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New structural data reveal benleonardite to be a member of the pearceite-polybasite group

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ABSTRACT

The determination of the crystal structure of benleonardite ($P\bar{3}m1$; $R = 0.0321$ for 1250 reflections and 102 parameters; refined formula $Ag_{15.00}Cu_{1.00}Sb_{1.58}As_{0.42}S_{7.03}Te_{3.97}$) 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 of the stacking of $[Ag_6(Sb,As)_2S_6Te]^{2-}$ *A* and $[Ag_9Cu(S,Te)_2Te_2]^{2+}$ *B* layer modules in which (Sb,As) forms isolated SbS_3 pyramids typically occurring in sulfosalts; Cu links two (S,Te) atoms with linear coordination, and Ag occupies sites with coordination geometries ranging from quasi-linear to almost triangular. The silver ions are found in the *B* layer module along two-dimensional diffusion paths and their electron densities are evidenced by means of a combination of a Gram-Charlier development of the atom displacement factors and a split model. In the structure, two S positions are completely replaced by Te (i.e. Te3 and Te4) and one is half occupied [S1: $S_{0.514(9)}Te_{0.486}$], whereas S2 is completely filled by sulfur. This distribution reflects the crystal-chemical environments of the different cations. On the basis of information gained from this characterization, the crystal-chemical formula of benleonardite was revised according to the structural results, yielding $Ag_{15}Cu(Sb,As)_2S_7Te_4$ ($Z = 1$) instead of $Ag_8(Sb,As)Te_2S_3$ ($Z = 2$) as previously reported. Thus, the mineral must be considered a member of the pearceite-polybasite group. A recalculation of the chemical data listed in the scientific literature for benleonardite according to the structural results obtained here leads to excellent agreement.

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

Introduction

Benleonardite, ideally $Ag_8(Sb,As)Te_2S_3$, was identified as a new mineral species by Stanley *et al.* (1986) by studying ore minerals collected from the spoil tips of the abandoned Bambolla mine, Moctezuma, Sonora (Mexico). It was described as forming thin black powdery crusts (1–2 mm thick) with native silver, acanthite, hessite, cervelleite, pyrite and sphalerite. By means of powder X-ray diffraction investigations, benleonardite was originally given as tetragonal with $a = 6.603(5)$ and $c = 12.726(6)$ Å, but the crystal structure remained unknown. Although benleonardite-like minerals have been found in several occurrences [Zyranov gold deposit, Russia (Aksenov *et al.*, 1969), Ivigtut cryolite deposit, Greenland (Karup-Møller and Pauly, 1979), Gies gold–silver telluride deposit, Montana (Zhang and Spry, 1994; Spry and Thieben, 1996), Mayflower gold–silver telluride deposit, Montana (Spry and Thieben, 1996), Um Samiuki Zn–Pb–Cu–Ag volcanogenic massive sulfide deposit, Egypt (Helmy *et al.*, 1999; Pals and Spry, 2003), black smoker chimney fragments from the Yaman Kasy massive sulfide deposit, southern Urals (Herrington *et al.*, 1998)], no additional structural investigations have been reported in the literature to date.

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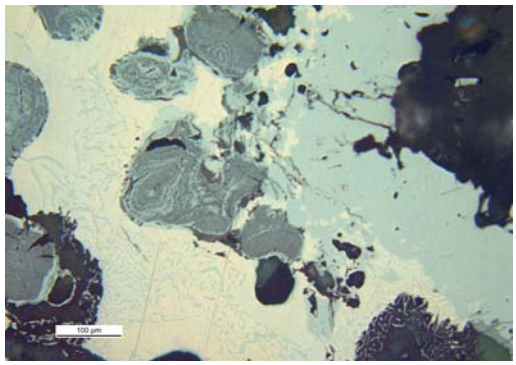


FIG. 1. Reflected plane-polarized light digital image in oil immersion illustrating a band of benleonardite on a ragged quartz grain to the right with rosettes of acanthite intergrown with low reflecting, unidentified phases in a mass of creamy white to off-white hessite. The hessite contains a vermiform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

The simplified formula for benleonardite was given as $Ag_8SbTe_2S_3$ by Stanley *et al.* (1986). However, such a chemical formula is unbalanced, which is a very unusual characteristic when dealing with Ag sulfosalts (Bindi and Evain, 2007; Moëlo *et al.*, 2008). Moreover, chemical data reported for benleonardite (and benleonardite-like minerals) in the literature show a general deficiency in Ag + Cu (i.e. <8 atoms per formula unit (a.p.f.u.)) coupled with an excess in S (i.e. 3–4 a.p.f.u.) when normalized on the basis of 14 atoms, thus reinforcing the suggestion by Spry and Thieben (1996) that the formula proposed by Stanley *et al.* (1986) needs to be modified.

