

Revision 1

Chemical composition and crystal structure of merrillite from the Suizhou meteorite

XIANDE XIE^{1,4}, HEXIONG YANG^{2*}, XIANGPING GU³ and ROBERT T. DOWNS²

¹Key Laboratory of Mineralogy and Metallogeny, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, 511 Kehua Street, Guangzhou, 510640, China

²Department of Geosciences, University of Arizona, 1040 E. 4th Street, Tucson, AZ 85721-0077, USA

³School of Geosciences and Info-Physics, Central South University, Changsha, Hunan 410083, China

⁴Guangdong Key Laboratory of Mineral Physics and Materials, Guangzhou, 510640 China

*E-mail: hyang@email.arizona.edu

Abstract

Merrillite, ideally $\text{Ca}_9\text{NaMg}(\text{PO}_4)_7$, is an important accessory phosphate mineral in many different groups of meteorites, including Martian meteorites, and a major carrier of rare earth elements (REE) in lunar rocks. By means of electron microprobe analysis, single-crystal X-ray diffraction, and Raman spectroscopy, we present the first structure determination of merrillite with a nearly ideal chemical composition, $\text{Ca}_{9.00}\text{Na}_{0.98}(\text{Mg}_{0.95}\text{Fe}_{0.06})_{\Sigma=1.01}(\text{P}_{1.00}\text{O}_4)_7$, from the Suizhou meteorite, a shock-metamorphosed L6-chondrite. Suizhou merrillite is trigonal with space group $R3c$ and unit-cell parameters $a = 10.3444(3)$, $c = 37.0182(11)$ Å, $V = 3430.5(2)$ Å³. Its crystal structure, refined to $R_1 = 0.032$, is characterized by a structural unit consisting of a $[(\text{Mg},\text{Fe})(\text{PO}_4)_6]^{16-}$ complex anion that forms a “bracelet-and-pinwheel” arrangement. Such structural units are linked by interstitial complexes with a formula of $[\text{Ca}_9\text{Na}(\text{PO}_4)]^{16+}$, which differs from that of $[\text{Ca}_9(\text{PO}_3[\text{OH}])]^{16+}$, $[\text{Ca}_9(\text{PO}_3\text{F})]^{16+}$, $[\text{Ca}_9(\text{Ca}_{0.5}\square_{0.5})(\text{PO}_4)]^{16+}$, or $[(\text{Ca}_{9-x}\text{REE})_x(\text{Na}_{1-x}\square_x)(\text{PO}_4)]^{16+}$ in terrestrial whitlockite, terrestrial/extraterrestrial bobdownsite, meteoritic Ca-rich merrillite, or lunar REE-rich merrillite, respectively. The Suizhou merrillite is found to transform to tuite at high pressures, pointing to the likelihood of finding REE-bearing tuite on the Moon as a result of shock events on REE-merrillite.

Key words: Merrillite, whitlockite, Suizhou meteorite, crystal structure, Raman

36 spectroscopy

37

38

INTRODUCTION

39 Merrillite, ideally $\text{Ca}_9\text{NaMg}(\text{PO}_4)_7$, is a primary accessory mineral in many
40 different groups of meteorites, including Martian meteorites, and a major storage of rare
41 earth elements (REE) in lunar rocks (e.g., Jolliff et al., 1993, McSween et al., 1996; Xie
42 et al., 2002; Terada et al. 2003; Shearer et al. 2011, 2015; Adcock et al. 2014). It is
43 considered to be an important phase in exploring the differences in petrogenesis, mantle
44 evolution, and other geologic processes among Earth, Mars, and other planetary bodies
45 (McSween et al, 1996; Treiman 2003; Shearer et al. 2015). Merrillite was originally
46 proposed by Wherry (1917) in honor of George P. Merrill, who first described this
47 mineral from four meteorites (Merrill 1915). However, owing to the chemical and
48 structural similarities between merrillite and terrestrial whitlockite, ideally
49 $\text{Ca}_9\text{Mg}(\text{PO}_4)_6(\text{PO}_3\text{OH})$, there has been a considerable overlap in the use of these two
50 mineral names in the literature. Fuchs (1962) noted the strong resemblances in powder
51 X-ray diffraction data among merrillite, whitlockite, and synthetic $\beta\text{-Ca}_3(\text{PO}_4)_2$, leading
52 him to argue that these three phases were actually the same and the term “merrillite”
53 should be abandoned in favor of “whitlockite”. Subsequent investigations, nevertheless,
54 demonstrated that the structures of merrillite and synthetic $\beta\text{-Ca}_3(\text{PO}_4)_2$ are similar, but
55 not identical to that of terrestrial whitlockite, especially in terms of their lack of an
56 essential hydrogen component that is found in whitlockite (Gopal and Calvo 1972; Calvo
57 and Gopal 1975; Prewitt and Rothbard 1975; Dowty 1977). Early work on lunar samples
58 also suggested that “lunar whitlockite” is actually more similar in structure to meteoritic
59 merrillite than to terrestrial whitlockite (Gay et al. 1970; Fuchs 1971). Thus, Dowty
60 (1977) recommended “merrillite” for the H-free form found in meteorites and
61 “whitlockite” for the terrestrial form. However, because of the lack of definitive
62 structural data for merrillite due to its small crystal size in meteorites, the term
63 “whitlockite” continues to occasionally be used synonymously or interchangeably when
64 describing extraterrestrial merrillite (e.g., Ruzsala and Kostiner 1980; Jolliff et al. 1993;

