase diagram in **Figure 9** rationalizes the variations in phase compositions and

296   proportions as a function of pressure. The opposite situation is seen for the coexisting garnet-

297   corundum assemblage. With bulk system compositions within the two-phase field, the garnet is

298   fixed at the pyrope composition (25 mol% Al_2O_3), and the proportion of garnet decreases with

299   increasing pressure as the MgSiO3 content of the coexisting corundum increases.

300   The phase boundaries between bridgmanite and two-phase region of bridgmanite and

301   corundum at 2000 and 2300 K, respectively, reported in the present study are close to those

302   obtained using thermodynamics calculation by Panero *et al.* [2006] and prediction by Irifune and

303   Tsuchiya [2007], respectively, although the rate of the increasing Al_2O_3 content in bridgmanite

304   with increasing pressure in the present study is slightly larger than that in the calculation and

305   prediction. On the contrary, the phase boundary between this two-phase region and corundum is

306   largely different from that obtained in the mentioned calculation and prediction, which may be

307   caused by the poorly constrained thermodynamics parameters of corundum.

14

308   We note that the compositions of the phases in the recovered samples from experiment runs

309   with the pyropic glass as the starting material are identical to those recovered from experiments

310   for the $En_{50}Cor_{50}$ oxide mixture within analytical errors, as shown in **Figure 9**. This fact suggests

311   that chemical equilibrium was achieved in our study. This idea is also supported by the identical

312   compositions of two phases obtained from a shorter (5 hours, IRIS 232) and longer (15 hours,

313   IRIS266) heating duration at the same conditions.

4.3 Host phases of Al_2O_3 in the lower mantle

315   Here, we discuss the Al_2O_3 host phases in the lower mantle at depths between 750 and 1250

316   km, corresponding to pressures of 27 and 50 GPa, respectively. The representative lower-mantle

317   temperatures at these depths are approximately 2000 K [Katsura *et al.*, 2010]. Temperatures in

318   subducted slabs under lower-mantle pressures are unknown, but must be substantially lower than

319   these ambient-mantle temperatures [Kirby *et al.*, 1996].

320   The pyrolite composition contains about 4 wt% of Al_2O_3 [Sun, 1982]. The phase diagram in

321   **Figure 9** suggests that bridgmanite can contain 13 and 29 wt% of Al_2O_3 at a depth of 750 and

322   1250 km, respectively. Therefore, all Al_2O_3 should be accommodated in bridgmanite in the

323   majority of the lower mantle, as already suggested by Irifune [1994]. In subducted slabs, the

324   estimated temperature profile may be at least 300 K lower than the ambient mantle depending on

325   whether the slabs are young or old [Kirby *et al.*, 1996]. At these lower temperatures, the Al_2O_3

326   solubility in bridgmanite is about 7 and 17 wt%, at depth of 750 and 1250 km, respectively.

327   Moreover, the MORB parts of slabs have an Al_2O_3 content up to 16 wt% [Green *et al.*, 1979].

328   Therefore, all Al_2O_3 cannot be fully accommodated in the cold peridotite parts of subducted slabs

329   at 750 km depth, and one additional aluminous phase such as the CF (a $MgAl_2O_4$ dominated phase

15

330 with a calcium ferrite-type structure) [Irifune et al., 1991] may therefore form to host the excess

331 Al_2O_3 in this region. At a depth of 1250 km, however, the Al_2O_3 solubility exceeds 16 wt% even

332 at lower temperature, and therefore CF is expected to disappear with increasing subduction depth.

333 Although phase relations in the $MgSiO_3$–Al_2O_3 system have been determined as a function of

334 pressure and temperature by our advanced multi-anvil experiments using SD technology and in

335 situ synchrotron XRD, the chemical systems in the lower mantle and subducted slabs are more

336 complicated. The $FeSiO_3$ and $FeAlO_3$ components may change the Al_2O_3 solubility in bridgmanite

337 [e.g., Kesson et al., 1995; Miyajima et al., 1999; Nishio-Hamane et al., 2005]. In particular, the

338 dominance of the $FeAlO_3$ component in bridgmanite should change the Al_2O_3 solubility relative

339 to that in the $MgSiO_3$–Al_2O_3 system [Miyajima et al., 1999; Nishio-Hamane et al., 2005]. The

340 presence of K_2O and Na_2O components would stabilize CF and NAL phases as host phases for the

341 Al_2O_3 component in MORB slabs [e.g., Irifune and Ringwood, 1993; Miyajima et al., 1999, 2001;

342 Ono et al., 2001; Hirose and Fei, 2002; Litasov and Ohtani, 2005], which would decrease the Al_2O_3

343 contents in bridgmanite. Therefore, further studies of phase relations in Fe-, K- and Na-bearing

344 systems are needed to constrain the host phases of Al_2O_3 and their compositions in the lower

345 mantle.

4. Conclusion

347 Phase relations in the system $MgSiO_3$–Al_2O_3 were determined at pressures between 27 and 45

348 GPa and temperatures of 1700, 2000 and 2300 K. At pressure just below 27 GPa, phase

349 assemblages of garnet+bridgmanite and garnet + corundum are stable for compositions of less and

350 more than 25 mol% Al_2O_3. At pressures above 27 GPa, another assemblage of bridgmanite and

351 corundum is stabilized for bulk compositions within the two-phase field. The Al_2O_3 and $MgSiO_3$

16

352 solubility in bridgmanite and corundum, respectively, increases with increasing temperature.

353 Moreover, bridgmanite becomes more aluminous with increasing pressure and can contain a

354 considerably higher Al_2O_3 component than the pyrope composition. In contrast, the $MgSiO_3$

355 solubility in corundum decreases with increasing pressure. Additionally, Al_2O_3 incorporation

356 significantly increases the molar volume of bridgmanite, while $MgSiO_3$ incorporation only slightly

357 increases the volume of corundum. The present study supports the idea that the entire Al_2O_3 content

358 of 4 wt% can be accommodated into bridgmanite in the pyrolitic lower mantle. On the other hand,

359 the Al_2O_3 solubility in bridgmanite is insufficient to accommodate the entire alumina inventory in

360 subducted slabs in the uppermost part of the lower mantle, owing to the low temperatures and

