

1 Revision1

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3 Elastic wave velocity anomalies of anorthite in subducting plate: In situ  
4 experiments

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25 **ABSTRACT**

26 To understand the origin of observed low-velocities in the crustal portion of subducting plates,  
27 we performed in situ measurements of elastic wave velocities of anorthite at temperatures up  
28 to 1373 K at pressure of ~1 GPa and up to 773 K at 2.0-7.0 GPa. A fine-grained  
29 polycrystalline anorthite which was synthesized using a gas pressure apparatus was used for  
30 the measurements. The high pressure experiments were performed using the multi-anvil  
31 apparatus installed on beam-line BL04B1 at SPring-8. The elastic wave velocity was  
32 measured by the ultrasonic pulse method with synchrotron X-ray radiographic imaging and  
33 X-ray diffraction techniques. At ~1.0 GPa, elastic wave velocities exhibited a sharp  
34 temperature-induced kink at ~500 K. Below 500 K, the elastic wave velocities decrease with  
35 increasing temperature. In contrast, above 500 K, the elastic wave velocities show an  
36 increasing trend in the range of 500-900 K, and then revert back to a decreasing trend at  
37 above 900 K. We also found a pressure-induced velocity anomaly of anorthite. At 300-373 K,  
38  $V_P$  is constant up to 4 GPa, but decrease above 4 GPa with increasing pressure, while  $V_S$   
39 decreases monotonously with increasing pressure. These elastic anomalies is considered to be  
40 attributable to the tilting behaviour of the corner-sharing  $TO_4$  (T = Al, Si) tetrahedra in three  
41 dimensional frameworks of anorthite. Our results suggest the presence of plagioclase feldspar  
42 has the potential to causes low velocity anomaly in the subducting oceanic crust when it  
43 survives as a metastable phase in the slab at higher pressure and lower temperature  
44 conditions.

45

46 Keywords: anorthite, plagioclase, elastic wave velocities, subduction, oceanic crust

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48

49 **INTRODUCTION**

50 Seismological observations have detected heterogeneous low-velocity structure in the  
51 crustal portion of subducting plates (e.g., Kawakatsu and Watada 2007; Rondenay et al. 2010).  
52 Plagioclase feldspars are one of the most abundant minerals in the crustal portion. Crusts with  
53 MORB-like composition contain large amount of plagioclase, normally more than 50 wt%.  
54 Therefore, the knowledge of the physical properties of plagioclase is important in order to  
55 resolve the detailed structure of the crust and crustal portions of subducted slabs based on  
56 such seismological observations. The purpose of our study is to determine the physical  
57 behaviour of anorthite ( $\text{CaAl}_2\text{Si}_2\text{O}_8$ , an end member of plagioclase), and to discuss the origin  
58 of the low-velocity layer in the crustal portion of subducting plates.

59 Elastic wave velocity of plagioclase minerals and rock aggregates has been measured  
60 using ultrasonic pulse technique (e.g., Ryzhova 1964; Wang et al. 1973; Liebermann and  
61 Ringwood 1976; Seront et al. 1993; Kono et al. 2008). Previous studies, however, encounter  
62 some experimental difficulties. In this technique, the elastic wave velocities are obtained from  
63 travel time and sample length. Thus, accurate measurement of the sample length is crucial for  
64 determining accurate elastic wave velocities (Li et al. 1998). In all previous studies for  
65 plagioclase, except for one study performed at room pressure (Ryzhova 1964), the sample  
66 lengths were not measured directly and were estimated by calculation using equation of state  
67 of minerals based on the assumption that only isotropic elastic deformation causes sample  
68 strain under high pressure and high temperature. In order to overcome this problem,  
69 synchrotron X-ray radiographic imaging technique has been applied in the elastic wave  
70 velocity measurements (Kung et al. 2002). When this method is used, direct measurement of  
71 the sample length in a high-pressure apparatus can be carried out. Recently, the experimental  
72 system for in situ ultrasonic measurement combined with X-ray radiographic imaging

73 technique has been installed at Spring-8, Japan (Higo et al. 2009). Here, we report the result  
74 of elastic wave velocity measurements on anorthite employing the ultrasonic pulse method  
75 under high pressure and high temperature with synchrotron X-ray radiographic imaging and  
76 X-ray diffraction techniques.

77

## 78 **EXPERIMENTAL METHODS**

### 79 **Synthesis of polycrystalline anorthite**

80 A polycrystalline anorthite was synthesised using the gas pressure apparatus installed  
81 at Tokyo Institute of Technology. The starting material was prepared from reagent grade  $\text{SiO}_2$ ,  
82  $\text{Al}_2\text{O}_3$  and  $\text{CaCO}_3$ , which were mixed in an appropriate ratio and ground in an agate mortar  
83 and pestle with ethanol. The mixed sample was decarbonated in a 1-atm furnace at 1273 K for  
84 24 hours. Then, it was melted at 1873 K and quenched to form glass. The glass sample was  
85 ground in ethanol and loaded into a sealed Pt tube container (3.0 mm inner diameter and 0.2  
86 mm thickness). The sample was preheated at 1173 K for 2 hours, and then it was kept at 1373  
87 K for 20 hours at pressure of 0.3 GPa. Figure 1a shows an orientation contrast image of the  
88 synthesised polycrystalline anorthite. The anorthite crystals are predominantly anhedral with  
89 mosaic texture, and some of crystals exhibit short columnar shape. The average grain size is  
90 less than 10  $\mu\text{m}$  across. Orientations of grains in the polycrystalline anorthite are estimated to  
91 be random based on observation of a thin section under an optical microscope, which showed  
92 random extinction of transmitted polarized light. The bulk density of the synthesised anorthite  
93 measured by the Archimedes method is  $2.72 \pm 0.02 \text{ g/cm}^3$ , which is 98.8% of the X-ray  
94 density (= porosity of 1.2%). The sample was formed into cylinders with 2.0 mm in diameter  
95 using ultrasonic cutter and ground to  $\sim 1.0$  mm in length, and both ends of cylinder were  
96 polished with 1  $\mu\text{m}$  diamond paste.

97

98 **In situ measurements of elastic wave velocities and X-ray diffraction**

99 In situ measurements of the elastic wave velocities ( $V_P$  and  $V_S$ ) of anorthite were  
100 performed at pressures between 0.6 and 7.0 GPa at temperatures of up to 1373 K. The  
101 experiments were performed using the Kawai-type multi-anvil apparatus (SPEED-1500) on  
102 beam-line BL04B1 at the synchrotron facility of Spring-8 (Utsumi et al., 1998). The  
103 experimental design for *in situ* elastic wave velocity measurement using the ultrasonic  
104 pulse-echo-overlap method at BL04B1 was presented by Higo et al. (2009). Pressure was  
105 generated by eight 26-mm tungsten carbide anvils (Tungaloy F grade) with truncated edge  
106 length of 11 mm. A Co-doped semi-sintered MgO octahedron with an 18-mm edge length was  
107 used as the pressure medium (Figure 2). A graphite sleeve was used as the heater and was  
108 inserted in a ZrO<sub>2</sub> thermal insulation sleeve with an MgO window for X-ray path to reduce  
109 potential temperature gradients. The temperature gradient of sample was estimated as ~25  
110 °C/mm at the maximum (Matsukage and Kawasaki 2014). The sample was enclosed in an  
111 hBN sleeve container, and then placed in the central part (hot part) of the furnace. Platinum  
112 foils (2.5 μm in thickness) were inserted on both side of the sample for the determination of  
113 sample length using the X-ray radiographic imaging technique (Figure 3a). The precision of  
114 the sample length measurement is estimated at 0.1-0.3 % of the nominal sample length (Higo  
115 et al., 2009). An Al<sub>2</sub>O<sub>3</sub> rod (5.3 mm in length and 2.0 mm in diameter) was used as the buffer  
116 rod for transmitting ultrasonic waves to the sample. The ultrasonic signals were generated and  
117 received by 10°Y-cut LiNbO<sub>3</sub> transducer having thickness of 50 μm and diameter of 3.2 mm.  
118 We used ultrasonic waves at frequencies of 30-60 MHz for 3 cycles (Figures 3b and 3c).

119 The diffracted X-ray from the sample was measured simultaneously with the  
120 measurement of elastic wave velocities. A solid-state detector connected to a multi-channel

121 analyzer combined with incident white X-ray beam was used for data collection. The  
122 multichannel analyzer was calibrated with the characteristic X-rays of Cu, Mo, Ag, Ta, Pt, Au  
123 and Pb. The X-ray diffractions were collected at a fixed  $2\theta$  angle ( $= 2.961^\circ$ ), which was  
124 determined using the unit-cell volume of MgO at room pressure and temperature. The  
125 incident X-ray beam was collimated to 0.2 and 0.1 mm in the vertical and horizontal  
126 dimensions, respectively. Slits of 2.0 mm in the vertical dimension and 0.1 mm in the  
127 horizontal dimension were used between the sample and the detector. MgO was used as a  
128 pressure marker, and it was mixed with hexagonal boron nitride (hBN) (MgO:hBN = 1:1 by  
129 weight) to prevent grain growth at high temperatures. Exposure times for collecting  
130 diffraction patterns of the sample and pressure marker were 300 and 180 s, respectively.  
131 Temperature was measured by a  $W_{97}Re_3$ - $W_{75}Re_{25}$  thermocouple. No pressure correction was  
132 made on the emf of the thermocouple. The pressure was calculated from the two diffraction  
133 peaks of MgO (111 and 200) using the equation of state of MgO presented by Jamieson et al.  
134 (1982) in program “XRayAna” available at the beam-line BL04B1.

135

## 136 **RESULTS**

137 The elastic wave velocities and X-ray diffraction measurements were carried out  
138 under pressures up to 7 GPa in a series of heating and cooling cycles (Table 1, Figure 4). First,  
139 we compressed the sample to  $\sim 2.0$  GPa (load = 80 ton), then heated it to 1373 K where it was  
140 kept for 60 minutes at 1373 K under constant oil pressure (cycle (1)). The purpose of the first  
141 heating and cooling cycle is to relax the stress on the sample and its surrounding materials,  
142 and to obtain better mechanical contact between the buffer rod and sample. This compression  
143 and preheating process is important for obtaining reliable signals of elastic waves (e.g., Li et  
144 al. 2004). After preheating,  $V_P$ ,  $V_S$  and X-ray diffraction measurements were performed in the

145 cooling stage of seven heating and cooling cycles (2)-(8). After each cooling stage, we  
146 increased the oil pressure, and then started the next heating and cooling cycle. The data of  
147 cycle (2) was collected up to 1373 K at  $P$ - $T$  conditions where anorthite is thermodynamically  
148 stable (Hays 1966). The data of cycles (3)-(8) were collected up to 773 K at metastable  
149 conditions.

150 In this study, we found a kink in elastic wave velocities with discontinuous change in  
151 temperature dependence at a temperature of about 500 K in cycle (2) (Figure 5). Below 500 K,  
152 the elastic wave velocities decrease with increasing temperature. In contrast, above 500 K, the  
153 elastic wave velocities show an increasing trend in the range of 500-900 K, and then revert  
154 back to a decreasing trend at above 900 K. Kinks similar to that of cycle (2) is observed for  
155 the cycles (3)-(5). At these cycles, temperatures at the kinks increase with increasing pressure,  
156 from ~500 K to ~720 K. In the cycles (6)-(8), kinks are not apparent within the studied  
157 temperature ranges, and only a monotonously decreasing trend is observed with increasing  
158 temperature. Elastic wave velocity measurement of anorthite was performed twice, and the  
159 temperature-induced elastic anomalies which are described here were observed in both  
160 experiments (see appendix). We also found a pressure-induced velocity anomaly of anorthite  
161 (Figure 6). At temperature of 300-373 K,  $V_P$  decreases with increasing pressure at above 4  
162 GPa, although it remains constant below 4 GPa. The  $V_S$  shows a decrease with increasing  
163 pressure. At 473 K, both  $V_P$  and  $V_S$  exhibit increasing trends below 4 GPa while showing a  
164 decreasing trend with increasing pressure above 4 GPa. At above 573 K,  $V_P$  and  $V_S$  decrease  
165 monotonously with increasing pressure up to 7 GPa.

