

1 **Revision 1**

2 **Crystal structure of the high-pressure phase of calcium hydroxide, portlandite: *In***  
3 ***situ* powder and single crystal X-ray diffraction study**

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19 **ABSTRACT**

20 The crystal structure of a high-pressure phase of calcium hydroxide, Ca(OH)<sub>2</sub>  
21 (portlandite), was clarified for the first time using the combination of *in situ* single  
22 crystal and powder X-ray diffraction measurements at high pressure and room  
23 temperature. A diamond anvil cell with a wide opening angle and cell-assembly was  
24 improved for single crystal X-ray diffraction experiments, which allowed us to  
25 successfully observe Bragg reflections in a wide range of reciprocal space. The  
26 transition occurred at 6 GPa and the crystal structure of the high-pressure phase was  
27 determined to be monoclinic at 8.9 GPa and room temperature [*I*121; *a* = 5.8882(10) Å,  
28 *b* = 6.8408(9) Å, *c* = 8.9334(15) Å, *β* = 104.798(15)°]. The transition involved a  
29 decrease in molar volume by approximately 5.8%. A comparison of the structures of the  
30 low- and high-pressure phases indicates that the transition occurs by a shift of CaO<sub>6</sub>  
31 octahedral layers in the *a-b* plane along the *a*-axis, accompanied by up-and-down  
32 displacements of Ca atoms from the *a-b* plane. The crystal structure of this  
33 high-pressure phase is considered to be an intermediate state between the low-pressure  
34 phase and the high-pressure–high-temperature phase. The complicated diffraction  
35 patterns of the high-pressure phase suggest that the phase transition occurred toward  
36 three directions around the *c*-axis of the low-pressure phase. This explains the  
37 difficulties encountered in previous structural analyses. The present results will provide  
38 key information for discussing the behavior of hydrogen bonds in these hydrous  
39 minerals under pressure.

40

41 **Keywords:** portlandite, phase transition, crystal structure, high pressure, X-ray  
42 diffraction, hydrogen bond

43

#### 44 INTRODUCTION

45 The pressure responses of hydrogen-bearing materials represent an interesting  
46 research topic in various fields of science. In over 20 years, hydroxides of a divalent  
47 metal,  $M(OH)_2$  ( $M = Mg, Ca, Mn, Co, Ni, Cd, \text{etc.}$ ), with a  $CdI_2$  structure (trigonal,  
48 space group  $P3m1$ ), have been investigated intensively by various methods such as  
49 optical spectroscopy, X-ray and neutron diffraction, and numerical simulations. These  
50 hydroxides are a research target because they show complicated structural and property  
51 changes, probably related to hydrogen bond interactions. In spite of their simple  
52 structure, diverse behaviors in  $M(OH)_2$  have been reported under high pressure,  
53 including high stability of the starting structure over a wide pressure range (Fei and  
54 Mao 1993), pressure-induced amorphization (Meade and Jeanloz 1990; Kruger et al.  
55 1989; Nguyen et al. 1997), phase transitions (Duffy et al. 1995; Ekbundit et al. 1996;  
56 Catalli et al. 2008; Iizuka et al. 2011), repulsion between hydrogen atoms within  
57 interlayers (Parise et al. 1998, 1999), and partial (H-sublattice) amorphization (Murli et  
58 al. 2001; Shieh and Duffy 2002). Proton disorder is predicted from theoretical  
59 simulations (Raugei et al. 1999; Mookherjee and Stixrude 2006). In addition to interest  
60 in the fields of material physics and crystallography,  $M(OH)_2$  is also important for  
61 geoscience because it is one of the simplest model structures of hydrous minerals,  
62 thereby providing insights into processes of water transport in subduction zones at

63 depths ranging from the Earth's surface to the deep mantle.

64  $\text{Ca(OH)}_2$  (portlandite), whose cation has the largest ionic radius among these  
65  $\text{M(OH)}_2$  hydroxides, undergoes various unique structural changes at relatively low  
66 pressures. In early studies, it was reported that a reversible pressure-induced  
67 amorphization occurs at 11 GPa and room temperature, based on broadening of the OH  
68 vibration mode in IR spectra (Kruger et al. 1989) and the disappearance of powder  
69 X-ray diffraction (XRD) peaks (Meade and Jeanloz 1990). However, the existence of a  
70 crystalline phase at high pressure and high temperature ( $\text{Ca(OH)}_2$ -II, hereafter "High-PT  
71 phase") was reported at >7 GPa and >200 °C, and its crystal structure was determined  
72 by an *in situ* XRD study by Kunz et al. (1996). Subsequently, Leinenweber et al. (1997)  
73 studied this phase using neutron diffraction and clarified the hydrogen positions. The  
74 authors recovered the High-PT phase to ambient pressure by quenching and  
75 decompression in liquid  $\text{N}_2$ , and measured the neutron diffraction at 0.1 MPa and 11 K.

