



UNIVERSITÀ
DEGLI STUDI
FIRENZE

FLORE

Repository istituzionale dell'Università degli Studi di Firenze

Cervelleite, Ag₄TeS: solution and description of the crystal structure

Questa è la Versione finale referata (Post print/Accepted manuscript) della seguente pubblicazione:

Original Citation:

Cervelleite, Ag₄TeS: solution and description of the crystal structure / Bindi, Luca; Stanley, Cristopher J.; Spry, Paul G.. - In: MINERALOGY AND PETROLOGY. - ISSN 0930-0708. - STAMPA. - 109:(2015), pp. 413-419.

Availability:

The webpage <https://hdl.handle.net/2158/1004385> of the repository was last updated on 2015-08-01T14:11:18Z

Terms of use:

Open Access

La pubblicazione è resa disponibile sotto le norme e i termini della licenza di deposito, secondo quanto stabilito dalla Policy per l'accesso aperto dell'Università degli Studi di Firenze (<https://www.sba.unifi.it/upload/policy-oa-2016-1.pdf>)

Publisher copyright claim:

La data sopra indicata si riferisce all'ultimo aggiornamento della scheda del Repository FloRe - The above-mentioned date refers to the last update of the record in the Institutional Repository FloRe

(Article begins on next page)

Title	Cervelleite, Ag ₄ TeS: solution and description of the crystal structure
Authors	Bindi, L; Spry, PG; Stanley, Christopher
Description	Copyright: Springer-Verlag Wien 2015. This is the final, post refereeing version. You are advised to consult the publisher's version if you wish to cite from it, http://link.springer.com/article/10.1007%2Fs00710-015-0384-4
Date Submitted	2016-03-15

Mineralogy and Petrology

Cervelleite, Ag₄TeS: solution and description of the crystal structure

--Manuscript Draft--

Manuscript Number:	MIPE-D-15-00008R1
Full Title:	Cervelleite, Ag ₄ TeS: solution and description of the crystal structure
Article Type:	Standard Article
Keywords:	cervelleite; Ag-Te-S system; Ag-Cu sulfotellurides; crystal structure; aguilrite; acanthite
Corresponding Author:	Luca Bindi, Prof University of Florence Florence, ITALY
Corresponding Author Secondary Information:	
Corresponding Author's Institution:	University of Florence
Corresponding Author's Secondary Institution:	
First Author:	Luca Bindi, Prof
First Author Secondary Information:	
Order of Authors:	Luca Bindi, Prof Christopher Stanley Paul G Spry
Order of Authors Secondary Information:	
Funding Information:	
Abstract:	<p>Examination of the type specimen of cervelleite throws new light on its structure demonstrating how earlier researchers erred in describing the mineral as cubic. It was found to be monoclinic, space group P21/n, with $a = 4.2696(4)$, $b = 6.9761(5)$, $c = 8.0423(7)$ Å, $\beta = 100.332(6)^\circ$, $V = 235.66(3)$ Å³, $Z = 4$. The crystal structure [$R1 = 0.0329$ for 956 reflections with $I > 2\sigma(I)$] is topologically identical to that of acanthite, Ag₂S, and aguilrite, Ag₄SeS. It can be described as a body-centered array of tetrahedrally coordinated X atoms (where X = S and Te) with Ag₂X₄ polyhedra in planes nearly parallel to (010); the sheets are linked by the other silver position (i.e., Ag1) that exhibits a three-fold coordination. Crystal-chemical features are discussed in relation to other copper and silver sulfides/tellurides, and pure metals. A SEM study of the cervelleite crystal used for the structural investigation showed that it is intergrown with an unnamed Ag₂FeS₂ phase in the type material.</p>
Response to Reviewers:	<p>Dear Anton,</p> <p>Please find herewith the revised copy of the manuscript entitled "Cervelleite, Ag₄TeS: solution and description of the crystal structure" by Luca Bindi, Christopher J. Stanley, and Paul G. Spry.</p> <p>We did the minor stylistic changes suggested by the reviewers. We think that it is not necessary to add the Table as suggested by Rev#2.</p> <p>With best regards, Luca Bindi</p>