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

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

Crystal data	
Space group	$P\bar{3}\,m1$
Cell parameters	$a = 7.623(1)$ (Å) $c = 12.708(1)$ (Å) $V = 639.5(2)$ (Å^3)
Z	1
Crystal colour	black
Crystal shape	block
Crystal size (mm)	0.031 × 0.045 × 0.062
Data collection	
Diffractometer	Oxford Diffraction Xcalibur 3
Radiation type	Mo$K\alpha$ ($\lambda = 0.71073$)
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	$-11 \le h \le 11$, $-13 \le k \le 13$, $-20 \le l \le 20$
Collected reflections	11,025
R_{int} before absorption correction	0.1054
R_{int} after absorption correction	0.0355
Refinement	
Refinement coefficient	F^2
No. of reflctions in refinement	1250
No. of observed reflections	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
w$R^{2\dagger}$ (obs) / w$R^{2\dagger}$ (all)	0.0167 / 0.0172
Difference Fourier (e$^-$/Å^3)	[–1.94, 1.13]

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

The holotype

A crystal for the X-ray investigation was selected from the type material (catalogue number E.1161 BM 1985, 354). The specimen was collected by the late Alan Criddle on a field excursion to the Sonora Desert led by the late Sid Williams. It consists of black powdery crusts (1–2 mm thick) of benleonardite, acanthite, hessite and cervelleite together with gangue quartz and dolomite (Fig. 1). The hessite contains a

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

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

s.o.f. – site occupancy factor.

vermiform or myrmekitic intergrowth of fine-grained cervelleite (pale greenish-grey in Fig. 1). The assemblage occupies irregular fractures in a highly altered rock described by Williams (1982) as an intensely silicified rhyolitic vitrophyre.

X-ray crystallography

A benleonardite crystal was hand-picked from a polished section of the type material and used for the room-temperature data collection, which was carried out on a Oxford Diffraction Xcalibur 3 diffractometer, fitted with a Sapphire 2 CCD detector (see Table 1 for details) using graphite-monochromatized Mo*K*α radiation (λ = 0.71069 Å). Because of the typical ionic conductivity observed in Ag sulfosalts and the probable presence of twinning (Bindi *et al.*, 2006*a*), a rather high sinθ/λ cutoff and a full sphere of data were considered. Intensity integration and standard Lorentz-polarization correction were performed with the *CrysAlis RED* (Oxford Diffraction,

TABLE 3. Anisotropic displacement parameters (Å^2) for the benleonardite crystal selected.

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

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2006) software package. The program *ABSPACK* in *CrysAlis RED* (Oxford Diffraction, 2006) was used for the absorption correction.

The unit cell found for the selected benleonardite crystal is trigonal (hexagonal setting), with a = 7.623(1) and c = 12.708(1) Å. The c parameter is almost the same as that found by Stanley *et al.* (1986), 12.726(6) Å, and the a parameter is related to that originally reported (6.606(5) Å) by a factor of sin120°, which explains the symmetry change from the trigonal to the tetragonal setting. The refined trigonal unit cell obtained for benleonardite is very similar to that observed for minerals belonging to the pearceite-polybasite group (Bindi *et al.*, 2007*a*). Taking into account this similarity, the structure was refined in space group $P\overline{3}m1$ using the program *JANA2006* (Petříček *et al.*, 2006) starting from the atom coordinates given by Bindi *et al.* (2007*b*) for the crystal structure of polybasite-*Tac*. The sites with partial (or total) substitution of S by Te were easily identified (S1, S3 and S4). To mimic the silver electron spreading along diffusion paths, up to third-order non-harmonic Gram-Charlier tensors were used for the Debye-Waller description of the Ag3, Ag4 and Ag5 atoms (Johnson and Levy, 1974; Kuhs, 1984). Full site occupation (Sb/As and S1/Te1) was assured through constraints and the overall charge balance was ascertained. The final residual R is 0.0179 for 609 reflections [$I > 2\sigma(I)$] and R = 0.0321 for all 1250 unique reflections and 102 parameters.