76 Even by compression at room temperature, a transition from an ambient pressure  
77 phase (hereafter "Low-P phase") into a crystalline high-pressure phase (hereafter  
78 "High-P phase") was observed at around 6–8 GPa (Ekbundit et al. 1996; Catalli et al.  
79 2008; Iizuka et al. 2011), instead of amorphization, when the applied pressure remained  
80 hydrostatic. Although the structure of this High-P phase remains unknown,  
81 spectroscopic measurements suggest that the hydrogen bonds show remarkable changes  
82 at the phase transition (Iizuka et al. 2011). Thus, the determination of the detailed  
83 crystal structure of this High-P phase is interesting from the viewpoints of both earth  
84 science and crystallography. Previous powder X-ray diffraction studies at high pressure

85 have revealed the difficulty encountered in clarifying the crystal structure of the High-P  
86 phase (Catalli et al. 2008; Iizuka et al. 2011) because: (1) the high-pressure behavior of  
87 portlandite is sensitive to the hydrostaticity of the applied pressure, and it is difficult to  
88 obtain reproducible results; (2) the Low-P and High-P phases coexist over a wide  
89 pressure range and it is difficult to obtain clear diffraction patterns from the single  
90 High-P phase; and (3) diffraction peaks of the High-P phase become broad and weak  
91 with increasing pressure. Although previous studies reported spectroscopic  
92 measurements using single crystal samples of portlandite (Ekbundit et al. 1996; Shinoda  
93 et al. 2000; Iizuka et al. 2011), there are no reports of single crystal X-ray diffraction  
94 studies, probably because the phase transition is reversible at room temperature and the  
95 High-P phase is unquenchable. In addition, even in single crystals the transition does  
96 not occur instantaneously, the Low- and High-P phases coexist over a wide pressure  
97 range, and the diffraction pattern of the High-P phase is complicated, as described  
98 below.

99 In this study, we clarified the crystal structure of the High-P phase by combining  
100 powder and single crystal X-ray diffraction measurements. We obtained high-quality  
101 X-ray diffraction patterns in the wide reciprocal lattice by improving upon existing  
102 experimental techniques, and analyzed the structure of the High-P phase with the aid of  
103 theoretical calculations. Based on the structure thus obtained, we discuss the structural  
104 relations of the three polymorphs of portlandite (i.e., the Low-P, High-P, and High-PT  
105 phases) and the mechanism of the phase transition.

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107

## EXPERIMENTAL

### 108 **Sample preparation**

109 Powder samples of  $\text{Ca}(\text{OH})_2$  or  $\text{Ca}(\text{OD})_2$  were synthesized by the hydration of  $\text{CaO}$   
110 powders (assay minimum of 99.9%; Wako Pure Chemical Industries Ltd) with pure  
111 water  $\text{H}_2\text{O}$  (milli-Q; Nihon Millipore Ltd) or  $\text{D}_2\text{O}$  (minimum isotope purity of 99.96  
112 atom%D; Aldrich Chemical Co. Inc.) at 235 °C for 1 week. Single crystals were  
113 obtained by gradually recrystallizing the synthesized powder sample on glass plates  
114 with excess  $\text{H}_2\text{O}$  or  $\text{D}_2\text{O}$  in desiccators. These synthesized samples were characterized  
115 using X-ray diffraction and Raman spectra as described in detail by Iizuka et al. (2011).  
116 Many hexagonal prismatic single crystals with a diameter of 30–300  $\mu\text{m}$  were grown,  
117 and the single crystals had a strong cleavage along the (001) plane. Microscopic  
118 observations under high pressure clarified that the shape of the single crystal remained  
119 almost unchanged by the phase transition, although the transition was clearly visible.  
120 The transition of the single crystal sample did not occur at once, but domains (around  
121 10–20  $\mu\text{m}$  thick) along the *c*-axis were transformed stepwise during the pressure  
122 increase from about 6 to 8 GPa. Thus, the Low- and High-P phases coexisted in this  
123 pressure range. In this study, therefore, single crystals of  $\sim 50 \times \sim 50 \times 10\text{--}20 \mu\text{m}^3$  in size  
124 were prepared by splitting large single crystals into the desired thickness along a (001)  
125 plane, following the cleavage.

126

### 127 **Improvements in single-crystal high-pressure apparatus**

128 In single crystal X-ray diffraction experiments, clamped diamond anvil cells

129 (DACs) were used. As described above, a platelet crystal was used. In conventional  
130 techniques, the X-ray beam is introduced parallel to the compression axis in the DAC.  
131 However, this geometry mainly yields information on the  $hk0$  lattice plane, because of  
132 the sample's strong cleavage (001) plane, which sits on the surface of the diamond anvil.  
133 This limitation makes it difficult to obtain reflections for the whole reciprocal lattice  
134 space. To obtain information from  $l \neq 0$  reflections, we made modifications to a  
135 Radial-DAC (Fig. 1(a)). The Radial-DAC was originally developed to observe uniaxial  
136 strain and preferred orientation in the sample by introducing X-rays perpendicular to the  
137 compression axis; consequently, the use of an X-ray-transparent gasket is indispensable  
138 (Merkel and Yagi 2005). Beryllium or a combination of boron-epoxy and kapton film  
139 has been widely used as a gasket material. A beryllium gasket has the disadvantage of a  
140 very strong background, whereas a boron-epoxy gasket cannot maintain the liquid  
141 pressure-transmitting medium during compression.