1
2
3
4
5
6
7
8 **Cervelleite, Ag₄TeS: solution and description of the crystal**
9 **structure**
10
11
12
13
14

15 **L. Bindi**^a · **C.J. Stanley**^b · **P.G. Spry**^c
16
17
18
19
20

21 ^a Dipartimento di Scienze della Terra, Università di Firenze, Via G. La Pira 4, I-50121 Firenze, Italy
22
23

24 ^b Department of Earth Sciences, Natural History Museum, Cromwell Road, London SW7 5BD, United
25
26 Kingdom
27

28 ^c Department of Geological and Atmospheric Sciences, 253 Science I, Iowa State University, Ames,
29
30 Iowa 50011-3212, U.S.A.
31
32
33
34
35
36
37

38 *Corresponding author:*
39

40 Luca Bindi
41 Dipartimento di Scienze della Terra,
42 Università di Firenze
43 Via G. La Pira 4, I-50121 Firenze, Italy
44 Tel. +39-055-2757532
45 Fax +39-055-2757455
46 e-mail: luca.bindi@unifi.it
47
48
49
50
51
52
53
54

55 **Keywords:** cervelleite · Ag-Te-S system · Ag-Cu sulfotellurides · crystal structure ·
56 aguilarite · acanthite
57
58
59
60
61
62
63
64
65

Abstract

Examination of the type specimen of cervelleite throws new light on its structure demonstrating how earlier researchers erred in describing the mineral as cubic. It was found to be monoclinic, space group $P2_1/n$, with $a = 4.2696(4)$, $b = 6.9761(5)$, $c = 8.0423(7)$ Å, $\beta = 100.332(6)^\circ$, $V = 235.66(3)$ Å³, $Z = 4$. The crystal structure [$R1 = 0.0329$ for 956 reflections with $I > 2\sigma(I)$] is topologically identical to that of acanthite, Ag_2S , and aguilarite, Ag_4SeS . It can be described as a body-centered array of tetrahedrally coordinated X atoms (where $X = \text{S}$ and Te) with Ag_2X_4 polyhedra in planes nearly parallel to (010); the sheets are linked by the other silver position (i.e., $\text{Ag}1$) that exhibits a three-fold coordination. Crystal-chemical features are discussed in relation to other copper and silver sulfides/tellurides, and pure metals. A SEM study of the cervelleite crystal used for the structural investigation showed that it is intergrown with an unnamed Ag_2FeS_2 phase in the type material.

Introduction

Silver chalcogenides have received much attention in recent years because of their important technological applications (e.g., Padma Kumar and Yashonath 2006). These compounds are known to be fast ionic conductors or semiconductors and, as such, find practical applications in silver photography as sensitizers or in optics and microelectronics as rewritable storage media. From a geological standpoint, silver sulfotellurides are trace constituents accompanying native gold and Au-Ag-tellurides in various deposit types that span the magmatic-hydrothermal spectrum.

In the system Ag-Te-S, cervelleite Ag_4TeS is of particular interest because it occurs as an accessory mineral in a range of hydrothermal precious mineral deposits (Cook and Ciobanu 2003). It was defined as a new mineral species by Criddle et al.

1 (1989) during a study of ore minerals collected from the spoil tips of the abandoned
2 Bambolla mine, Moctezuma, Sonora (Mexico). By means of X-ray photographic
3 techniques, these authors studied fragments of cervelleite intergrown with acanthite
4 from a structural point of view and reported a cubic symmetry (with $P23$, $Pm3$, $P432$,
5 $P43m$, $Pm3m$, $P2_13$, $P4_232$, $P4_132$, $P4_332$, $Pa3$ as possible space groups) with $a =$
6 $14.03(1)$ and $Z = 24$. Criddle et al. (1989) also noticed that cervelleite, acanthite and
7 hessite were altered rapidly and profoundly by light, in a surface reaction interpreted
8 as photo-chemical in origin.
9

