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Revised version 1134R**New structural data reveal benleonardite to be a member of the pearceite-polybasite group**LUCA BINDI^{1,*}, CHRISTOPHER J. STANLEY², PAUL G. SPRY³¹*Dipartimento di Scienze della Terra, Università di Firenze, Via G. La Pira 4, I-50121 Firenze, Italy*²*Natural History Museum, Cromwell Road, London SW7 5BD, United Kingdom*³*Department of Geological and Atmospheric Sciences, 253 Science I, Iowa State University, Ames, Iowa 50011-3210, U.S.A.** e-mail address: luca.bindi@unifi.it**ABSTRACT**

The determination of the crystal structure of benleonardite (S.G. $P\bar{3}m1$; $R = 0.0321$ for 1250 reflections and 102 parameters; refined formula $\text{Ag}_{15.0}\text{Cu}_{1.0}\text{Sb}_{1.58}\text{As}_{0.42}\text{S}_{7.03}\text{Te}_{3.97}$) obtained using data from a gem-quality, untwinned crystal recovered from the type material, revealed that benleonardite exhibits the structure observed for minerals of the pearceite-polybasite group. The structure consists in the stacking of $[\text{Ag}_6(\text{Sb,As})_2\text{S}_6\text{Te}]^{2-}$ *A* and $[\text{Ag}_9\text{Cu}(\text{S,Te})_2\text{Te}_2]^{2+}$ *B* layer modules in which (Sb,As) forms isolated SbS_3 pyramids typically occurring in sulfosalts, Cu links two (S,Te) atoms in a linear coordination, and Ag occupies sites with coordination ranging from quasi linear to almost triangular. The silver d^{10} ions are found in the *B* layer module along two-dimensional diffusion paths and their electron densities, which are evidenced by means of a combination of a Gram-Charlier development of the atomic displacement factors and a split model. In the structure, two S-positions are completely replaced by Te (i.e., Te3 and Te4) and one for one half [S1: $\text{S}_{0.514(9)}\text{Te}_{0.486}$],

26 whereas S2 is completely filled by sulfur. This distribution reflects on the crystal-chemical
27 environments of the different cations. On the basis of information gained from this
28 characterization, the crystal-chemical formula of benleonardite was revised according to the
29 structural results, yielding $\text{Ag}_{15}\text{Cu}(\text{Sb,As})_2\text{S}_7\text{Te}_4$ ($Z = 1$) instead of $\text{Ag}_8(\text{Sb,As})\text{Te}_2\text{S}_3$ ($Z = 2$)
30 as previously reported. Thus, the mineral must be considered a member of the pearceite-
31 polybasite group. A recalculation of the chemical data listed in the scientific literature for
32 benleonardite according to the structural results obtained here leads to an excellent agreement.

33

34 **Keywords:** benleonardite, crystal structure, pearceite, polybasite, Ag-sulfosalt, Bambolla.

35

36 INTRODUCTION

37 Benleonardite, ideally $\text{Ag}_8(\text{Sb,As})\text{Te}_2\text{S}_3$, was identified as a new mineral species by
38 Stanley *et al.* (1986) by studying ore minerals collected from the spoil tips of the abandoned
39 Bambolla mine, Moctezuma, Sonora (Mexico). It was described as forming thin black
40 powdery crusts (1–2 mm thick) with native silver, acanthite, hessite, cervelleite, pyrite and
41 sphalerite. By means of powder-diffraction X-ray investigations, benleonardite was originally
42 given as tetragonal with $a = 6.603(5)$ and $c = 12.726(6)$ Å, but the crystal structure remained
43 unknown. Although benleonardite-like minerals have been found in several occurrences
44 [Zyranov gold deposit, Russia (Aksenov *et al.*, 1969), Ivigtut cryolite deposit, Greenland
45 (Karup-Møller and Pauly, 1979), Gies gold–silver telluride deposit, Montana (Zhang and
46 Spry, 1994; Spry and Thieben, 1996), Mayflower gold–silver telluride deposit, Montana
47 (Spry and Thieben, 1996), Um Samiuki Zn–Pb–Cu–Ag volcanogenic massive sulfide deposit,
48 Egypt (Helmy *et al.*, 1999; Pals and Spry, 2003), black smoker chimney fragments from the
49 Yaman Kasy massive sulfide deposit, southern Urals (Herrington *et al.*, 1998)], no additional
50 structural investigations have been reported in the literature so far.