142 To overcome these difficulties, we processed to make a small hole in one of the  
143 anvils and compressed the sample in the hole with a smaller culet anvil using a stainless  
144 steel (SUS) gasket, as follows. First, a small cup-shaped, flat-bottomed hole (125  $\mu\text{m}$  in  
145 diameter and  $\sim 20$   $\mu\text{m}$  deep) was drilled in the center of the large culet (800  $\mu\text{m}$  in  
146 diameter) using an excimer laser (excitation wavelength: 248 nm of KrF). The sample  
147 was loaded into the hole, and a SUS gasket with a 175  $\mu\text{m}$ -diameter-hole was placed on  
148 the sample. Then, the holes were filled with glycerin as a pressure medium (as  
149 described below). The assembly was compressed with the smaller culet anvil (350  $\mu\text{m}$   
150 in diameter), toward which the SUS gasket gradually bent with increasing pressure.

151 This enabled incident and diffracted X-rays to pass through the sample and the top part  
152 of the larger anvil without being disturbed by the gasket, thereby yielding clear  
153 reflections with a high signal-to-noise ratio, even from such a thin sample under  
154 hydrostatic conditions. This also allowed us to obtain crystallographic information in  
155 the direction perpendicular to the platelet-shaped single crystal. A DAC with similar  
156 X-ray geometry was reported by Glinnemann et al. (1992). In the present design,  
157 however, X-ray beam never hits the metal gasket directly by passing through the  
158 diamond with a hole, and we can obtain much clear diffraction patterns from the  
159 sample.

160 In most powder and single crystal diffraction experiments, conventional clamped  
161 DACs with an aperture angle of  $\pm 40^\circ$  were additionally used. Some of the powder  
162 X-ray diffraction experiments employed a lever-and-spring type DAC. A hybrid gasket  
163 assembly was adopted, consisting of a SUS outer and a PFA (Teflon®) ring inner,  
164 following Komatsu et al. (2011). The PFA ring (100–300  $\mu\text{m}$ , inner–outer diameter) was  
165 placed in a 300  $\mu\text{m}$  hole of the 100- $\mu\text{m}$ -thick SUS gasket. The PFA ring worked to keep  
166 the sample in the center of the culet during compression, and to prevent the  
167 contamination of scattering and attenuation by the SUS gasket. Initially, a 4:1  
168 methanol–ethanol mixture was used as a pressure-transmitting medium to maintain  
169 hydrostatic conditions, however, the single crystal sample was susceptible to dissolution.  
170 Moreover, fractures commonly developed in the anvil when an anvil with a hole was  
171 used. In this study, therefore, glycerin was used as a pressure medium because of its  
172 high viscosity and reduced volatility compared with methanol–ethanol. The use of



173 glycerin resulted in relatively simple sample preparation. Although the freezing pressure  
174 of glycerin is reported to be around 6.5–7.0 GPa (Osakabe and Kakurai 2008; Klotz et  
175 al. 2012), it remains quite soft above the freezing pressure, and no notable difference  
176 was found in the transition behavior of portlandite when using glycerin versus  
177 methanol–ethanol as the pressure medium. Pressure was determined by the ruby  
178 fluorescence method by Mao et al. (1986), or from the pressure dependence of the  
179 Raman shift of the OH stretching peaks of portlandite by Catalli et al. (2008) and Iizuka  
180 et al. (2011).

181

#### 182 **X-ray diffraction measurements**

183 The single crystal X-ray diffraction measurements were performed using both a  
184 laboratory X-ray source and synchrotron radiation. For the laboratory measurement, we  
185 used a micro-focused X-ray generator (MicroMax-007; Rigaku) with a Mo rotating  
186 target ( $\lambda = 0.7107 \text{ \AA}$ , 50 kV, 24 mA) and confocal mirror optics (Varimax-Mo; Rigaku),  
187 housed at the Geochemical Research Center (GCRC), the University of Tokyo. Incident  
188 X-rays were collimated using a single pinhole collimator with a diameter of 300  $\mu\text{m}$  or  
189 50  $\mu\text{m}$ . Single crystal oscillation photographs were taken using an imaging plate (IP)  
190 X-ray diffractometer (R-Axis IV<sup>++</sup>; Rigaku), with the sample being oscillated by  $\pm 0.5^\circ$   
191 and the diffraction recorded. The measurement was repeated by rotating the sample  
192 stepwise at  $1^\circ$  increments. The Radial DAC used in the present study has four  
193 side-windows, each of which has  $\pm 25^\circ$  openings, and measurements were performed in  
194 each window. The investigated pressures ranged from ambient condition up to about 9.0