166 All X-ray diffraction peaks correspond to anorthite with triclinic structure (Figure 7)  
167 (e.g., Foit and Peacor, 1973). For anorthite, the  $P(-1)$  structure is stable at ambient condition,  
168 and it changes to  $I(-1)$  structures with increasing temperature (e.g., Redfern and Salje 1987;

169 Redfern et al. 1988) and with increasing pressure (e.g., Angel 1988, 1992; Hackwell and  
170 Angel 1995) (Figure 4). Because there is no significant difference in the position of atoms  
171 between these structures, X-ray diffraction patterns resemble one another. Previous studies  
172 (e.g., Hackwell and Angel 1995; Tribaudino and Angel 2012) distinguished I(-1) phase from  
173 P(-1) by using the disappearance of 11(-1) reflection (c-type reflection:  $h + k = \text{even}$ ,  $l = \text{odd}$ )  
174 that is absent in I(-1) phase due to the symmetry of body centered structure. In our  
175 experiments, 11(-1) reflection was observed at 300-473 K in cycle (2) and at ambient  
176 condition before and after the experiments. The X-ray diffraction patterns of sample exhibit  
177 no additional peaks at any of the pressure and temperature conditions, although a small  
178 amount of reaction products ( $< 1\%$ ) were observed at the grain boundaries of anorthite  
179 crystals from the recovered sample (Figure 1b). Unit cell parameters and volume of the  
180 sample are determined by Le Bail method in program GSAS (Von Dreele and Larson 2001)  
181 using all diffraction lines shown in Figure 7. The unit cell parameters  $a$ ,  $b$ ,  $c$ ,  $\alpha$  and  $\beta$  decrease  
182 with increasing pressure and  $\gamma$  increase with increasing pressure (Figure 8). The change in  
183 temperature dependence of unit cell angles ( $\beta$  and  $\gamma$ ) at about 500-550 K is observed in cycles  
184 (2) and (3). The unit cell volume at ambient pressure ( $V_0 = 1341 \text{ \AA}^3$ ) agrees well with that of  
185 Tribaudino and Angel (2012) ( $V_0 = 1340.1 \text{ \AA}^3$ ). The unit cell volume gradually decreases with  
186 increasing pressure, though a weak kink is observed at about 4 GPa (Figure 9).

187         The adiabatic bulk modulus ( $K_S$ ) and shear modulus ( $G$ ) are represented by the  
188 equations:  $K_S = \rho(V_P^2 - V_S^2 \times 4/3)$  and  $G = \rho V_S^2$ , where  $\rho$  is density. To calculate the  $K_S$  and  $G$   
189 from the velocities and density data, we obtained density from the equation,  $\rho = (m Z/N_A) \times$   
190  $(1/V)$ , where  $m$ ,  $Z$ ,  $N_A$  and  $V$  are formula weight, formula number ( $Z = 8$  for anorthite), the  
191 Avogadro constant and unit cell volume, respectively. The calculated  $\rho$ ,  $K_S$  and  $G$  are listed in  
192 Table 1. In cycles (2), (3) and (4), kinks of  $K_S$  and  $G$  are observed at ~500-750 K. Adiabatic



193 bulk modulus ( $= K_{S0}$ ) and shear modulus ( $= G_0$ ) at room temperature and room pressure were  
194 estimated by polynomial fitting using data at 300 K. We obtained  $K_{S0} = 83$  GPa and  $G_0 = 38.6$   
195 GPa. Based on Angel's (2004) data on plagioclase feldspars, isothermal bulk modulus ( $K_{T0}$ ) at  
196 ambient condition was estimated by Tribaudino et al. (2011) to be  $K_{T0} = 82.5$  GPa.  $K_{S0}$  is  
197 calculated as 82.7 GPa from the formula  $K_{S0} = K_{T0}(1 + \alpha\gamma T)$  where  $\alpha$  and  $\gamma$  are thermal  
198 expansion coefficient and Grüneisen parameter, and are  $1.379 \times 10^{-5} \text{ K}^{-1}$  and 0.46 (Tribaudino  
199 et al. 2011), respectively. The  $K_{S0}$  determined by our experiments is sufficiently consistent  
200 with those of previous study.

201

## 202 **DISCUSSION AND CONCLUSIONS**

### 203 **Relationship with the phase transitions and the crystal structure**

204 Anorthite is known for undergoing a reversible phase transition from  $P(-1)$  to  
205 high-temperature  $I(-1)$  at temperature of 510 K at pressures of less than  $\sim 2$  GPa (e.g., Foit and  
206 Peacor 1973; Redfern et al. 1988). Temperature and pressure conditions of the discontinuous  
207 elasticity change at 500 K of cycle (2) agree well with the phase boundary of  $P(-1)$  and  
208 high-temperature  $I(-1)$  (Figure 4). Based on this observation, it is thought that anomalous  
209 behaviour at  $> 500$  K is caused by successive structural changes in the high-temperature  $I(-1)$   
210 phase, followed by the phase transition. In our experiments, the temperature-induced anomaly  
211 is observed at higher pressure, at the  $P$ - $T$  conditions near the extrapolated phase boundary by  
212 Hackwell and Angel (1995) (Figure 4). The structure of anorthite comprises a flexible three  
213 dimensional framework of rigid, corner sharing  $\text{TO}_4$  tetrahedra ( $T = \text{Si}$  and  $\text{Al}$ ) with  $\text{Ca}^{2+}$   
214 occupying interstitial sites of the framework (e.g., Angel et al., 2013). Molecular dynamics  
215 (MD) simulation (Noritake et al. 2013) suggests that the temperature-induced anomalies of  
216 the  $K_S$  and  $G$  could be caused by a combination of two different thermal expansion

217 mechanisms due to atomic motions and displacements: (1) expansion of inter-atomic  
218 distances of near neighbor atoms and (2) increase in T-O-T angles of the framework. Below  
219 the phase transition temperature, thermal expansion is mainly caused by the expansion of the  
220 inter-atomic distances. In high-temperature  $I(-1)$  stability field, two mechanisms contribute to  
221 the thermal expansion. The T-O-T angles increase with increasing temperature, which  
222 subsequently causes shortening of bridging bond length of T-O (e.g., Newton and Gibbs 1980)  
223 that contributes to increase in elastic moduli ( $K_S$  and  $G$ ). This structural change in the  $I(-1)$   
224 stability field provides a reasonable explanation why the elastic wave velocities of anorthite  
225 increase with increasing temperature in the range of 500-900 K. Above 900 K, thermal  
226 expansion is dominated by the expansion of inter-atomic distance and results in the reduction  
227 of elasticity.

228         Angel (1992) performed single crystal X-ray diffraction experiments on five samples  
229 with various degrees of Al and Si cation disordering, and found that the pressure of phase  
230 transition from  $P(-1)$  to high-pressure  $I(-1)$  was dependent on the state of Si and Al order.  
231 When  $Q_{OD}$  (where  $Q_{OD}$  quantifies the state of order, varying from unity for complete Al and  
232 Si order to zero for complete disorder) decreases from 0.92 to 0.78, the pressure of the phase  
233 transition increases from 2.5 GPa to 4.8 GPa. In our sample, existence of the 11(-1) reflection  
234 seems to have suggested a possibility that the sample was ordered because the 11(-1)  
235 reflection should become less intense when the  $Q_{OD}$  decreases (Carpenter, 1991). However,  
236 for the synthesis method and condition of the anorthite in our study, it can be estimated that  
237 the state of Al and Si order should be partly disordered (Carpenter, 1991). The pressure  
238 condition of weak kink in the velocities and compression curves at ~4.0 GPa (Figures 6 and 9)  
239 is consistent with the phase boundary between  $P(-1)$  and high-pressure  $I(-1)$  for partly  
240 disordered anorthite for  $Q_{OD} \cong 0.8$ . The unit cell angles of  $\alpha$  and  $\gamma$  are known to be sensitive to

241 the state of order, and the partly disordered anorthite ( $Q_{OD} \cong 0.7-0.8$ ) has unit cell angles  $\alpha =$   
242  $93.2^\circ$  and  $\gamma = 91.2^\circ$  (Carpenter 1991; Angel 1992). At ambient condition, the sample used in  
243 this study has  $\alpha = 93.1^\circ$  and  $\gamma = 91.2^\circ$  which are quite consistent with that of previous studies  
244 for the partly disordered anorthite. Consequently, we conclude that the anorthite sample in the  
245 ultrasonic measurements is possible to be partly disordered and the kink of slope at  $\sim 4$  GPa is  
246 caused by the phase transition.

247 The velocities decrease accompanying pressure increase was observed in wide  
248 pressure and temperature conditions of the experiments at above 4 GPa where  $I(-1)$  structures  
249 are stable (Figure 6). This pressure-induced velocities anomaly (with the negative pressure  
250 dependence) is in contrast to the positive effect for typical minerals such as olivine (e.g.,  
251 Birch 1961, 1963). First, it is considered a possibility that the anomaly is an experimental  
252 artefact originated by an influence of differential stress. The pressure increment induces a  
253 differential stress in the sample, and the stress may influence to the elasticity. In this study, a  
254 soft material (hBN) was used as the sample container to minimize the differential stress at the  
255 compression, and the measurements were performed after heating to reduce the stress. Based  
256 on the in situ X-ray diffraction measurements, the reduction of the stress was observed in the  
257 sample and pressure maker at the heating. Consequently the influence of the differential stress  
258 to the elasticity was not large in our experiments, and we considered that the pressure induced  
259 anomaly is not an experimental artefact. Here, we suggest that the pressure induced anomaly  
260 with the negative pressure dependence is caused by the tilting behavior of T-O-T angles in the  
261 network of  $TO_4$  tetrahedra. The MD simulation indicated that the average T-O-T angle of  
262 anorthite decreases with increasing pressure, and this structural behaviour happens especially  
263 at the high-temperature phase and the high-pressure phase with  $I(-1)$  symmetry (Noritake et al.  
264 2013, 2014). When the T-O-T angle decrease and hence bridging bond length of T-O increase

265 with increasing pressure, elastic wave velocities are likely to decrease. In our experiments, the  
266 anomaly mainly occurs in the  $I(-1)$  stability fields irrespective of the existence of  $P(-1)$   
267 structure.

268

### 269 **Comparison with previous plagioclase studies**

270 Previous determinations of elastic wave velocities of plagioclase at room temperature  
271 in the thermodynamically stability field are compared with our data (Figure 10). Ryzhova  
272 (1964) was the first to measure elastic wave velocities of plagioclase single crystals with  
273 various chemical compositions at room temperature and room pressure. These data suggest  
274 that velocities of plagioclase have a positive linear correlation with anorthite content. After  
275 that, Liebermann and Ringwood (1976) and Kono et al. (2008) measured the elastic wave  
276 velocities of polycrystalline plagioclase with An100 at 0.75 GPa and with An51 at 1 GPa,  
277 respectively, employing an ultrasonic pulse transmission technique using a piston cylinder  
278 apparatus without X-ray radiographic imaging. The data of Liebermann and Ringwood (1976)  
279 and Kono et al. (2008) do not agree with Ryzhova's data, and were faster. Liebermann and  
280 Ringwood (1979) speculated that Ryzhove had underestimated the data, possibly due to the  
281 presence of cracks, pores or inclusions in the single crystal measured at atmospheric pressure.  
282 Here, we point out another possibility that the velocities measured using piston cylinder  
283 apparatus had been the ones overestimated resulting, from overestimation of sample length  
284 because the sample lengths could not be measured directly in their studies. Higo et al. (2009)  
285 observed that sample length measured by X-ray radiographic imaging is shorter than that  
286 estimated from unit-cell volumes in high pressure for their cell assembly. Their observation  
287 indicates that the sample deforms not only through isotropic elastic deformation but also  
288 through plastic deformation owing to uniaxial compression of the sample by a hard buffer rod.

