

1 **Revision 2**

2 **Compressibility, thermal expansion and Raman scattering of synthetic**
3 **whitlockite $\text{Ca}_9\text{Mg}(\text{PO}_3\text{OH})(\text{PO}_4)_6$ at high pressures and high temperatures**

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16 **Abstract** In-situ X-ray diffraction and Raman scattering of synthetic whitlockite,
17 $\text{Ca}_9\text{Mg}(\text{PO}_3\text{OH})(\text{PO}_4)_6$, have been systematically measured at high pressures and high
18 temperatures, respectively. The results show that whitlockite is stable up to ~ 15 GPa
19 at ambient temperature and undergoes a temperature-induced dehydrogenation to
20 merrillite above 973 K at ambient pressure. The obtained pressure-volume data were
21 fitted using a third-order Birch-Murnaghan equation of state to yield the isothermal
22 bulk modulus as $K_0 = 79(4)$ GPa with pressure derivative $K_0' = 4.3(6)$. When K_0' was
23 fixed at 4, the refined isothermal bulk modulus was 81(1) GPa. The volumetric
24 thermal expansion coefficient (α_V) is equal to $4.05(8) \times 10^{-5} \text{ K}^{-1}$. The axial thermal
25 expansion coefficients (α_a and α_c) are $1.07(5) \times 10^{-5} \text{ K}^{-1}$ and $1.91(6) \times 10^{-5} \text{ K}^{-1}$. Both
26 compressibility and thermal expansion show an axial anisotropy. The effects of
27 pressure and temperature on the Raman spectra of whitlockite have been
28 quantitatively analyzed. The isothermal and isobaric mode Grüneisen parameters, and
29 the intrinsic anharmonic mode parameters of whitlockite were calculated. Some
30 amounts of OH-bearing whitlockite may be preserved and could be discovered in
31 meteorites if whitlockite undergoes a low temperature process.

32

33 **Keywords:** Whitlockite; $\text{Ca}_9\text{Mg}(\text{PO}_3\text{OH})(\text{PO}_4)_6$; High-pressure; High-temperature;
34 Compressibility; Thermal expansion; Raman spectra; Dehydrogenation

35 **1. Introduction**

36 Whitlockite, $\text{Ca}_9\text{Mg}(\text{PO}_3\text{OH})(\text{PO}_4)_6$, is one important natural calcium phosphate,
37 commonly occurring in the terrestrial rocks (Lagier et al. 2003; Hughes et al. 2008;
38 Adcock et al. 2014). $\text{Ca}_9\text{Mg}(\text{PO}_3\text{OH})(\text{PO}_4)_6$ is the hydrogenated end member of the
39 whitlockite-merrillite solid solution series (Adcock et al. 2017), with merrillite
40 $[\text{Ca}_9\text{NaMg}(\text{PO}_4)_7]$ being the anhydrous end-member (Xie et al. 2015). Merrillite is an
41 accessory mineral found in many meteorites and it is a major carrier of rare earth
42 elements, whereas whitlockite has not been confirmed in any type of meteorites
43 (Adcock et al. 2017). Recently, natural merrillite was found as an inclusion in
44 lower-mantle diamonds from the Rio Soriso area, Brazil (Kaminsky and Zedgenizov
45 2022). Previous studies indicated that whitlockite can transform into merrillite by
46 heating at 1323 K (Hughes et al. 2008) or shock-compression (Adcock et al. 2017).

47 Whitlockite crystallizes in the trigonal system with the space group of $R\bar{3}c$
48 (Gopal et al. 1974). It consists of structural unit $[\text{Mg}(\text{PO}_4)_6]^{16-}$ and interstitial complex
49 $[\text{Ca}_9(\text{PO}_3)(\text{OH})]^{16+}$ (Xie et al. 2002; Hughes et al. 2006). The structural unit yields a
50 “bracelet-and-pinwheel” arrangement (Moore 1973), which is composed of Mg
51 octahedra decorated by six PO_4 tetrahedra in two kinds, as shown in Figure 1.

52 Some previous studies investigated the stability of whitlockite at high
53 temperatures (Gopal et al. 1972; Hughes et al. 2006; Adcock et al. 2017). Gopal (1972)
54 heated the natural whitlockite at 1200 °C overnight and refined the atomic
55 arrangement to examine the structural relationships of $\text{Ca}_9\text{Mg}(\text{PO}_3\text{OH})(\text{PO}_4)_6$ and
56 $\beta\text{-Ca}_3(\text{PO}_4)_2$. Hughes et al. (2008) heated whitlockite at 773 K and 1323 K for 24
57 hours. Their results showed that whitlockite is stable at 773 K and dehydrogenates
58 into merrillite at 1323 K. Adcock et al. (2017) showed whitlockite transforms into
59 merrillite by shock-compression at conditions relevant to meteorites, which indicated

60 that meteoritic merrillite may originally be formed from H⁺-bearing whitlockite.

61 However, the physical properties of whitlockite at high pressures and high
62 temperatures have been rarely investigated. The temperature for the dehydrogenation
63 of whitlockite has not been well constrained since no continuous observation for the
64 dehydrogenation at various temperatures is available. In the present study, the
65 compressibility, thermal expansion, and the effect of pressure and temperature on the
66 Raman active modes of whitlockite [Ca₉Mg(PO₃OH)(PO₄)₆] have been systematically
67 investigated at high pressures up to ~ 15 GPa and high temperatures up to 1273 K by
68 using in-situ X-ray diffraction and Raman spectroscopic measurements, respectively.
69 In particular, the temperature-induced dehydrogenation of whitlockite into merrillite
70 was observed in-situ.