65 McSween et al. 1996; Xie et al. 2001, 2002, 2003, 2013; Terada et al. 2003; Orlova et al.
66 2009).

67 Another confusion about merrillite arises from its chemical variations. In addition to
68 the ideal chemical formula approved by the Commission on New Minerals,
69 Nomenclature and Classification of the International Mineralogical Association
70 (IMA), there are also two other ideal endmembers commonly found in meteorites and
71 lunar rocks: a Na-free but Ca-excess form, $\text{Ca}_9(\text{Ca}_{0.5}\square_{0.5})(\text{Mg},\text{Fe}^{2+})(\text{PO}_4)_7$ and a Na-free
72 but REE-bearing form, $(\text{Ca}_8\text{REE})\square(\text{Mg},\text{Fe}^{2+})(\text{PO}_4)_7$ (e.g., Dowty 1977; Jolliff et al. 1993,
73 2006; Shearer et al. 2015). These two phases are isostructural with merrillite, but have no
74 official names approved by IMA. To facilitate the following discussion, we will
75 temporarily follow the proposal by Jolliff et al. (2006), whenever it is necessary, by
76 calling the three forms $\text{Ca}_9\text{NaMg}(\text{PO}_4)_7$, $\text{Ca}_9(\text{Ca}_{0.5}\square_{0.5})(\text{Mg},\text{Fe}^{2+})(\text{PO}_4)_7$, and
77 $(\text{Ca}_8\text{REE})\square(\text{Mg},\text{Fe}^{2+})(\text{PO}_4)_7$ as Na-, Ca-, and REE-merrillites, respectively.

78 Although there have been a number of structure determinations on synthetic or
79 heat-treated merrillites (e.g., Malozov et al. 1997; Hughes et al. 2008; Adcock et al.
80 2014), the first high-quality single-crystal X-ray structural refinement from a natural
81 sample was only conducted recently by Hughes et al. (2006) using a REE-rich but
82 Na-poor lunar merrillite with the chemistry
83 $(\text{Ca}_{8.42}\text{REE}_{0.69})_{\Sigma 9.11}\text{Na}_{0.20}(\text{Mg}_{0.72}\text{Fe}^{2+}_{0.31}\text{Mn}^{2+}_{0.01})_{\Sigma 1.04}(\text{P}_{0.99}\text{O}_4)_7$. Based on this study,
84 Hughes et al. (2006) illustrated the detailed structural differences among lunar merrillite,
85 merrillite reported from meteorites, and terrestrial whitlockite. Jolliff et al. (2006) further
86 suggested that significant structural differences between terrestrial whitlockite and lunar
87 (and meteoritic) varieties warrant the use of “merrillite” for the H-free extraterrestrial
88 material, and the systematic enrichment of REE in lunar merrillite warrants the use of
89 “REE-merrillite”. Yet, there has been no crystal structure report on any, natural or
90 synthetic, Na-rich merrillite to date. This paper presents the first single-crystal X-ray
91 diffraction and Raman spectroscopic study on a natural merrillite with nearly ideal
92 chemistry, $\text{Ca}_{9.00}\text{Na}_{0.98}(\text{Mg}_{0.95}\text{Fe}_{0.06})_{\Sigma=1.01}(\text{P}_{1.00}\text{O}_4)_7$, from the Suizhou meteorite.

93 The Suizhou meteorite is a shock-metamorphosed L6-chondrite, with an estimated

104 shock stage S5 (Xie et al. 2001, 2011). The meteorite contains shock-produced melt veins
105 ranging from 20 to 200 μm in width with a bulk chondritic composition. Major
106 rock-forming minerals in the host meteorite are olivine, pyroxene, plagioclase, kamacite,
107 taenite, and troilite. Accessory minerals include chromite, ilmenite, merrillite, and apatite.
108 Both olivine and pyroxene display moderate mosaic texture, and most of the
109 plagioclase grains were shock-melted and quenched to maskelynite. The shock veins
110 contain abundant high-pressure minerals (e.g., ringwoodite, majorite, akimotoite, vitrified
111 perovskite, lingunite, tuite, xieite, CF-phase, magnesiowüstite, majorite-pyrope garnet
112 solid solution), for which the shock-produced pressure and temperature of 24 GPa and
113 1,900~2,000 $^{\circ}\text{C}$ is inferred (Xie et al. 2011).

105

106

EXPERIMENTAL METHODS

119 Merrillite in the Suizhou meteorite makes up about 2 volume % of the chondritic
120 portions (Xie et al. 2002). It occurs as single grains of irregular shape up to 0.5 mm in
121 length (Fig.1). The grains of merrillite are heavily fractured by shock. The merrillite
122 sample used in this study was selected from a polished section of the shock vein-bearing
123 fragment, which was deposited in the RRUFF Project with the deposition number
124 R150063 (<http://rruff.info/R150063>). Its chemical composition was determined with a
125 Shimadzu 1720 electron microprobe operated at 15 kV and 10 nA with the beam
126 diameter of 1 μm . The standards include albite for Na, MgO for Mg, CaSiO_3 for Ca,
127 Fe_2O_3 for Fe, fluorapatite for P. The average composition (wt. %) of 16 analysis points on
128 10 different grains is CaO 46.76(49), Na_2O 2.82(17), MgO 3.53(15), FeO 0.40(29), and
129 P_2O_5 46.06(43), with a total of 99.62(40), yielding an empirical chemical formula
130 $\text{Ca}_{9.00}\text{Na}_{0.98}(\text{Mg}_{0.95}\text{Fe}_{0.06})_{\Sigma=1.01}(\text{P}_{1.00}\text{O}_4)_7$ on the basis of 28 O atoms, in remarkable
131 agreement with the ideal formula $\text{Ca}_9\text{MgNa}(\text{PO}_4)_7$.

123 The Raman spectrum of merrillite was collected from a randomly oriented
124 crystal on a Thermo Almega microRaman system, using a 532-nm solid-state laser
125 with a thermoelectric cooled CCD detector. The laser is partially polarized with 4 cm^{-1}
126 resolution and a spot size of 1 μm .