289 This implies that plagioclase sample lengths estimated in previous studies of plagioclase  
290 possible to be overestimated if the samples were uniaxially compressed using a piston  
291 cylinder apparatus. In contrast, sample lengths measured in our study are considered to be  
292 accurate because they were measured directly using synchrotron X-ray radiography.

293 Our anorthite velocity data are compatible with the trends reported by Ryzhova  
294 (1964), and are slower than that of Liebermann and Ringwood (1979). There are two factors  
295 which may explain this inconsistency. One is the preferred orientation of the anorthite crystals,  
296 which may have developed during the experiment. Anorthite has strong elastic anisotropy,  
297 thus the ultrasonic measurements on a highly textured sample would not yield correct  
298 aggregate velocities. In this study, the sample experienced not only isotropic elastic  
299 deformation but also weak plastic deformation owing to uniaxial compression by a hard  $\text{Al}_2\text{O}_3$   
300 buffer rod. In order to eliminate this possibility, crystallographic orientation of the recovered  
301 sample was measured by electron backscatter diffraction method. As a result, the preferred  
302 orientation was not observed (Figure 11). Therefore, it is thought that lowering of velocity  
303 accompanying elastic deformation had not occurred during the high pressure experiment. The  
304 second is the presence of pores in the sintered polycrystalline anorthite during the  
305 measurement of elastic wave velocities. Our sintered polycrystalline anorthite contained  
306  $\sim 1.2\%$  of pore before the experiments. After the experiments (Figure 1b), the pores were not  
307 completely closed although they were considerably lessened ( $< \sim 0.5\%$ ). To evaluate the  
308 influence of pore on velocity lowering, we estimated elastic wave velocities of pore-free  
309 polycrystalline sample using the theory of Takei (2002). Since the shape of pores was fairly  
310 globular, calculation was performed assuming a dihedral angle of larger than  $70^\circ$ . The  
311 calculated elastic wave velocities of a pore-free polycrystalline anorthite are very close to the  
312 original data and are only higher than those of the pore-bearing sample by  $0.4\%$  and  $0.8\%$

313 for  $V_S$  and  $V_P$ , respectively (Figure 10). It is concluded that the elastic wave velocities  
314 measured in our experiment is considered to be appropriate as aggregate velocities although it  
315 is slightly slower than the value of a sample without pores.

316

### 317 **Implications for the crustal rocks in the subducting slab**

318 Thin low-velocity layer having thickness of about several km has been observed in  
319 the upper portion of the subducting plate in the Japan arcs (e.g., Fukao et al. 1983; Hasegawa  
320 et al. 1994; Nakajima et al. 2009). It reaches depths of  $\sim 150$  km ( $P = \sim 5$  GPa) in central Japan  
321 and  $\sim 100$  km ( $P = \sim 3$  GPa) in northeast Japan, and disappears with increasing depths.  
322 Nakajima and his co-workers interpreted the low-velocity layer as a metamorphosed crust  
323 coexisting with interstitial aqueous fluid, because the observed  $V_P$  at depths of  $< 100$  km in  
324 this layer is  $\sim 10\%$  lower than that of fully-hydrous metamorphic MORB in blueschist facies  
325 (Shiina et al. 2013). This model is the basis for the hypothesis that subducting mafic rocks  
326 suffer complete metamorphic hydration before subduction. Plagioclase feldspars are one of  
327 most abundant minerals in gabbroic rocks that are subducted into the Earth's interior.  
328 Therefore the elastic anomaly in plagioclase has the potential to cause the low velocity  
329 anomaly in the slab in case of the cold slab in which the hydration reaction from gabbro to  
330 hydrous metamorphic rock is slow (Hasegawa et al. 1994). Our experimental results suggest  
331 that anorthite is metastable to at least less than 800 K and 7.0 GPa within the timescale of the  
332 experiments, although plagioclase will transform to a garnet-bearing assemblage at a depth of  
333  $\sim 35$  km when thermodynamic equilibrium is achieved at high temperature ( $> 1300$  K) (Green  
334 and Ringwood, 1967). Consequently, plagioclase may potentially survive in the slab to higher  
335 pressures if the slab is sufficiently cold.

336 Here, seismic velocities of gabbro and eclogite with NMORB composition were

337 calculated for the range of pressure and temperature assumed to be present in the subducting  
338 slab. The one-dimensional geotherms along the slab-wedge interface for the central and  
339 northeast Japan arcs were used as reference models for temperature (Iwamori, 2007). The  
340 modal and chemical compositions of minerals were estimated using software for  
341 thermodynamic calculation “PerpleX667” (Connolly 2012). The value of thermoelastic  
342 parameters for coesite, kyanite, olivine, pyroxenes and garnet are after Hacker et al. (2003)  
343 and Matsukage et al. (2005). The gabbro with MORB composition contains Na-bearing  
344 plagioclase with An55-80. However the pressure dependence of the elastic wave velocity of  
345 Na-bearing plagioclase has not been investigated. Therefore, the data of anorthite measured in  
346 our experiment was used. Because the slab temperature is consistent with that of  
347 high-temperature  $I(-1)$  stability field, we modelled temperature and pressure dependent elastic  
348 wave velocities of anorthite with high-temperature  $I(-1)$  structure using a quadratic expression  
349 with least squares fit:  $V_X = a_0 + a_1T + a_2T^2 + bP$ , where  $V_X$  ( $X = P, S$ ),  $T$  and  $P$  is the wave  
350 velocity, temperature and pressure. The parameters were determined to be  $a_0 = 6.407$  km/s,  $a_1$   
351  $= 1.085 \times 10^{-3}$  km/s/K,  $a_2 = -5.630 \times 10^{-7}$  km/s/K<sup>2</sup>,  $b = -0.0280$  km/s/GPa at  $V_P$ , and to be  $a_0 =$   
352  $3.247$  km/s,  $a_1 = 7.198 \times 10^{-4}$  km/s/K,  $a_2 = -3.601 \times 10^{-7}$  km/s/K<sup>2</sup> and  $b = -0.0400$  km/s/GPa at  $V_S$ .  
353 Elastic wave velocities of An55 are estimated to be slower by ~5 % compared with that of  
354 An100 (Figure 10). Since ~60 % of plagioclase is contained in the gabbroic rock, the  
355 maximum bulk velocity lowering due to the compositional effect in plagioclase is estimated to  
356 be ~3%. As shown in Figure 12, the observed  $V_S$  structures in the Japan arcs (Nakajima et al.  
357 2009) are consistent with those of gabbro but lower than those of eclogite at a depth of < ~100  
358 km. For central Japan, the  $V_P$  structure reported by Nakajima et al. (2009) is consistent with  
359 the gabbro data. However, for northeast Japan, the eclogite velocities are more consistent with  
360 the  $V_P$  by Nakajima et al. (2009). Nakajima et al. (2009) estimated the  $V_P$  structure by direct P

361 wave. Recently, the  $V_p$  structure was estimated by using P-to-S-converted wave, which is  
362 considered to be useful for the estimation of  $V_p$  structure at the upper portion of the  
363 subducting plate (Shiina et al. 2013). The data by P-to-S-converted wave is slower than the  
364 data by direct P wave. The  $V_p$  reported by Shiina et al. (2013) slightly lower than that of  
365 gabbro (Figure 12). The above comparison of the mineralogical model with existing seismic  
366 observations shows that the presence of metastable gabbro may reasonably explain observed  
367 low velocity in the slab without necessitating the introduction of hydration processes or a  
368 fluid phase. At present, it is difficult to determine whether the subducting crust is comprised  
369 of gabbroic or metamorphic mineral assemblies with aqueous fluid. Further studies are  
370 needed on elastic wave velocity measurements for Na-bearing plagioclase and on the reaction  
371 kinetics of metamorphic hydration of gabbro and gabbro-eclogite transition to address this  
372 issue.

373

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380

#### 381 **References**

- 382 Angel, R.J. (1988) High-pressure structure of anorthite. *American Mineralogist*, 73,  
383 1114-1119.
- 384 Angel, R.J. (1992) Order-disorder and the high-pressure  $P(-1)$ - $I(-1)$  transition in anorthite.



- 385 American Mineralogist, 77, 923-929.
- 386 Angel, R.J. (2004) Equation of state of plagioclase feldspars. *Contribution to Mineralogy and*  
387 *Petrology*, 146, 506-512.
- 388 Angel, R.J., Sochalski-Kolbus, L.M., and Tribaudino, M. (2012) Tilts and tetrahedra: the  
389 origin of the anisotropy of feldspars. *American Mineralogist*, 97, 765-778.
- 390 Birch, F. (1961) The velocity of compressional waves in rocks to 10 kilobars, Part 2. *Journal*  
391 *of Geophysical Research*, 66, 2199-2224.
- 392 Birch, F. (1963) Some geophysical applications of high-pressure research. *In Solids under*  
393 *Pressure*, edited by W. Paul, and D. M. Warschauer, pp. 137-162, McGraw Hill, New York.
- 394 Carpenter, M.A. (1991) Mechanisms and kinetics of Al-Si ordering in anorthite: II. Energetics  
395 and a Ginzburg-Landau rate law. *American Mineralogy*, 76, 1120-1133.
- 396 Christy, A.G., and Angel R.J. (1995) A Model for the origin of the cell-doubling phase  
397 transitions in clinopyroxene and body-centred anorthite. *Physics and Chemistry of*  
398 *Minerals*, 22, 129-135.
- 399 Connolly, J.A.D. (2012) PerpleX667 report, <http://www.perplex.ethz.ch/>.
- 400 Connolly, J.A.D., and Kerrick, D.M. (2002) Metamorphic controls on seismic velocity of  
401 subducting oceanic crust at 100-250 km. *Earth and Planetary Science Letters*, 204, 61-74.
- 402 Foit, F.F., and Peacor, D.R. (1973) The anorthite crystal structure at 410 and 830°C. *American*  
403 *Mineralogist*, 58, 665-675.
- 404 Fukao, Y., Hori, S., and Ukawa, M. (1983) A seismological constraint on the depth of  
405 basalt-eclogite transition in a subducting oceanic crust. *Nature*, 303, 413-415.
- 406 Gibbs, G.V. (1982) Molecules as models for bonding in silicates. *American Mineralogist*, 67,  
407 421-450.
- 408 Green, D.H. and Ringwood, A.E. (1966) An experimental investigation of the gabbro to

- 409 eclogite transformation and its petrological applications. *Geochimica et Cosmochimica*  
410 *Acta*, 31, 767-833.
- 411 Hacker, B.R., Abers, G.A. and Peacock, S.M. (2003) Subduction factory: 1. Theoretical  
412 mineralogy, densities, seismic wave speeds, and H<sub>2</sub>O contents. *Journal of Geophysical*  
413 *Research*, 108, B1, 2029, doi:10.1029/2001JB001127.
- 414 Hackwell, T.P., and Angel, R.J. (1995) Reversed brackets for the *P(-1)-I(-1)* transition in  
415 anorthite at high pressure and temperature. *American Mineralogist*, 80, 239-246.
- 416 Hasegawa, A., Horiuchi, S., and Umino, N. (1994) Seismic structure of the northeastern Japan  
417 convergent margin: A synthesis. *Journal of Geophysical Research*, 99, 22295-22311.
- 418 Hays, J.F. (1966) Lime-alumina-shilica. *Carnegie Inst. Washington Year Book*, 65, 234-239.
- 419 Higo, Y., Kono, Y., Inoue, T., Irifune, T., and Funakoshi, K. (2009) A system for measuring  
420 elastic wave velocity under high pressure and high temperature using a combination of  
421 ultrasonic measurement and the multi-anvil apparatus at Spring-8. *Journal of Synchrotron*  
422 *Radiation*, 16, 762-768, doi:10.1107/S0909049509034980.
- 423 Iwamori, H. (2007) Transportation of H<sub>2</sub>O beneath the Japan arcs and its implications for  
424 global water circulation. *Chemical Geology*, 239, 182-198.
- 425 Jamieson, J.C., Fritz, J.N., and Manghnani, M.H. (1982) Pressure measurement at high  
426 temperature in x-ray diffraction studies: Gold as a primary standard. In *High-Pressure*  
427 *Research: Application to Earth and Planetary Sciences*, *Geophys. Monogr. Ser.*, vol. 67,  
428 edited by S. Akimoto and M. H. Manghnani, pp. 27-48, Terra Sci., Tokyo.
- 429 Kono, Y., Miyake, A., Ishikawa, M., and Arima, M. (2008) Temperature derivatives of elastic  
430 wave velocities in plagioclase (An<sub>50±1</sub>) above and below the order-disorder transition  
431 temperature. *American Mineralogist*, 93, 558-564.
- 432 Koziol, A.M., and Newton, R.C. (1988) Redetermination of the anorthite breakdown reaction