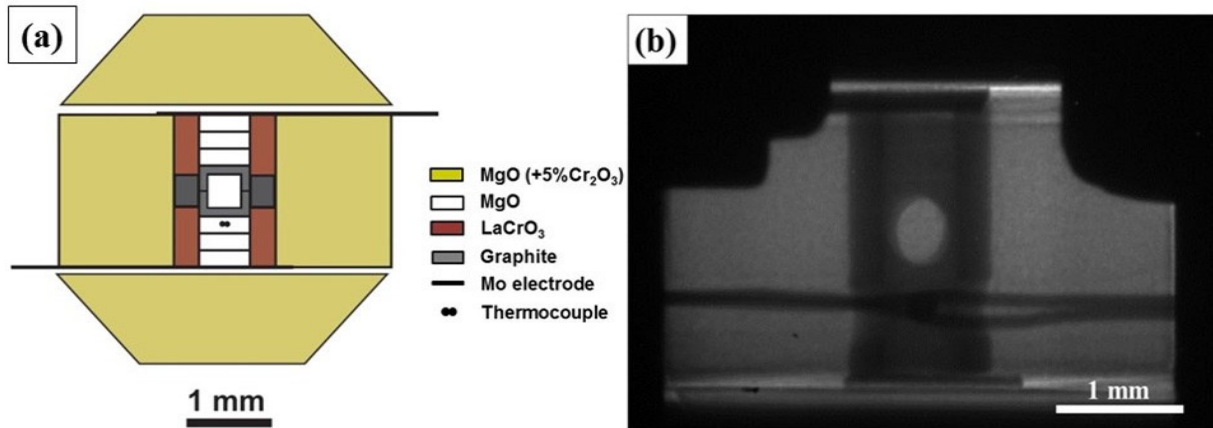361 limited pressures, and additional Al phases may therefore be present at these conditions.

362

379

380 **References**

381 Akaogi, M., A. Tanaka, and E. Ito (2002), Garnet-ilmenite-perovskite transitions in the system $Mg_4Si_4O_{12}$–
382     $Mg_3Al_2Si_3O_{12}$ at high pressures and high temperatures: phase equilibria, calorimetry and implications
383   for mantle structure. Phys. Earth Planet. Inter. 132, 303–324.

384 Andrault, D., N. Bolfan-Casanova, M. Bouhifd, N. Guignot, and T. Kawamoto (2007), The role of Al-
385   defects on the equation of state of Al-(Mg, Fe)SiO_3 perovskite, Earth Planet. Sci. Lett. 263 (3–4), 167–
386   179.

387 Brodholt, J. P. (2000), Pressure-induced changes in the compression mechanism of aluminous perovskite
388   in the Earth's mantle, Nature, 407, 620–622.

389 D'Amour, H., D. Schiferl, W. Denner, H. Schulz, and W. B. Holzapfel (1978), High-pressure single-crystal
390   structure determinations for ruby up to 90 kbar using an automatic diffractometer P = 0 kbar. J. Appl.
391   Phys., 49, 4411–4416.

392 Hirose, K., Y. Fei, T. Yagi, and K. Funakoshi (2001), In situ measurements of the phase transition boundary
393   in $Mg_3Al_2Si_3O_{12}$: implications for the nature of the seismic discontinuities in the Earth's mantle. Earth
394   Planet. Sci. Lett. 184, 567–573.

395 Hirose, K., and Y. Fei (2002), Subsolidus and melting phase relations of basaltic composition in the
396   uppermost lower mantle. Geochim. Cosmochim. Acta 66, 2099–2108.

397 Hirsch, L. M., and T. J. Shankland, (1991), Point defects in silicate perovskite. Geophys. Res. Lett.18,
398   1305–1308.

399 Fei, Y., Y. Wang, and L. W. Finger (1996), Maximum solubility of FeO in (Mg,Fe)SiO_3 perovskite as a
400   function of temperature at 26 GPa: Implication for the FeO content in the lower mantle. J. Geophys.
401   Res., 101, 11525–11530.

402 Funamori, N., Yagi, T., Miyajima, N., Fujino, K. (1997), Transformation in garnet: from orthorhombic
403   perovskite to $LiNbO_3$ phase on release of pressure. Science 275, 513–515.

404 Irifune, T. (1987), An experimental investigation of the pyroxene-garnet transformation in a pyrolite
405   composition and its bearing on the constitution of the mantle. Phys. Earth Planet. Inter. 45, 324–336.

406 Irifune, T., K. Fujino, and E. Ohtani (1991), A new high-pressure form of $MgAl_2O_4$ Nature 349, 409-411.

18

407   Irifune, T., and A.E. Ringwood (1993), Phase transformations in subducted oceanic crust and buoyancy
408   relationships at depths of 600–800 km in the mantle. Earth Planet. Sci. Lett., 117, 101–11.

409   Irifune, T. (1994), Absence of an aluminous phase in the upper part of the Earth's lower mantle. Nature
410   370, 131–133.

411   Irifune, T., T. Koizumi, and J. Ando (1996), An experimental study of the garnet-perovskite transformation
412   in the system $MgSiO_3$–$Mg_3Al_2Si_3O_{12}$. Phys. Earth Planet Inter. 96, 147–157.

413   Irifune, T. and T. Tsuchiya (2007), Phase transition and mineralogy of the lower mantle, in: G.D. Price
414   (Ed.), Treatise on Geophysics, vol. 2 Elsevier, pp. 33–62.

415   Ishii, T., L. Shi, R. Huang, N. Tsujino, D. Druzhbin, R. Myhill, Y. Li, L.Wang, T. Yamamoto, N. Miyajima,
416   T. Kawazoe, N. Nishiyama, Y. Higo, Y. Tange, and T. Katsura (2016), Generation of pressure over 40
417   GPa using Kawai-type multi–anvil press with tungsten carbide anvils. Rev. Sci. Instr. 87, 024501–1–
418   024501–6.

419   Ishii, T., R. Sinmyo, T. Komabayashi, T. Boffa-Ballaran, T. Kawazoe, N. Miyajima, K. Hirose and T.
420   Katsura (2017), Synthesis and crystal structure of $LiNbO_3$-type $Mg_3Al_2Si_3O_{12}$: A possible indicator of
421   shock conditions of meteorites, *Am. Min.* 102, 1947–1952.

422   Ito, E., and Y. Matsui (1978), Synthesis and crystal-chemical characterization of $MgSiO_3$ perovskite. Earth.
423   Planet. Sci. Lett. 38, 443–450.

424   Ito, E., A. Kubo, T. Katsura, M. Akaogi, and T. Fujita (1998), High-pressure transformation of pyrope
425   ($Mg_3Al_2Si_3O_{12}$) in a sintered diamond cubic anvil assembly. Geophys. Res. Lett. 25, 821–824.

426   Green, D. H., W. O. Hibberson, and A. L. Jaques (1979), Petrogenesis of mid-ocean ridge basalts. In:
427   McElhinny MW (ed.) The Earth: Its Origin, Structure and Evolution, pp. 269–299. London: Academic
428   Press.

429   Katsura, T., K. Funakoshi, A. Kubo, N. Nshiyama, Y. Tange, Y. Sueda, T. Kubo, and W. Utsumi (2004),
430   A large-volume high-pressure and high-temperature apparatus for in situ X-ray observation, SPEED-
431   Mk.II. Phys. Earth Planet. Inter. 143–144, 497–506.