195 GPa. A sample-to-detector distance was 150 mm, and the exposure time was 20 min for  
196 each measurement.

197       Synchrotron X-rays ( $\lambda \approx 0.41 \text{ \AA}$ , ca. 30 keV) were used at the NE1 beamline of the  
198 Photon Factory, Advanced Ring (PF-AR), High Energy Accelerator Research  
199 Organization (KEK), Tsukuba. The shorter wavelength of the synchrotron X-ray  
200 allowed us to obtain higher-index diffractions and reciprocal lattice images with less  
201 distortion. The incident X-rays were collimated to a diameter of 75  $\mu\text{m}$ , and  
202 measurements were made in the same manner as those in the laboratory experiments.  
203 The sample was oscillated by  $\pm 2.5^\circ$  and measurements were repeated at  $5^\circ$  increments  
204 of sample rotation. The diffraction data in the pressure range of 8.0–9.0 GPa were  
205 complementally obtained from both geometry using the Radial-DAC and the  
206 conventional DAC (along the compression axis). The exposure time for each  
207 measurement was 5–10 min.

208       The powder diffraction measurements were conducted using synchrotron X-rays at  
209 the same beamline (PF-AR-NE1) as for the single crystal measurements. Diffraction  
210 patterns were measured at high pressure up to above 20 GPa every 2–3 GPa (Iizuka et  
211 al., 2011). The two-dimensional diffraction image from the powder sample on an IP was  
212 converted into an intensity– $2\theta$  diffraction pattern up to  $25^\circ$  in  $2\theta$  using the software  
213 IPAnalyzer, as developed by Seto et al. (2010)

214

215 **Indexing and structure refinement analyses**

216 Indexing of the powder pattern was performed using two methods, DICVOL  
217 (Boultif and Louër 2004) and Cell Finder in the software PDIndexer (Seto et al. 2010).  
218 Crystal structure refinement was performed using the Rietveld method (Rietveld 1969)  
219 as coded in the General Structure Analysis System (GSAS) software (Larson and Von  
220 Dreele 2000). For the Low-P phase, an initial structure model for the refinement was  
221 taken from Iizuka et al. (2011) and Nagai et al. (2000). For the High-P phase, we used a  
222 new structure derived from a molecular dynamics simulation based on density  
223 functional theory (see below).

224

225 **RESULTS**

226 **Powder X-ray diffraction**

227 In the powder X-ray diffraction analyses, the High-P phase started to appear above  
228 about 6 GPa. With further compression, the amount of the Low-P phase decreased and  
229 the amount of the High-P phase increased, but the overall peaks gradually became broad  
230 and weak. The pressure dependence of the diffraction patterns has been demonstrated  
231 previously by Iizuka et al. (2011). The diffraction data obtained at 8.9 GPa were used  
232 for structure analysis of the Low-P and High-P phases, because at this pressure the  
233 diffraction pattern of the High-P phase was strong enough for analysis and the  
234 broadening of the diffraction was not yet severe (Fig. 2). Using 14 clear diffraction lines  
235 from the High-P phase with  $d$ -values ranging from 5.3 to 1.7 Å, we performed powder  
236 diffraction pattern indexing to determine the unit cell. Cells with symmetry higher than

237 orthorhombic were not consistent with the observed diffraction for both indexing  
238 methods (DICVOL and Cell finder). When the symmetry was lowered to monoclinic,  
239 several possible unit cells were found, with the best fit yielding the following cell  
240 parameters:  $a = 5.96 \text{ \AA}$ ,  $b = 6.84 \text{ \AA}$ ,  $c = 8.93 \text{ \AA}$ ,  $\beta = 103.94^\circ$ . However, there were other  
241 possible unit cells, and it was difficult to uniquely determine the unit cell from these  
242 analyses alone.

243

#### 244 **Single crystal X-ray diffraction**

245 Table 1 provides a summary of the experimental conditions of the single crystal  
246 diffraction analyses, which were performed parallel or normal to the  $c$ -axis. At each of  
247 the side-windows of the Radial-DAC, a set of 41 diffraction images, each covering a  
248 range of  $\pm 0.5^\circ$ , were obtained by varying the initial angle from  $-20$  to  $+20^\circ$ . Figure 1(b)  
249 shows a combined image of 41 images at 8.5 GPa. Data were measured through the four  
250 side-windows of the Radial-DAC in the same manner, and then all the images were  
251 accumulated into a single reciprocal space using CrystalClear software (Rigaku Corp.).  
252 After eliminating the reflections from the anvils and gasket, the unit cell was derived to  
253 satisfy the reflections from the sample, yielding the following cell parameters:  $a = 5.8 \text{ \AA}$ ,  
254  $b = 7.1 \text{ \AA}$ ,  $c = 9.0 \text{ \AA}$ ,  $\beta = 104.0^\circ$  of the monoclinic system. This result is consistent with  
255 that obtained from powder diffraction analyses at 8.9 GPa (see above). However, the  
256 orientation matrix could not be determined accurately and integrated intensities had a  
257 large  $R$ -factor for equivalent reflections, resulting from the elongate nature of the  
258 diffraction spots. By including the images with more reflections of lower  $d$ -values ( $\sim 1$

259 Å) obtained by using synchrotron X-rays, all the reflections satisfied the following  
260 selection rules for a monoclinic cell:

261

262 For  $hkl$ :  $h + k + l = 2n$ ;  $0kl$ :  $k + l = 2n$ ;  $hk0$ :  $h + k = 2n$ ;

263  $h0l$ :  $h + l = 2n$ ;  $h00$ :  $h = 2n$ ;  $00l$ :  $l = 2n$ ;

264  $0k0$ :  $k = 2n$ .