- 433 and improvement of the plagioclase-garnet- $\text{Al}_2\text{SiO}_5$ -quartz geobarometer. American  
434 Mineralogist, 73, 216-223.
- 435 Kung, J., Li, B., Weidner, D.J., Zhang, J., Liebermann, R.C. (2002) Elasticity of  $(\text{Mg}_{0.83}$ ,  
436  $\text{Fe}_{0.17})\text{O}$  ferropicicase at high pressure: ultrasonic measurements in conjunction with  
437 X-radiation techniques. Earth and Planetary Science Letters, 203, 557-566.
- 438 Li, B., Kung, J., and Liebermann, R.C. (2004) Modern techniques in measuring elasticity of  
439 Earth materials at high pressure and high temperature using ultrasonic interferometry in  
440 conjunction with synchrotron X-radiation in multi-anvil apparatus. Physics of the Earth  
441 and Planetary Interior, 143-144, 559-574.
- 442 Li, B., Liebermann, R.C., and Weidner, D.J. (1998) Elastic moduli of wadsleyite ( $\beta\text{-Mg}_2\text{SiO}_4$ )  
443 to 7 Gigapascals and 873 Kelvin. Science, 281, 675-677.
- 444 Liebermann, R.C., and Ringwood, A.E. (1976) Elastic properties of anorthite and the nature  
445 of the lunar crust. Earth and Planetary Science Letters, 31, 69-74.
- 446 Matsukage, K.N., and Kawasaki, T. (2014) Hydrous origin of the continental cratonic mantle.  
447 Earth, Planets and Space, 66:29, doi:10.1186/1880-5981-66-29.
- 448 Matsukage, K.N., Nishihara, Y., and Karato, S. (2005) Seismological signature of chemical  
449 differentiation of Earth's upper mantle. Journal of Geophysical Research, 110, B12305,  
450 doi:10.1029/2004JB003504.
- 451 Nakajima, J., Tsuji, Y., and Hasegawa, A. (2009) Seismic evidence for thermally-controlled  
452 dehydration reaction in subducting oceanic crust. *Geophysical Research Letters*, 36,  
453 L03303, doi:10.1029/2008GL036865.
- 454 Newton, M.D., and Gibbs, G.V. (1980) *Ab initio* calculated geometries and charge  
455 distributions for  $\text{H}_4\text{SiO}_4$  and  $\text{H}_6\text{Si}_2\text{O}_7$  compared with experimental values for silicates and  
456 siloxanes. Physics and Chemistry of Minerals, 6, 221-246.

- 457 Noritake, F., Kawamura, K., and Matsukage, K.N. (2013) Elastic anomalies of anorthite:  
458 molecular dynamics simulation. Abstract of the meeting of *Japan Association of*  
459 *Mineralogical Sciences*, R2, 14 (Japanese with English abstract).
- 460 Noritake, F., Kawamura, K., and Matsukage, K.N. (2014) Elastic wave velocity anomalies of  
461 anorthite in subducting plate: molecular dynamics simulations. Submitted to *Physics of the*  
462 *Earth and Planetary Interior*.
- 463 Ohuchi, T., Kawazoe, T., Nishihara, Y., Nishiyama, N., and Irifune, T. (2011) High pressure  
464 and temperature fabric transitions in olivine and variations in upper mantle seismic  
465 anisotropy. *Earth and Planetary Science Letters*, 304, 55-63.
- 466 Prior, D., Boyle, A.P., Brenker, F., Cheadle, M., Day, A., Lopez, G., Peruzzo, L., Potts, G.J.,  
467 Reddy, S., Spiess, R., Timms, N.E., Trimby, P., Wheeler, J., and Zetterström, L. (1999) The  
468 application of electron backscatter diffraction and orientation contrast imaging in the SEM  
469 to textural problems in rocks. *American Mineralogist*, 84, 1741-1759.
- 470 Redfern, S.A.T., Graeme-Barber, A., and Salje, E. (1988) Thermodynamics of plagioclase III:  
471 Spontaneous Strain at the  $I(-1)$ - $P(-1)$  phase transition in Ca-rich plagioclase. *Physics and*  
472 *Chemistry of Minerals*, 16, 157-163.
- 473 Redfern, S.A.T., and Salje, E. (1987) Thermodynamics of plagioclase II: temperature  
474 evolution of the spontaneous strain at the  $I(-1)$ - $P(-1)$  phase transition in anorthite. *Physics*  
475 *and Chemistry of Minerals*, 14, 189-195.
- 476 Rondenay, S., Abers, G.A., and Van Keken, P.E. (2010) Seismic imaging of subduction zone  
477 metamorphism. *Geology*, 36, 275-278.
- 478 Ryzhova, T.V. (1964) Elastic properties of plagioclase. *Izv. Acad. Sci. USSR, Geophys. Ser.*, 7,  
479 633-635.
- 480 Seront, B., Mainprice, D., and Christensen, N.I. (1993) A determination of the

- 481 three-dimensional seismic properties of anorthite: comparison between values calculated  
482 from the petrofabric and direct laboratory measurements. *Journal of Geophysical Research.*,  
483 98, 2209-2221.
- 484 Shiina, T., Nakajima, J., and Matsuzawa, T. (2013) Seismic evidence for high pore pressures  
485 in the oceanic crust: Implications for fluid-related embrittlement. *Geophysical Research*  
486 *Letters*, 40, doi: 10.1002/grl.50468.
- 487 Takei, Y. (2002) Effect of pore geometry on  $V_P/V_S$ : from equilibrium geometry to crack.  
488 *Journal of Geophysical. Research*, 107, doi:10.1029/2001JB000522.
- 489 Tribaudino, M., and Angel, R.J. (2012) The thermodynamics of the I(-1)-P(-1) phase  
490 transition in Ca-rich plagioclase from an assessment of the spontaneous strain. *Physics and*  
491 *Chemistry of Minerals*, doi:10.1007/s00269-012-0524-x.
- 492 Tribaudino, M., Bruno, M., Nestola, F., Pasqual, D., and Angel, R.J. (2011) Thermoelastic and  
493 thermodynamic properties of plagioclase feldspars from thermal expansion measurements.  
494 *American Mineralogist*, 96, 992-1002.
- 495 Utsumi, W., Funakoshi, K., Urakawa, S., Yamakata, M., Tsuji, K., Konishi, H., Shimomura, O.  
496 (1998) Spring-8 beam lines for high pressure science with multi-anvil apparatus. *Review*  
497 *of High Pressure Science Technique*. 7, 1484–1486.
- 498 Von Dreele, R.B., and Larson, A.C. (2001) GSAS (General Structure Analysis System).  
499 Copyright, Regents of the University of California.
- 500 Wang, H., Todd, T., Richter, D., and Simmons, G. (1973) Elastic properties of plagioclase  
501 aggregates and seismic velocities in the moon. *Proceedings of the Fourth Lunar Science*  
502 *Conference*, 3, 2663-2671.
- 503 Weidner, D.J., Wang, H., and Ito, J. (1978) Elasticity of orthoenstatite. *Physics of the Earth*  
504 *and Planetary Interior*, 17, 7-13

505

506 **Figure captions**

507 Figure 1. Orientation contrast images of the synthesized polycrystalline anorthite taken using  
508 forescatter detectors in scanning electron microprobe equipped with field emission gun  
509 (FE-SEM) with the polished sample inclined at 70° (Prior et al. 1999). a) Before experiment,  
510 b) after experiment. Bright particles in (b) are reaction products at high pressure.

511

512 Figure 2. A schematic illustration of cell assembly for elastic wave velocity measurements.

513

514 Figure 3. A typical example of the X-ray radiographic image (a) and the ultrasonic signals (b  
515 and c) at 1373 K and 1.2 GPa. R1, R2 and R3 are shown in Figure 2.

516

517 Figure 4. Experimental pressure and temperature paths in elastic wave velocity measurements  
518 on anorthite. Open diamonds denote the preheating stage. Phase relations of anorthite are after  
519 Hackwell and Angel (1995) and Koziol and Newton (1988). The pressure of the phase  
520 transition from P(-1) to high-pressure I(-1) was dependent on the state of Si and Al order, and  
521 when  $Q_{OD}$  (see text) decreases from 0.92 to 0.78, the pressure of the phase transition increases  
522 from 2.5 GPa to 4.8 GPa (Angel, 1992). Open circles indicate the pressure and temperature  
523 conditions corresponding to the temperature-induced kink in velocities.

524

525 Figure 5. Variations in  $V_P$  (a-c),  $V_S$  (d-f) of cycles (2)-(8) as a function of temperature. Error of  
526 velocities is listed in Table 1.

527

528 Figure 6. Variations in a)  $V_P$ , and b)  $V_S$  as a function of pressure at temperatures of 300-773 K.

529 Error of velocities is listed in Table 1.

530

531 Figure 7. A typical diffraction pattern for anorthite at room temperature and room pressure.

532

533 Figure 8. Unit cell parameters of anorthite as a function of temperature. Error of the unit cell  
534 parameters (one standard deviation) is smaller than symbols.

535

536 Figure 9. Unit cell volume of anorthite as a function of pressure. Error of the unit cell volume  
537 (one standard deviation) is smaller than symbols.

538

539 Figure 10. Elastic wave velocities of plagioclase with various chemical compositions at room  
540 temperature and at pressures of  $\leq 1$  GPa. The Ryzhova's data are Voigt-Reuss-Hill averages of  
541 single crystals. Gray circles show the velocities after correction for pore effect.

542

543 Figure 11. Pole figures showing crystallographic orientations of anorthite grains in recovered  
544 sample from S2708 (equal area lower hemisphere projections of [100] and  $[(-1)00]$  directions,  
545 (010) and (001) planes). The orientations of grains were measured by electron backscatter  
546 diffraction method using FE-SEM (Ohuchi et al. 2011). 404 measurements are used. The  
547 cylinder axis is vertical.