432   Katsura, T., A. Yoneda, D. Yamazaki, T. Yoshino, E. Ito (2010), Adiabatic temperature profile in the
433   mantle. Phys. Earth Planet. Inter. 183, 212–218.

434   Kesson, S. E., J. D. Fitzgerald, J. M. G. Shelley, and R. L.Withers (1995), Phase relations, structure and
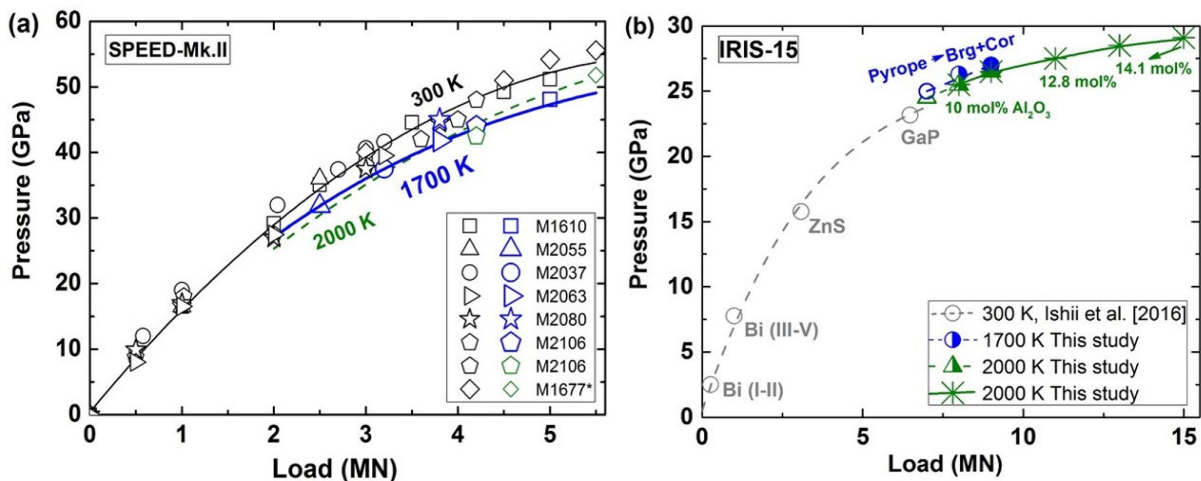435   crystal chemistry of some aluminous perovskites. Earth Planet. Sci. Lett. 134, 187–201.

436　Keppler, H., and D. J. Frost (2005), Introduction to minerals under extreme conditions. In: R. Miletich
437　　　(Ed.), EMU Notes in Mineralogy, 7, Eötvös University Press, Budapest, pp. 1–30.

438　Kirby, S. H., S. Stein, E. A. Okal, and D. C. Rubie (1996), Metastable mantle phase transformations and
439　　　deep earthquakes in subducting oceanic lithosphere, Rev. Geophys. 34, 261– 306.

440　Kröger, F.A. and H. H. Vink (1956), Relations between the concentrations of imperfections in crystalline
441　　　solids. Solid State Phys. 307–435.

442　Kubo, A., and M. Akaogi (2000), Post–garnet transitions in the system $Mg_4Si_4O_{12}$–$Mg_3Al_2Si_3O_{12}$ up to 28
443　　　GPa: phase relations of garnet, ilmenite and perovskite. Phys. Earth Planet Int. 121, 85–102.

444　Liu, Z. D., T. Irifune, M., Nishi, Y. Tange, T. Arimoto, and T. Shinmei (2016), Phase relations in the system
445　　　$MgSiO_3$–Al_2O_3 up to 52 GPa and 2000 K. Phys. Earth Planet Inter. 257, 18–27.

446　Litasov, K. D., and E. Ohtani (2005), Phase relations in hydrous MORB at 18−28 GPa: Implications for

447　　　heterogeneity of the lower mantle, Phys. Earth Planet. Inter. 150, 239−263.

448　McCammon, C. A. (1997), Perovskite as a possible sink for ferric iron in the lower mantle. Nature 387,
449　　　694–696.

450　McDonough, W. F., and S.-S. Sun (1995), The composition of the Earth, Chem. Geol., 120, 223–253.

451　Miyajima, N., K. Fujino, N. Funamori, T. Kondo, and T. Yagi (1999), Garnet-perovskite transformation
452　　　under conditions of the Earth's lower mantle: an analytical transmission electron microscopy study.
453　　　Phys. Earth Planet. Inter. 116, 117–131.

454　Miyajima, N., T. Yagi, K. Hirose, T. Kondo, K. Fujino, and H. Miura (2001), Potential host phase of
455　　　aluminium and potassium in the Earth's lower mantle. American Mineralogist, 86, 740–746.

456　Navrotsky, A. (1990), A lesson from ceramics. Science 284, 1788–1789.

457　Navrotsky, A., Schoenitz, M., Kojitani, H., Xu, H., Zhang, J., Weidener, D. J., Jeanloz, R. (2003),
458　　　Aluminum in magnesium silicate perovskite: formation, structure, and energetics of magnesium-rich
459　　　defect solid solutions. J. Geophys. Res. 108, 2330.

460   Nishio-Hamane, D., T. Nagai, K. Fujino, Y. Seto, and N. Takafuji (2005), Fe^{3+} and Al solubilities in

461        $MgSiO_3$ perovskite: implication of the $Fe^{3+}AlO_3$ substitution in $MgSiO_3$perovskite at the lower mantle

462   condition. Geophys. Res. Lett., 32, L16306.

463   Ono, S., E. Ito, and T. Katsura (2001), Mineralogy of subducted basaltic crust (MORB) from 25 to 37 GPa,

464   and chemical heterogeneity of the lower mantle. Earth Planet. Sci. Lett. 190, 57–63.

465   Panero, W. R., S. Akber-Knutson, and L. Stixrude (2006), Al_2O_3 incorporation in $MgSiO_3$ perovskite and

466   ilmenite. Earth Planet. Sci. Lett. 252, 152–161.

467   Richmond, N. C., and J. P. Brodholt, (1998) Calculated role of aluminum in the incorporation of ferric iron

468   into magnesium silicate perovskite, Am. Mineral. 83, 947–951.

469   Ringwood, A. E. (1967), The pyroxene-garnet transformation in the Earth's mantle. Earth Planet. Sci. Lett.

470   2, 255–63.

471   Ringwood, A. E. (1975), Composition and Petrology of the Earth's Mantle. McGraw–Hill, New York.

472   Ringwood, A. E. (1991), Phase transformations and their bearing on the constitution and dynamics of the

473   mantle. Geochim. Cosmochim. Acta, 55, 2083–2110.