265

(1)

266 Given the above reflection conditions, we identified three possible body-centered space  
267 groups:  $I121$ (#5),  $I1m1$ (#8), and  $I12/m1$ (#12).

268

#### 269 **Analysis of crystal structure of the high-pressure phase**

270 Among the three possible space groups listed above, only  $I121$ (#5) is consistent  
271 with a reasonable arrangement of Ca and O atoms in the observed unit cell with a  
272 chemical composition of  $\text{Ca}(\text{OH})_2$ . The structure was also estimated using a  
273 first-principles molecular dynamic simulation based on density functional theory as our  
274 previous studies on high-pressure behavior of hydrous minerals by Tsuchiya et al. (2002,  
275 2005). When the portlandite structure was compressed up to 10 GPa at 0 K, the  
276 structure was compressed but remained basically unchanged. The temperature was then  
277 increased to 500 K and a stable structure was calculated at constant temperature. Some  
278 of Ca atoms shifted to the  $c$ -axis direction, and the Ca and O configurations changed  
279 into those quite similar to the structure model of a space group  $I121$ . Using this  
280 structure as an initial structure model, further refinements of the unit cell parameters  
281 and atomic positions were carried out using Rietveld analysis for the powder diffraction

282 pattern shown in Figure 2. The coexisting Low-P phase was also successfully refined by  
283 means of multi-phase Rietveld analysis. The cell parameters and the atomic positions  
284 (except for the positions of hydrogen atoms) were clarified (Tables 2 and 3,  
285 respectively).

286

287

## DISCUSSION

### 288 **Crystal structure of the High-P phase**

289 The reversible change from the Low-P phase to the High-P phase at room  
290 temperature suggests that the phase transition was accompanied not by significant  
291 atomic diffusion but by small displacements of atoms. Figure 3 compares the two  
292 crystal structures at 8.9 GPa, viewed from the same direction. A comparison of the cell  
293 parameters of the Low-P and High-P phases reveals the following relations:

$$\begin{aligned} a_{\text{HP}} &\approx \sqrt{3}a_{\text{LP}}; \\ b_{\text{HP}} &\approx 2b_{\text{LP}}; \\ c_{\text{HP}} &\approx 2c_{\text{LP}}. \end{aligned} \tag{2}$$

296 A comparison of Figure 3(a) with 3(b) shows that the *a-b* plane, which is formed by  
297 a network of CaO<sub>6</sub> polyhedrons, is preserved. However, the *c* axis, which was originally  
298 perpendicular to the *a-b* plane, was inclined from 90° to 104.80°. At the phase transition,  
299 the *a-b* plane shifted to the *a*-axis direction, and Ca atoms aligned in the *b*-axis direction  
300 in the *a-b* plane shifted alternately up and down. The molar volume decreased by  
301 approximately 5.8% at 8.9 GPa.

302 Komatsu et al. (2007) reported a similar transition mechanism in gibbsite,

303  $\gamma$ -Al(OH)<sub>3</sub>, which also has a layered structure and transforms into a High-P phase of  
304  $\eta$ -Al(OH)<sub>3</sub> at 3 GPa. The authors reported that the main mechanism of the phase  
305 transformation is a layer shift of the *a-b* plain, which is formed by a network of AlO<sub>6</sub>  
306 octahedrons. In the case of portlandite, however, the transformation involved both a  
307 layer shift and vertical displacements of in-plane Ca atoms. As a result, Ca atoms  
308 shifted closer to one of the oxygen atoms in the neighboring layer, forming a new bond.  
309 The coordination number of Ca effectively increased from six to seven at the phase  
310 transition (Table 4).

311

### 312 **Structure relations**

313 Here, the structure of the High-P phase is compared with that of the High-PT phase  
314 (Ca(OH)<sub>2</sub>-II). The High-PT phase was identified using powder X-ray diffraction at 7.2  
315 GPa and 300 °C by Kunz et al. (1996). Subsequently, Leinenweber et al. (1997)  
316 performed a detailed analysis of the crystal structure of the High-PT phase synthesized  
317 at 9 GPa and 400 °C, using powder neutron diffraction data obtained at 0.1 MPa and 11  
318 K. The authors reported a detailed structure including the hydrogen positions. Figure 4  
319 compares the High-P and High-PT phases viewed along the *a* and *b* directions. To  
320 enable a visual comparison, the *a*- and *c*- axes of the High-PT phase are exchanged  
321 from the original literature (see footnote in Fig. 4). These crystal structures show similar  
322 arrangements of atoms in both phases, but each *a-b* plane in the High-PT phase is more  
323 “expanded” in the *c*-axis direction than that in the High-P phase. This observation  
324 suggests that increasing temperature enhanced the structural relaxation and resulted in

325 further displacements of Ca atoms from the High-P phase to the High-PT phase.