548

549 Figure 12. Comparison of  $V_P$  and  $V_S$  in the crustal portion of the subducting slab in the Japan  
550 arcs with those of gabbro and eclogite. Solid circles show  $V_P$  and  $V_S$  values along A-A' and  
551 B-B' sections of northeastern and central Japan of Nakajima et al. (2009). Open diamonds  
552 denote averaged  $V_P$  in northeastern Japan estimated using P-to-S-converted waves (Shiina et

553 al. 2013)

554

Table 1. Experimental conditions, density, elastic wave velocities and elastic parameters for anorthite

Temperature (K)	Load (ton)	Pressure (GPa)	$V_p$ (km/s)	$V_s$ (km/s)	$\rho$ (g/cm <sup>3</sup> )	$K_s$ (GPa)	$G$ (GPa)
Run No. S2708							
before experiment							
300	0	0.0001			2.754		
heating (2)							
1373	150	1.21(10)	6.81(1)	3.51(1)	2.765	82.6(4)	34.1(2)
1273	150	1.09(7)	6.85(1)	3.54(<1)	2.765	83.6(3)	34.6(1)
1173	150	1.07(8)	6.87(1)	3.55(1)	2.767	84.1(7)	34.8(1)
1073	150	0.99(13)	6.89(1)	3.56(1)	2.768	84.4(4)	35.2(2)
973	150	0.95(11)	6.90(2)	3.57(1)	2.769	85.1(7)	35.2(1)
873	150	0.90(9)	6.90(<1)	3.57(1)	2.770	84.9(2)	35.3(1)
773	150	0.82(8)	6.89(1)	3.56(1)	2.771	84.8(4)	35.1(2)
673	150	0.75(9)	6.87(<1)	3.55(1)	2.772	84.2(2)	34.8(2)
573	150	0.66(10)	6.82(1)	3.51(1)	2.773	83.5(3)	34.2(2)
473	150	0.67(7)	6.81(1)	3.48(<1)	2.775	84.0(4)	33.7(1)
373	150	0.62(7)	6.95(<1)	3.66(1)	2.777	84.5(2)	37.3(1)
300	150	0.63(4)	7.01(1)	3.73(<1)	2.778	84.9(4)	38.6(1)
heating (3)							
773	220	2.83(6)	6.84(3)	3.47(1)	2.847	87.7(11)	34.3(2)
673	220	2.82(9)	6.79(3)	3.45(1)	2.850	86.3(10)	33.8(1)
573	220	2.67(10)	6.83(3)	3.46(<1)	2.853	87.6(12)	34.1(1)
473	220	2.62(4)	6.88(3)	3.51(1)	2.855	88.4(12)	35.2(1)
373	220	2.56(6)	6.95(2)	3.60(1)	2.857	88.6(9)	37.1(3)
300	220	2.53(2)	7.00(1)	3.66(1)	2.858	88.8(6)	38.4(2)
heating (4)							
773	250	3.79(18)	6.81(1)	3.44(1)	2.879	88.0(4)	34.1(2)
673	250	3.71(7)	6.80(1)	3.44(<1)	2.880	87.8(4)	34.1(<1)
573	250	3.63(8)	6.83(1)	3.46(<1)	2.882	88.5(5)	34.5(1)
473	250	3.60(4)	6.90(3)	3.53(<1)	2.884	89.2(10)	36.0(<1)
373	250	3.54(3)	6.95(2)	3.61(<1)	2.885	89.5(9)	37.6(<1)



300	250	3.53(4)	7.00(1)	3.65(1)	2.885	90.1(5)	38.4(2)
heating (5)							
773	280	4.55(14)	6.78(1)	3.41(1)	2.898	88.2(5)	33.7(2)
673	280	4.42(8)	6.78(3)	3.42(1)	2.898	88.0(13)	33.9(2)
573	280	4.35(7)			2.900		
473	280	4.26(3)	6.89(2)	3.53(1)	2.902	89.5(9)	36.1(1)
373	280	4.28(1)	6.95(7)	3.61(2)	2.902	89.8(28)	37.7(4)
302	280	4.24(4)	6.97(1)	3.64(1)	2.903	89.7(6)	38.4(2)
573	280	4.45(6)	6.82(2)	3.46(1)	2.902	88.9(7)	34.7(1)
300	280	4.37(4)	6.96(2)	3.64(1)	2.907	89.7(8)	38.4(2)
heating (6)							
773	320	5.05(4)	6.74(2)	3.39(1)	2.922	88.1(7)	33.6(1)
673	320	4.84(7)	6.77(2)	3.41(1)	2.921	88.6(7)	34.1(1)
573	320	4.76(9)	6.82(2)	3.46(1)	2.923	89.2(8)	35.0(1)
473	320	4.71(5)	6.87(2)	3.53(1)	2.923	89.5(9)	36.4(2)
373	320	4.68(1)	6.92(2)	3.59(1)	2.923	89.7(10)	37.7(2)
300	320	4.64(9)	6.94(3)	3.63(1)	2.926	89.7(12)	38.5(2)
heating (7)							
773	390	5.66(14)	6.72(1)	3.38(1)	2.944	88.2(4)	33.6(1)
673	390	5.60(3)	6.75(2)	3.41(<1)	2.943	88.6(6)	34.2(1)
573	390	5.52(5)	6.81(2)	3.47(1)	2.944	89.5(7)	35.4(2)
473	390	5.33(2)	6.86(3)	3.53(1)	2.945	89.9(12)	36.6(3)
373	390	5.15(7)	6.89(2)	3.58(1)	2.944	89.7(9)	37.6(2)
300	390	5.00(35)	6.92(1)	3.61(1)	2.948	89.9(6)	38.4(2)
heating (8)							
773	480	6.99(1)	6.67(1)	3.36(<1)			
673	480	6.71(12)	6.70(1)	3.40(1)	2.988	88.4(5)	34.5(1)
573	480	6.59(13)	6.77(2)	3.46(1)	2.988	89.4(7)	35.7(2)
473	480	6.60(3)	6.81(2)	3.51(1)	2.989	89.5(10)	36.8(2)
373	480	6.51(8)	6.84(2)	3.55(1)	2.989	89.6(10)	37.7(1)
300	480	6.52(3)	6.86(2)	3.57(1)	2.991	89.7(9)	38.2(1)

Numbers in parentheses are the one standard deviation ( $1\sigma$ ) in the last digit.  $1\sigma$  of density is less than  $0.001 \text{ (g/cm}^3\text{)}$

555

556

557

558

559

560 **APPENDIX**

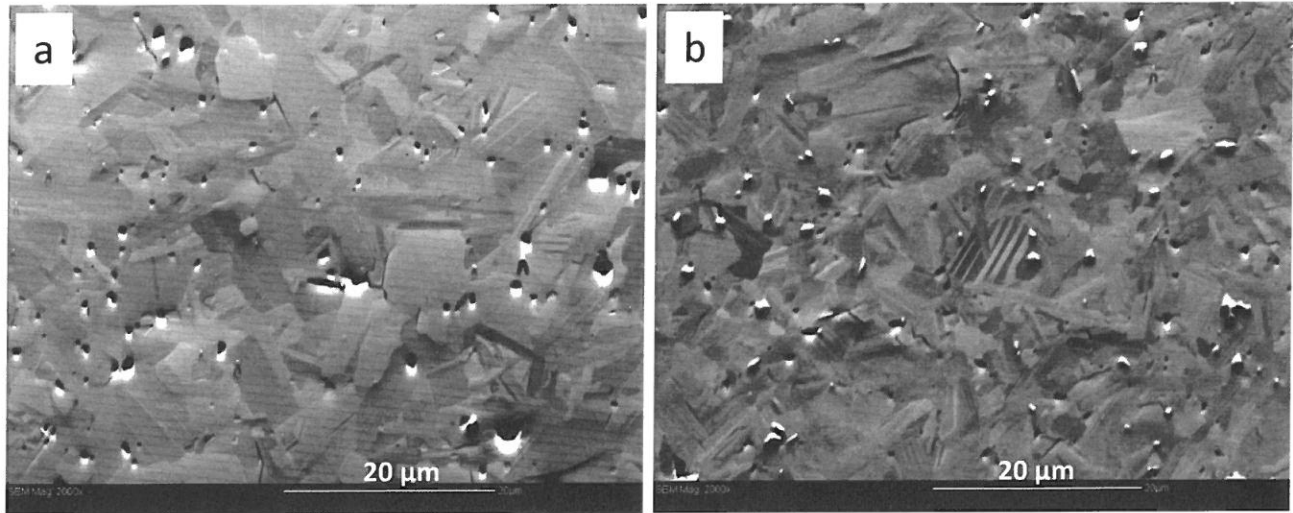
561 The in situ elastic wave velocity measurements of anorthite were performed twice. In first  
562 experiments (S2646), the measurements were carried out under load of 150 ton and 250 ton  
563 after preheating process. We, however, could not obtain reliable temperature and pressure data  
564 at except for room temperature because thermocouple was broken during preheating process.  
565 In second experiment (S2708), we succeeded to measure the temperature directly by  
566 thermocouple, and the reliable data in wide pressure and temperature range were corrected  
567 (see text). Therefore, only the second experiment was used for the discussion. Here, in order  
568 to prove reproducibility of the elastic wave velocity anomalies observed by S2708, the results  
569 of S2646 are compared. Temperature in S2646 was estimated using relation between  
570 temperature and electric power at the same loads in S2708. In S2646, pressures at room  
571 temperature after heating was calculated from the EOS of MgO as 1.5 GPa for 150 ton and  
572 3.1 GPa for 250 ton, respectively. The pressure at 150 tons was higher than that of 150 tons of  
573 S2708, and, in the case of 250 tons, it becomes lower. Therefore there may be larger  
574 uncertainty in this temperature estimation. As shown in Figure A1, the elastic wave velocity  
575 anomalies were evident in the experiment of S2646. The variation of  $V_P$  of S2646 agrees well  
576 with that of S2706. In the experiments at 150 ton, the  $V_S$  of S2646 becomes slower than that  
577 of S2708. The lower  $V_S$  in S2646 are considered to originate from the difference in pressure  
578 because the  $dV_S/dP$  shows a negative though  $dV_P/dP$  is constant at below  $\sim 4$  GPa. In  
579 conclusion, these comparisons demonstrate the reproducibility of our experiments.