474   Shcheka, S. S., M. Wiedenbeck, D. J. Frost, and H. Keppler, (2006), Carbon solubility in mantle minerals.

475   Earth Planet. Sci. Lett., 245, 730–742.

476   Stebbins, J. F., S. Kroeker, and D. Andrault, (2001), The mechanism of solution of aluminum oxide in

477        $MgSiO_3$ perovskite. Geophys. Res. Lett. 28, 615-618.

478   Sun, S. (1982), Chemical composition and the origin of the Earth's primitive mantle. Geochimica et

479   Cosmochimica Acta 46, 179–192.

480   Tange, Y., T. Irifune, and K. Funakoshi. (2008), Pressure generation to 80 GPa using multianvil apparatus

481   with sintered diamond anvils. High Pressure Res., 28, 245−254.

482   Tange, Y., E. Takahashi, Y. Nishihara, K. Funakoshi, and N. Sata (2009), Phase relations in the system

483        $MgO–FeO–SiO_2$ to 50 GPa and 2000°C: An application of experimental techniques using multianvil

484   apparatus with sintered diamond anvils. J. Geophys. Res. 114, B02214.

485 Tsuchiya, T. (2003), First–principles prediction of the P–V–T equation of state of gold and the 660–km
486   discontinuity in Earth's mantle. J. Geophys. Res. 108, B10.

487 Van Cappellen, V., and J. C. Doukhan, (1994), Quantitative transmission X-ray microanalysis of ionic
488   compounds. Ultramicroscopy, 53, 343–349.

489 Walter, M., A. Kubo, T. Yoshino, J. Brodholt, K. T. Koga, and Y. Ohishi (2004), Phase relations and
490   equation-of-state of aluminous Mg-silicate perovskite and implications for Earth's lower mantle. Earth
491   Planet. Sci. Lett. 222, 501–516.

492 Walter, M., R. G. Trønnes, L. S. Armstrong, O. Lord, W. A. Caldwell, A. M. Clark (2006), Subsolidus
493   phase relations and perovskite compressibility in the system $MgO–AlO_{1.5}–SiO_2$ with implications for
494   Earth's lower mantle. Earth Planet. Sci. Lett. 248,77–89.

495 Weng, K., H. K. Mao, and P. M. Bell (1981), Lattice parameters of the perovskite phase in the system
496      $MgSiO_3–CaSiO_3 –Al_2O_3$. Carnegie Inst. Washington, Year Book. 81, 273–277.

497 Xu, Y., C. A. McCammon, and B. T. Poe (1998), The effect of alumina on the electrical conductivity of
498   silicate perovskite. Science, 282, 922–924.

499 Yagi, T., K. Okabe, N. Nishiyama, A. Kubo, and T. Kikegawa (2004), Complicated effects of aluminum
500   on the compressibility of silicate perovskite. Phys. Earth Planet. Inter. 143–144, 81–89.

501 Zhang, J., and D. J. Weidner (1999), Thermal equation of state of aluminium-enriched silicate perovskite.
502   Science, 284, 782–784.
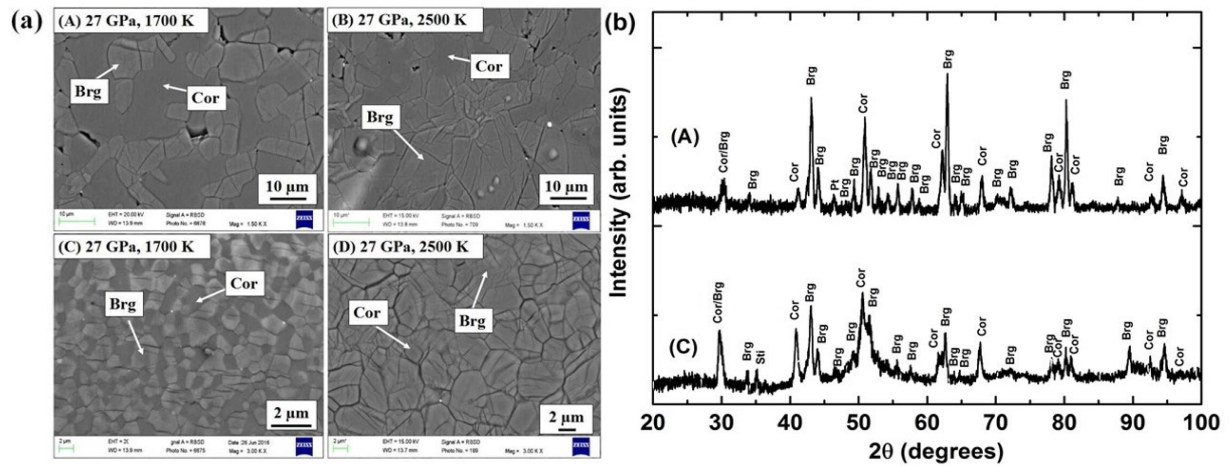
503

504

505

506

507

508

509 **Figure 1.** (a) Schematic illustration of the high-pressure cell assembly for *in situ* SD experiments. (b) X-ray radiographic images

510 of SD cell assembly at ambient conditions. The hot junction of the thermocouple was placed at the bottom of the capsule, and the

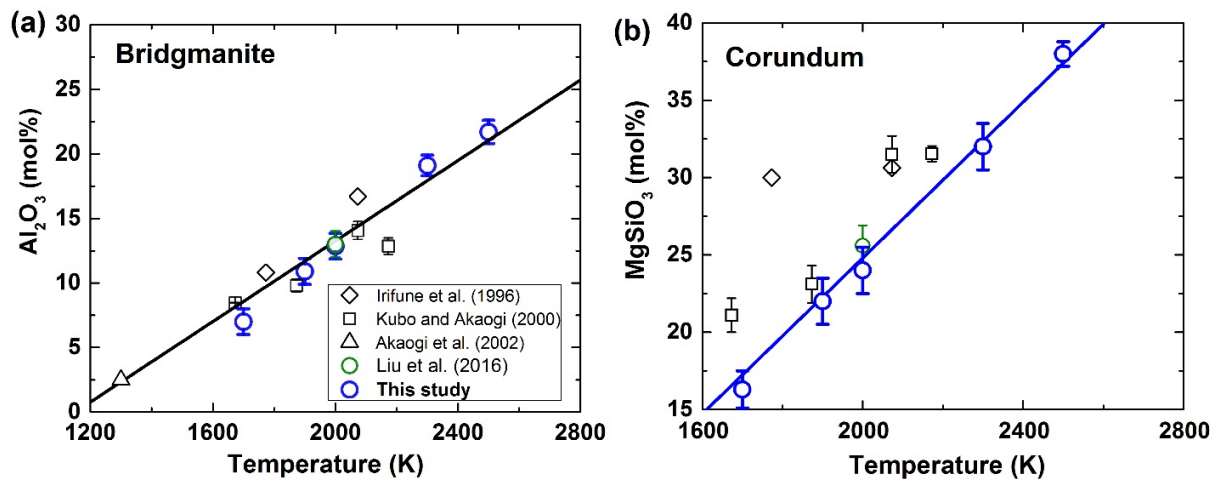511 diffracted X-ray signals were acquired through the graphite windows.