326 Although the Ca-O atomic distances of the High-P phase show a wide scatter from  
327 2.18 to 2.70 Å (Table 4), those in the High-PT phase are much less scattered and  
328 remained in the range from 2.23 to 2.43 Å (Leinenweber et al. 1997). This finding  
329 indicates that with increasing temperature, Ca atoms move to stable position, with a  
330 more regular seven-fold coordination in the High-PT phase. To date, no study has  
331 observed the transition from the High-PT phase to the High-P phase with decreasing  
332 temperature. This suggests that the High-P phase might be a metastable phase that exists  
333 only as an intermediate state between the six-fold coordinated Low-P phase and the  
334 seven-fold coordinated High-PT phase.

335

### 336 **Microscopic observations and phase transition mechanism**

337 Figure 5(a) shows a representative oscillation X-ray photograph of the single  
338 crystal, which was observed when the *c*-axis of portlandite was placed parallel to the  
339 X-ray beam. New diffraction spots from the High-P phase started to appear at above 6  
340 GPa. Some of the new spots appeared very close to those of the Low-P phase without  
341 any overlaps, but the intensity of these specific spots became much denser. Initially,  
342 strong diffraction spots appeared near the 100 and 010 reflections of the Low-P phase  
343 (Fig. 5(b1)), and several weak spots appeared surrounding these strong spots. This  
344 complicated reflection pattern observed on the *hk*0 reciprocal lattice can be explained  
345 by the overlap of reflections of the High-P phase, which was formed in three different  
346 directions by the phase transition. Figure 6 shows the *hk*0 reciprocal lattices. Using the



347 lattice parameters of the Low-P and High-P phases listed in Table II, the reciprocal  
348 lattice parameters were calculated to be  $a_{LP}^* = b_{LP}^* = 0.333 \text{ \AA}^{-1}$ ,  $c_{LP}^* = 0.225 \text{ \AA}^{-1}$ ,  $\gamma_{LP}^*$   
349  $= 60^\circ$  for the Low-P phase; and  $a_{HP}^* = 0.176 \text{ \AA}^{-1}$ ,  $b_{HP}^* = 0.146 \text{ \AA}^{-1}$ ,  $c_{HP}^* = 0.115 \text{ \AA}^{-1}$ ,  
350  $\beta_{HP}^* = 75.2^\circ$  for the High-P phase. Figure 6(a) shows these two reciprocal lattices  
351 overlapping with each other. Figure 6(b) shows three reciprocal lattices of the High-P  
352 phase, rotated by  $60^\circ$  and  $120^\circ$  about the origin of the reciprocal lattice (black dot in the  
353 figure). Many of the lattice points of the High-P phase appear very close to those of the  
354 Low-P phase (largest yellow dots) when the High-P phase is rotated. In Figures 5(b2)  
355 and 5(c2), all the reflections with high intensity can be explained by these yellow dots.  
356 All the other weak reflection spots can also be indexed by the lattice points of one of the  
357 three rotated High-P phases. As a result, the complicated diffraction pattern from the  
358 High-P phase is well explained by the overlap of the reciprocal lattices. In the real space,  
359 the Low-P phase has trigonal symmetry and there are three equivalent directions in the  
360  $a$ - $b$  plane. Therefore, the layer shift of the  $a$ - $b$  plane at the transition may occur toward  
361  $0^\circ$ ,  $120^\circ$ , or  $240^\circ$ , with equal probability in each case.

362       Optical microscope observations under high pressure revealed that the crystalline  
363 shape of the Low-P phase remained almost unchanged through the phase transition, but  
364 cracks appeared perpendicular to the  $c$ -axis. In addition, before the phase transition,  
365 when the crystal was observed perpendicular to the  $c$ -axis under crossed nicols, the  
366 entire crystal showed extinction simultaneously. In contrast, after the transition, the  
367 crystal contained many domains of lamellae with different extinction angles. These  
368 observations are consistent with the transition mechanism described above.

369 A reversible single-crystal to single-crystal transition was reported in  $\text{Zn}(\text{OH})_2$  at  
370 about 1.1 GPa at room temperature (Kusaba et al. 2007). In this case, the Low-P phase  
371 is orthorhombic and the High-P phase is tetragonal. Because of this symmetry, there is  
372 only one possible direction for the transformation to occur when the crystal transforms  
373 from the Low-P to the High-P phase, and the High-P phase retains good crystallinity. In  
374 portlandite, however, the crystallinity of the High-P phase is low because there are three  
375 possible equivalent directions for the layer shift of the  $a$ - $b$  plane at the transition, which  
376 results in many twins in the High-P phase.