10
11
12
13
14
15
16
17
18
19 Cervelleite, along with other cervelleite-like minerals, has been reported from
20 various ore types including the intrusion-hosted San Martin deposit, Argentina (Paar
21 and De Brodtkorb 1996), the epithermal Mayflower Au-Ag deposit, Montana (Spry
22 and Thieben 1996), the Um Samiuki volcanogenic massive sulfide deposit, Egypt
23 (Helmy 1999), epithermal (Larga, Roşia Montană) and skarn (Băiţa Bihor and Ocna
24 de Fier) occurrences in Romania (Cook and Ciobanu 2003; Ciobanu et al. 2004), the
25 Eniovche epithermal deposit, Bulgaria (Dobrev et al. 2002), the intrusion-hosted
26 Funan Au deposit, China (Gu et al. 2003), and several volcanic-hosted massive
27 sulfide deposits in the southern Urals (Novoselov et al. 2006). Unnamed Ag-
28 sulfotellurides $[(Ag,Cu)_6TeS_2 - (Ag,Cu)_4TeS]$ were described from the Funan deposit
29 (Gu et al. 2003), and a phase with the composition Ag_2Cu_2TeS was reported by Cook
30 and Ciobanu (2003) from the Băiţa Bihor and Ocna de Fier skarns in Romania. In
31 Greece, cuprian cervelleite and unnamed Ag-Cu sulfotellurides $[(Ag,Cu)_{12}Te_3S_2$ and
32 $(Ag,Au,Cu)_9Te_2S_3]$ were described from the intrusion-related deposit at Panormos
33 Bay, Tinos Island (Tombros et al. 2004, 2010; Spry et al. 2006). In the Kallianou area
34 (southern Evia Island, Greece), gold-bearing quartz veins contain an exotic ore
35 mineralogy including cervelleite-like sulfotellurides $[Ag_2CuTeS$ and $(Ag,Cu)_2Te]$ and
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

Te-rich polybasite (Voudouris and Spry 2008; Voudouris et al. 2011; Bindi et al. 2013b).

In the course of a research project dealing with the description and structural characterization of natural copper and silver tellurides (Bindi 2008, 2009, 2014; Bindi and Cipriani 2004; Bindi and Pinch 2014; Bindi and Pingitore 2013; Bindi et al. 2004, 2005, 2009, 2013a, 2013b), we have examined a fragment of cervelleite from the holotype material (catalogue number E.1161 BM 1985, 354).

The holotype

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 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.

Crystal-structure solution and refinement

A small crystal fragment (40 × 55 × 60 μm) was selected from the type specimen for the X-ray single-crystal diffraction study that was done with an Oxford Diffraction Xcalibur 3 CCD single-crystal diffractometer (Table 1). Surprisingly, most of the X-ray reflections (89% of the total) match the following monoclinic unit cell: $a \sim 4.30$, $b \sim 6.98$, $c \sim 8.04$ Å and $\beta \sim 100^\circ$, being very close to those of acanthite, Ag₂S (Frueh 1958) and aguilarite (Bindi and Pingitore 2013). The other 11% of the total reflections could be indexed according to the following monoclinic (primitive) unit cell:

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

$a \sim 9.00$, $b \sim 12.56$, $c \sim 5.76$ Å, $\beta = 94^\circ$ (*vide infra*). The data were reduced taking into account the first monoclinic cell. Systematic absences ($h0l$: $h + l = 2n$; $h00$: $h = 2n$; $0k0$: $k = 2n$; $00l$: $l = 2n$) were consistent with the space groups $P2_1/n$ ($P2_1/c$ as standard). Statistical tests on the distribution of $|E|$ values strongly indicate the presence of an inversion centre ($|E^2-1| = 0.922$), thus supporting the choice of the space group $P2_1/n$. We decided to refine the cervelleite structure in the non-standard space group $P2_1/n$ in order to have the same orientation reported for acanthite and aguilarite. The program SHELXL (Sheldrick 2008) was used for the refinement of the structure, which was carried out starting from the atomic coordinates of acanthite by Frueh (1958). The occupancy of all the sites was left free to vary (Ag vs. vacancy; Te vs. S) and then fixed to the resulting value. The refined values are given in Table 2. Neutral scattering curves for Ag, S and Te were taken from the *International Tables for X-ray Crystallography* (Ibers and Hamilton 1974). At the last stage, with anisotropic atomic displacement parameters for all atoms and no constraints, the residual value settled at $R = 0.0298$ for 418 observed reflections [$2\sigma(I)$ level] and 29 parameters and at $R = 0.0329$ for all 956 independent reflections. Experimental details and R indices are given in Table 1. Fractional atomic coordinates and isotropic displacement parameters are reported in Table 2 (anisotropic ADPs can be found in the accompanying CIF). Bond distances are given in Table 3. The calculated X-ray powder-diffraction pattern, computed with the atom coordinates and occupancies reported in Table 2, is given in Table 4. Structure factors and CIF are available from the authors upon request.