123 Single-crystal X-ray diffraction data of merrillite were collected from a nearly
124 equidimensional crystal (0.06 x 0.07 x 0.07 mm) on a Bruker X8 APEX2 CCD X-ray
125 diffractometer equipped with graphite-monochromatized MoK_α radiation with frame
126 widths of 0.5° in ω and 30 s counting time per frame. All reflections were indexed on
127 the basis of a hexagonal unit-cell (Table 1). The intensity data were corrected for
128 X-ray absorption using the Bruker program SADABS. The systematic absences of
129 reflections suggest possible space group $R3c$ or $R-3c$. The crystal structure was solved
130 and refined using SHELX97 (Sheldrick 2008) based on space group $R3c$, because it
131 produced the better refinement statistics in terms of bond lengths and angles, atomic
132 displacement parameters, and R factors. The positions of all atoms were refined with
133 the full occupancies and anisotropic displacement parameters. The ratio of Mg vs. Fe
134 at the M site was also refined, yielding Mg = 0.95 and Fe = 0.05, matching that
135 measured from the chemical composition analysis. Final coordinates and
136 displacement parameters of atoms in merrillite are listed in Table 2, and selected
137 bond-distances in Table 3.

138

139

RESULTS AND DISCUSSION

Crystal Structure

141 The crystal structure of merrillite from the Suizhou meteorite is directly comparable
142 with that reported by Hughes et al. (2006) for the REE-rich merrillite from the Apollo 14
143 lunar rocks. It is characterized by a structural unit consisting of a $[(\text{Mg,Fe})(\text{PO}_4)_6]^{16-}$
144 complex anion that forms a “bracelet-and-pinwheel” arrangement (Moore 1973) (Fig. 2).
145 The central octahedral cation and the six coordinating phosphate tetrahedra form a
146 pinwheel, which is characteristic of whitlockite-type compounds. Such structural units
147 are linked by interstitial complexes with a formula of $[\text{Ca}_9\text{Na}(\text{PO}_4)]^{16+}$. The major
148 structural difference between the Suizhou merrillite and the lunar REE-rich merrillite is
149 that, due to the coupled substitution of $(\text{REE}^{3+} + \square) \leftrightarrow (\text{Ca}^{2+} + \text{Na}^+)$, the Na site in lunar
150 REE-merrillite is only about 20% occupied, resulting in an average Na-O bond distance
151 (2.71 Å) slightly longer than that (2.625 Å) in the Suizhou merrillite. According to

152 Hughes et al. (2006, 2008) and Jolliff et al. (2006), the Na site in the interstitial complex
153 unit plays a critical role in maintaining the charge balance in various merrillites. In
154 Ca-merrillite (Calvo and Gopal 1975; Prewitt and Rothbard 1975; Dowty 1977), this site
155 is occupied by $(0.5\text{Ca} + 0.5\text{□})$. In other words, it is the configuration and the chemistry of
156 the interstitial complex that defines the differences between whitlockite and merrillite, as
157 well as among Na-, Ca-, and REE-merrillites. The chemical formulas of the interstitial
158 complex units are $[\text{Ca}_9(\text{PO}_3[\text{OH}])]^{16+}$, $[\text{Ca}_9(\text{Ca}_{0.5}\text{□}_{0.5})(\text{PO}_4)]^{16+}$, and
159 $[(\text{Ca}_{9-x}\text{REE})_x(\text{Na}_{1-x}\text{□}_x)(\text{PO}_4)]^{16+}$ in whitlockite, Ca-merrillite, and REE-merrillite,
160 respectively.

161 The chief structural difference between merrillite-type and whitlockite-type
162 compounds consists in the configuration of the phosphate tetrahedron in the interstitial
163 complex unit. In whitlockite-type minerals, one of the O^{2-} anions in the phosphate group
164 is substituted by OH^- in whitlockite or F^- in bobdownsite (the F-analogue of whitlockite)
165 and the $\text{PO}_3(\text{OH})$ or PO_3F group exhibits an inversed configuration with respect to that in
166 merrillite (e.g., Hughes et al. 2008; Tait et al. 2011). Interestingly, the $\text{PO}_3(\text{OH})$ or PO_3F
167 tetrahedron in natural whitlockite or bobdownsite, respectively, is found to be disordered
168 between the two opposite orientations (with the O-H or P-F bond pointing to either $+\mathbf{c}$ or
169 $-\mathbf{c}$) and the smaller portion of it apparently possesses the same configuration as that in
170 merrillite.

171

172 **Raman spectroscopy**

173 There have been several investigations on merrillite with Raman spectroscopy
174 and the detailed assignments of major Raman bands have been proposed (e.g., Chen et al.,
175 1995; Jolliff et al. 1996, 2006; Cooney et al. 1999; Wang et al. 2004; Xie and Chen
176 2008). The Raman spectrum of the Suizhou merrillite is displayed in Figure 3, which
177 resembles that of weakly- to moderately-shocked merrillite in the Sixiangkou meteorite
178 (Chen et al., 1995; Xie and Chen 2008), merrillite from Martian meteorites (Wang et al.
179 2004), and synthetic REE-poor merrillite (Jolliff et al., 2006). The spectrum of the
180 Suizhou merrillite contains a well-resolved strong doublet at 960 and 976 cm^{-1} , which are

181 attributable to the ν_1 symmetric stretching vibrations of the P-O bonds within the PO₄
182 tetrahedra. The weak bands between 1018 and 1106 cm⁻¹ correspond to ν_3 asymmetric
183 stretching vibrations of the PO₄ groups. The bands ranging from 561 to 524 cm⁻¹ are due
184 to the O-P-O bending modes within the PO₄ tetrahedra and those below 479 cm⁻¹ to the
185 lattice mode (Jolliff et al., 1996).

186 The Raman spectrum of the Suizhou merrillite is, however, obviously different
187 from that of the REE-rich merrillite, natural or synthetic, which exhibits an asymmetric
188 single peak or a very poorly resolved doublet (Jolliff et al., 2006). The Raman spectrum
189 of terrestrial whitlockite is similar to that of the REE-rich merrillite, but exhibits an
190 additional weak peak at ~924 cm⁻¹ (Fig. 3) that is not observed in the spectra of the
191 H-free merrillite. This peak, according to Jolliff et al. (2006), is attributable to the ν_1
192 symmetric stretching vibrations of the PO₃(OH) group.