51 The simplified formula for benleonardite was given as $\text{Ag}_8\text{SbTe}_2\text{S}_3$ by Stanley *et al.*,
52 (1986). However, such a chemical formula is unbalanced, which is a very unusual
53 characteristic when dealing with Ag-sulfosalts (Bindi and Evain, 2007; Mořlo *et al.*, 2008).
54 Moreover, chemical data reported for benleonardite (and benleonardite-like minerals) in the
55 literature show a general deficiency in Ag+Cu (i.e., <8 atoms per formula unit) coupled with
56 an excess in S (i.e., 3 to 4 atoms per formula unit) when normalized on the basis of 14 atoms,
57 thus reinforcing the suggestion by Spry and Thieben (1996) that the formula proposed by
58 Stanley *et al.* (1986) needs to be modified.

59 Here we present the determination of the crystal structure of benleonardite obtained
60 using data from a gem-quality, untwinned benleonardite crystal recovered from the type
61 material. We show that benleonardite exhibits the structure observed for the minerals of the
62 pearceite-polybasite group (Bindi *et al.*, 2006a, 2006b, 2007a, 2007b, 2007c, 2013; Bindi and
63 Menchetti, 2009; Evain *et al.*, 2006a, 2006b).

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THE HOLOTYPE

67 A crystal for the X-ray investigation was selected from the type material (catalogue
68 number E.1161 BM 1985, 354). The specimen was collected by the late Alan Criddle on a
69 field excursion to the Sonora Desert led by the late Sid Williams. It consists of black powdery
70 crusts (1–2 mm thick) of benleonardite, acanthite, hessite and cervelleite together with gangue
71 quartz and dolomite (Fig. 1). The hessite contains a vermiform or myrmekitic intergrowth of
72 fine-grained cervelleite (pale-greenish-grey in Fig. 1). The assemblage occupies irregular
73 fractures in a highly altered rock described by Williams (1982) as an intensely silicified
74 rhyolitic vitrophyre.

75
76

77 **X-RAY CRYSTALLOGRAPHY**

78 A benleonardite crystal was hand-picked from a polished section of the type material,
79 glued to a glass rod and used for the room temperature data collection, which was carried out
80 on a Oxford Diffraction Xcalibur 3 diffractometer, fitted with a Sapphire 2 CCD detector (see
81 Table 1 for details) using graphite-monochromatized MoK α radiation ($\lambda = 0.71069$ Å).
82 Because of the typical ionic conductivity observed in Ag-sulfosalts and the probable presence
83 of twinning (see Bindi *et al.*, 2006a), a rather high $\sin(\theta)/\lambda$ cutoff and a full sphere exploration
84 were considered. Intensity integration and standard Lorentz-polarization correction were
85 performed with the *CrysAlis* RED (Oxford Diffraction, 2006) software package. The program
86 ABSPACK in *CrysAlis* RED (Oxford Diffraction, 2006) was used for the absorption
87 correction.

88 The unit-cell found for the selected benleonardite crystal is trigonal (hexagonal setting),
89 with $a = 7.623(1)$ and $c = 12.708(1)$ Å. The c -parameter is almost the same as that found by
90 Stanley *et al.* (1986), 12.726(6) Å, and the a -parameter is related to that originally reported
91 [i.e., 6.606(5) Å] by a factor of $\sin(120^\circ)$ [i.e., 7.623 Å \times $\sin(120^\circ) = 6.602$ Å], which
92 explains the symmetry change from the trigonal to the tetragonal setting. The refined trigonal
93 unit-cell obtained for benleonardite is very similar to that observed for minerals belonging to
94 the pearceite-polybasite group (Bindi *et al.*, 2007a). Taking into account this similarity, the
95 structure was refined in the space group $P\bar{3}m1$ using the program JANA2006 (Petříček *et al.*,
96 2006) starting from the atomic coordinates given by Bindi *et al.* (2007b) for the crystal
97 structure of polybasite-*Tac*. The sites with partial (or total) substitution of S by Te were easily
98 identified (i.e., S1, S3 and S4). To mimic the silver electron spreading along diffusion paths,
99 up to third-order non-harmonic Gram-Charlier tensors were used for the Debye-Waller
100 description of the Ag3, Ag4 and Ag5 atoms (Johnson and Levy, 1974; Kuhs, 1984).

101 Full site occupation (Sb/As and S1/Te1) was assured through constraints and the overall
 102 charge balance was ascertained. The final residual R is 0.0179 for 609 reflections [$I > 2\sigma(I)$]
 103 and $R = 0.0321$ for all 1250 unique reflections and 102 parameters.

104 Atomic parameters are reported in Tables 2 to 4, whereas bond distances are given in
 105 Table 5. Structure factors and CIF are deposited with the Principal Editor of Mineralogical
 106 Magazine at http://www.minersoc.org/pages/e_journals/dep_mat.html.