71

72 **2. Methods**

73 2.1 Sample synthesis

74 By using pure reagents of Mg(NO₃)·6H₂O, CaO and H₃PO₄, high-purity
75 whitlockite was obtained through a hydrothermal synthesis method. The method and
76 procedure were similar to a previous study (Li et al. 2017). Firstly, according to the
77 molality concentration of (Ca+Mg) of 0.1mol/L and molar ratio of Mg/(Ca+Mg) of
78 0.3, CaO and Mg(NO₃)·6H₂O were added to deionized water to form a suspension.
79 Secondly, H₃PO₄ was mixed with deionized water at desired concentration at a molar
80 ratio of P/(Ca+Mg) of 1.67, stirring while pouring the solution into the suspension.
81 Thirdly, HNO₃ was added to the mixture, and then the mixture was allowed to rest for
82 a period of time until the precipitate dissolved. After the mixture was clarified,
83 acetamide was added as the precipitation agent. The mixture was then enclosed into
84 the autoclave and heated at 453 K for 6 hours. Finally, after natural cooling, the

85 precipitation was washed, filtered, and dried at 333 K. The synthesized sample was
86 characterized and confirmed as a single phase by powder X-ray diffraction method.

87

88 2.2 High- pressure X-ray diffraction and Raman spectra

89 The in-situ high-pressure X-ray diffraction measurements were carried out at the
90 BL15U1 beamline in Shanghai Synchrotron Radiation Facility (SSRF) (Zhang et al.
91 2015). A symmetric piston cylinder diamond anvil cell (DAC) with 300- μm culets
92 was adopted. The central part of a Re gasket was pre-intended to a thickness of 45 μm
93 in which a cylindrical hole of 180 μm in diameter was drilled as the sample chamber.
94 Small pieces of sample and gold were loaded into the chamber. A mixture of 4:1
95 deuterated methanol–ethanol was loaded as the pressure medium. The experimental
96 pressures were calculated based on the equation of state (*EoS*) of gold given by Fei et
97 al. (2007). Monochromatic X-ray with a wavelength of 0.6199 Å and a beam size of 2
98 μm (width) \times 3 μm (height) was used in all the experiments. 2D images were recorded
99 by a MAR-165 charge-couple device detector and integrated using the Dioptas
100 program (Prescher and Prakapenka, 2015) to obtain one-dimensioned diffraction
101 patterns. The sample-to-detector distance and the geometrical parameters of the
102 detector were calibrated with cerium dioxide (CeO_2). All obtained X-ray diffraction
103 patterns were analyzed by GSAS software package (Larson et al. 2004) to determine
104 the unit-cell parameters and volume.

105 High-pressure Raman spectroscopic measurements were conducted with a
106 symmetric piston cylinder DAC with 400- μm culets. The central part of T301
107 stainless steel gasket was pre-intended to a thickness of 70 μm in which a cylindrical
108 hole of 240 μm in diameter was drilled as the sample chamber. Argon was used as
109 pressure medium. A small piece of sample was loaded into the sample chamber with a

110 ruby sphere as the pressure marker. Pressures were determined by the ruby
111 fluorescence method (Mao et al. 1986). Raman spectra of whitlockite at different
112 pressures and room temperature were recorded by a Horiba LabRam HR Evolution
113 micro-Raman spectrometer with an 1800 lines/mm grating. A YAG: Nd³⁺ laser with a
114 wavelength of 532 nm was used as an exciting source. The accumulation time of each
115 spectrum was 60 s and the final spectrum at each pressure was the average of three
116 measurements. The obtained Raman spectra were analyzed by using the PeakFit
117 program (SPSS Inc., Chicago).

118

119 2.3 High-temperature X-ray diffraction and Raman spectra

120 In-situ synchrotron angle dispersive X-ray diffraction patterns at different
121 temperatures were collected at the beamline BL14B1 of SSRF (Yang et al. 2015). A
122 powdered sample was loaded into a fused quartz capillary, which was heated in a
123 custom-made furnace to reach the target temperature in a speed of 30 K/min. The
124 temperature was measured by a K-type thermocouple and controlled with an accuracy
125 of about ± 1 K. A monochromatic X-ray beam with a wavelength of 0.6886 Å and a
126 beam size of 180 μm (width) \times 200 μm (height) was used. The Mythen 1K linear
127 detector was adopted to collect the data in transmission mode (Gao et al. 2016). The
128 wavelength of the X-ray was calibrated by LaB₆ standard from NIST (660b). The
129 sample was kept at a desired temperature about 5 mins for thermal equilibration
130 before each measurement. One-dimensional X-ray diffraction patterns were collected
131 in the 2θ range of 5~30° with a step of 0.01°. All collected X-ray diffraction patterns
132 were analyzed by GSAS software package (Larson and Von Dreele 2004) to obtain
133 the unit-cell parameters and volume.

134 The Raman spectra of synthetic whitlockite at various temperatures and ambient
135 pressure were collected using a Horiba LabRam HR Evolution micro-Raman
136 spectrometer with an 1800 gr/mm grating. A YAG: Nd³⁺ laser with a wavelength of
137 532 nm and a power of 20 mW was adopted. The Raman spectrometer was calibrated
138 with a single crystal of silicon to the peak at 520 cm⁻¹. Polycrystalline whitlockite of
139 approximate 100 × 100 × 60 μm in size was placed on sapphire window which was
140 put into an alumina chamber in Linkam TS 1500, and the experiment was performed
141 up to 1173 K by using a heating stage consisting of an electric-resistance heater with a
142 water-cooling system which was used to prevent damages to the optical system and
143 the sample stage. The temperature was measured by an S-type thermocouple and
144 controlled by a program. The sample was hold at each temperature for about 10 min
145 for thermal equilibrium. The accumulation time for each collection was 60 s, and the
146 final spectrum at each temperature was the average of three measurements. The
147 Raman spectra were analyzed by the PeakFit program (SPSS Inc., Chicago).