193

194 IMPLICATIONS

195 The Suizhou merrillite has a rather simple composition with 0.98 Na apfu. This value
196 is much higher than that (0.05-0.20 Na apfu) in lunar merrillites (Hughes et al. 2006;
197 Jolliff et al. 2006), most of which exhibit characteristic enrichment in REE. In
198 comparison, on the one hand, Martian merrillite contains significantly higher Na
199 concentrations (up to 0.86 apfu) and much lower REE concentrations (Shearer et al. 2015
200 and references therein). On the other hand, meteoritic merrillite has relatively low REE
201 contents, but exists in both Ca-rich and Na-rich varieties. Clearly, the simple chemical
202 formula for merrillite, Ca₉NaMg(PO₄)₇, approved by IMA is insufficient and inadequate
203 to describe various merrillites documented thus far. Accordingly, Jolliff et al. (2006)
204 proposed three merrillite endmember compositions: Ca-merrillite
205 Ca₉(Ca_{0.5}□_{0.5})Mg(PO₄)₇, Na-merrillite Ca₉NaMg(PO₄)₇, and REE-merrillite
206 [Ca₈(REE)]□Mg(PO₄)₇. These merrillite endmembers are linked by coupled substitutions:
207 (0.5Ca_{Na-site} + 0.5□_{Na-site}) ⇌ Na_{Na-site}, Ca_{Ca-site} + 0.5Ca_{Na-site} ⇌ REE_{Ca-site} + 0.5□_{Na-site}, and
208 0.5Ca_{Ca-site} + 0.5Na_{Na-site} ⇌ 0.5REE_{Ca-site} + 0.5□_{Na-site}. The nomenclature proposed by
209 Jolliff et al. (2006) for various merrillites appears to have its merits, as it reflects their

210 chemical differences and provides considerable conveniences in their descriptions.
211 Tuite, ideally $\text{Ca}_3(\text{PO}_4)_2$, was first discovered from the Suizhou meteorite as the
212 high-pressure polymorph of merrillite (Xie et al. 2002) or the high-pressure
213 decomposition product of chlorapatite (Xie et al. 2013). It is stable at Earth's mantle
214 temperature-pressure conditions and is proposed to be a potential host for REE and
215 incompatible elements, such as Na, Sr and Ba (Murayama et al. 1986; Xie et al. 2002).
216 Based on chemical analyses of numerous tuite grains from the Suizhou meteorite, Xie et
217 al. (2013) noticed that tuite converted from merrillite retains similar amounts of MgO and
218 Na_2O as merrillite, whereas that formed through the decomposition of chlorapatite
219 contains little MgO or Na_2O , but significant Cl, suggesting that the Na_2O , MgO, and Cl
220 contents in natural tuite may serve as good indicators for distinguishing its precursor
221 phosphate mineral, merrillite or chlorapatite. It thus begs the question whether
222 REE-bearing tuite could be found on the Moon as a consequence of the REE-merrillite
223 transformation under impacts, as only lunar merrillite exhibits high REE concentrations
224 of all extraterrestrial merrillites documented thus far.

225

226

ACKNOWLEDGEMENTS

227 We gratefully acknowledge the funding support from the National Natural Science
228 Foundation of China (Grant No. 41172046 to X.X.) and the Science Foundation Arizona.
229

230

REFENRECES CITED

231 Adcock, C.T., Hausrath, E.M., Forster, P.M., Tschauner, O., and Sefein, K. J. (2014) Synthesis
232 and characterization of the Mars-relevant phosphate minerals Fe- and Mg-whitlockite and
233 merrillite and a possible mechanism that maintains charge balance during whitlockite to
234 merrillite transformation. *American Mineralogist*, 99, 1221–1232.
235 Calvo, C. and Gopal, R. (1975) The crystal structure of whitlockite from the Palermo Quarry.
236 *American Mineralogist*, 60, 120-133.
237 Chen, M., Wopenka, B., Xie, X., El Goresy, A. (1995) A new high-pressure polymorph of
238 chlorapatite in the shocked Sixiangkou (L6) chondrite. *Lunar and Planetary Science*, XXVI,
239 237-238.
240 Cooney, T.F., Scott, E.R.D., Krot, A.N., Sharma, S.K., and Yamaguchi, A. (1999) Vibrational
241 spectroscopic study of minerals in the Martian meteorite ALH84001. *American*
242 *Mineralogist*, 84, 1569-1576.
243 Dowty, E. (1977) Phosphate in Angra dos Reis: structure and composition of the $\text{Ca}_3(\text{PO}_4)$