107 Unfortunately, the crystal used for the structural study was lost in an attempt to embed
 108 it in epoxy to get electron microprobe data. However, the final refined formula can be written
 109 as: $\text{Ag}_{15.00}\text{Cu}_{1.00}(\text{Sb}_{1.58}\text{As}_{0.42})\text{S}_{7.03}\text{Te}_{3.97}$, which is in good agreement with those reported by
 110 Stanley *et al.* (1986) for benleonardite from the type material, i.e. $\text{Ag}_{16.0-16.1}\text{Cu}_{0.0-0.1}\text{Sb}_{1.6-}$
 111 $_{1.7}\text{As}_{0.4-0.6}\text{S}_{6.7-6.8}\text{Te}_{3.9-4.0}$.

112

113 DESCRIPTION OF THE STRUCTURE

114 On the whole, the benleonardite structure resembles that of the trigonal polytype (*Tac*)
 115 of polybasite (Bindi *et al.*, 2007b). It can be described as the succession, along the c axis, of
 116 two layer modules: a $[\text{Ag}_6(\text{Sb,As})_2\text{S}_6\text{Te}]^{2-}$ A module layer and a $[\text{Ag}_9\text{Cu}(\text{S,Te})_2\text{Te}_2]^{2+}$ B
 117 module layer (Fig. 2).

118 In the A module layer, Ag atoms (Ag1 and Ag2) are triangularly coordinated by S and
 119 Te atoms in a quasi-planar environment. Benleonardite represents the first member of the
 120 pearceite-polybasite group showing structural disorder also in the Ag positions of the A layer.
 121 The disorder has been modeled with two split Ag-positions ($\text{Ag1}-\text{Ag2} = 0.51 \text{ \AA}$) with partial
 122 occupancy (Table 2). The (Sb,As) atoms are also in a threefold coordination, but in a trigonal
 123 pyramidal configuration. The $[\text{Ag}(\text{S,Te})_3]$ and $[(\text{Sb,As})\text{S}_3]$ subunits are linked together
 124 through corners to constitute the A module layer.

125 In the *B* module layer, the silver d^{10} cations are distributed along 2D diffusion paths, in
126 a structure skeleton made of face-sharing tetrahedra (as in argyrodite-type ionic-conductor
127 compounds; Boucher *et al.*, 1993) around the Cu atom (see Fig. 3). It is worth noting that the
128 modes (maxima of density) observed in the diffusion paths do not correspond to the Ag
129 refined positions (Ag3, Ag4 and Ag5) and that and the refined atomic positions do not lie
130 along diffusion paths between modes, the Gram-Charlier expansion of the Debye-Waller
131 factor providing the connecting density. For this reason, the refined Ag positions should not
132 be used to calculate distances (although meaningful distances could be obtained with mode
133 positions).

134 In the structure, two S-positions are completely replaced by Te (i.e., Te3 and Te4) and
135 one for one half [S1: $S_{0.514(9)}Te_{0.486}$], whereas S2 is completely filled by sulfur. This
136 distribution reflects on the crystal-chemical environments of the different cations. The Cu-
137 S1/Te1 distance [2.317(4) Å] is much longer than both the Cu-S1/Se1' distance in
138 selenopolybasite [2.199(2) Å – Evain *et al.*, 2006b] and that observed for Te-rich polybasite
139 [2.201(2) Å; Bindi *et al.*, 2013], with an ‘S1’ occupation of $S_{0.91(1)}Te_{0.09}$. Although strongly
140 enhanced (given the high amount of tellurium present in benleonardite), most of the metal-
141 anion bond distances for the crystal studied here show a similar tendency to those in both Te-
142 rich polybasite (Bindi *et al.*, 2013) and selenopolybasite (Evain *et al.*, 2006b).

143 Table 6 compares the X-ray powder pattern reported by Stanley *et al.* (1986) with that
144 calculated using the structural parameters obtained in this study. Calculated and observed data
145 are in very good agreement.