148

149 **3. Result and discussion**

150 3.1 High-pressure in situ X-ray diffraction

151 Figure 2 displays the typical X-ray diffraction patterns of whitlockite at different
152 pressures, where all the peaks shift to higher 2θ region with increasing pressure. No
153 pressure-induced phase transition is observed. The unit-cell parameters and volume of
154 whitlockite at ambient conditions are $a = 10.357(1) \text{ \AA}$, $c = 37.119(5) \text{ \AA}$, $V = 3448.0(6)$
155 \AA^3 , which are consistent with previous results of Gopal (1974).

156 The refined unit-cell parameters and volume of whitlockite are listed in Table 1.
157 The relative changes of the unit-cell parameters and volume with pressures for
158 whitlockite are plotted in Figure 3, with a following third-order Birch-Murnaghan EoS

159 (Birch 1947) fitting to obtain the elastic parameters:

$$160 \quad P = \frac{3K_0}{2} \left[\left(\frac{V_0}{V} \right)^{\frac{7}{3}} - \left(\frac{V_0}{V} \right)^{\frac{5}{3}} \right] \left\{ 1 + \frac{3}{4} (K'_0 - 4) \left[\left(\frac{V_0}{V} \right)^{\frac{2}{3}} - 1 \right] \right\} \quad (1)$$

161 where P , V , V_0 , K_0 , and K'_0 are pressure, volume, zero-pressure volume, isothermal
162 bulk modulus and its pressure derivative, respectively. The least-squares fitting was
163 performed by using *EoSFit* program (Angel 2000), giving $V_0 = 3459.1(56) \text{ \AA}^3$, $K_0 =$
164 $79(4) \text{ GPa}$, $K'_0 = 4.3(6)$. When K'_0 was fixed at 4, a second-order Birch-Murnaghan
165 *EoS*, the fitting yields $K_0 = 81(1) \text{ GPa}$. The $V_0 = 3459.1 \text{ \AA}^3$ obtained by fitting was
166 used for normalization shown in Figure 3. The obtained bulk modulus is comparable
167 to some other phosphates, as listed in Table 2. It is noted that different crystal
168 structure and chemical composition have effects on the bulk modulus of phosphates.
169 In trigonal structure with a space group of $R3c$, three kinds of PO_4 tetrahedra with
170 averaged P-O bond lengths of 1.540, 1.561 and 1.538 \AA exist in $\text{Ca}_9\text{Mg}(\text{PO}_4)_7(\text{OH})$,
171 $\text{Ca}_9\text{NaMg}(\text{PO}_4)_7$ and $\beta\text{-Ca}_3(\text{PO}_4)_2$, respectively, at ambient conditions (Gopal et al.
172 1974; Moore 1973; Yashima et al. 2003). Three kinds of CaO_8 and one MgO_6
173 polyhedra present in $\text{Ca}_9\text{Mg}(\text{PO}_4)_7(\text{OH})$. Two kinds of CaO_8 , one CaO_9 , one NaO_6 and
174 one MgO_6 polyhedra present in $\text{Ca}_9\text{NaMg}(\text{PO}_4)_7$. Two kinds of CaO_8 , one CaO_7 , one
175 CaO_3 and one CaO_6 polyhedra present in $\beta\text{-Ca}_3(\text{PO}_4)_2$. In trigonal structure with a
176 space group of $R-3m$, one kind of PO_4 tetrahedron with averaged P-O bond lengths of
177 1.533, 1.553 and 1.549 \AA exists in $\gamma\text{-Ca}_3(\text{PO}_4)_2$, $\text{Sr}_3(\text{PO}_4)_2$, and $\text{Pb}_3(\text{PO}_4)_2$, respectively,
178 at ambient conditions (Sugiyama and Tokonami 1987; Qin et al. 2014). Two kinds of
179 metal-oxygen polyhedra with coordination of 12 and 10 present in $\gamma\text{-Ca}_3(\text{PO}_4)_2$,
180 $\text{Sr}_3(\text{PO}_4)_2$ and $\text{Pb}_3(\text{PO}_4)_2$ with different metal-oxygen bond lengths due to different
181 cations. In hexahonal apatites with a space group of $P6_3/m$, one PO_4 tetrahedron, one
182 CaO_9 and one CaO_6X ($\text{X} = \text{F}, \text{Cl}, \text{OH}$) polyhedra exist (Hughes et al. 1989). In

183 monoclinic apatites with a space group of $P2_1/b$, three kinds of PO_4 tetrahedra, three
184 kinds of CaO_9 and two kinds of CaO_6X ($\text{X} = \text{Cl}, \text{OH}$) polyhedra exist (Suetsugu et al.
185 2001).

186 In order to obtain the axial compressibility of whitlockite, simply by substituting
187 the cube of the lattice parameter (a^3 or c^3) for the volume, the values of a^3 and c^3 were
188 fitted by a “linearized” third-order Birch-Murnaghan EoS and following the
189 procedure implemented in the $EoSFit$ program (Angel 2000). The refined initial
190 incompressible parameters (that is 1/3 of the axial incompressibilities; see Angel
191 (2000)) are $K_a = 82.5(15)$ GPa and $K_c = 77.0(14)$ GPa when K_0' fixed at 4, which
192 indicates that whitlockite has an axial elastic anisotropy since the c -axis is more
193 compressible than the a -axis based on the bracelet-and-pinwheel structure (Figure 1).