- 244 minerals. *Earth and Planetary Science Letters*, 35, 347-351.
- 245 Fuchs, L.H. (1962) Occurrence of whitlockite in chondritic meteorites. *Science*, 137, 425-426.
- 246 Fuchs, L.H. (1971) Orthopyroxene and orthopyroxene-bearing rock fragments rich in K, REE,
247 and P in Apollo 14 soil sample 14163. *Earth and Planetary Science Letters*, 12, 170-174.
- 248 Gopal, R. and Calvo, C. (1972) Structure relationship of whitlockite and β -Ca₃(PO₄). *Nature*
249 *Physical Sciences*, 237, 30-32.
- 250 Jolliff, B.L., Haskin, L.A., Colson, R.O., and Wadhwa, M. (1993) Partitioning in REE-
251 saturating minerals: Theory, experiment, and modeling of whitlockite, apatite, and
252 evolution of lunar residual magmas. *Geochimica et Cosmochimica Acta*, 57, 4069-4094.
- 253 Jolliff, B.L., Freeman, J.J., Wopenka, B. (1996) Structural comparison lunar, terrestrial, and
254 synthetic whitlockite using laser Raman microprobe spectroscopy. *Lunar and Planetary*
255 *Science*, XXII, 613-614 (Abstract).
- 256 Jolliff, B.L., Hughes, J.M., Freeman, J.J., and Zeigler, R.A. (2006) Crystal chemistry of lunar
257 merrillite and comparison to other meteoritic and planetary suites of whitlockite and merrillite.
258 *American Mineralogist*, 91, 1583-1595.
- 259 Malozov, V.A., Presnyakov, I.A., Belik, A.A., Khasarov, S.S., and Lazoryak, B.I. (1997) Crystal
260 structure of calcium, magnesium and alkali metal phosphates Ca₉MgM(PO₄)₇ (M = Li, Na, K).
261 *Krystallografiya*, 42, 825-836.
- 262 McSween, H.Y., Eisenhour, D.D., Taylor, L.A., Wadhwa, M., and Crozaz, G. (1996) QUE94201
263 shergottite: Crystallization of a Martian basaltic magma. *Geochimica et Cosmochimica Acta*,
264 60, 4563-4569.
- 265 Merrill, G.P. (1915) On the monticellite-like mineral in meteorites and on oldhamite as a
266 meteoritic constituent. *Proceedings of the Natural Academy of Science*, 1, 302-308.
- 267 Moore, P.B. (1973) Bracelets and pinwheels: a topological-geometric approach to the calcium
268 orthosilicates and alkali sulfate structures. *American Mineralogist*, 58, 32-42.
- 269 Murayama, J.K., Nakai, S., Kato, M., and Kumazawa, M. (1986) A dense polymorph of
270 Ca₃(PO₄)₂: A high pressure phase of apatite decomposition and its geochemical significance.
271 *The Physics of the Earth and Planetary Interiors*, 44, 293-303.
- 272 Orlova, A.I., Khainakov, S., Loginova, E., Oleneva, T., Granda, S.G., and Kurazhkovskaya, V.S.
273 (2009) Calcium thorium phosphate (whitlockite-type mineral). Synthesis and structure
274 refinement. *Crystallography Reports*, 54, 591-597.
- 275 Prewitt, C.T. and Rothbard, D.R. (1975) Crystal structures of meteoritic and lunar whitlockites
276 (abstract). *Lunar and Planetary. Science*, VI, 646-648.
- 277 Ruzsala, F., and Kostiner, E. (1980) The hydrothermal synthesis and crystal growth of various
278 whitlockites and a manganese containing graftonite. *Journal of Crystal Growth*, 48, 473-474.
- 279 Shearer, C., Papike, J., Burger, P., Sutton, S., McCubbin, F., and Newville, M. (2011) Direct
280 determination of europium valence state by XANES in extraterrestrial merrillite: Implications
281 for REE crystal chemistry and martian magmatism. *American Mineralogist*, 96, 1418-1421.
- 282 Shearer, C.K., Burger, P.V., Papike, J.J., McCubbin, F.M., and Bell, A.S. (2015) Crystal chemistry
283 of merrillite from Martian meteorites: Mineralogical recorders of magmatic processes and
284 planetary differentiation. *Meteoritics & Planetary Science*, 50, 649-673.
- 285 Sheldrick, G. M. (2008). A short history of SHELX. *Acta Crystallographica*, A64, 112-122.
- 286 Tait, K.T., Barkley, M.C., Thompson, R.M., Origlieri, M.J., Evans, S.H., Prewitt, C.T., Yang, H.
287 (2011) Bobdownsite, a new mineral species from Big Fish River, Yukon, Canada, and its

- 288 structural relationship with whitlockite-type compounds. *The Canadian Mineralogist*, 49,
289 1065-1078.
- 290 Terada, K., Monde, T., and Sano, Y. (2003) Ion microprobe U-Th-Pb dating of phosphates in
291 martian meteorite ALH 84001. *Meteoritics & Planetary Science*, 38, 1697–1703.
- 292 Treiman, A.H. (2003) Chemical compositions of martian basalts (shergottites): Some inferences
293 on basalt formation, mantle metasomatism, and differentiation on Mars. *Meteoritics and*
294 *Planetary Science*, 38, 1849–1864.
- 295 Wang, A., Kuebler, K., Jolliff, B., and Haskin, L.A. (2004) Mineralogy of a Martian meteorite as
296 determined by Raman spectroscopy. *Journal of Raman Spectroscopy*, 35, 504-514.
- 297 Wherry, E.T. (1917) Merrillite, meteoritic calcium phosphate. *American Mineralogist*, 2, 119.
- 298 Xie, X., Chen, M., Wang, D. (2001) Shock-related mineralogical features and P-T history of the
299 Suizhou L6 chondrite. *European Journal of Mineralogy*, 13, 1177-1190.
- 300 Xie, X., Minitti, M.E., Chen, M., Mao, H.K., Wang, D., Shu, J., Fei, Y. (2002) Natural
301 high-pressure polymorph of merrillite in the shock vein of the Suizhou meteorite. *Geochimica*
302 *et Cosmochimica Acta*, 66, 2439-2444.
- 303 Xie, X., Minitti, M. E., Chen, M., Wang, D., Mao, H. K., Shu, J., and Fei, Y. W. (2003) Tuite,
304 γ -Ca₃(PO₄)₂, a new phosphate mineral from the Suizhou L6 chondrite. *European Journal of*
305 *Mineralogy*, 15, 1001–1005.
- 306 Xie, X., and Chen, M. (2008) Formation conditions of tuite. *Geochimica (Beijing)* 37, 297–303.
307 In Chinese with English abstract.
- 308 Xie, X., Sun, Z., and Chen, M. (2011) The distinct morphological and petrological features of
309 shock melt veins in the Suizhou L6 chondrite. *Meteoritics and Planetary Science*, 6, 459-469.
- 310 Xie, X., Zhai, S., Chen, M., and Yang, H. (2013) Tuite, γ -Ca₃(PO₄)₂, formed from chlorapatite
311 decomposition in the shock vein of the Suizhou L6 chondrite. *Meteoritics and Planetary*
312 *Science*, 48, 1515–1523.
- 313
- 314
- 315
- 316
- 317
- 318
- 319
- 320
- 321