146

147 NOMENCLATURE REMARKS

148 The crystal structure of benleonardite is topologically identical to all compounds of the
149 pearceite/polybasite group in their higher temperature form [i.e., 111 pearceite-type structure

150 (*Tac* polytype); Bindi *et al.*, 2007a]. The real difference is the presence of pure (Te₃ and Te₄)
151 and partial (S₁/Te₁) Te-sites. Evain *et al.* (2006b) and Bindi *et al.* (2007d, 2013) already
152 noted that these anion sites are the same where the S-for-(Se,Te) substitution occurs in
153 selenopolybasite and Te-rich polybasite. However, the concentration of Te in benleonardite is
154 much higher, almost dominating three structural sites. Bindi *et al.* (2013) suggested the
155 possible existence of a “*telluropolybasite*” in nature. In this context, benleonardite clearly
156 represents the missing “*telluropolybasite*” member of the pearceite-polybasite group. A
157 recalculation of the chemical data listed in the scientific literature (Table 7) for benleonardite
158 (and benleonardite-like minerals), according to the structural results obtained here, leads to an
159 excellent agreement. Indeed, the mean values for the sums (Ag+Cu), (Sb+As) and (Te+S) in
160 atoms per formula unit (when the data are normalized on the basis of 29 atoms) are 16.11(13),
161 1.98(19) and 10.91(22), in good accord with the (Ag,Cu)₁₆(Sb,As)₂(S,Te)₁₁ stoichiometry of
162 the pearceite-polybasite minerals.

163 It is interesting to note that very high amounts of Te and Se substituting for S are always
164 associated with low Cu contents and with disordered trigonal structures (*Tac* polytype). Such
165 a feature was already observed and discussed by Evain *et al.* (2006b) and Bindi *et al.* (2013).
166 Benleonardite exhibits this even more strongly, given the fact that some of the analyses given
167 in Table 7 (corresponding to benleonardite and benleonardite-like minerals) show no
168 appreciable concentrations of Cu. This fact seems to contradict what is known for pearceite-
169 polybasite minerals, wherein copper is an essential element for the linearly-coordinated
170 structural site of the *B* module layer. The case of benleonardite shows that the linearly
171 coordinated structural site is able to accommodate larger amounts of silver than recognized
172 previously, thus corroborating the suggestions of Bindi and Menchetti (2009) and raising the
173 possibility that a mineral with Ag > Cu at this site deserves its own name.

174

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272 **FIGURE CAPTIONS**

273 Figure 1 – Reflected plane polarized light digital image in oil immersion illustrating a band of
274 benleonardite on a ragged quartz grain to the right with rosettes of acanthite
275 intergrown with low reflecting unidentified phases in a mass of creamy white to off-
276 white hessite. The hessite contains a vermiform or myrmekitic intergrowth of fine-
277 grained cervelleite (pale-greenish-grey). The sample (catalogue number E.1161 BM
278 1985, 354) is the type specimen for both benleonardite and cervelleite.

279 Figure 2 – Projection of the benleonardite structure along the a axis. The figure emphasizes
280 the succession of the $[\text{Ag}_6(\text{Sb,As})_2\text{S}_6\text{Te}]^{2-}$ A and $[\text{Ag}_9\text{Cu}(\text{S,Te})_2\text{Te}_2]^{2+}$ B module
281 layers. Grey, light blue, yellow, orange and red circles refer to Ag, Cu, S (S2), S/Te
282 (S1) and Te (Te3 and Te4), respectively.

283 Figure 3 – Non-harmonic joint probability density isosurface of silver for benleonardite at
284 room temperature. S/Te and Cu atoms have an arbitrary size. Level of the 3D map:
285 0.05 \AA^{-3} . The figure illustrates the silver diffusion in the ab plane among the various
286 S/Te tetrahedral sites.

TABLE 1. Details pertaining to the single-crystal X-ray data collection and structure refinement of benleonardite

| <i>Crystal data</i> | |
|-----------------------------------------------|-------------------------------------------------------------------------------|
| space group | $P\bar{3}m1$ (#164) |
| cell parameters | $a = 7.623(1)$ (Å) $c = 12.708(1)$ (Å) $V = 639.5(2)$ (Å ³) |
| Z | 1 |
| crystal color | black |
| crystal shape | block |
| crystal size (mm) | $0.031 \times 0.045 \times 0.062$ |
| <i>Data collection</i> | |
| diffractometer | Oxford Diffraction Xcalibur 3 |
| radiation type | MoK α ($\lambda = 0.71073$) |
| monochromator | oriented graphite (002) |
| scan mode | ϕ/ω |
| temperature (K) | 293 |
| detector to sample distance (cm) | 5 |
| number of frames | 598 |
| rotation width per frame (°) | 0.15 |
| measuring time (s) | 90 |
| maximum covered 2θ (°) | 75.52 ($d = 0.86$ Å) |
| range of h, k, l | $-11 \leq h \leq 11, -13 \leq k \leq 13, -20 \leq l \leq 20$ |
| collected reflections | 11025 |
| R_{int} before absorption correction | 0.1054 |
| R_{int} after absorption correction | 0.0355 |
| <i>Refinement</i> | |
| refinement coefficient | F^2 |
| No. of refl. in refinement | 1250 |
| No. of observed refl. | 609 |
| No. of refined parameters | 102 |
| weighting scheme | $w = 1 / [\sigma^2(I) + (0.044 \times I)^2]$ |
| R^\dagger (obs) / R^\dagger (all) | 0.0179 / 0.0321 |
| $wR^{2\dagger}$ (obs) / $wR^{2\dagger}$ (all) | 0.0167 / 0.0172 |
| diff. Fourier ($e^-/\text{Å}^3$) | [-1.94, 1.13] |