194

195 3.2 High-pressure Raman spectra

196 As mentioned above, whitlockite has a trigonal structure belonging to the space
197 group $R3c$. The Raman active modes of whitlockite can be predicted by
198 symmetry-adapted modes (Kroumova et al. 2003) as following:

$$199 \quad \Gamma = 44A_1 + 89E \quad (2)$$

200 where A_1 , E and Γ represent non-degenerate, double-degenerate, and the total
201 irreducible Raman vibrations, respectively. Thus, a total of 133 Raman active modes
202 are predicated. However, due to some undetected weak Raman active modes and/or
203 overlapping, the numbers of observed Raman bands are fewer than the theoretically
204 predicted. The Raman spectrum of whitlockite at ambient conditions is consistent
205 with previous studies (Jolliff et al. 1996; 2006), and some Raman modes can be
206 distinguished (Figure 4). In the high frequency range (above 900 cm^{-1}), the spectrum
207 contains peaks at 989 , 971 and 961 cm^{-1} for the ν_1 symmetric stretching vibrations of

208 P-O bonds in PO₄ tetrahedron. The peak at 920 cm⁻¹ is assigned to the ν_1 symmetric
209 stretching vibration of the HPO₄²⁻ group. Moreover, the peaks at 1093, 1064 and 1025
210 cm⁻¹ are assigned to ν_3 anti-symmetric stretching vibrations of the P-O bonds in PO₄
211 tetrahedron. In the middle frequency range (350-700 cm⁻¹), the peaks at 486, 460, 430
212 and 405 cm⁻¹ are assigned to the ν_2 bending vibrations of the O-P-O bonds in PO₄
213 tetrahedron, and the peaks at 625, 604 and 560cm⁻¹ are assigned to the ν_4 bending
214 vibrations of the O-P-O bonds in PO₄ tetrahedron. In the low frequency range (below
215 350 cm⁻¹), the peaks at 280 and 160 cm⁻¹ are the external modes.

216 The Raman spectra of whitlockite were collected to 15.3 GPa and the
217 representative spectra at various pressures were also showed in Figure 4. It is noted
218 that no new peaks appear during compression, which indicates that whitlockite does
219 not exhibit any pressure-induced phase transition. This is consistent with the
220 observation of high-pressure X-ray diffraction measurements. Figure 5 shows the
221 changes of Raman shifts for different modes with pressure. It is clear that all the peaks
222 systematically shift to higher frequency with different slope with increasing pressure.
223 The correlations between Raman shift of different modes and pressure fitted by linear
224 regressions are listed in Table 3. The pressure dependence of anti-symmetric and
225 symmetric stretching modes (ν_3 and ν_1) (3.40 ~ 5.25 cm⁻¹/GPa) are larger than those of
226 the bending modes (ν_4 and ν_2) and the external modes (1.38 ~ 2.88 cm⁻¹/GPa)
227 excluding the band at 430 cm⁻¹, indicating that the stretching vibrations in high
228 frequency range are more sensitive to pressure than the bending vibrations and the
229 external modes in the low frequency range.

230 The isothermal bulk modulus and pressure-dependence of Raman vibrations can
231 be used to obtain the isothermal mode Grüneisen parameters γ_{iT} , defined by the
232 following equation (Grüneisen 1912):

233
$$\gamma_{iT} = \frac{\left(\frac{\delta v_i}{\delta P}\right) K_0}{v_i} \quad (3)$$

234 where v_i , P , and K_0 are the frequency of the i^{th} mode, the pressure and the isothermal
235 bulk modulus, respectively. The isothermal bulk modulus $K_0 = 79$ GPa obtained in
236 this study was used. The values of γ_{iT} for different modes of whitlockite are also listed
237 in Table 3.

238 The average value for the mode Grüneisen parameters (Table 3) of the bands
239 associated to phosphate group vibrations is 0.38, which is larger than that of merrillite
240 and smaller than that of fluorapatite. PO_4^{3-} groups exist in whitlockite, merrillite and
241 fluorapatite with different geometrical arrangement. This difference may be caused by
242 different crystal structure and other components (such as halogens and/or OH)
243 excluding phosphorus oxygen tetrahedron. On the other hand, the average value for
244 the lattice modes is 0.44, which is larger than the average of the internal PO_4 modes,
245 illustrating the lattice modes largely affect the isothermal mode Grüneisen parameters.
246 The pressure dependence of the Raman mode frequency is affected by the "stiffness"
247 of the local interatomic interactions in the structural unit that most directly contributes
248 to that vibrational mode. Therefore, the different Grüneisen parameters might be due
249 to the result that calcium/magnesium polyhedron is more compressible (flexible) than
250 the phosphate tetrahedral (Comodi et al. 2001; Pankrushina et al. 2022).