322

323

324

325

326

327 **List of Tables**

328

329 Table 1. Comparison of crystallographic data for various merrillite

330

331 Table 2. Coordinates and displacement parameters of atoms in Suizhou merrillite

332

333 Table 3. Selected interatomic distances (Å) in Suizhou merrillite

334

335

336 **List of Figure Captions**

337

338 Figure 1. Back-scattered electron image showing a large merrillite (Mer) grain in the
339 Suizhou meteorite. Ol = olivine, Pyx = Low Ca-pyroxene, Mas = maskelynite,
340 M = FeNi metal.

341

342 Figure 2. The arrangement of the bracelet-and-pinwheel structural units in Suizhou
343 merrillite. A $[(\text{Mg,Fe})(\text{PO}_4)_6]^{16-}$ structure unit is indicated separately at the
344 lower-right corner.

345 Figure 3. Raman spectrum of Suizhou merrillite, along with that of whitlockite for
346 comparison.

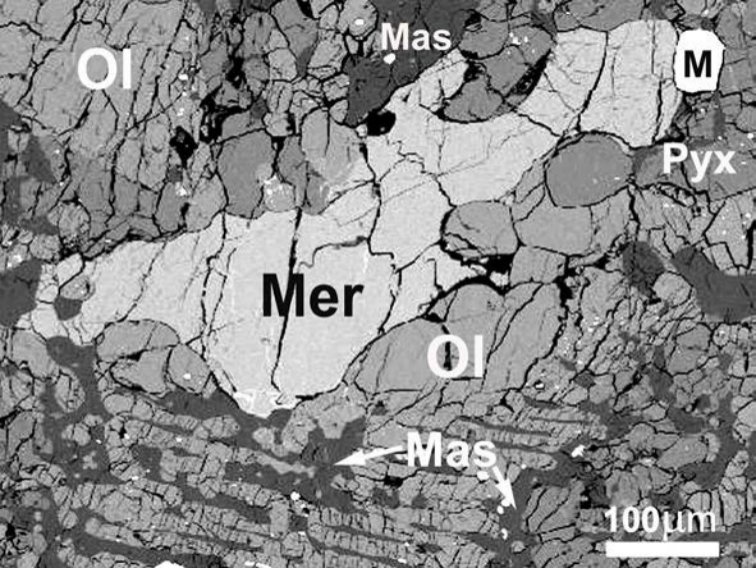
347

348

349

350

351



Ol

Mas

M

Pyx

Mer

Ol

Mas

100 μ m

Figure 2

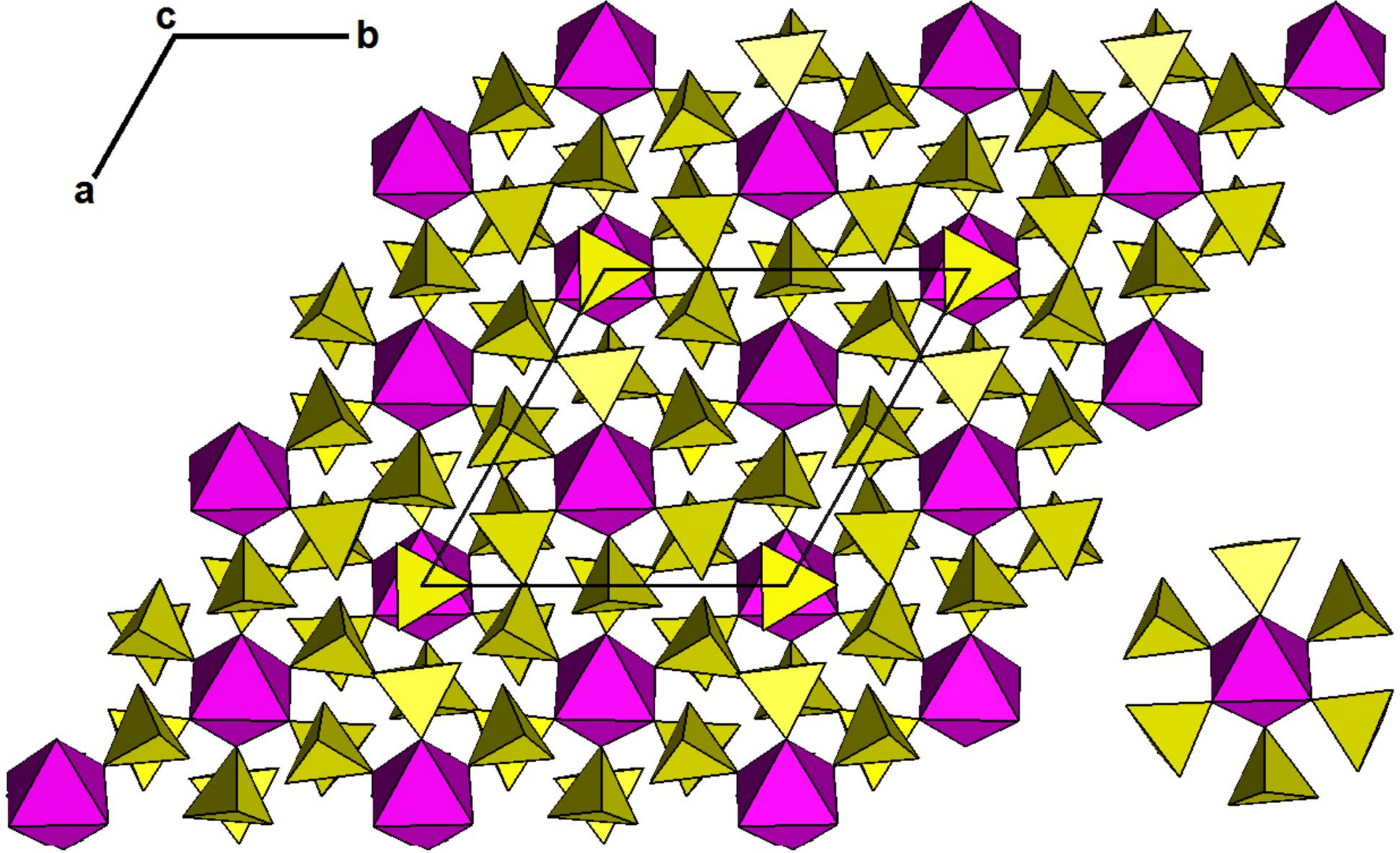


Figure 3

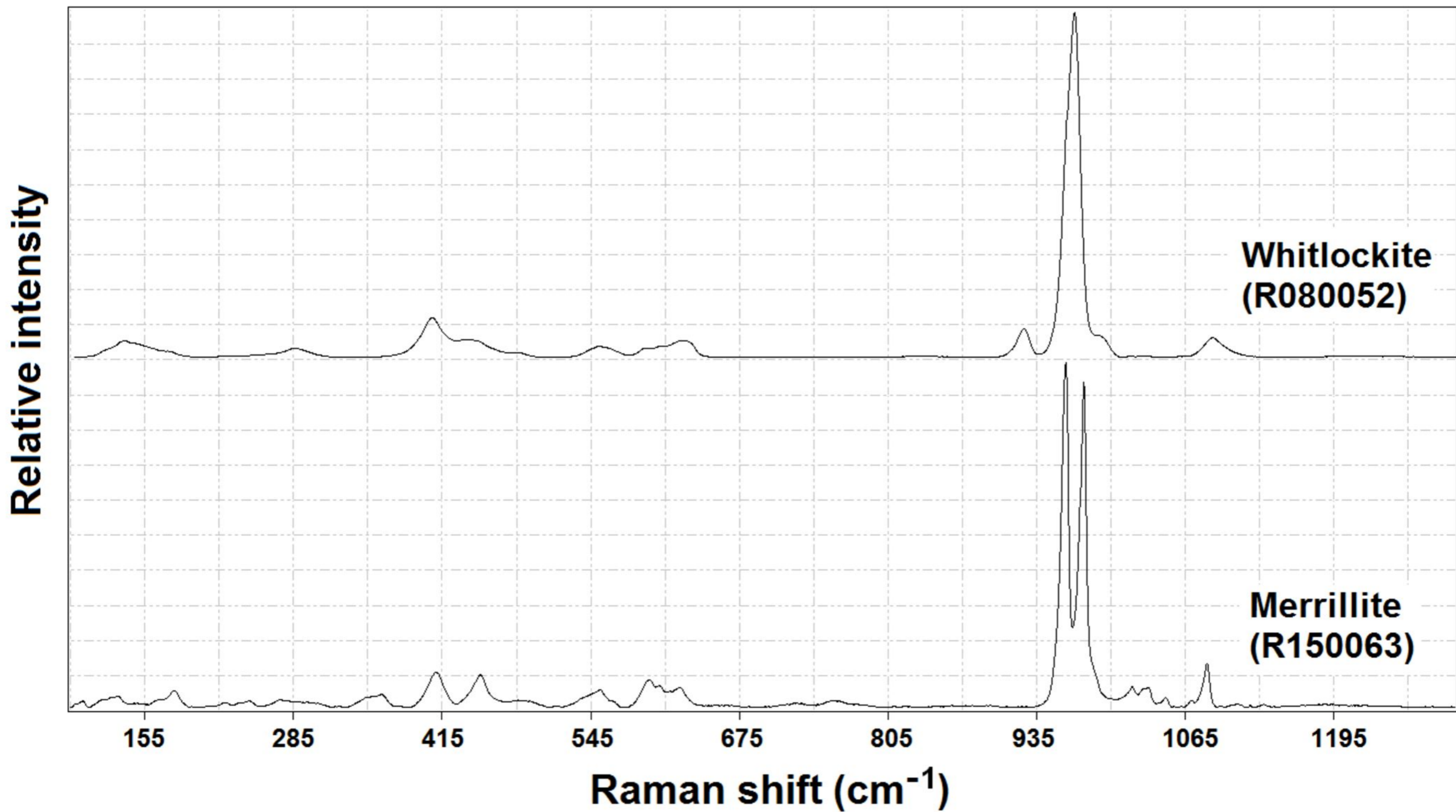