580

581 Figure A1. Elastic wave velocities as a function of temperature in S2646 and S2708.

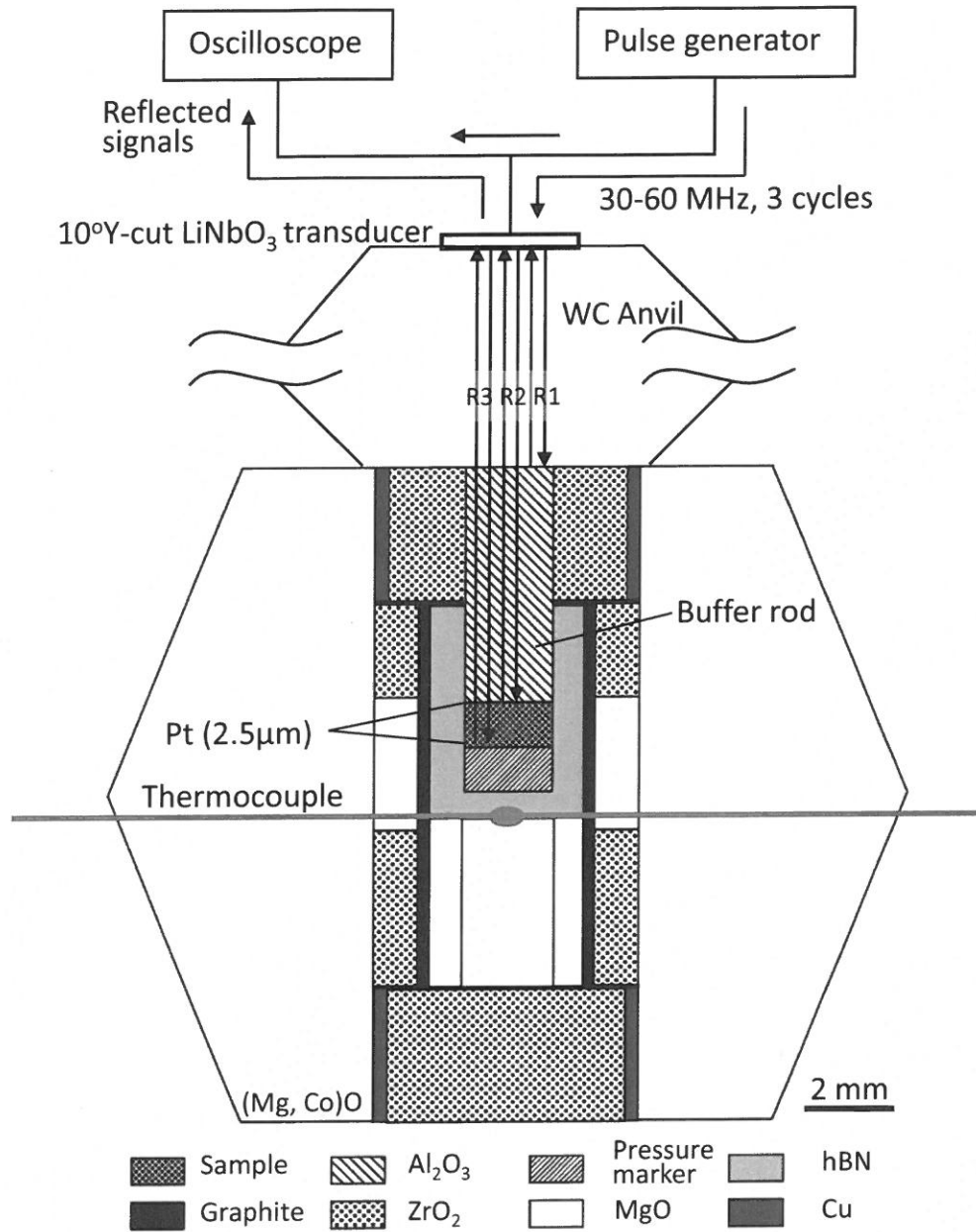
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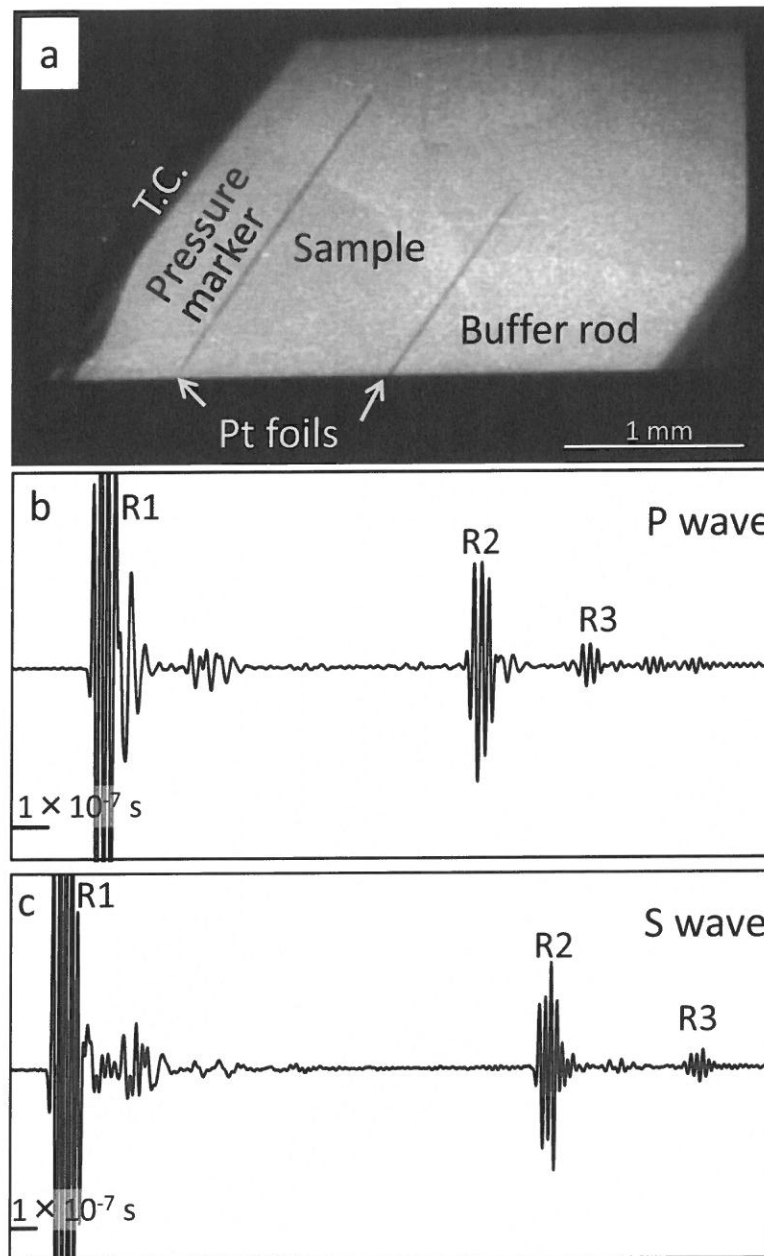
**Figure 1.** Orientation contrast images of the synthesized polycrystalline anorthite taken using forescatter detectors in scanning electron microprobe equipped with field emission gun (FE-SEM) with the polished sample inclined at 70 ° (Prior et al., 1999). a) Before experiment, b) after experiment. Bright particles in (b) are reaction products at high pressure.

Matsukage et al.



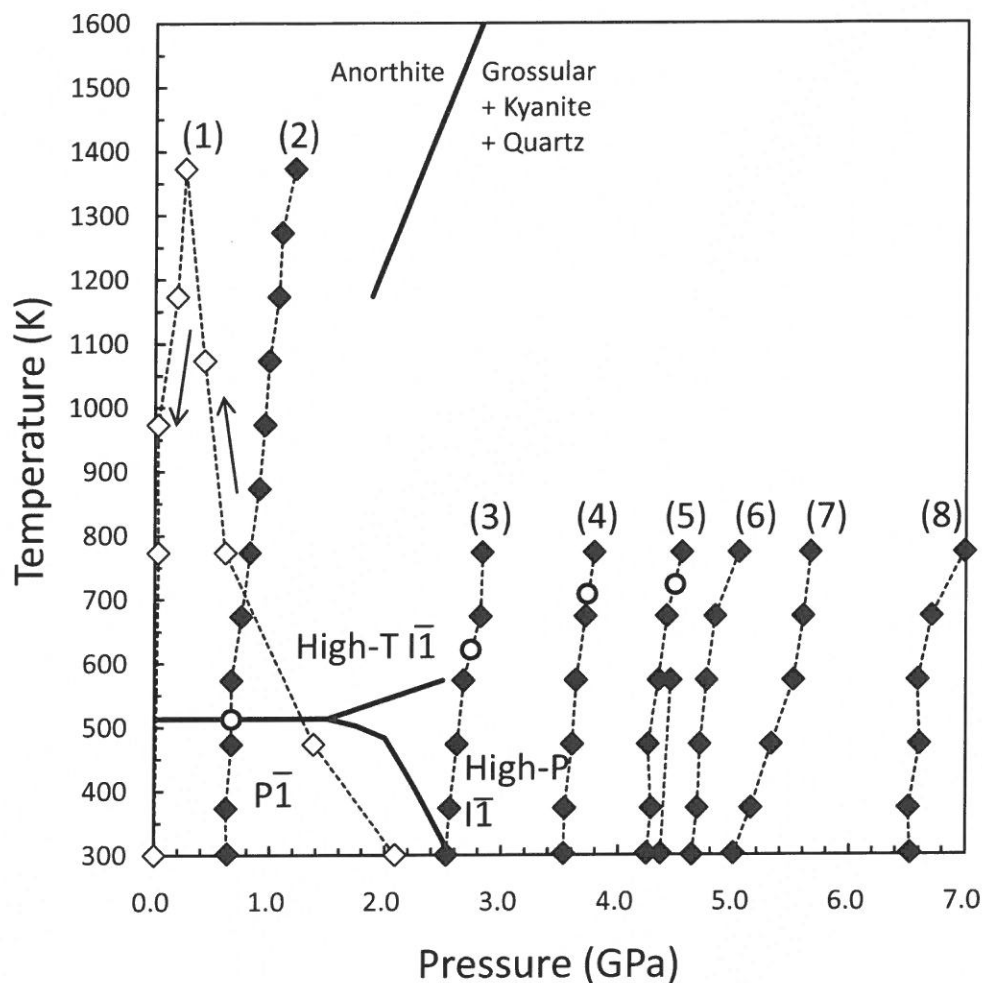
**Figure 2.** A schematic illustration of cell assembly for elastic wave velocity measurements.

Matsukage et al.



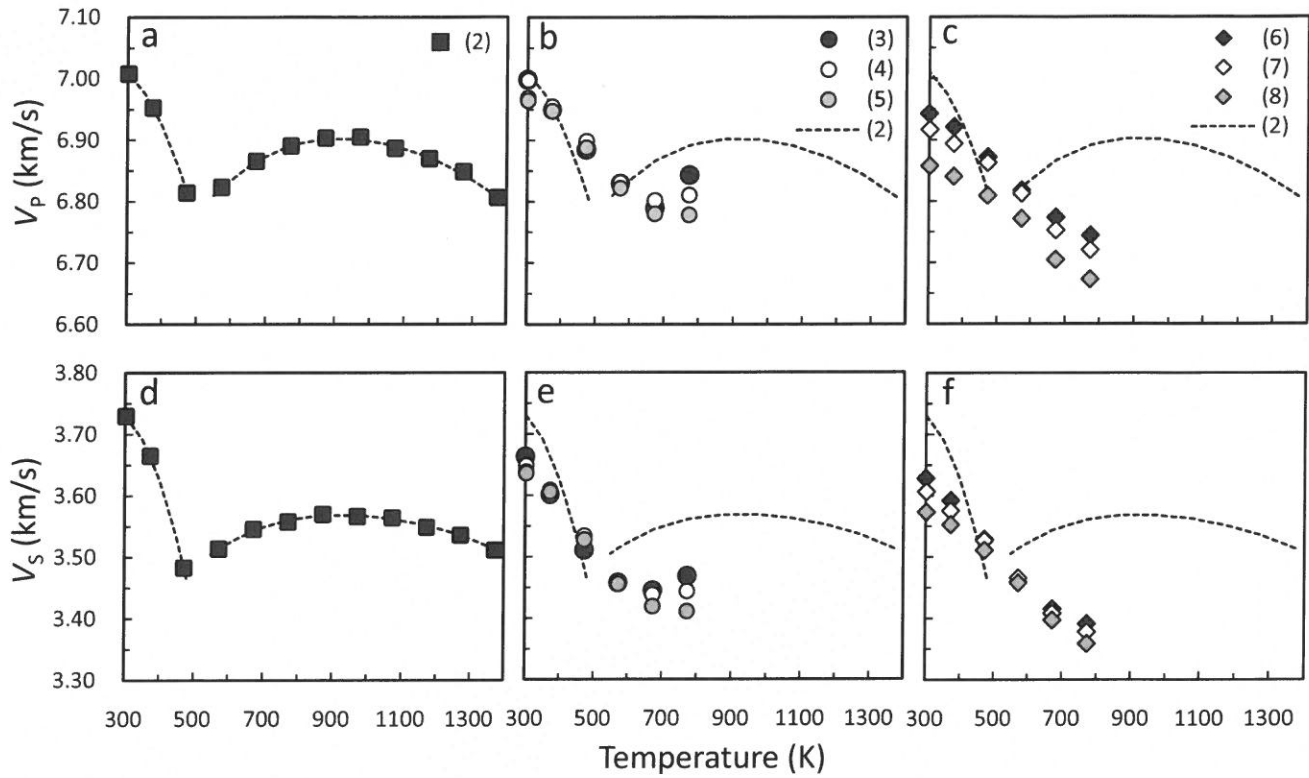
**Figure 3.** A typical example of the X-ray radiographic image (a) and the ultrasonic signals (b and c) at 1373 K and 1.2 GPa. R1, R2 and R3 are shown in Figure 2.

Matsukage et al.



**Figure 4.** Experimental pressure and temperature paths in elastic wave velocity measurements on anorthite. Open diamonds denote the preheating stage. Phase relations of anorthite are after Hackwell and Angel (1995) and Koziol and Newton (1988). The pressure of the phase transition from P(-1) to high-pressure I(-1) was dependent on the state of Si and Al order, and when  $Q_{OD}$  (see text) decreases from 0.92 to 0.78, the pressure of the phase transition increases from 2.5 GPa to 4.8 GPa (Angel, 1992). Open circles indicate the pressure and temperature conditions corresponding to the temperature-induced kink in velocities.