Atom parameters are reported in Tables 2 to 4, whereas bond distances are given in Table 5. Structure factors and a crystallographic information file have been deposited with the Principal Editor of *Mineralogical Magazine* and are available from www.minersoc.org/pages/e_journals/dep_mat_mm.html. Unfortunately, the crystal used for the structural study was lost in an attempt to embed it in epoxy to obtain electron microprobe data. However, the final refined formula can be written as $Ag_{15.00}Cu_{1.00}(Sb_{1.58}As_{0.42})S_{7.03}Te_{3.97}$, which is in good agreement with that reported by Stanley *et al.* (1986) for benleonardite from the type material, $Ag_{16.0–16.1}Cu_{0.0–0.1}Sb_{1.6–1.7}As_{0.4–0.6}S_{6.7–6.8}Te_{3.9–4.0}$.

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

	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)

†Third-order tensor elements C^{ijk} are multiplied by 10^3.

Description of the structure

On the whole, the benleonardite structure resembles that of the trigonal polytype (*Tac*) of polybasite (Bindi *et al.*, 2007*b*). It can be described as the succession, along the c axis, of two layer modules, a $[Ag_6(Sb,As)_2S_6Te]^{2-}$ *A* module layer and a $[Ag_9Cu(S,Te)_2Te_2]^{2+}$ *B* module layer (Fig. 2). In the *A* module layer, Ag atoms (Ag1 and Ag2) are triangularly coordinated by S and Te atoms in a

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

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						

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

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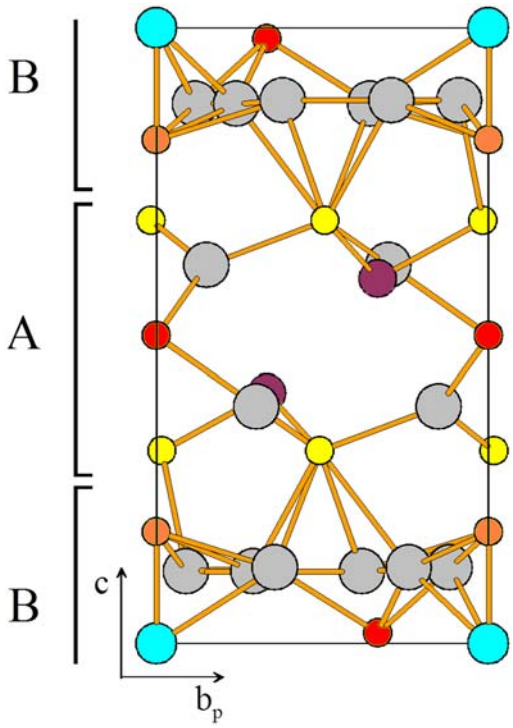


FIG. 2. Projection of the benleonardite structure along the *a* axis. The figure emphasizes the succession of the $[Ag_6(Sb,As)_2S_6Te]^{2-}$ *A* and $[Ag_9Cu(S,Te)_2Te_2]^{2+}$ *B* module layers. Grey, light blue, yellow, orange and red circles refer to Ag, Cu, S (S2), S/Te (S1) and Te (Te3 and Te4), respectively.

quasi-planar fashion. Benleonardite represents the first member of the pearceite-polybasite group showing structural disorder in the Ag positions of the *A* layer. The disorder has been modelled with two split Ag positions (Ag1–Ag2 = 0.51 Å) with partial occupancy (Table 2). The (Sb,As) atoms are also in threefold coordination, but in a trigonal pyramidal configuration. The $[Ag(S,Te)_3]$ and $[(Sb,As)S_3]$ subunits are linked together through corners to constitute the *A* module layer. In the *B* module layer, the silver ions are distributed along 2D diffusion paths, in a structure skeleton made of face-sharing tetrahedra (as in argyrodite-type ionic conductor compounds; Boucher *et al.*, 1993) around the Cu atom (Fig. 3). It is worth noting that the modes (maxima of density) observed in the diffusion paths do not correspond to the refined Ag positions (Ag3, Ag4 and Ag5) and that the refined atom positions do not lie along diffusion paths between modes, the Gram-Charlier expansion of the Debye-Waller factor providing the connecting density. For this reason, the refined Ag positions should not be used to calculate distances (although meaningful distances could be obtained with mode positions).

In the structure, two S positions are completely replaced by Te (Te3 and Te4) and one is half occupied by S (S1: $S_{0.514(9)}Te_{0.486}$), whereas S2 is completely filled by sulfur. This distribution reflects the crystal-chemical environments of the different cations. The Cu-S1/Te1 distance [2.317(4) Å] is much longer than both the Cu-S1/Se1′ distance in selenopolybasite (2.199(2) Å; Evain *et al.*, 2006*b*) and that observed for Te-rich polybasite (2.201(2) Å; Bindi *et al.*, 2013), with an 'S1' occupation of $S_{0.91(1)}Te_{0.09}$. Although strongly enhanced (given the large amount of tellurium present in benleonardite), most of the metal–anion bond distances for the crystal studied here show a similar tendency to those in both Te-rich polybasite (Bindi *et al.*, 2013) and selenopolybasite (Evain *et al.*, 2006*b*). Table 6 compares the powder X-ray pattern reported by Stanley *et al.* (1986) with that calculated using the structural parameters obtained in this study. Calculated and observed data are in very good agreement.