Table 1. Comparison of crystallographic data for various merrillite

	Merrillite	REE-Merrillite	Ca-Merrillite
Sample source	Suizhou meteorite	Apollo 14 lunar rocks	Angra dos Reis achondrite
Ideal chemical formula	$\text{Ca}_9\text{NaMg}(\text{PO}_4)_7$	$(\text{Ca}_8\text{REE})\square(\text{Mg,Fe}^{2+})(\text{PO}_4)_7$	$\text{Ca}_9(\text{Ca}_{0.5}\square_{0.5})(\text{Mg,Fe}^{2+})(\text{PO}_4)_7$
Space group	<i>R3c</i>	<i>R3c</i>	<i>R3c</i>
<i>a</i> (Å)	10.3444(3)	10.2909(10)	10.362(1)
<i>c</i> (Å)	37.0182(11)	36.8746(68)	37.106(5)
<i>V</i> (Å ³)	3430.5(2)	3381.9	3450.3
<i>Z</i>	6	6	6
ρ_{cal} (g/cm ³)	3.121	3.058	3.104
λ (Å)	0.71073	0.71073	0.7107
μ (mm ⁻¹)	2.776		2.85
2θ range for data collection	≤ 65.16	≤ 57	
No. of reflections collected	13704	10015	2401
No. of independent reflections	2781	1103	
No. of reflections with $I > 2\sigma(I)$	2279	922	1972
No. of parameters refined	142	147	
R(int)	0.046	0.051	
Final R_1 , wR_2 factors [$I > 2\sigma(I)$]	0.032, 0.054	0.045, 0.113	0.041
Final R_1 , wR_2 factors (all data)	0.050, 0.059	0.063	
Goodness-of-fit	1.010	1.055	
Reference	This work	Hughes et al. (2006)	Dowty (1977)