Results and Discussion

Description of the crystal structure

1 The crystal structure of cervelleite (Fig. 2) is topologically identical to that of
 2 acanthite (Frueh 1958) and aguilarite (Bindi and Pingitore 2013). It can be described
 3 as a body-centered array of tetrahedrally coordinated X atoms (where X = S, Se and
 4 Te) with Ag₂-polyhedra in planes nearly parallel to (010); the sheets are linked by the
 5 other silver position (i.e., Ag1) that exhibits a three-fold coordination. Due to the
 6
 7
 8
 9
 10
 11
 12
 13
 14
 15
 16
 17
 18
 19
 20
 21
 22
 23
 24
 25
 26
 27
 28
 29
 30
 31
 32
 33
 34
 35
 36
 37
 38
 39
 40
 41
 42
 43
 44
 45
 46
 47
 48
 49
 50
 51
 52
 53
 54
 55
 56
 57
 58
 59
 60
 61
 62
 63
 64
 65

Te) with Ag₂-polyhedra in planes nearly parallel to (010); the sheets are linked by the other silver position (i.e., Ag1) that exhibits a three-fold coordination. Due to the greater size of Te compared to S and Se, Ag1 and Ag2 atoms in cervelleite increase their coordination number to 3 and 4, respectively, with respect to that observed in acanthite and aguilarite (2 and 3 for Ag1 and Ag2, respectively). Results indicate that $Z = 4$ [with an unit-cell volume of $235.66(3) \text{ \AA}^3$ and formula $\text{Ag}_2(\text{Te}_{0.50}\text{S}_{0.50})$], unlike the findings of Criddle et al. (1989) that reported $Z = 24$ [with unit-cell volume of $2762(2) \text{ \AA}^3$ and formula Ag_4TeS]. As such, the computed density should be 8.247 g/cm^3 rather than the value of 8.53 g/cm^3 reported previously.

In the structure, the bond distances observed for the two silver positions (i.e., $\langle \text{Ag1-X} \rangle = 2.660 \text{ \AA}$ and $\langle \text{Ag2-X} \rangle = 2.729 \text{ \AA}$) are larger than those observed in acanthite [$\langle \text{Ag1-X} \rangle = 2.503 \text{ \AA}$ and $\langle \text{Ag2-X} \rangle = 2.602 \text{ \AA}$, Frueh (1958)] and aguilarite [$\langle \text{Ag1-X} \rangle = 2.511 \text{ \AA}$ and $\langle \text{Ag2-X} \rangle = 2.628 \text{ \AA}$, Bindi and Pingitore (2013)], due to the greater size of Te compared to Se and S (Shannon 1976). On the whole, the observed Ag–X bond distances (Table 3) are intermediate with respect to the Ag–Te distances observed in hessite, Ag_2Te (2.84–3.03 Å; Van der Lee and de Boer 1993), sylvanite, $(\text{Au,Ag})_2\text{Te}_4$ (2.74–3.23 Å; Pertlik 1984), muthmannite, AuAgTe_2 (2.69–2.97 Å; Bindi and Cipriani 2004), and empressite, AgTe (2.84–2.96 Å; Bindi et al. 2004), and those observed for some Ag–Se minerals (e.g., naumannite, Ag_2Se , 2.62–2.86 Å, Wieggers 1971; aguilarite, Ag_4SeS , 2.51–2.63 Å, Bindi and Pingitore 2013).