512

513 **Figure 2. (a)** Generated pressure versus the press load at room temperature (300 K, open black symbols), 1700 (blue symbols, this

514 study) and 2000 K (green symbols, this study) for *in situ* XRD experiments using a DIA-type apparatus (SPEED-MK.II) at SPring–

515 8. The black and blue solid lines represent the fitting results of the data at 300 and 1700 K in the present study, and that at 2000 K

516 together with the symbol of M1677 is from Liu *et al.* [2016]. **(b)** Pressure calibration curve at 1700 (circle) and 2000 K (triangle)

517 for the IRIS–15 multi-anvil apparatus, based on the phase transition of pyrope to bridgmanite and corundum [Hirose *et al.*, 2001]

518 and various Al_2O_3 solubility (mol%) in bridgmanite at 2000 K [Liu *et al.*, 2016]. Pressure calibration at room temperature condition

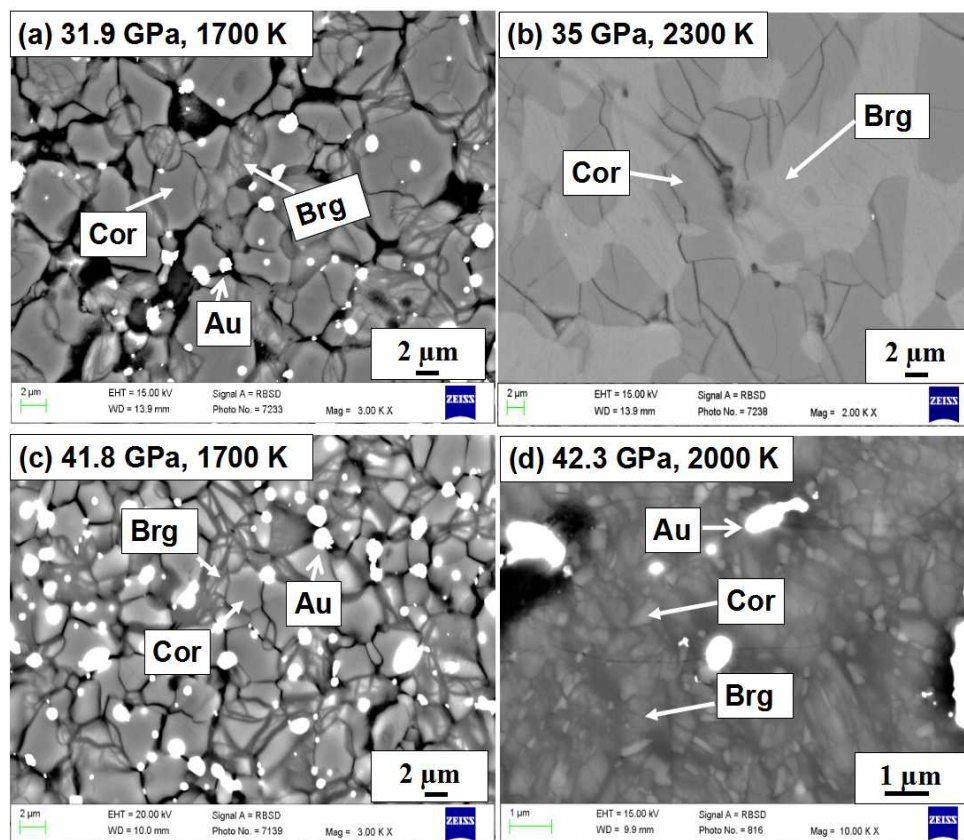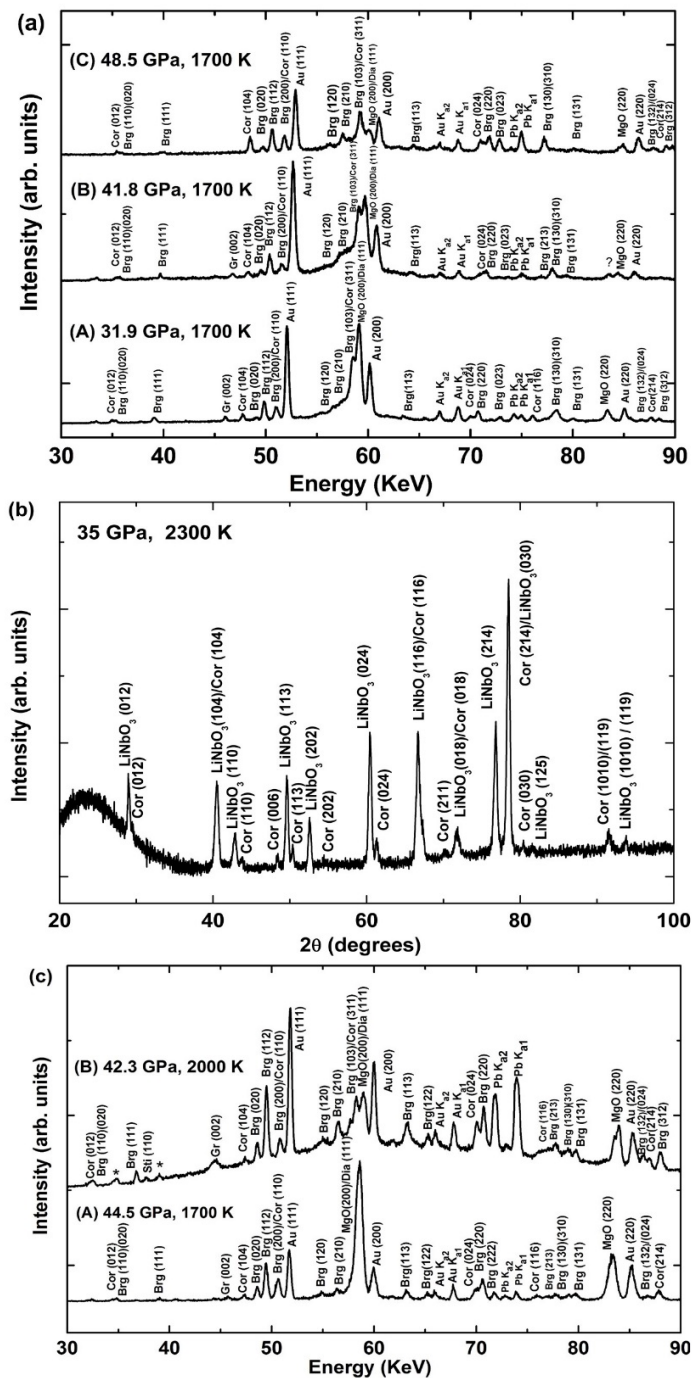519 is from Ishii *et al.* [2016].