251

252 3.3 High-temperature in situ X-ray diffraction

253 Figure 6 illustrates the typical X-ray diffraction patterns of
254 $\text{Ca}_9\text{Mg}(\text{PO}_3\text{OH})(\text{PO}_4)_6$ up to 1223 K. It is clear that the X-ray diffraction peaks shift
255 to the lower 2θ region with increasing temperature. At 1073 K new peaks appear at 2θ
256 $= 12.97^\circ$ and 13.54° and become stronger with further heating (Figure 6b). At 1173 K
257 several other new peaks appear at $2\theta = 9.57^\circ$, 12.64° , 13.05° , 13.93° , 14.03° and 14.20°

258 (Figure 6b). Additionally, the split peaks at $2\theta = 14.58^\circ$ become one peak at 1223 K.
259 Hughes et al. (2008) heated whitlockite at 773 K and 1323 K for 24 hours and found
260 that whitlockite is stable at 773 K and completely dehydrogenates into merrillite at
261 1323 K. They only heated the sample at two temperatures and didn't constrain the
262 dehydrogenated temperature. These new peaks we observe indicate some part of
263 whitlockite undergoes a temperature-induced dehydrogenation above 973 K.
264 Therefore, it is reasonable to infer that whitlockite dehydrogenates to merrillite in the
265 present study. The refined unit-cell parameters and volume for whitlockite at different
266 temperatures before dehydrogenation are listed in Table 4.

267 The relative variations of unit-cell parameters and volume of whitlockite at
268 different temperatures up to 973 K are plotted in Figure 7. The thermal expansion
269 coefficient of whitlockite can be obtained by the following expression (Fei 1995):

$$270 \quad \ln(V/V_0) = \alpha_V(T - T_0) \quad (4)$$

271 Similarly, the axial thermal expansion coefficients can also be obtained as follows:

$$272 \quad \ln(a/a_0) = \alpha_a(T - T_0) \quad (5)$$

$$273 \quad \ln(c/c_0) = \alpha_c(T - T_0) \quad (6)$$

274 The calculated thermal expansion coefficients are listed in Table 5. The thermal
275 expansion coefficients of whitlockite were obtained as $4.05(8) \times 10^{-5} \text{ K}^{-1}$, $1.07(5) \times$
276 10^{-5} K^{-1} , and $1.91(6) \times 10^{-5} \text{ K}^{-1}$ for volume, *a*- and *c*-axis, respectively. The axial
277 thermal expansion along the *a*-axis is 44% smaller than that along the *c*-axis,
278 indicating an axial anisotropic thermal expansion.

279 Whitlockite anisotropic axial thermal expansivity and compressibility can be
280 explained by the “path” of the structure (Cameron et al. 1973). As mentioned above,
281 the structural units have a “bracelet-and-pinwheel” arrangement (Figure 1), and the
282 path along *a*-axis crosses the structural unit with larger atom density and tighter

283 arrangement, but the path parallel to the *c*-axis does not (Hughes et al. 2008).

284 For comparison, the thermal expansion coefficients of other phosphate minerals
285 are also listed in Table 5. The thermal expansion coefficient of whitlockite is smaller
286 than that of merrillite (Jia et al. 2020b), and larger than those of hydroxyapatite
287 (Hovis et al. 2014), β -Ca₃(PO₄)₂ (Zhai et al. 2014), tuite (Zhai et al. 2011a),
288 fluorapatite (Chernorukov et al. 2011; Hovis et al. 2015) and chlorapatite (Hovis et al.
289 2015), which might be attributed to different chemical composition, crystal structure,
290 crystallinity, and bond strength. Different chemical composition is important - for
291 example, the different proportions of F, Cl, OH (and amount of vacancies) in apatite is
292 an important factor, because halogens in binary and ternary apatites are difficult to
293 accommodate in solid solution. An additional off-mirror F site appears in
294 F-Cl-apatites (OH-free) (Hughes et al. 2014). The chemical composition of
295 β -Ca₃(PO₄)₂ and tuite is same, but the crystal structure and bond strength are different,
296 resulting in different thermal expansion coefficient. Therefore, it is difficult to
297 conclude which factor is the most important to influence the thermal expansion
298 coefficient.

299

300 3.4 High-temperature Raman spectra

301 The typical Raman spectra at various temperatures are plotted in Figure 8, where
302 all the Raman bands become broader and shift to lower frequency regions with
303 increasing temperature. It is noted that the peak at 920 cm⁻¹ attributed to the ν_1
304 symmetric stretching vibrations of HPO₄²⁻ becomes weak with increasing temperature
305 and disappears at 1023 K. This phenomenon is consistent with the results of
306 high-temperature X-ray diffraction measurements, indicating a temperature-induced
307 dehydrogenation of whitlockite. After cooling to 298 K, the temperature-induced

308 dehydrogenated product does not transform back into its initial structure, which
309 means an irreversible reaction. In previous studies (Hughes et al. 2006; Adcock et al.
310 2017), by the analysis of the crystal structure and the obtained from whitlockite at
311 high temperature, it has been demonstrated that merrillite is the dehydrogenated
312 product of whitlockite.

313 Figure 9 displays the variations of Raman shift for different modes with
314 temperature. All Raman modes shift linearly and continuously. The relationships
315 between vibration mode ν and temperature T fitted by linear regressions are listed in
316 Table 3. The range of temperature dependence for whitlockite is from -0.049 to
317 -0.006 cm⁻¹/K. The temperature dependences of anti-symmetric stretching modes and
318 symmetric stretching modes (ν_3 and ν_1) are -0.045~- 0.015 cm⁻¹/K, whereas those of
319 bending modes (ν_4 and ν_2) are -0.017~ -0.006 cm⁻¹/K. Thus, the effect of temperature
320 on ν_3 and ν_1 modes is stronger than that on ν_4 and ν_2 bending modes.

321 For the internal PO₄ vibrations of whitlockite, the symmetric stretching modes
322 are more susceptible to temperature and pressure than the bending modes. It might be
323 attributed to the stretching modes of PO₄ with less spatial hindrance to move easily as
324 temperature and pressure increase, whereas bending modes of PO₄ may encounter
325 more spatial hindrance because they vibrate in directions with more repulsion.