Note: $\dagger R = \sum ||F_o| - |F_c|| / \sum |F_o|$. $wR^2 = [\sum w (|F_o|^2 - |F_c|^2)^2 / \sum w (|F_o|^4)]^{1/2}$.

TABLE 2. Wyckoff positions, site occupation factors, fractional atomic coordinates, and equivalent isotropic displacement parameters (\AA^2) for the selected benleonardite crystal.

| atom | Wyckoff | s.o.f. | x | y | z | U_{iso} |
|------|---------|----------|------------|------------|------------|------------------|
| Sb | $2d$ | 0.789(4) | 0.3333 | 0.6667 | 0.38572(2) | 0.0251(7) |
| As | $2d$ | 0.211 | 0.3333 | 0.6667 | 0.38572(2) | 0.0251(7) |
| Ag1 | $6i$ | 0.677(7) | 0.2848(3) | 0.1424(3) | 0.3804(1) | 0.0526(3) |
| Ag2 | $6i$ | 0.311(7) | 0.3422(3) | 0.1711(3) | 0.3537(3) | 0.0700(8) |
| Ag3 | $12j$ | 0.307(5) | 0.252(3) | 0.3641(4) | 0.1192(3) | 0.0555(8) |
| Ag4 | $12j$ | 0.134(6) | 0.382(3) | 0.402(3) | 0.1065(8) | 0.0635(6) |
| Ag5 | $12j$ | 0.315(7) | 0.3503(4) | 0.2803(18) | 0.1234(4) | 0.0670(6) |
| Cu | $1a$ | 1.000 | 0 | 0 | 0 | 0.0320(2) |
| S1 | $2c$ | 0.514(9) | 0 | 0 | 0.1823(2) | 0.0271(9) |
| Te1 | $2c$ | 0.486 | 0 | 0 | 0.1823(2) | 0.0271(9) |
| S2 | $6i$ | 1.000 | 0.01458(5) | 0.50729(5) | 0.30681(8) | 0.0404(2) |
| Te3 | $2d$ | 1.000 | 0.6667 | 0.3333 | 0.01650(3) | 0.0475(1) |
| Te4 | $1b$ | 1.000 | 0 | 0 | 0.5 | 0.0422(1) |

TABLE 3 – Anisotropic displacement parameters U_{ij} (\AA^2) for the selected benleonardite crystal

| atom | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|------|-----------|-----------|-----------|------------|------------|------------|
| Sb | 0.0235(9) | 0.0235(9) | 0.037(1) | 0.0118(5) | 0 | 0 |
| As | 0.0235(9) | 0.0235(9) | 0.037(1) | 0.0118(5) | 0 | 0 |
| Ag1 | 0.0542(5) | 0.0502(2) | 0.0547(6) | 0.0271(3) | -0.0002(3) | -0.0001(1) |
| Ag2 | 0.093(1) | 0.0447(5) | 0.089(1) | 0.0464(6) | 0.042(2) | 0.0208(8) |
| Ag3 | 0.26(2) | 0.0381(7) | 0.0516(9) | -0.016(3) | -0.035(3) | 0.0024(4) |
| Ag4 | 0.169(7) | 0.240(9) | 0.085(4) | 0.170(8) | 0.073(5) | 0.078(6) |
| Ag5 | 0.0356(8) | 0.29(1) | 0.050(1) | -0.016(2) | 0.0068(5) | -0.009(2) |
| Cu | 0.0388(2) | 0.0388(2) | 0.0186(3) | 0.0194(1) | 0 | 0 |
| S1 | 0.038(3) | 0.038(3) | 0.006(2) | 0.019(1) | 0 | 0 |
| Te1 | 0.038(3) | 0.038(3) | 0.006(2) | 0.019(1) | 0 | 0 |
| S2 | 0.0227(3) | 0.0418(3) | 0.0503(4) | 0.0113(1) | -0.0031(2) | -0.0015(1) |
| Te3 | 0.0454(1) | 0.0454(1) | 0.0519(2) | 0.02269(7) | 0 | 0 |
| Te4 | 0.0424(2) | 0.0424(2) | 0.0417(3) | 0.02120(8) | 0 | 0 |