377 As mentioned in the Introduction, brucite-type layered hydroxides show a wide  
378 range of high-pressure behaviors, and no structurally-related mineral is known to have a  
379 similar phase transition to that of portlandite. In many isostructural oxides (e.g., olivine,  
380 spinel, and perovskite), the high-pressure behavior changes systematically depending on  
381 the cation size. In layered hydroxides, however, the behavior is much more complicated  
382 and shows greater variety, probably because the hydrogen bond in the structure plays an  
383 important role in controlling the high-pressure behavior. In fact, it is expected that the  
384 phase transition of portlandite is accompanied by a large geometrical change in  
385 hydrogen bonds, as deduced from spectroscopic measurements of OH vibration modes  
386 (Ekbundit et al. 1996; Catalli et al. 2008; Iizuka et al. 2011). However, little is known  
387 about the behavior of hydrogen bonds under high pressure, because hydrogen atoms are  
388 almost invisible to X-rays. The present results of X-ray diffraction had also difficulty in  
389 the refinement of the hydrogen positions. Alternatively, it is therefore important to  
390 clarify this behavior by using neutron diffraction analyses, and the results of this paper

391 will provide key information for such detailed structure analyses, including the  
392 hydrogen positions.

393

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496

### Figure captions

497 FIGURE 1. (a) Schematic diagram of the newly designed cell assembly for  
498 single-crystal diffraction measurements. (b) Representative oscillation photograph of  
499 the single crystal portlandite obtained at 8.5 GPa using the assembly shown in (a).  
500 Forty-one images taken at  $90^\circ \pm 20^\circ$  were combined into a single image. Most of the  
501 diffracted reflections in the upper hemisphere were behind the shadow of the SUS  
502 gasket. Several diffraction lines and a big spot at the left below come from the gasket,  
503 and the diamond anvil, respectively.

504

505 FIGURE 2. Result of the Rietveld refinement of  $\text{Ca}(\text{OH})_2$  at 8.9 GPa. Crosses and lines  
506 represent observed diffraction and calculated profiles, respectively. Vertical bars  
507 indicate the positions of Bragg reflections for the High- (upper) and Low-P (lower)  
508 phases. The line below the profile indicates the difference profiles between the observed  
509 and calculated patterns.

510

511 FIGURE 3. Crystal structure of (a) the Low-P phase and (b) the High-P phase of  
512 portlandite from the perspective of (upper) the  $a$ - $b$  plane, and (lower) the  $b$ -axis. Frames  
513 indicate the unit cell of the Low-P phase and the High-P phase, respectively.

514

515 FIGURE 4. Structural relation between (a) the High-P phase and (b) the High-PT phase.

516 The crystal structure of the High-PT phase was determined at 0.1 MPa and 11 K

517 (Leinenweber et al. 1997). For comparison, the  $a$ - and  $c$ -axes of the High-PT phase



518 were changed from the original figure, from  $(a, b, c)$  to  $(a', b', c')$ , via the following  
519 transformation matrix:

$$520 \quad \begin{pmatrix} a' & b' & c' \end{pmatrix} = \begin{pmatrix} a & b & c \end{pmatrix} \begin{pmatrix} 0 & 0 & 1 \\ 0 & -1 & 0 \\ 1 & 0 & 0 \end{pmatrix}.$$

521

522 FIGURE 5. Typical X-ray diffraction patterns of single crystal (a) before and (b, c) after  
523 the phase transition, observed parallel to the  $c$ -axis. Debye rings originate from the SUS  
524 gasket. New diffraction spots appeared at around 6.3 GPa, as shown in (b1). The  
525 diffraction patterns of (a) and (b) are from the same sample observed using a laboratory  
526 X-ray source, and (c) was measured at 9.0 GPa using synchrotron X-rays. (b2) and (c2)  
527 represent the lattice points (Fig. 6(b)). All the lattice points can be explained by the  
528 overlap of three reciprocal lattices (see text).

529

530 FIGURE 6. Reciprocal lattices of the  $hk0$  plane of (a) The thin-line (red) and thick-line  
531 (blue) nets represent the reciprocal lattices of the Low-P and High-P phases,  
532 respectively, which are drawn so that one of the lattice points (represented by a solid  
533 black dot) coincides. (b) Reciprocal lattices of the High-P phase (denoted by purple and  
534 green rectangular nets) overlapped by rotating  $60^\circ$  and  $120^\circ$  about the center black dot,  
535 together with the reciprocal lattice of the Low-P phase. The largest yellow dots  
536 represent the positions where the lattice points from the four reciprocal lattices are  
537 located very close to each other.

538

539

**TABLES**

540 **TABLE 1.** Experimental conditions of single crystal X-ray diffraction measurements.

Diamond anvil cell	Boehler-Almax	Radial-DAC
Pressure transmitting medium	4:1Methanol-ethanol	Glycerin
X-ray source	MoK $\alpha$ or Synchrotron (PF-AR-NE1)	
Wavelength ( $\text{\AA}$ )	0.71069 / 0.41138	
Exposure time (sec)	120–240	300–600
Oscillation angle ( $^{\circ}$ )	$\pm 38$	$\pm 20 \times 4$

541

542

543

544 **TABLE 2.** Summary of Rietveld refinement of powder X-ray diffraction data of  
 545  $\text{Ca}(\text{OD})_2$ .