23

520

Figure 3. (a) Representative back-scattered electron images of the run products for $En_{50}Cor_{50}$ (A-B) and pyropic compositions (C-D) synthesized at 27 GPa and 1700 and 2500 K, respectively. **(b)** Selected XRD patterns of the run products of (A) $En_{50}Cor_{50}$ and (C) pyropic compositions at 27 GPa and 1700 K, respectively. Abbreviations: Brg, bridgmanite; Cor, corundum; Sti, stishovite.
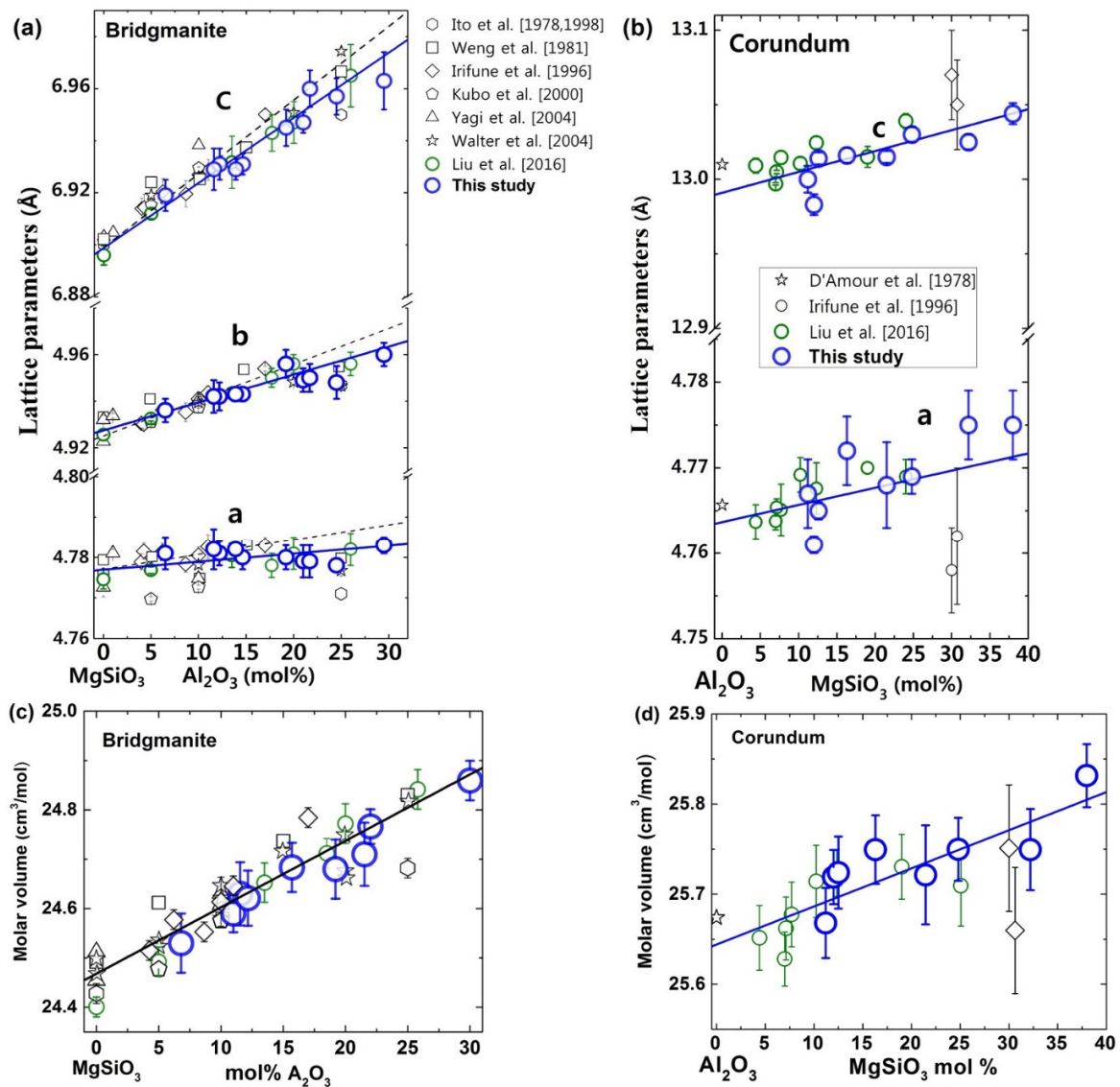

525

Figure 4. (a) Al_2O_3 solubility in bridgmanite and **(b)** $MgSiO_3$ solubility in corundum, respectively, as a function of temperature at a constant pressure of 27 GPa. The solid black and blue lines are the least-squares fitting of all the data and only the data in the present study, respectively.

529

530

Figure 5. Selected back-scattered electron images of the run products for $En_{50}Cor_{50}$ at 31.9–41.8 GPa and 1700 and 2300 K (a–c) and pyropic glass (d) at 42.3 GPa and 2000 K. Abbreviations: Brg, bridgmanite; Cor, corundum; Au: gold.

540

Figure 6. Selected (**a**) *in situ* and (**b**) quench XRD profiles of En$_{50}$Cor$_{50}$ and (**c**) *in situ* XRD profiles of the pyropic glass at various pressure and temperature conditions. Abbreviations: Brg, bridgmanite; Cor, corundum; Dia, diamond; Sti, stishovite; Gr: graphite. The stars represent the fluorescence of X-ray beam.