1 The shortest Ag–Ag contact in cervelleite ($\text{Ag}_2\text{–Ag}_2 = 2.968 \text{ \AA}$) is nearly
2 identical to the corresponding value in naumannite ($\text{Ag–Ag} = 2.93 \text{ \AA}$, Wiegiers 1971),
3
4 and is very similar to those observed in *fcc* silver ($\text{Ag–Ag} = 2.89 \text{ \AA}$; Suh et al. 1988)
5
6 or *hcp* silver [$\text{Ag–Ag} = 2.93 \text{ \AA}$; Petruk et al. 1970]. The mean electron number refined
7
8 for the X position [$0.527(3)\text{Te} + 0.473\text{S} = 34.97$] is in excellent agreement with the
9
10 chemical formula reported in the literature for cervelleite, i.e. Ag_4TeS .
11
12
13

14 In Figure 3, the unit-cell volumes of synthetic members belonging to the two
15
16 solid solutions, the monoclinic ‘acanthite-like’ $\text{Ag}_2\text{S} - \text{Ag}_2\text{S}_{0.4}\text{Se}_{0.6}$ series and the
17
18 orthorhombic ‘naumannite-like’ $\text{Ag}_2\text{S}_{0.3}\text{Se}_{0.7} - \text{Ag}_2\text{Se}$ series (Pingitore et al. 1992),
19
20 are plotted against the selenium contents. A good linear trend is observed
21
22 corresponding to the expansion of the lattice dimensions as the larger Se^{2-} anion
23
24 replaces S^{2-} , following Vegard’s law for the properties of solid solutions. Taking into
25
26 consideration the ionic radii of Te, Se and S, if we calculate a mean value for
27
28 cervelleite ($\text{Te}_{0.50}\text{S}_{0.50}$) and then extrapolate the potential amount of Se (to plot it in
29
30 Figure 3), we can see that the studied crystal (filled circle) occurs along this trend.
31
32
33
34
35
36
37
38
39

40 Discussion of the previous results obtained by Criddle et al. (1989)

41
42 We have here unambiguously shown for the first time that cervelleite represents
43
44 the Te-analogue of aguilarite. However, a puzzling aspect of the current study is that
45
46 Criddle et al. (1989) described cervelleite as an optically isotropic mineral with a
47
48 cubic symmetry. We note here that the same set of *d* spacings reported by Criddle et
49
50 al. (1989), which are indexed with a primitive cubic lattice with $a = 14.03 \text{ \AA}$, can be
51
52 obtained with the monoclinic unit cell found in this study and matching the 11% of the
53
54 total reflections collected from our ‘cervelleite’ crystal. The refined monoclinic unit cell
55
56 can be written as $a = 8.994(8)$, $b = 12.56(1)$, $c = 5.761(6) \text{ \AA}$, $\beta = 93.90(8)^\circ$, $V =$
57
58
59
60
61
62
63
64
65

649.3(9) Å³ and the comparison with the diffraction pattern originally reported by Criddle et al. (1989) is given in Table 5.

We surmise that Criddle et al. (1989) obtained chemical and optical data on cervelleite but carried out X-ray data on this second monoclinic unknown phase. This unknown phase is intergrown with cervelleite, and occurs in variable amounts. To corroborate these findings, we embedded the cervelleite grain in epoxy used for the structural investigation and studied the polished section by means of a scanning electron microscope. The grain appears to be formed of two phases (Fig. 4): a brighter phase which shows the composition typically observed for cervelleite (i.e., Ag₄TeS, when the data are normalized on the basis of 6 atoms per formula unit), and a darker phase with stoichiometry Ag₂FeS₂, which is likely responsible for the diffraction peaks belonging to the second monoclinic unit cell [i.e., $a = 8.994(8)$, $b = 12.56(1)$, $c = 5.761(6)$ Å, $\beta = 93.90(8)^\circ$]. Unfortunately, the very low number of reflections for this unnamed Ag₂FeS₂ phase precludes any *ab initio* structure determination. The search for grains composed of this potential new mineral only failed.

Thus, the holotype sample contains cervelleite, benleonardite and an unknown (likely) new Ag-Fe-S phase exhibiting the second monoclinic unit-cell identified here (which replaced the cubic cell given by Criddle et al. 1989).