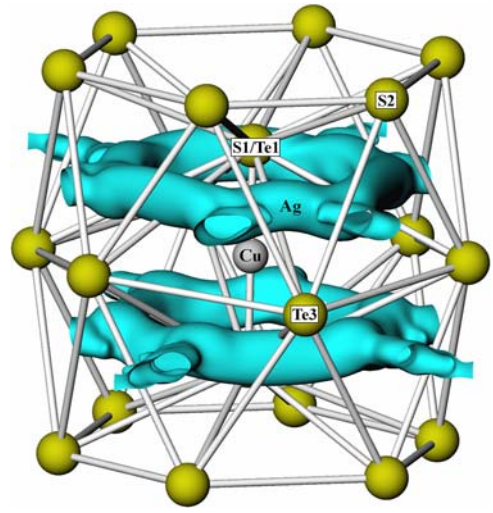


FIG. 3. Non-harmonic joint probability density isosurface of silver for benleonardite at room temperature. S/Te and Cu atoms have an arbitrary size. The level of the 3D map is 0.05 $Å^{-3}$. The figure illustrates silver diffusion in the *ab* plane among the various S/Te tetrahedral sites.

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

1			2		
hkl	d_{calc} (Å)	I_{calc}	*hkl*	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, 202	2.9292	100	022	2.936	100
014	2.8628	2	014	2.863	25
113	2.8334	5	–	–	–
023	2.6037	21	023	2.608	35
005	2.5416	1	005	2.542	10
210	2.4952	3	–	–	–
211	2.4485	5	n.i.	2.453	15
114	2.4404	54	–	–	–
105	2.3719	1	015	2.376	15
122, 212	2.3225	2	220	2.328	20
024, 204	2.2890	26	221, 024	2.291	10
300	2.2006	22	030	2.206	10
031, 301	2.1683	23	124	2.158	35
123, 213	2.1499	31			
006	2.1180	1	006	2.120	20
115	2.1146	29			
032, 302	2.0794	11	130, 032	2.084	10
106	2.0168	4	016	2.020	15
205	2.0138	19			
214	1.9623	1	n.i.	1.965	10
033	1.9528	7	–	–	–
220	1.9058	43	n.i.	1.914	15
221	1.8847	3	–	–	–
116	1.8514	8	–	–	–
310	1.8310	1	007	1.819	15
222	1.8254	1			
026, 206	1.7826	14	026	1.786	10
125, 215	1.7806	4			
017	1.7504	4	–	–	–
223	1.7380	12	134	1.744	15
313, 133	1.6807	6	–	–	–
401	1.6367	2	–	–	–
224	1.6343	2	–	–	–
216	1.6147	4	–	–	–
042, 402	1.5974	10	008	1.591	15
027, 207	1.5907	3			
008	1.5885	9			
403	1.5378	3	n.i.	1.531	15
306	1.5260	2			
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	–	–	–
$00\bar{1}0$	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	–	–	–
$02\bar{1}0$	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	–	–	–
$03\bar{1}0$	1.1005	1	–	–	–
600	1.1003	3	–	–	–
426	1.0750	3	–	–	–
155	1.0745	1	–	–	–
063	1.0649	1	–	–	–
$22\bar{1}0$	1.0573	1	–	–	–
520	1.0571	1	–	–	–
239	1.0328	2	–	–	–
247	1.0282	1	–	–	–
$11\bar{1}2$	1.0203	2	–	–	–
$02\bar{1}2$	1.0084	2	–	–	–
$40\bar{1}0$	1.0069	2	–	–	–

*1: Calculated powder pattern and indexing for benleonardite from this study; *d* values are calculated on the basis of $a = 7.623(1)$ Å, $c = 12.708(1)$ Å, and with the atom coordinates and occupancies reported in Table 2; intensities were calculated using *XPOW* software version 2.0 (Downs *et al.*, 1993).
2: Observed powder pattern and indexing reported originally by Stanley *et al.* (1986). n.i. – not indexed.