Table 2. Coordinates and displacement parameters of atoms in merrillite

Atom	x	y	z	U _{eq}	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
Ca1	0.26876(7)	0.14531(7)	0.67512(2)	0.0138(1)	0.0157(3)	0.0137(3)	0.0130(3)	-0.0026(3)	-0.0012(2)	0.0083(3)
Ca2	0.27190(7)	0.14172(7)	0.56756(1)	0.0121(1)	0.0127(3)	0.0133(3)	0.0107(2)	-0.0009(2)	-0.0002(2)	0.0069(3)
Ca3	0.38354(7)	0.17613(7)	0.76894(1)	0.0122(1)	0.0131(3)	0.0126(3)	0.0103(2)	-0.0002(3)	-0.0013(2)	0.0060(3)
Na	0	0	0.81343(7)	0.0278(6)	0.0267(9)	0.0267(9)	0.0300(16)	0	0	0.0134(5)
M	0	0	-0.00066(5)	0.0108(5)	0.0113(6)	0.0113(6)	0.0100(7)	0	0	0.0056(3)
P1	0	0	0.73382(3)	0.0113(3)	0.0110(4)	0.0110(4)	0.0120(5)	0	0	0.0055(2)
P2	0.31245(9)	0.13793(9)	0.86509(2)	0.0108(2)	0.0107(3)	0.0115(4)	0.0103(3)	0.0007(3)	0.0000(3)	0.0055(3)
P3	0.34393(10)	0.15077(9)	0.96893(2)	0.0104(2)	0.0104(4)	0.0110(4)	0.0096(3)	0.0006(3)	0.0002(3)	0.0051(3)
O1	0	0	0.6928(1)	0.0139(8)	0.0148(12)	0.0148(12)	0.0120(17)	0	0	0.0074(6)
O2	-0.0040(3)	0.1384(2)	0.7475(1)	0.0166(4)	0.0165(10)	0.0137(12)	0.0223(10)	-0.0017(10)	0.0044(8)	0.0094(10)
O3	0.2576(3)	0.0803(3)	0.8265(1)	0.0156(5)	0.0165(11)	0.0171(11)	0.0111(10)	-0.0006(8)	0.0005(9)	0.0067(10)
O4	0.2421(3)	0.2273(3)	0.8792(1)	0.0164(5)	0.0186(12)	0.0202(12)	0.0142(10)	0.0028(9)	0.0038(9)	0.0125(10)
O5	0.2767(2)	-0.0008(2)	0.8880(1)	0.0126(4)	0.0132(10)	0.0119(10)	0.0111(9)	0.0017(8)	0.0009(8)	0.0052(9)
O6	0.4851(2)	0.2392(2)	0.8672(1)	0.0124(4)	0.0117(10)	0.0118(11)	0.0126(9)	0.0008(9)	0.0008(8)	0.0051(10)
O7	0.3784(2)	0.1809(2)	0.0092(1)	0.0127(4)	0.0123(10)	0.0157(11)	0.0092(8)	-0.0007(8)	-0.0022(8)	0.0063(9)
O8	0.3969(3)	0.0427(2)	0.9565(1)	0.0153(5)	0.0162(11)	0.0182(12)	0.0134(10)	-0.0026(9)	-0.0005(9)	0.0102(10)
O9	0.4208(3)	0.2997(3)	0.9488(1)	0.0164(5)	0.0175(11)	0.0143(11)	0.0133(10)	0.0026(9)	0.0003(9)	0.0047(9)
O10	0.1741(2)	0.0767(3)	0.9619(1)	0.0119(4)	0.0101(10)	0.0142(11)	0.0104(9)	-0.0006(9)	-0.0016(8)	0.0053(10)

Note: (1) The M site is occupied by (0.95 Mg + 0.05 Fe).

(2) The labeling scheme of the atomic sites given by Hughes et al. (2006) is adopted here to facilitate a better comparison with the REE-rich merrillite.

Table 3. Selected interatomic distances (Å) in the Suizhou merrillite

Ca1--O8	2.386(2)	Ca2--O9	2.313(2)	Ca3--O2	2.363(2)
--O5	2.413(2)	--O7	2.361(2)	--O5	2.373(2)
--O7	2.472(2)	--O2	2.450(3)	--O10	2.418(2)
--O1	2.497(1)	--O8	2.467(2)	--O10	2.431(2)
--O4	2.517(2)	--O5	2.477(2)	--O3	2.436(2)
--O7	2.531(2)	--O6	2.479(2)	--O4	2.443(2)
--O3	2.626(2)	--O6	2.489(2)	--O8	2.634(2)
--O9	2.628(2)	--O4	2.833(3)	--O9	2.689(2)
Ave.	2.509		2.434		2.473
Na--O3	2.411(2) ×3	Mg--O6	2.070(2) ×3		
--O2	2.839(3) ×3	--O10	2.089(2) ×3		
Ave.	2.625		2.080		
P1--O1	1.520(4)	P2--O4	1.527(2)	P3--O9	1.529(2)
--O2	1.5385(2)	--O3	1.541(2)	--O7	1.529(2)
--O2	1.5385(2)	--O5	1.545(2)	--O8	1.541(2)
--O2	1.539(2)	--O6	1.556(2)	--O10	1.547(2)
Ave.	1.534		1.542		1.536