TABLE 4. Higher-order displacement parameters[†] for the selected benleonardite crystal

| | Ag3 | Ag4 | Ag5 |
|-----------|------------|----------|------------|
| C^{111} | -0.01(4) | 0.08(3) | 0.001(1) |
| C^{112} | 0.001(9) | 0.08(3) | -0.002(2) |
| C^{113} | -0.008(5) | 0.028(7) | -0.0001(4) |
| C^{122} | 0.000(3) | 0.09(4) | 0.02(1) |
| C^{123} | 0.002(1) | 0.028(8) | -0.0005(7) |
| C^{133} | 0.0009(9) | 0.006(2) | -0.0001(2) |
| C^{222} | -0.001(1) | 0.11(4) | -0.06(5) |
| C^{223} | 0.0002(3) | 0.028(9) | 0.005(3) |
| C^{233} | -0.0005(2) | 0.005(3) | -0.0006(6) |
| C^{333} | -0.0001(2) | 0.001(1) | 0.0007(2) |

Note: [†]Third-order tensor elements C^{ijk} are multiplied by 10^3 ;

TABLE 5. Main interatomic distances (Å) for the selected benleonardite crystal

| | | | | | |
|---------------------------|---------------|---------------------------|---------------|------------------------|---------------|
| Sb/As - S2 | 2.331(1) (×3) | Cu - S1/Te1 | 2.317(4) (×2) | Ag1 - S2 | 2.591(2) (×2) |
| <Sb/As-S> | 2.331 | <Cu-S/Te> | 2.317 | - Te4 | 2.418(2) |
| | | | | <Ag1-S/Te> | 2.533 |
| Ag2 - S2 | 2.302(4) (×2) | Ag3 [‡] - S1/Te1 | 2.589(6) | Ag4 [‡] - Te3 | 2.726(3) |
| - Te4 | 2.926(4) | - Te3 | 2.692(6) | - Te3 | 2.720(2) |
| <Ag2-S/Te> | 2.510 | <Ag3-S/Te> | 2.638 | <Ag4-Te> | 2.723 |
| Ag5 [‡] - S1/Te1 | 2.559(5) | | | | |
| - Te3 | 2.618(6) | | | | |
| <Ag5-S/Te> | 2.589 | | | | |

Note: [‡] the bond distances calculated for Ag3, Ag4 and Ag5 correspond to the most probable distance calculated from the modes (maxima) of *jpdf* (joint probability density function) maps.

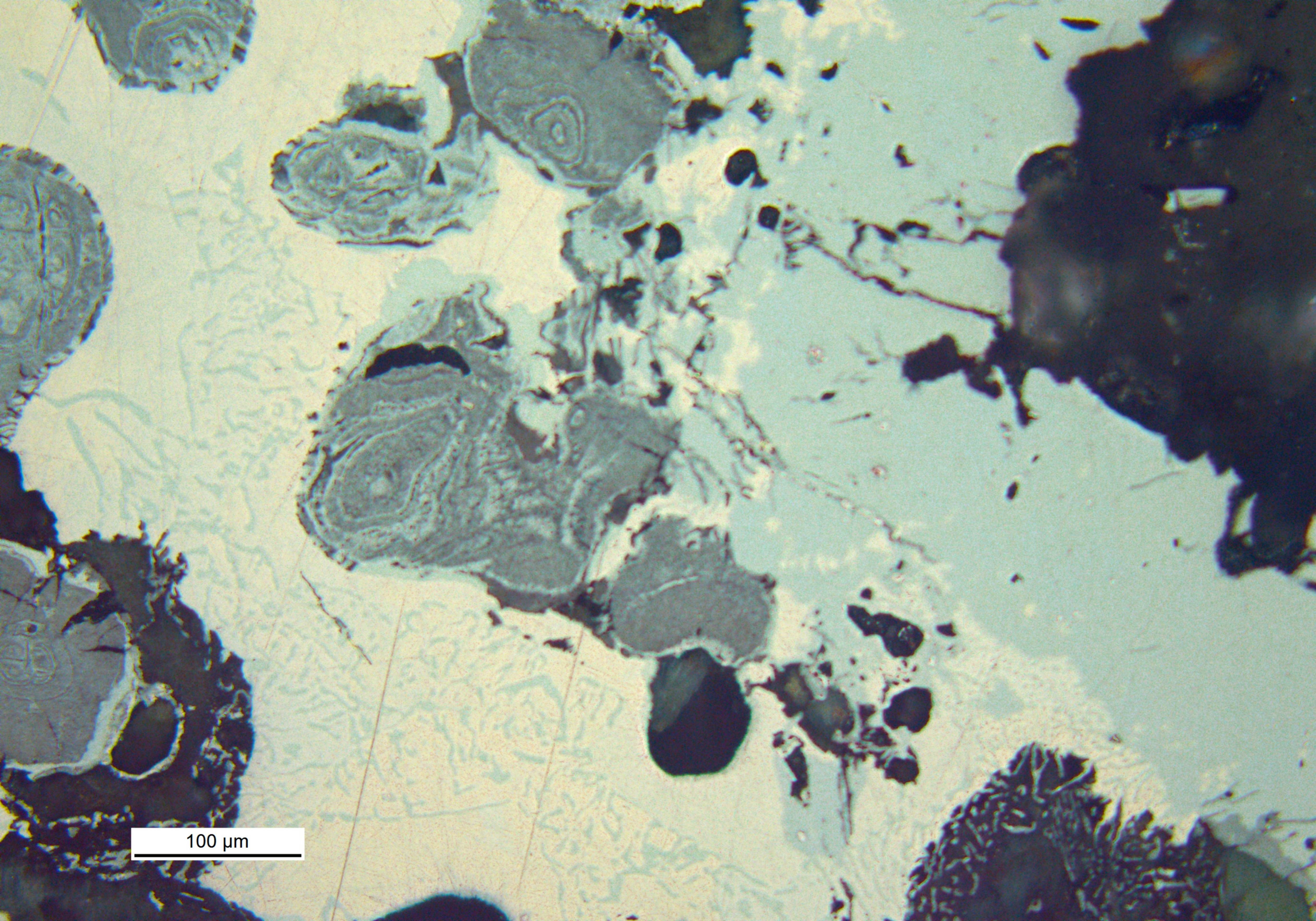
TABLE 6. X-ray powder diffraction patterns for benleonardite.