Conclusions

1. Cervelleite is monoclinic, space group $P2_1/n$, with $a = 4.2696(4)$, $b = 6.9761(5)$, $c = 8.0423(7)$ Å, $\beta = 100.332(6)^\circ$, $V = 235.66(3)$ Å³, $Z = 4$. The crystal structure [$R1 = 0.0329$ for 956 reflections with $I > 2\sigma(I)$], solved for the first time, demonstrates that the mineral is the Te-analogue of aguilrite.

- 1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
2. Cervelleite coexists with an unnamed Ag_2FeS_2 phase in the type sample. The unnamed phase exhibits a monoclinic symmetry with cell dimensions: $a = 8.994(8)$, $b = 12.56(1)$, $c = 5.761(6)$ Å, $\beta = 93.90(8)^\circ$ and $V = 649.3(9)$ Å³. The comparison with the diffraction pattern originally reported by Criddle et al. (1989) gave an excellent match.
 3. The museum specimen studied here (catalogue number E.1161 BM 1985, 354) is the type sample for cervelleite, benleonardite and a new previously unidentified Ag-Fe-S phase.

24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

Acknowledgements Mike Rumsey is thanked for providing us with the holotype sample of cervelleite. The paper benefited by the official reviews made by Panagiotis Voudouris and an anonymous reviewer. Associate Editor Anton Beran is thanked for his efficient handling of the manuscript. This work was supported by “Progetto d’Ateneo 2012, University of Firenze” to LB.

References

- 1
2
3 Bindi L (2008) Commensurate-incommensurate phase transition in muthmannite,
4
5 AuAgTe₂: First evidence of a modulated structure at low-temperature. *Phil Mag*
6
7 *Lett* 88:533–541
8
9
- 10 Bindi L (2009) Thermal expansion behavior of empressite, AgTe: A structural study
11
12 by means of in situ high-temperature single-crystal X-ray diffraction. *J Alloys*
13
14 *Comp* 473:262–264
15
16
- 17 Bindi L (2014) Chemical and structural characterization of henryite, (Cu,Ag)_{3+x}Te₂ (*x*
18
19 ~ 0.40): A new structure type in the (Ag)-Cu-Te system. *Solid State Sci* 38:108–
20
21 111
22
23
- 24 Bindi L, Arakcheeva A, Chapuis G (2009) The role of silver on the stabilization of the
25
26 incommensurately modulated structure in calaverite, AuTe₂. *Am Mineral*
27
28 94:728–736.
29
30
- 31 Bindi L, Carbone C, Belmonte D, Cabella R, Bracco R (2013a) Weissite from
32
33 Gambatesa mine, Val Graveglia, Liguria, Italy: occurrence, composition and
34
35 determination of the crystal structure. *Mineral Mag* 77:475–483
36
37
38
- 39 Bindi L, Cipriani C (2004) Ordered distribution of Au and Ag in the crystal structure of
40
41 muthmannite, AuAgTe₂, a rare telluride from Sacarîmb, western Romania. *Am*
42
43 *Mineral* 89:1505–1509
44
45
- 46 Bindi L, Pinch WW (2014) Cameronite, Cu_{5-x}(Cu,Ag)_{3+x}Te₁₀ (*x* = 0.43), from the Good
47
48 Hope Mine, Vulcan, Colorado: Crystal structure and revision of the chemical
49
50 formula. *Can Mineral* 52:423–432
51
52
53
- 54 Bindi L, Pingitore NE (2013) On the symmetry and crystal structure of aguilarite,
55
56 Ag₄SeS. *Mineral Mag* 77:21–31
57
58
59
60
61
62
63
64
65