Crystallographic data			
Phase	Low-P [This study]	High-P [This study]	High-PT [Leinenweber et al. 1997]
Measurement condition	8.9 GPa, 300K		0.1 MPa, 11K (synthesized at 9 GPa, 400 °C)
Space group	$P-3m1$ (#164)	$I121$ (#5)	$P2_1/c$ (#14)
Lattice parameter (Å)	<i>a</i>	<i>b</i>	<i>c</i>
	3.4631(3)	5.8882(10)	5.3979(4)
	3.4631(3)	6.8408(9)	6.0931(4)
	4.4471(8)	8.9334(15)	5.9852(4)
Monoclinic angle (°)	$\beta$	104.798(18)	103.581(6)
Unit cell volume (Å <sup>3</sup> )	$V_c$	46.188(10)	347.90(10)
		191.34(1)	
Z	Z	1	8
		4	
Molecular weight	$M_r$	76.1	76.1
Molar volume (calculated) (cm <sup>3</sup> mol <sup>-1</sup> )	$V_m$	27.8	26.18
Density (calculated) (g cm <sup>-3</sup> )	<i>d</i>	2.74	2.91
		2.64	
Condition of Rietveld analysis			
source	Synchrotron X-ray (PF-AR NE1)		Neutron
Wavelength (Å)	0.41138		
Exposure time (sec)	600		
<i>d</i> -range (Å)	0.9–5.9		
No. data points	1024		
No. parameters	28		
$R_p$ *(%)	0.47		
$R_{wp}$ †(%)	0.63		
$R_e$ ‡(%)	0.25		
$R(F^2)$ § (%)	17.4		
$ S $	2.09		

546

547 Notes:  $* R_p(\%) = \frac{\sum_i |y_i - f_i(x)|}{\sum_i y_i} \times 100$ ,

548  $\dagger R_{wp}(\%) = \left\{ \frac{\sum_i w_i [y_i - f_i(x)]^2}{\sum_i w_i y_i^2} \right\}^{1/2} \times 100$ ,  $\ddagger R_e(\%) = \left( \frac{N - P}{\sum_i w_i y_i^2} \right)^{1/2} \times 100$ ,

549  $\S R(F^2)(\%) = \frac{\sum |F_o^2 - KF_c^2|}{\sum F_o^2} \times 100$   $\parallel S = R_{wp} / R_e$ ,

550 where  $y_i$ , observed intensity;  $f_i(x)$ , calculated intensity;  $w_i$ , statistical weight;  $N$ , number  
 551 of data points;  $P$ , number of variables;  $F_o$ , observed structure factor;  $F_c$ , calculated  
 552 structure factor;  $K$ , scale factor for which the sum extends over all the observed  
 553 reflections. Calculation was made after background has been subtracted.

554

555 **TABLE 3.** Structure parameters of Ca(OD)<sub>2</sub> at 8.9 GPa and 300 K.

Phase	Atoms	site	g	x	y	z	$U_{iso}^* \times 100 (\text{\AA}^2)$
High-P	Ca1	4c	1	0.208(3)	0†	0.1980(14)	0.78(9)
	Ca2	4c	1	0.710(2)	0.736(2)	0.1683(14)	0.78(9)
	O1	4c	1	0.390(6)	0.267(12)	0.137(4)	2.6(4)
	O2	4c	1	0.727(9)	0.587(4)	0.407(5)	2.6(4)
	O3	4c	1	0.560(6)	-0.032(9)	0.367(4)	2.6(4)
	O4	4c	1	0.316(6)	0.744(7)	0.079(4)	2.6(4)
Low-P	Ca1	1a	1	0	0	0	0.78(9)
	O2	2d	1	1/3	2/3	0.256(3)	2.6(4)

556

557

558 Note: \*The isotropic atomic displacement parameters ( $U_{iso}$ ) of Ca and O atoms between  
 559 the Low- and High-P phases were constrained to be the same, respectively (i.e.,  
 560  $U_{iso}(\text{Ca}_{LP}) = U_{iso}(\text{Ca}_{HP})$ ,  $U_{iso}(\text{O}_{LP}) = U_{iso}(\text{O}_{HP})$ ). †The y position of Ca of the High-P  
 561 phase was fixed to be 0.

562

563 **TABLE 4.** Ca-O inter-atomic distances of the two Ca sites in the High-P phase at 8.9

564 GPa.

Atoms	Distance (Å)	Atoms	Distance (Å)
Ca1-O4	2.22(5)	Ca2-O4	2.18(4)
Ca1-O3	2.24(3)	Ca2-O4	2.25(4)
Ca1-O1	2.25(7)	Ca2-O3	2.34(5)
Ca1-O1	2.34(6)	Ca2-O3	2.35(6)
Ca1-O2	2.56(5)	Ca2-O2	2.55(3)
Ca1-O4	2.63(4)	Ca2-O1	2.55(3)
Ca1-O2	2.70(5)	Ca2-O3	2.69(5)
Ca1-O3	3.55(6)	Ca2-O3	3.70(8)
Average of 7-bond length (Å)	2.422		2.416

565

