544

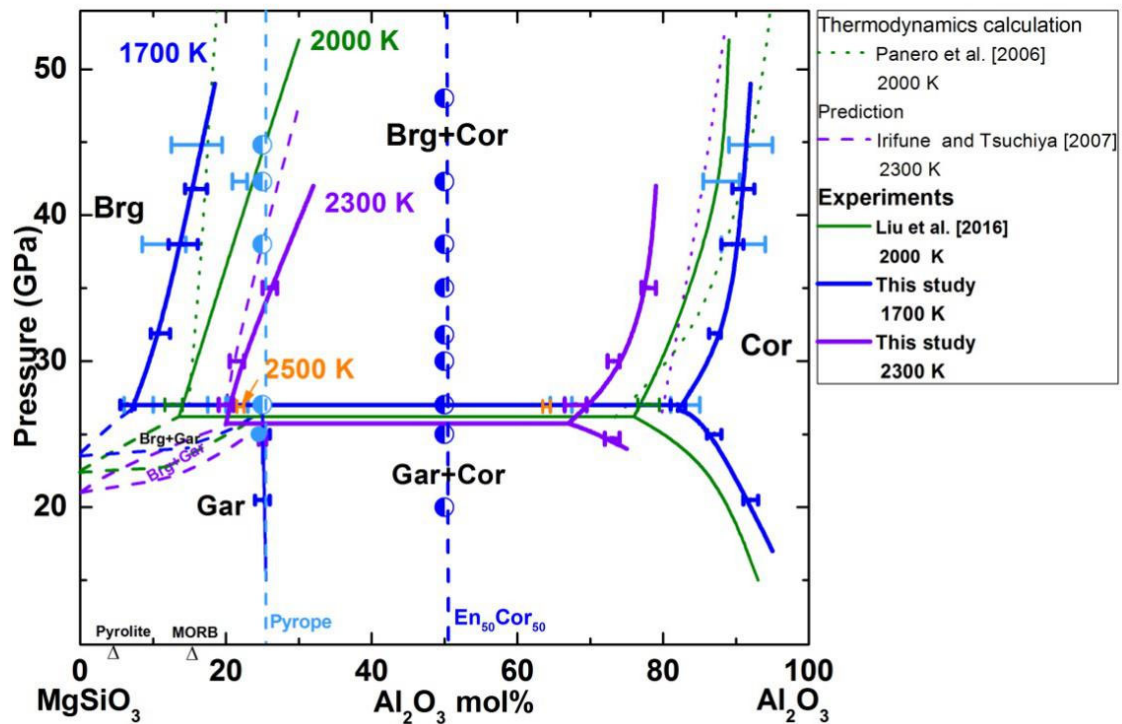**Figure 7.** Lattice parameter and molar volume of (**a** and **c**) bridgmanite and (**b** and **d**) corundum versus the Al_2O_3 and $MgSiO_3$ content, respectively, in the present and previous work. Solid lines are the linear fitting of the present data and Liu *et al.* [2016], and the dashed lines are results of Irifune *et al.* [1996].

550

Figure 8. (a) The ratio between Mg and Si cation and **(b)** Si cation number versus the Al per formula unit (pfu, based on 3 oxygens) in bridgmanite in the present study and previous works [Irifune *et al.*, 1996; Kubo and Akaogi, 2000; Liu *et al.*, 2016]. Solid blue and black lines indicate the trend expected for trivalent cation incorporation by the charge-coupled substitution mechanism (CCM) and oxygen vacancy substitution mechanism (OVM), respectively.

555

556

557

558

Figure 9. Phase relations in the MgSiO$_3$–Al$_2$O$_3$ system at 24–45 GPa and 1700, 2000 and 2300 K in the present and previous studies. Dark and light blue dashed lines represent the chemical compositions of the starting materials in the present study. Dark blue circular symbols indicate the high pressure runs using the En$_{50}$Cor$_{50}$ oxide mixture as the starting material, while light blue circular symbols indicate those for the pyropic glass. The corresponding horizontal-lined symbols mark the compositions of the coexisting phases for the En$_{50}$Cor$_{50}$ oxide mixture and the pyropic glass. The phase loop of bridgmanite plus garnet was referenced from Irifune *et al.* [1996], Kubo and Akaogi [2000] and Irifune and Tsuchiya [2007]. The triangles represent the Al$_2$O$_3$ content in the pyrolite and MORB models. Error bars indicate the uncertainties of chemical compositions. Abbreviations: Brg, bridgmanite; Cor, corundum; Sti, stishovite; Gar, garnet.

574   **Table 1** Experimental run conditions and products.

Run no.	Starting sample	Pressure (GPa)	Temperature (K)	Duration (hours)	Phases
S6778	$En_{50}Cor_{50}$ oxide	20	1700	6	Gar + Cor
S6607	$En_{50}Cor_{50}$ oxide	25	1700	6	Gar + Cor
	$En_{75}Cor_{25}$ glass				Gar
S6636	$En_{50}Cor_{50}$ oxide	24	2300	3	Gar + Cor
IRIS232	$En_{50}Cor_{50}$ oxide	27	1700	5	Al-Brg + Cor
IRIS266	$En_{50}Cor_{50}$ oxide	27	1700	15	Al-Brg + Cor
	$En_{75}Cor_{25}$ glass				Al-Brg + Cor + tr (Sti)
IRIS276	$En_{50}Cor_{50}$ oxide	27	1900*	2	Al-Brg + Cor
IRIS256	$En_{50}Cor_{50}$ oxide	27	2000	5	Al-Brg + Cor
	$En_{75}Cor_{25}$ glass				Al-Brg + Cor
IRIS244	$En_{50}Cor_{50}$ oxide	27	2300	2	Al-Brg + Cor + tr (Sti)
	$En_{75}Cor_{25}$ glass				Al-Brg + Cor
IRIS300	$En_{50}Cor_{50}$ oxide	27	2500*	0.5	Al-Brg + Cor+ tr (Sti)
	$En_{75}Cor_{25}$ glass				Al-Brg + Cor
IRIS252	$En_{50}Cor_{50}$ oxide	30	2300	1.5	Al-Brg + Cor
M2055	$En_{50}Cor_{50}$ oxide	31.9	1700	5	Al-Brg + Cor
S6615	$En_{50}Cor_{50}$ oxide	35	2300	1.5	Al-Pv + Cor
M2037	$En_{50}Cor_{50}$ oxide	38.5	1700	5.5	Al-Brg + Cor
M2063	$En_{50}Cor_{50}$ oxide	41.8	1700	6	Al-Brg + Cor
M2080	$En_{75}Cor_{25}$ glass	44.8	1700	5	Al-Brg + Cor + tr (Sti)
M2106	$En_{75}Cor_{25}$ glass	42.3	2000	3	Al-Brg + Cor + tr (Sti)
M1610	$En_{50}Cor_{50}$ oxide	48.5	1700[a]	2	Al-Brg + Cor + tr (Sti)
M1677#	$En_{50}Cor_{50}$ oxide	51.8	2000	3	Al-Brg + Cor

575   * temperature was evaluated from a calibrated power curve derived from the low temperature of 1500 K for IRIS276, and 2400 K for IRIS300.

576   # the run is from Liu et al. [2016].

577   a: temperature is around 1700-1800 K due to the instability of the heater

578   Abbreviations: Gar: garnet, Cor: corundum, Sti: stishovite, Al-Brg: aluminous bridgmanite, Al-Pv: aluminous perovskite; tr: trace.