| 1 | | | 2 | | |
|------------|----------------|------------|------------|---------------|---------|
| <i>hkl</i> | d_{calc} (Å) | I_{calc} | <i>hkl</i> | d_{obs} (Å) | I/I_o |
| 001 | 12.7080 | 79 | 001 | 12.7 | 70 |
| 100 | 6.6017 | 33 | 010 | 6.62 | 15 |
| 002 | 6.3540 | 10 | 002 | 6.34 | 15 |
| 101, 011 | 5.8584 | 20 | 011 | 5.87 | 15 |
| 102, 012 | 4.5780 | 2 | 012 | 4.61 | 15 |
| 003 | 4.2360 | 2 | — | — | — |
| 110 | 3.8115 | 1 | — | — | — |
| 013, 103 | 3.5652 | 23 | — | — | — |
| 200 | 3.3009 | 1 | — | — | — |
| 112 | 3.2685 | 28 | — | — | — |
| 021, 201 | 3.1948 | 31 | 021, 004 | 3.188 | 30 |
| 004 | 3.1770 | 56 | 022 | 2.936 | 100 |
| 022, 202 | 2.9292 | 100 | 014 | 2.863 | 25 |
| 014 | 2.8628 | 2 | — | — | — |
| 113 | 2.8334 | 5 | 023 | 2.608 | 35 |
| 023 | 2.6037 | 21 | 005 | 2.542 | 10 |
| 005 | 2.5416 | 1 | — | — | — |
| 210 | 2.4952 | 3 | n.i. | 2.453 | 15 |
| 211 | 2.4485 | 5 | — | — | — |
| 114 | 2.4404 | 54 | 015 | 2.376 | 15 |
| 105 | 2.3719 | 1 | 220 | 2.328 | 20 |
| 122, 212 | 2.3225 | 2 | 221, 024 | 2.291 | 10 |
| 024, 204 | 2.2890 | 26 | 030 | 2.206 | 10 |
| 300 | 2.2006 | 22 | 124 | 2.158 | 35 |
| 031, 301 | 2.1683 | 23 | 006 | 2.120 | 20 |
| 123, 213 | 2.1499 | 31 | 130, 032 | 2.084 | 10 |
| 006 | 2.1180 | 1 | 016 | 2.020 | 15 |
| 115 | 2.1146 | 29 | n.i. | 1.965 | 10 |
| 032, 302 | 2.0794 | 11 | — | — | — |
| 106 | 2.0168 | 4 | n.i. | 1.914 | 15 |
| 205 | 2.0138 | 19 | — | — | — |
| 214 | 1.9623 | 1 | — | — | — |
| 033 | 1.9528 | 7 | 007 | 1.819 | 15 |
| 220 | 1.9058 | 43 | 026 | 1.786 | 10 |
| 221 | 1.8847 | 3 | — | — | — |
| 116 | 1.8514 | 8 | — | — | — |
| 310 | 1.8310 | 1 | 134 | 1.744 | 15 |
| 222 | 1.8254 | 1 | — | — | — |
| 026, 206 | 1.7826 | 14 | — | — | — |
| 125, 215 | 1.7806 | 4 | — | — | — |
| 017 | 1.7504 | 4 | — | — | — |
| 223 | 1.7380 | 12 | — | — | — |
| 313, 133 | 1.6807 | 6 | — | — | — |
| 401 | 1.6367 | 2 | — | — | — |
| 224 | 1.6343 | 2 | — | — | — |
| 216 | 1.6147 | 4 | — | — | — |