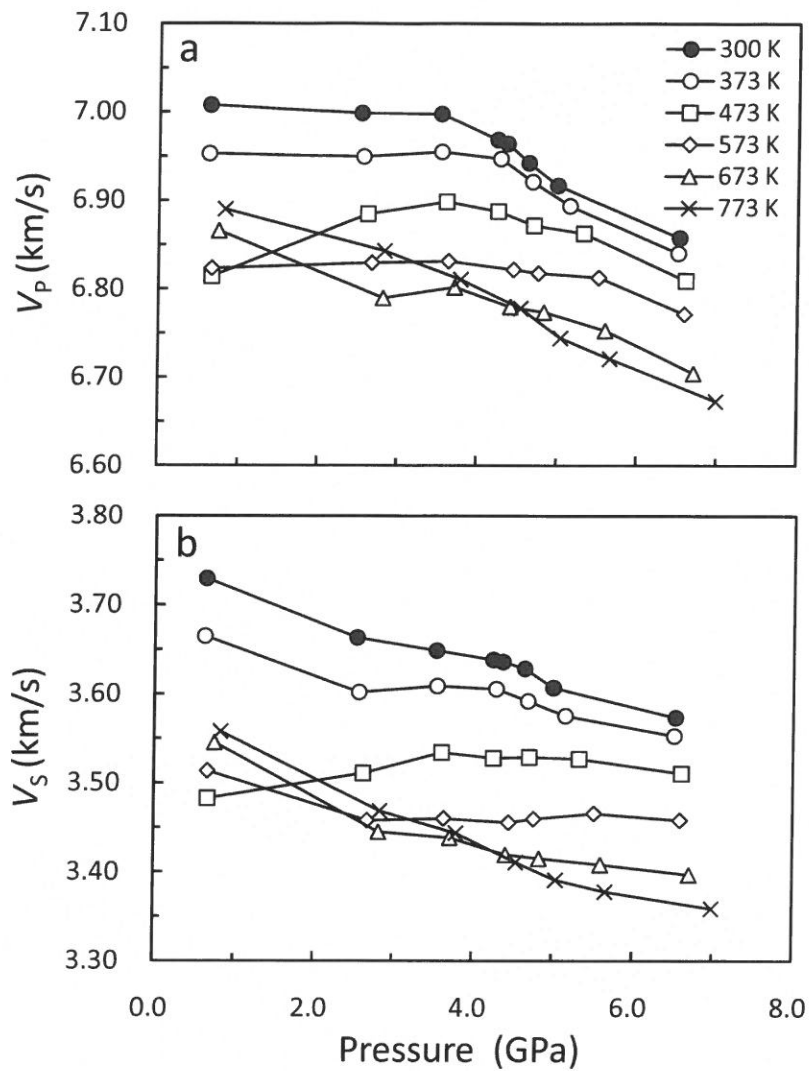
Matsukage et al.



**Figure 5.** Variations in  $V_p$  (a-c),  $V_s$  (d-f) of cycles (2)-(8) as a function of temperature. Error of velocities is listed in Table 1.

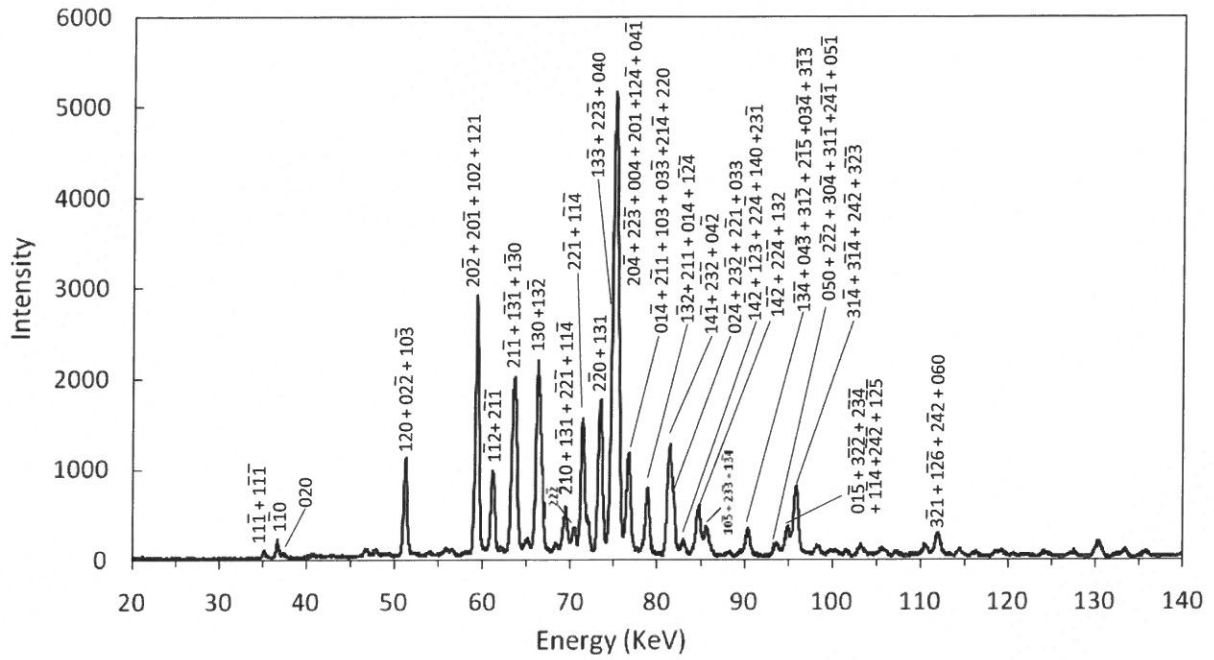
Matsukage et al.





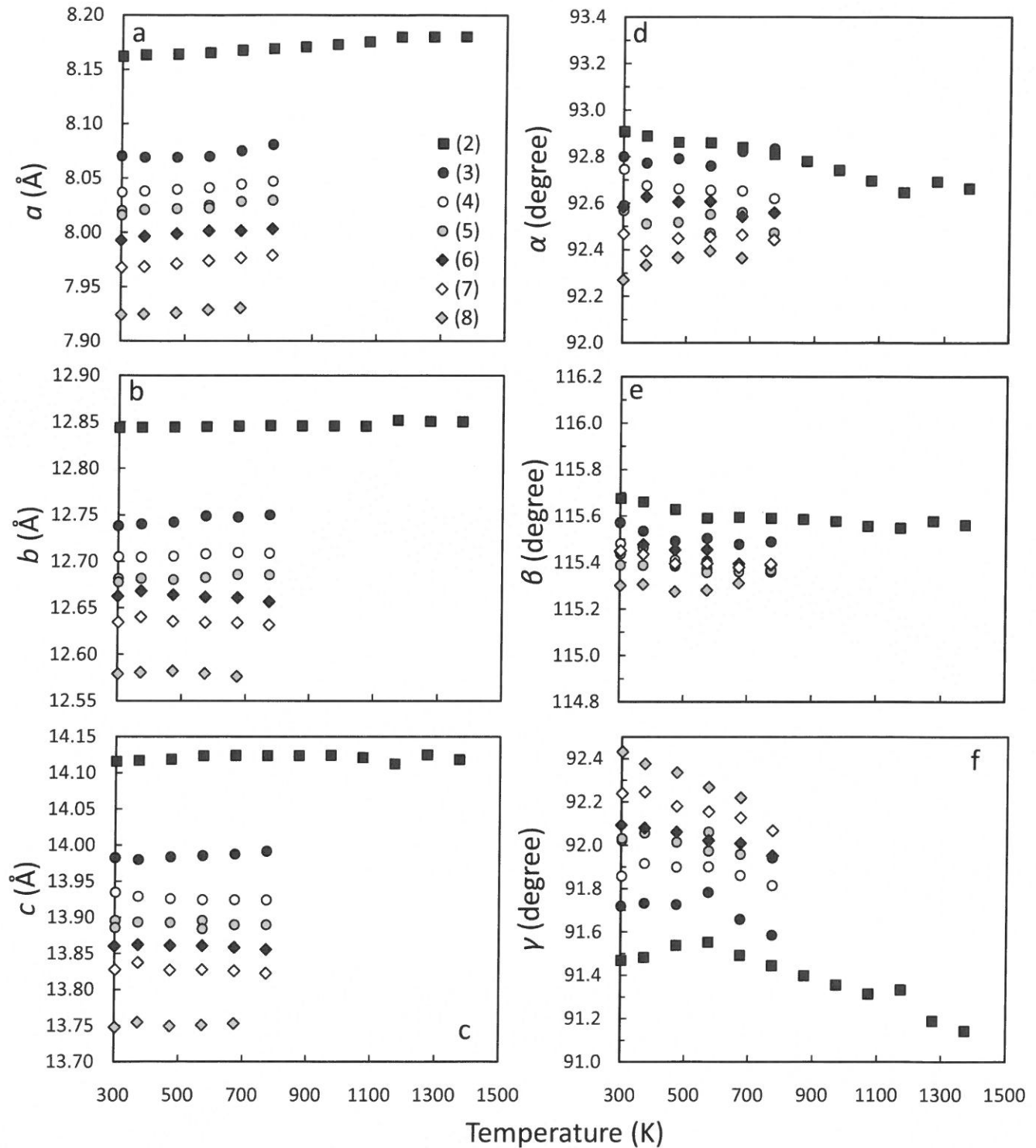
**Figure 6.** Variations in a)  $V_P$  and b)  $V_S$  as a function of pressure at temperatures of 300-773 K. Error of velocities is listed in Table 1.

Matsukage et al.



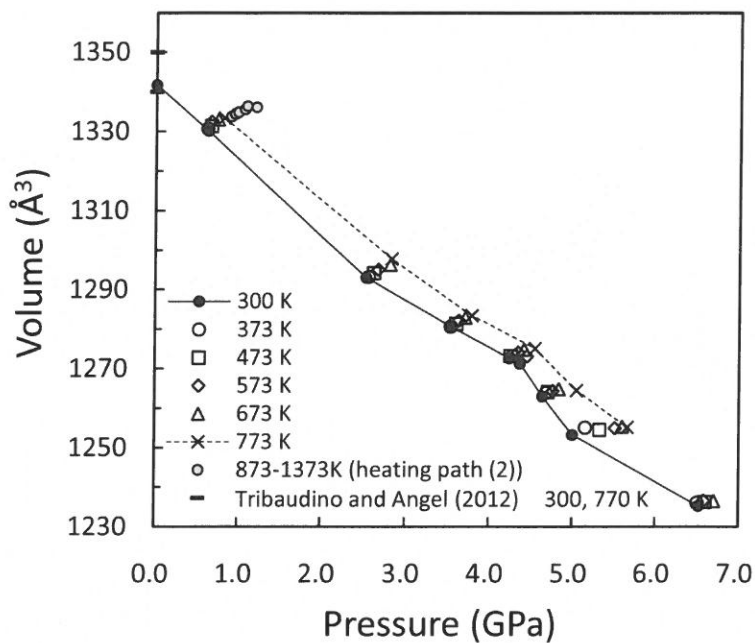
**Figure 7.** A typical diffraction pattern for anorthite at room temperature and room pressure.

Matsukage et al.