579

580

581   **Table 2**. Chemical compositions of the coexisting mineral phases in the run products at pressure above 27 GPa

Run no.	Start Comp	Phases	MgO	Al$_2$O$_3$	SiO$_2$	Total	Mg	Al	Si	Sum
IRIS232	En$_{50}$Cor$_{50}$	Brg (n = 15)	37.79 (62)	6.79 (41)	55.33 (78)	99.11 (115)	3.776 (35)	0.521 (35)	3.722 (19)	8.018 (13)
		Cor (n = 12)	6.73 (33)	82.46 (90)	9.19(69)	98.18 (45)	0.671 (35)	6.706 (48)	0.635 (37)	8.012 (19)
IRIS266	En$_{50}$Cor$_{50}$	Brg (n = 15)	37.45 (66)	6.93 (36)	55.33 (88)	99.80 (132)	3.754 (26)	0.548 (32)	3.714 (17)	8.014 (19)
		Cor (n = 12)	6.84 (49)	82.07 (27)	9.91(42)	98.82 (70)	0.699 (56)	6.629 (60)	0.679 (26)	8.006 (17)
IRIS256	En$_{50}$Cor$_{50}$	Brg (n = 11)	35.67 (26)	12.49 (27)	52.94 (25)	101.10 (63)	3.523 (48)	0.975 (25)	3.507 (14)	8.005 (19)
		Cor (n = 12)	9.74 (29)	74.98 (17)	14.58 (42)	99.05 (57)	0.989 (28)	6.017 (37)	0.993 (24)	7.999 (12)
IRIS276	En$_{50}$Cor$_{50}$	Brg (n = 10)	35.36 (27)	11.66 (14)	52.40 (45)	99.42 (81)	3.552 (10)	0.925 (6)	3.530 (7)	8.007 (5)
		Cor (n = 10)	8.61 (37)	79.26 (28)	12.67 (23)	100.54 (46)	0.864 (34)	6.287 (13)	0.853 (17)	8.004 (17)
IRIS244	En$_{50}$Cor$_{50}$	Brg (n = 15)	31.50 (54)	20.60 (24)	49.97 (56)	98.79 (93)	3.243 (33)	1.541 (28)	3.222 (14)	8.007 (12)
		Cor (n = 12)	13.08 (17)	67.41 (29)	18.30 (31)	98.80 (19)	1.335 (15)	5.439 (34)	1.253 (19)	8.027 (4)
	En$_{75}$Cor$_{25}$	Brg (n = 15)	33.34 (38)	20.04 (35)	49.37 (27)	102.75 (39)	3.243 (33)	1.541 (28)	3.222 (14)	8.007 (12)
		Cor (n = 12)	11.74 (17)	68.73 (39)	17.51 (31)	98.27 (73)	1.203 (12)	5.586 (34)	1.204 (37)	8.000 (14)
IRIS300	En$_{50}$Cor$_{50}$	Brg (n = 15)	31.39 (36)	22.38 (52)	47.46 (51)	101.24 (59)	3.100 (31)	1.735 (49)	3.149 (28)	7.984 (11)
		Cor (n = 12)	15.08 (11)	63.14 (83)	23.09 (28)	101.33 (79)	1.497 (7)	4.953 (33)	1.537 (24)	7.987 (8)
	En$_{75}$Cor$_{25}$	Brg (n = 15)	31.25 (49)	22.09 (25)	46.97 (31)	100.28 (76)	3.114 (32)	1.740 (18)	3.138 (16)	7.992 (15)
		Cor (n = 12)	14.69 (42)	63.72 (63)	22.10 (128)	100.21	1.474 (26)	5.034 (93)	1.487 (68)	7.996 (18)
IRIS252	En$_{50}$Cor$_{50}$	Brg (n = 15)	32.32 (55)	21.66 (69)	47.58 (79)	101.56	3.183 (31)	1.687 (53)	3.143 (31)	8.013 (11)
		Cor (n = 12)	10.97 (30)	72.26 (74)	15.93 (44)	99.16 (26)	1.115 (32)	5.808 (73)	1.086 (31)	8.009 (11)
S6615	En$_{50}$Cor$_{50}$	Brg (n = 8)	29.69 (49)	27.76 (23)	42.55 (32)	100#	2.983 (22)	2.197 (17)	2.861 (38)	8.041 (14)
		Cor (n = 10)	8.82 (19)	77.76 (34)	12.44 (25)	99.01 (37)	0.899 (12)	6.277 (25)	0.854 (15)	8.016 (5)
M2055	En$_{50}$Cor$_{50}$	Brg (n = 8)	35.26 (27)	11.76 (24)	52.71 (39)	99.73 (58)	3.530 (29)	0.930 (17)	3.538 (21)	7.997 (13)
		Cor (n = 10)	4.75 (51)	87.84 (45)	6.83 (48)	99.42 (81)	0.482 (29)	7.058 (57)	0.465 (29)	8.006 (3)
M2037	En$_{50}$Cor$_{50}$	Brg (n = 8)	34.52 (27)	13.72 (40)	51.82 (56)	99.96 (53)	3.414 (17)	1.195 (23)	3.397 (19)	8.005 (12)
		Cor (n = 10)	4.50 (49)	90.10 (53)	6.72 (51)	101.12 (76)	0.450 (36)	7.118 (48)	0.437 (32)	8.004 (5)
M2063	En$_{50}$Cor$_{50}$	Brg (n = 5)	34.27 (77)	15.41 (54)	50.95 (90)	101.64 (89)	3.369 (54)	1.275 (22)	3.359 (22)	8.003 (24)
		Cor (n = 11)	3.61 (28)	92.41 (62)	5.23 (22)	101.37 (51)	0.360 (22)	7.283 (34)	0.358 (15)	8.001 (2)
M2106	En$_{75}$Cor$_{25}$	Brg (n = 8)	31.55 (69)	22.35 (82)	46.99 (82)	100.89 (98)	3.127 (57)	1.751 (38)	3.124 (47)	8.001 (33)
M1677	En$_{50}$Cor$_{50}$	Brg (n = 12)	28.08 (47)	30.00 (64)	42.57 (69)	100.63 (30)	2.789 (58)	2.357 (48)	2.838 (38)	7.984 (27)
		Cor (n = 16)	4.62 (58)	88.98 (80)	6.40 (52)	100.01 (17)	0.467 (6)	7.110 (60)	0.434 (35)	8.010 (23)

582   Oxide analyses are reported in wt%. Cations are reported based on the oxygen number is normalised to 12. Number in parentheses represents

583   standard deviation and is placed in the last digit (s). n: the number of analysis points. #: normalized to 100 due to some amounts (~1 wt%) of WO$_3$

584   in bridgmanite. Abbreviations: Brg, bridgmanite; Cor, corundum; Comp, composition.