326 Based on the thermal expansion coefficient and the temperature dependence of
327 active Raman modes, the isobaric mode Grüneisen parameter γ_{iP} can be obtained by
328 the following equation (Gillet et al. 1989; Okada et al. 2008):

$$329 \quad \gamma_{iP} = - 1/ \alpha (\partial \ln \nu_i / \partial T)_P \quad (7)$$

330 where ν_i and α are the frequency of the i^{th} mode and the thermal expansion coefficient,
331 respectively. The obtained thermal expansion coefficient of $4.05 \times 10^{-5} \text{ K}^{-1}$ for
332 whitlockite in this study was adopted. The calculated values of γ_{iP} are also listed in

333 Table 3, in the range of 0.37~4.25. In fact, the values of isobaric mode Grüneisen
334 parameters of the internal PO₄ modes are smaller than those of the lattice modes. This
335 phenomenon might be due to differences in coordination numbers and charges (Gillet
336 et al. 1989). For the internal PO₄ modes, low coordination (four for P) and higher
337 charged atoms lead to small γ_{iP} . For the lattice modes, lower charged atoms, and
338 higher coordination account for large γ_{iP} (Gillet et al. 1989). Such behavior is not only
339 observed in whitlockite, but also found in some other minerals for which
340 high-temperature data are available, including merrillite (Jia et al. 2020b), Mg₂SiO₄
341 (Dietrich and Arndt 1982), pyrope and andradite (Gillet et al. 1992).

342

343 3.5 Intrinsic anharmonicity

344 Based on the obtained results, the intrinsic anharmonicity of whitlockite can be
345 calculated. As shown in Table 3, the values of isothermal mode Grüneisen parameters
346 and those of isobaric mode Grüneisen parameters for the same vibrations are not equal.
347 Therefore, an intrinsic anharmonicity exists. The intrinsic anharmonic mode
348 parameter β_i , can be estimated using the values of Grüneisen parameters γ_{iP} and γ_{iT} as
349 follows (Mammone et al. 1979):

$$350 \quad \beta_i = \left(\frac{\partial \ln \nu_i}{\partial T} \right)_v = \alpha (\gamma_{iT} - \gamma_{iP})_T \quad (8)$$

351 The calculated values of β_i for different vibrational modes are also list in Table 3,
352 ranging from $-15.80 \times 10^{-5} \text{ K}^{-1}$ to $0.69 \times 10^{-5} \text{ K}^{-1}$ with an average intrinsic anharmonic
353 mode parameter for PO₄ of $-1.01 \times 10^{-5} \text{ K}^{-1}$. The absolute average intrinsic anharmonic
354 mode parameter of whitlockite is higher than that of tuite ($-0.80 \times 10^{-5} \text{ K}^{-1}$) (Zhai et al.
355 2011a) and merrillite ($0.98 \times 10^{-5} \text{ K}^{-1}$) (Jia et al. 2020a). Compared with SiO₄ vibrations
356 in silicate minerals such as grossular ($-1.75 \times 10^{-5} \text{ K}^{-1}$) (Gillet et al. 1992), the PO₄
357 vibrations in whitlockite show lower absolute average intrinsic anharmonic mode

358 parameter.

359 The data of X-ray diffraction and Raman spectra under high temperature indicate
360 that a temperature-induced dehydrogenation of whitlockite forms anhydrous
361 end-member merrillite. Combined with previous study by Hughes et al. (2008), the
362 atomic arrangement of the whitlockite is changed by heating and the charge-balancing
363 substitution between whitlockite and merrillite is $H \leftrightarrow Ca_{0.5}$. The whitlockite-merrillite
364 solid solution series differ due to the temperature and content of hydrogen.

365

366 **4. Implication**

367 Previous studies on Martian and lunar meteorites suggest they contain water.
368 Detectable amounts of OH in Martian and lunar apatite were found in previous studies
369 (Watson et al. 1994; Leshin 2000; Boyce et al. 2010; McCubbin et al. 2010;
370 Greenwood et al. 2011; Liu et al. 2012; Gross et al. 2013; Smith et al. 2020).
371 Merrillite was also found in Martian and lunar meteorites, as well as in carbonaceous
372 chondrites (Martinez 2021; Martinez and Brearley 2022), while whitlockite has not
373 been confirmed in any type of meteorite (Adcock et al. 2017). According to this study,
374 the dehydrogenation of whitlockite begins above 973 K at ambient pressure. Though
375 there is no information about the effect of pressure on the dehydrogenation of
376 whitlockite, it is reasonable to deduce that some meteoritic merrillites may be
377 produced by OH-bearing whitlockite due to some kinds of high-temperature
378 processes. If the temperature of such process is not so high, some part of OH-bearing
379 whitlockite may remain and could be distinguished in meteorites.

380

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393

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583 **Figure captions**

584 **Fig. 1** The arrangement of the bracelet-and-pinwheel structure units in whitlockite.