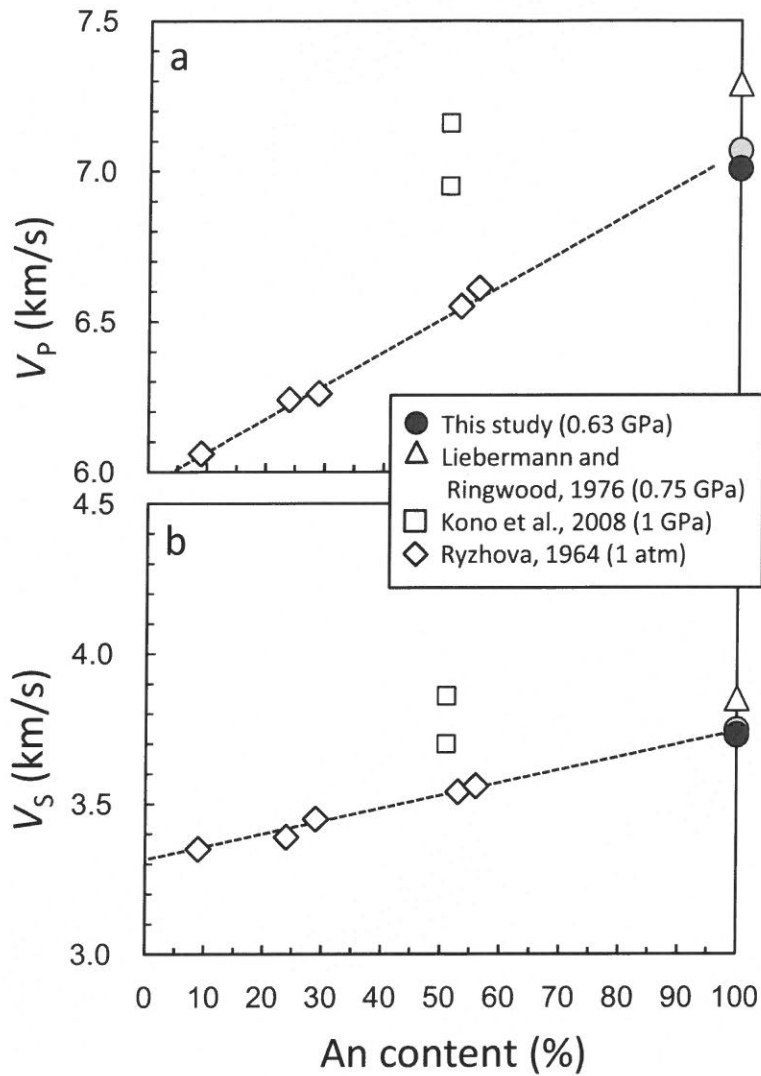
**Figure 8.** Unit cell parameters of anorthite as a function of temperature. Error of the unit cell parameters (one standard deviation) is smaller than symbols.

Matsukage et al.



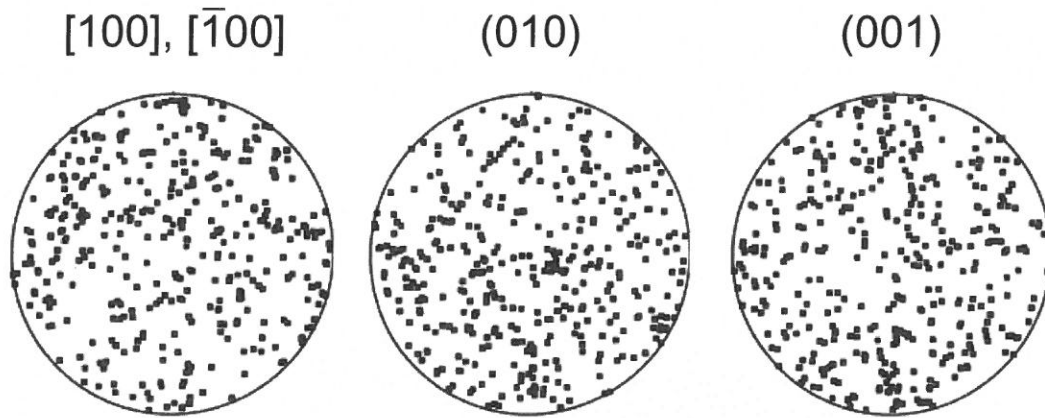
**Figure 9.** Unit cell volume of anorthite as a function of pressure. Error of the unit cell volume (one standard deviation) is smaller than symbols.

Matsukage et al.



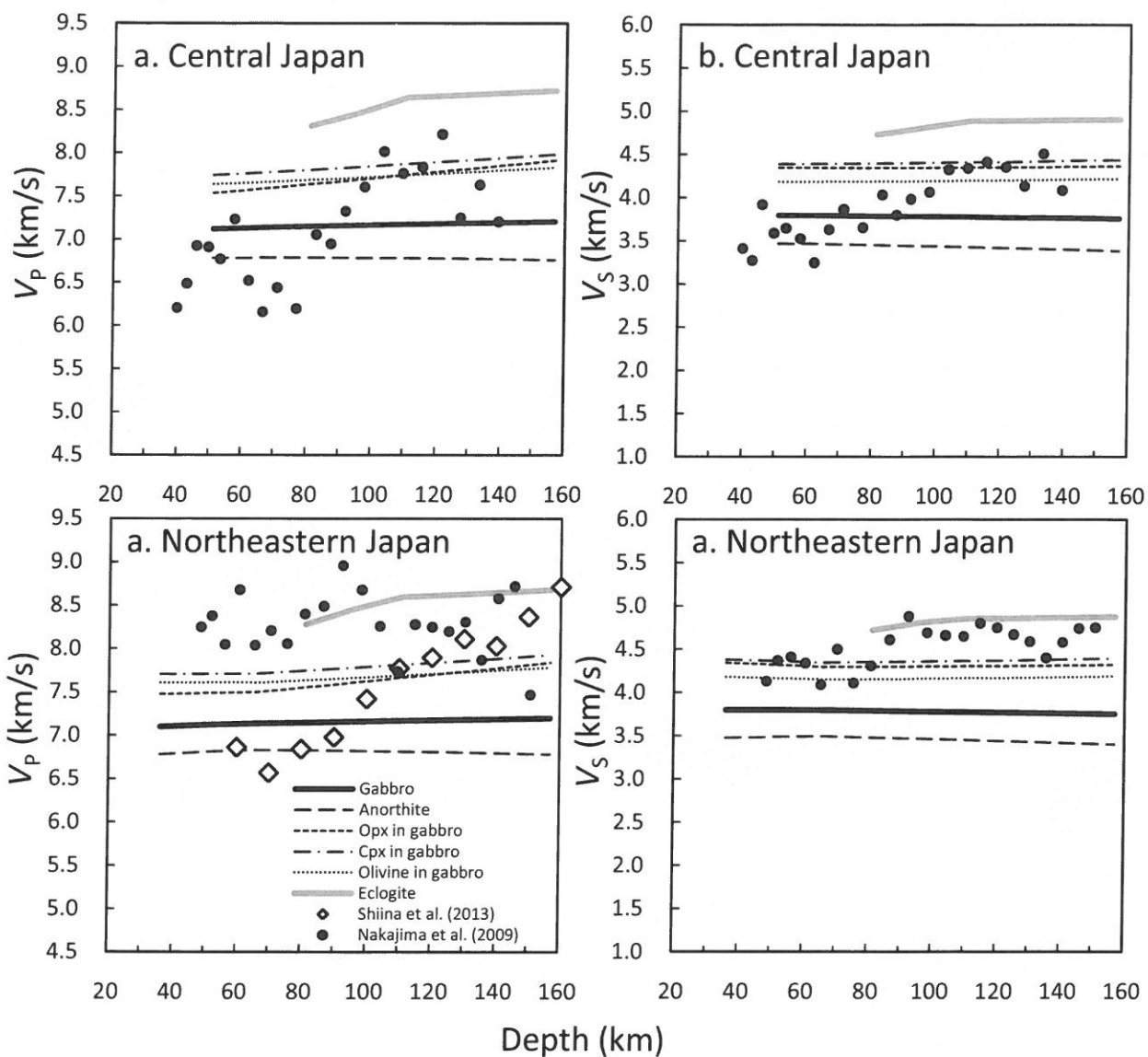
**Figure 10.** Elastic wave velocities of plagioclase with various chemical compositions at room temperature and at pressures of  $\leq 1$  GPa. The Ryzhova's data are Voigt-Reuss-Hill averages of single crystals. Gray circles show the velocities after correction for pore effect.

Matsukage et al.



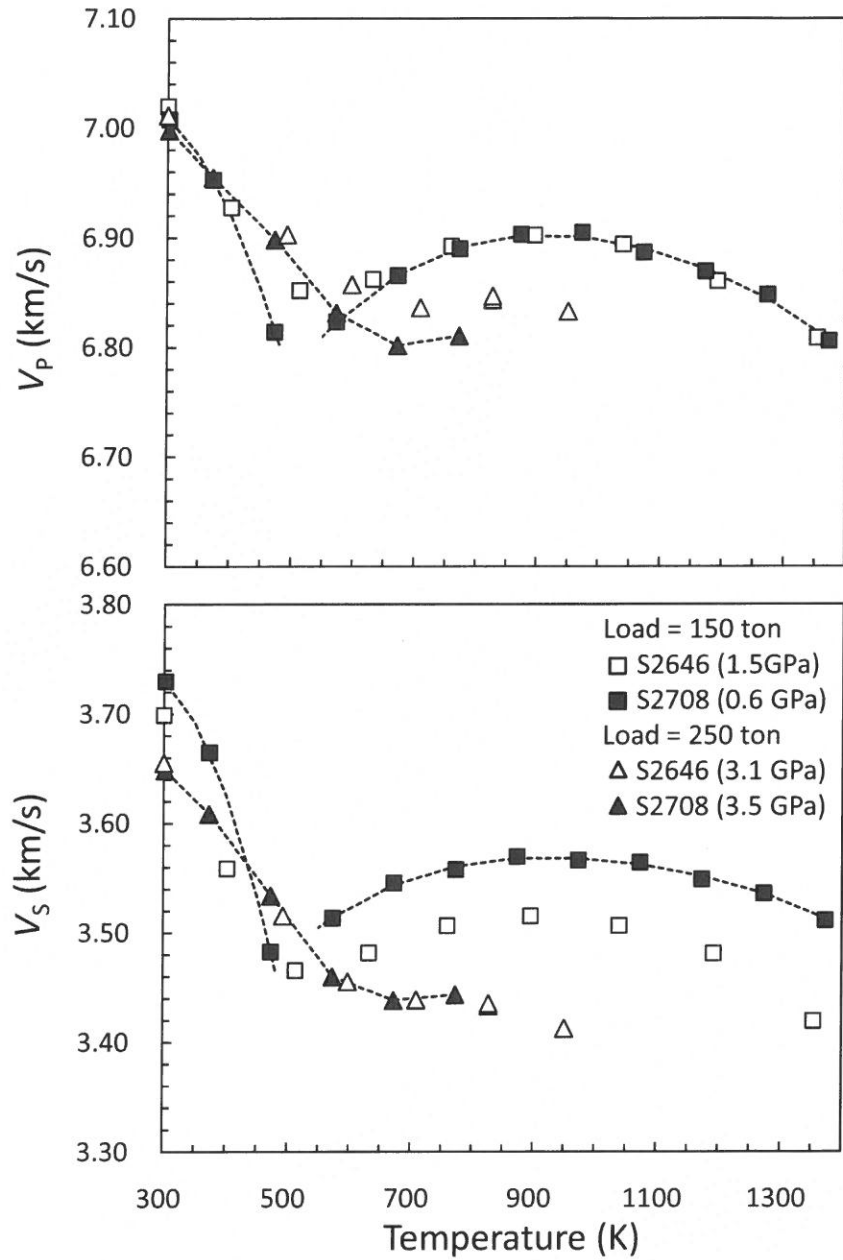
**Figure 11.** Pole figures showing crystallographic orientations of anorthite grains in recovered sample from S2708 (equal area lower hemisphere projections of [100] and  $[\bar{1}00]$  directions, (010) and (001) planes). The orientations of grains were measured by electron backscatter diffraction method using FE-SEM (Ohuchi et al. 2011). 404 measurements are used. The cylinder axis is vertical.

Matsukage et al.



**Figure 12.** Comparison of  $V_P$  and  $V_S$  in the crustal portion of the subducting slab in the Japan arcs with those of gabbro and eclogite. Solid circles show  $V_P$  and  $V_S$  values along A-A' and B-B' sections of northeastern and central Japan of Nakajima et al. (2009). Open diamonds denote averaged  $V_P$  in northeastern Japan estimated using P-to-S-converted waves (Shiina et al. 2013).

Matsukage et al.



Appendix

**Figure A1.** Elastic wave velocities as a function of temperature in S2646 and S2708.

Matsukage et al.