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TABLE 7. Electron microprobe data (wt.% of elements) of 'benleonardite' minerals from different deposits (data from the literature) and atom ratios calculated on the basis of 29 atoms per formula unit.*

	Bambolla						Gies				Mayflower		Ivigtut	Emperor	Um Samiuki		
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
Ag	63.80	65.00	65.00	65.10	65.60	64.50	62.52	62.99	62.70	63.40	60.76	63.07	61.70	63.00	64.87	65.50	64.83
Cu	0.10	0.00	0.00	0.00	0.00	0.10	1.90	1.65	1.90	2.10	2.68	0.55	0.00	0.18	0.30	0.00	0.31
Sb	9.00	7.40	7.80	7.60	7.20	7.30	6.25	5.33	6.70	4.40	6.94	6.98	7.10	5.81	6.60	6.99	6.88
As	0.70	1.80	1.20	1.10	1.80	1.40	1.16	1.70	0.90	2.60	1.15	1.01	0.00	1.57	1.71	1.20	1.66
Te	18.60	18.40	18.70	18.50	18.70	18.70	19.38	19.06	19.60	18.80	18.97	18.75	17.00	19.99	19.24	18.78	19.98
S	8.00	8.10	8.20	8.10	8.00	8.00	8.16	8.33	8.40	8.60	8.78	8.56	8.80	8.22	8.47	8.27	8.38
Total	100.20	100.70	100.90	100.40	101.30	100.00	99.37	99.06	100.20	99.90	99.28	98.92	94.60	98.77	101.19	100.74	102.04
Ag	16.01	16.11	16.10	16.23	16.22	16.14	15.52	15.60	15.41	15.38	14.85	15.74	15.98	15.85	15.88	16.22	15.81
Cu	0.04	0.00	0.00	0.00	0.00	0.04	0.80	0.69	0.79	0.87	1.11	0.23	0.00	0.08	0.12	0.00	0.13
Sb	2.00	1.63	1.71	1.68	1.58	1.62	1.37	1.17	1.46	0.95	1.50	1.54	1.63	1.30	1.43	1.53	1.48
As	0.25	0.64	0.43	0.39	0.64	0.50	0.41	0.61	0.32	0.91	0.40	0.36	0.00	0.57	0.60	0.43	0.58
Te	3.95	3.86	3.92	3.90	3.91	3.96	4.07	3.99	4.07	3.86	3.92	3.95	3.72	4.25	3.98	3.93	4.12
S	6.75	6.76	6.84	6.80	6.65	6.74	6.83	6.94	6.95	7.03	7.22	7.18	7.67	6.95	6.99	6.89	6.88
Ag + Cu	16.05	16.11	16.10	16.23	16.22	16.18	16.32	16.29	16.20	16.25	15.96	15.97	15.98	15.93	16.00	16.22	15.94
Sb + As	2.25	2.27	2.14	2.07	2.22	2.12	1.78	1.78	1.78	1.86	1.90	1.90	1.63	1.87	2.03	1.96	2.06
Te + S	10.70	10.62	10.76	10.70	10.56	10.70	10.90	10.93	11.02	10.89	11.14	11.13	11.39	11.20	10.97	10.82	11.00

*Analyses 1–6: Stanley *et al.* (1986); analyses 7–8: Spry and Thieben (1996); analyses 9–10: Zhang and Spry (1994); analyses 11–12: Spry and Thieben (1996); analysis 13: Karup-Møller and Pauly (1979); analysis 14: Pals and Spry (2003); analyses 15–17: Pals and Spry (2003).

Nomenclature remarks

The crystal structure of benleonardite is topologically identical to all compounds of the pearceite/polybasite group in their higher temperature form [i.e. the 111 pearceite-type structure (*Tac* polytype); Bindi *et al.*, 2007*a*]. The real difference is the presence of purely (Te3 and Te4) and partial (S1/Te1) Te sites. Evain *et al.* (2006*b*) and Bindi *et al.* (2007*d*, 2013) have noted that these anion sites are the same where the S-for-(Se,Te) substitution occurs in selenopolybasite and Te-rich polybasite. However, the concentration of Te in benleonardite is much larger, almost dominating three structural sites. Bindi *et al.* (2013) suggested the possible existence of a 'telluropolybasite' in nature. In this context, benleonardite clearly represents the missing 'telluropolybasite' member of the pearceite-polybasite group. A recalculation of the chemical data listed in the scientific literature (Table 7) for benleonardite (and benleonardite-like minerals), according to the structural results obtained here, leads to an excellent agreement. Indeed, the mean values for the sums (Ag + Cu), (Sb + As) and (Te + S) in atoms per formula unit (when the data are normalized on the basis of 29 atoms) are 16.11(13), 1.98(19) and 10.91(22), in good accord with the $(Ag,Cu)_{16}(Sb,As)_2(S,Te)_{11}$ stoichiometry of the pearceite-polybasite minerals.

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

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