| | | | | | |
|----------|--------|----|------|-------|----|
| 042, 402 | 1.5974 | 10 | | | |
| 027, 207 | 1.5907 | 3 | 008 | 1.591 | 15 |
| 008 | 1.5885 | 9 | | | |
| 403 | 1.5378 | 3 | | | |
| 306 | 1.5260 | 2 | n.i. | 1.531 | 15 |
| 225 | 1.5247 | 5 | | | |
| 320 | 1.5145 | 1 | — | — | — |
| 321 | 1.5039 | 4 | — | — | — |
| 404, 044 | 1.4646 | 6 | — | — | — |
| 410 | 1.4406 | 3 | — | — | — |
| 028, 208 | 1.4314 | 6 | — | — | — |
| 226 | 1.4167 | 5 | — | — | — |
| 142, 412 | 1.4050 | 5 | — | — | — |
| 037 | 1.4004 | 2 | — | — | — |
| 045 | 1.3842 | 3 | — | — | — |
| 019 | 1.3808 | 2 | — | — | — |
| 119 | 1.3241 | 2 | — | — | — |
| 414, 144 | 1.3120 | 4 | — | — | — |
| 046 | 1.3018 | 3 | — | — | — |
| 325 | 1.3011 | 2 | — | — | — |
| 317 | 1.2892 | 2 | — | — | — |
| 038, 308 | 1.2880 | 4 | — | — | — |
| 0010 | 1.2708 | 1 | — | — | — |
| 330 | 1.2705 | 1 | — | — | — |
| 145, 415 | 1.2533 | 3 | — | — | — |
| 332 | 1.2458 | 1 | — | — | — |
| 421 | 1.2416 | 1 | — | — | — |
| 422, 242 | 1.2242 | 6 | — | — | — |
| 228 | 1.2202 | 3 | — | — | — |
| 054 | 1.2192 | 1 | — | — | — |
| 243 | 1.1968 | 3 | — | — | — |
| 146 | 1.1912 | 2 | — | — | — |
| 0210 | 1.1859 | 4 | — | — | — |
| 237 | 1.1630 | 4 | — | — | — |
| 048 | 1.1445 | 2 | — | — | — |
| 153, 513 | 1.1418 | 3 | — | — | — |
| 335 | 1.1364 | 3 | — | — | — |
| 056 | 1.1205 | 1 | — | — | — |
| 425 | 1.1200 | 4 | — | — | — |
| 319 | 1.1181 | 1 | — | — | — |
| 0310 | 1.1005 | 1 | — | — | — |
| 600 | 1.1003 | 3 | — | — | — |
| 426 | 1.0750 | 3 | — | — | — |
| 155 | 1.0745 | 1 | — | — | — |
| 063 | 1.0649 | 1 | — | — | — |
| 2210 | 1.0573 | 1 | — | — | — |
| 520 | 1.0571 | 1 | — | — | — |
| 239 | 1.0328 | 2 | — | — | — |
| 247 | 1.0282 | 1 | — | — | — |
| 1112 | 1.0203 | 2 | — | — | — |
| 0212 | 1.0084 | 2 | — | — | — |

| | | | | | | | | | |
|------|--------|---|--|--|---|--|---|--|---|
| 4010 | 1.0069 | 2 | | | - | | - | | - |
|------|--------|---|--|--|---|--|---|--|---|

Note: 1 = calculated powder pattern and indexing for benleonardite of this study. *d* values calculated on the basis of $a = 7.623(1) \text{ \AA}$, $c = 12.708(1) \text{ \AA}$, and with the atomic coordinates and occupancies reported in Table 2. Intensities calculated using XPOW software version 2.0 (Downs *et al.*, 1993). 2 = observed powder pattern and indexing originally reported by Stanley *et al.* (1986).



100 μm