585 A $[\text{Mg}(\text{PO}_4)_6]^{16-}$ structural unit is shown separately at the right corner

586

587 **Fig. 2** Representative X-ray diffraction patterns of whitlockite up to 14.90 GPa at

588 room temperature

589

590 **Fig. 3** Relative changes of unit-cell parameters and volume of whitlockite at different

591 pressures. The values of $V_0 = 3459.1 \text{ \AA}^3$, $a_0 = 10.357 \text{ \AA}$ and $c_0 = 37.119 \text{ \AA}$ were

592 adopted for normalization

593

594 **Fig. 4** Typical Raman spectra of whitlockite at different pressures and room

595 temperature

596

597 **Fig. 5** Pressure dependence of the Raman bands of whitlockite at room temperature,

598 the solid, open and half-open symbols represent the measured Raman shifts at different

599 pressures, and the dot-dashed lines represent linear fittings. The error bar is the

600 standard deviation

601

602 **Fig. 6** Representative X-ray diffraction patterns of whitlockite up to 1223 K at

603 ambient pressure in the 2 theta ranges of 5~25° (a) and 9~15° (b). The asterisk

604 symbols indicate new XRD peaks. The XRD pattern labelled with 314 K was

605 collected after cooling to room temperature

606

607 **Fig. 7** Relative changes in unit-cell parameters and volume with temperature. The

608 values of $a_0 = 10.3564 \text{ \AA}$, $c_0 = 37.1247 \text{ \AA}$ and $V_0 = 3448.3 \text{ \AA}^3$ obtained from the XRD
609 pattern collected at 306 K before heating were adopted for normalization

610

611 **Fig. 8** Typical Raman spectra of whitlockite at different temperatures and ambient
612 pressure. The spectrum labelled with 298 K* was collected after cooling to room
613 temperature

614

615 **Fig. 9** Temperature dependence of the Raman bands of whitlockite at ambient
616 pressure

Table 1 Unit-cell parameters and volume of whitlockite at different pressures

| $P(\text{GPa})$ | $a(\text{\AA})$ | $c(\text{\AA})$ | $V(\text{\AA}^3)$ |
|-----------------|-----------------|-----------------|-------------------|
| 0.0001 | 10.357(1) | 37.119(5) | 3448.0(6) |
| 1.12(1) | 10.305(1) | 37.117(7) | 3413.5(8) |
| 2.80(1) | 10.264(1) | 36.762(3) | 3353.8(4) |
| 3.47(1) | 10.235(1) | 36.647(5) | 3324.5(6) |
| 4.49(1) | 10.199(1) | 36.523(4) | 3290.1(4) |
| 4.92(1) | 10.181(1) | 36.464(4) | 3273.5(5) |
| 5.66(1) | 10.156(1) | 36.369(4) | 3248.6(4) |
| 6.96(1) | 10.109(1) | 36.234(5) | 3206.6(6) |
| 7.63(1) | 10.098(1) | 36.146(4) | 3191.9(5) |
| 8.54(1) | 10.066(1) | 36.093(5) | 3166.9(5) |
| 9.04(1) | 10.047(1) | 36.004(6) | 3147.1(6) |
| 9.56(1) | 10.035(1) | 35.926(3) | 3133.3(3) |
| 10.4(1) | 10.014(1) | 35.825(5) | 3111.1(8) |
| 10.76(1) | 10.000(1) | 35.814(5) | 3101.6(5) |
| 11.18(1) | 9.989(1) | 35.749(4) | 3089.3(4) |
| 11.74(1) | 9.970(1) | 35.688(4) | 3072.5(5) |
| 12.72(1) | 9.955(1) | 35.616(5) | 3056.7(5) |
| 13.68(1) | 9.938(1) | 35.531(5) | 3039.1(6) |
| 14.32(1) | 9.924(1) | 35.512(6) | 3029.0(7) |
| 14.90(2) | 9.918(1) | 35.460(4) | 3020.6(5) |

Pressure was determined by the EoS of Au (Fei et al. 2007). The number in the parentheses represents one standard deviation in the right-most digit. The measurement at 0.0001 GPa was obtained after decompression.

Table 2 Parameters of the Birch-Murnaghan EoS derived for some phosphates

| Chemical formula | Space group | K_0 (GPa) | K_0' | Reference |
|--|-------------------------|-------------|-------------|-----------------------|
| Ca ₉ Mg(PO ₄) ₇ (OH) | <i>R3c</i> | 79(4) | 4.3(6) | This study |
| | | 81(1) | 4.0 (fixed) | |
| Ca ₉ NaMg(PO ₄) ₇ | <i>R3c</i> | 87.3(32) | 3.2(4) | Jia et al. 2020a |
| | | 81.6(10) | 4.0 (fixed) | |
| β-Ca ₃ (PO ₄) ₂ | <i>R3c</i> | 79.5(20) | 4.0 (fixed) | Zhai et al. 2010 |
| γ-Ca ₃ (PO ₄) ₂ | <i>R-3m</i> | 100.2(13) | 5.48(16) | Zhai et al. 2009 |
| | | 113.1(12) | 4.0 (fixed) | |
| Sr ₃ (PO ₄) ₂ | <i>R-3m</i> | 89.5(17) | 6.57(34) | Zhai et al. 2011b |
| | | 104.4(12) | 4.0 (fixed) | |
| Pb ₃ (PO ₄) ₂ | <i>R-3m</i> | 89(4) | 5.8(2) | Qin et al. 2014 |
| Ca ₅ (PO ₄) ₃ F _{0.94} Cl _{0.06} | <i>P6₃/m</i> | 91.5(38) | 4.0(11) | Matsukage et al. 2004 |
| | | 91.6(10) | 4.0 (fixed) | |
| Ca ₅ (PO ₄) ₃ F | <i>P6₃/m</i> | 93(4) | 5.8(18) | Comodi et al. 2001 |
| | | 97.8(10) | 4.0 (fixed) | |
| Ca ₅ (PO ₄) ₃ (F _{0.975} ,OH _{0.025}) | <i>P6₃/m</i> | 97.9(19) | 4.0 (fixed) | Brunet et al. 1999 |
| Ca ₅ (PO ₄) ₃ OH | <i>P2₁/b</i> | 97.5(18) | 4.0 (fixed) | Brunet et al. 1999 |
| Ca ₅ (PO ₄) ₃ (Cl _{0.7} ,OH _{0.3}) | <i>P2₁/b</i> | 93.1(42) | 4.0 (fixed) | Brunet et al. 1999 |

Table 3 Frequencies of Raman modes, corresponding pressure/temperature derivatives, isobaric mode Grüneisen parameters, isothermal mode Grüneisen parameters, and intrinsic anharmonic parameters of whitlockite

| Modes | ν_{i0} at ambient conditions (cm^{-1}) | $(\partial\nu_i/\partial P)_T$ ($\text{cm}^{-1} \text{ GPa}^{-1}$) | γ_{iT} | $(\partial\nu_i/\partial T)_P$ ($\text{cm}^{-1} \text{ K}^{-1}$) | γ_{iP} | β_i (10^{-5} K^{-1}) |
|-----------------------|--|---|---------------|---|---------------|---|
| PO ₄ modes | | | | | | |
| ν_3 | 1093 | 5.25(6) | 0.38 | -0.045(2) | 1.02 | -2.60 |
| | 1064 | 4.62(18) | 0.34 | -0.028(2) | 0.65 | -1.26 |
| | 1025 | 4.84(5) | 0.37 | -0.038(4) | 0.92 | -2.23 |
| ν_1 | 989 | 4.63(4) | 0.37 | -0.015(1) | 0.37 | 0 |
| | 971 | 4.47(1) | 0.36 | -0.017(1) | 0.42 | -0.24 |
| | 961 | 3.40(1) | 0.28 | -0.017(1) | 0.43 | -0.61 |
| | 920 | 4.21(1) | 0.36 | -0.039(1) | 1.05 | -2.79 |
| ν_4 | 625 | 1.62(3) | 0.20 | -0.017(1) | 0.66 | -1.86 |
| | 604 | 1.79(13) | 0.23 | -0.010(1) | 0.39 | -0.65 |
| | 560 | 1.38(2) | 0.19 | -0.008(2) | 0.37 | -0.73 |
| ν_2 | 485 | 2.88(5) | 0.47 | -0.016(3) | 0.82 | -1.42 |
| | 460 | 2.27(9) | 0.39 | -0.010(4) | 0.56 | -0.69 |
| | 430 | 3.89(9) | 0.74 | -0.012(1) | 0.68 | 0.24 |
| | 405 | 2.65(1) | 0.52 | -0.006(1) | 0.34 | 0.69 |
| External modes | | | | | | |
| | 280 | 1.26(6) | 0.36 | -0.049(5) | 4.25 | -15.80 |
| | 160 | 1.06(8) | 0.52 | -0.011(1) | 1.73 | -4.90 |

Table 4 Unit-cell parameters and volume of whitlockite at various temperatures

| T(K) | $a(\text{\AA})$ | $c(\text{\AA})$ | $V(\text{\AA}^3)$ |
|------|-----------------|-----------------|-------------------|
| 306 | 10.3564(1) | 37.1247(7) | 3448.3(1) |
| 373 | 10.366(1) | 37.1684(7) | 3458.7(1) |
| 473 | 10.3798(1) | 37.2393(7) | 3474.6(1) |
| 573 | 10.3904(1) | 37.2970(6) | 3487.2(1) |
| 673 | 10.4032(1) | 37.3720(5) | 3502.8(1) |
| 773 | 10.4159(1) | 37.4464(5) | 3518.3(1) |
| 873 | 10.4242(1) | 37.4998(5) | 3528.9(1) |
| 973 | 10.4277(1) | 37.6147(5) | 3542.1(1) |

Values in parentheses are errors

Table 5 Thermal expansion coefficients for whitlockite and comparison with other phosphate minerals

| Mineral | Formula | $\alpha_V (\times 10^{-5} \text{ K}^{-1})$ | $\alpha_a (\times 10^{-5} \text{ K}^{-1})$ | $\alpha_c (\times 10^{-5} \text{ K}^{-1})$ | Reference |
|----------------|--|--|--|--|-------------------------|
| whitlockite | $\text{Ca}_9\text{Mg}(\text{PO}_4)_7(\text{OH})$ | 4.05(8) | 1.07(5) | 1.91(6) | This study |
| | $\beta\text{-Ca}_3(\text{PO}_4)_2$ | 3.35 | | | Zhai et al. 2014 |
| merrillite | $\text{Ca}_9\text{NaMg}(\text{PO}_4)_7$ | 4.86(5) | 1.46(1) | 1.94(5) | Jia et al.2020b |
| tuite | $\gamma\text{-Ca}_3(\text{PO}_4)_2$ | 3.67(3) | 1.18(1) | 1.32(3) | Zhai et al. 2011a |
| hydroxyapatite | $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ | 3.95(5) | 1.36(2) | 1.24(2) | Hovis et al. 2014 |
| fluorapatite | $\text{Ca}_5(\text{PO}_4)_3\text{F}$ | 3.70(10) | 1.25(3) | 1.22(4) | Chernorukov et al. 2011 |
| | | 3.85(4) | 1.30(1) | 1.26(1) | Hovis et al. 2015 |
| chlorapatite | $\text{Ca}_5(\text{PO}_4)_3\text{Cl}$ | 3.80(3) | 0.91(8) | 1.98(3) | Hovis et al. 2015 |

