- 1 Bindi L, Rossell Abrodos M, Van Tendeloo G, Spry PG, Cipriani C (2005) Inferred
2 phase relations in part of the system Au-Ag-Te: an integrated analytical study of
3 gold ore from the Golden Mile, Kalgoorlie, Australia. *Mineral Petrol* 83:283–293
4
5 Bindi L, Spry PG, Cipriani C (2004) Empressite, AgTe, from the Empress-Josephine
6 Mine, Colorado, USA: composition, physical properties and determination of the
7 crystal structure. *Am Mineral* 89:1043–1047
8
9 Bindi L, Voudouris P, Spry PG (2013b) Structural role of tellurium in the minerals of
10 the pearceite-polybasite group. *Mineral Mag* 77:419–428
11
12 Ciobanu CL, Cook NJ, Tămaş C, Leary S, Manske S, O'Connor G, Minuţ A (2004)
13 Tellurides-gold-base metal associations at Roşia Montană: the role of hessite
14 as gold carrier. In: Cook N, Ciobanu CL (eds) Au-Ag-telluride deposits of the
15 Golden Quadrilateral, Apuseni Mts., Romania, IAGOD Guidebook Ser 12, 187–
16 202
17
18 Cook NJ, Ciobanu CL (2003) Cervelleite, Ag₄TeS, from three, localities in Romania,
19 substitution of Cu, and the occurrence of the associated phase, Ag₂Cu₂TeS. *N*
20 *Jb Miner Mh* 7:321–336
21
22 Criddle AJ, Chisholm JE, Stanley CJ (1989) Cervelleite, Ag₄TeS, a new mineral from
23 the Bambolla mine, Mexico, and a description of a photo-chemical reaction
24 involving cervelleite, acanthite and hessite. *Eur J Miner* 1:371–380
25
26 Dobrev S, Strashimirov S, Vassileva M, Dragiev H (2002) Silver and silver-bearing
27 phases from Chala and Pcheloiad deposits (Eastern Rhodopes) and Eniovche
28 deposit (Central Rhodopes). *Univ Mining and Geology "St. Ivan Rilski" Annual:*
29 1–6
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

- 1 Downs RT, Bartelmehs KL, Gibbs GV, Boisen MB Jr (1993) Interactive software for
2 calculating and displaying X-ray or neutron powder diffractometer patterns of
3 crystalline materials. *Am Mineral* 78:1104–1107
4
5
6
7 Frueh AJ Jr (1958) The crystallography of silver sulfide, Ag₂S. *Zeit Kristallogr*
8
9 110:136–144
10
11 Gu XP, Watanabe M, Hoshino K, Shibata Y (2003) New find of silver tellurosulphides
12 from the Funan gold deposit, East Shandong, China. *Eur J Miner* 15:147–155
13
14
15
16 Helmy HM (1999) The Um Samiuki volcanogenic Zn-Cu-Pb-Ag deposit, Eastern
17 Desert, Egypt: a possible new occurrence of cervelleite. *Can Miner* 37:143–158
18
19
20
21 Ibers JA, Hamilton WC Eds (1974) *International Tables for X-ray Crystallography*,
22 vol. IV, 366p. Kynock, Dordrecht, The Netherlands
23
24
25
26 Novoselov KA, Belogub EV, Zykov VV, Yakovleva VA (2006) Silver sulfotellurides
27 from volcanic-hosted massive sulphide deposits in the Southern Urals. *Mineral*
28
29 *Petrol* 87:327–349
30
31
32
33 Oxford Diffraction (2006) *CrysAlis* RED (Version 1.171.31.2) and ABSPACK in
34 *CrysAlis* RED. Oxford Diffraction Ltd, Abingdon, Oxfordshire, England
35
36
37
38 Paar W, De Brodtkorb MK (1996) Presencia de cervelleíta y hessita en la galena del
39 yacimiento San Martín, Valcheta, prov. de Río Negro. 3° Reunión de
40 Mineralogía y Metalogenia, Instituto de Recursos Minerales. Univ. Nacional de
41 La Plata, Argentina Publ. No. 5: 173–175
42
43
44
45
46
47
48 Padma Kumar P, Yashonath S (2006) Ionic conduction in the solid state. *J Chem Sci*
49 118:135–154
50
51
52
53 Pertlik F (1984) Kristallchemie natürlicher Telluride I: Verfeinerung der Kristallstruktur
54 des Sylvanits, AuAgTe₄. *Tsch Mineral Petrograph Mitt* 33:203–212
55
56
57
58
59
60
61
62
63
64
65

- 1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65
- Petruk W, Cabri LJ, Harris DC, Stewart JM, Clark LA (1970) Allargentum, redefined. *Can Mineral* 10:163–172
- Pingitore NE, Ponce BF, Moreno F, Podpora C (1992) Solid solutions in the system Ag_2S – Ag_2Se . *J Mat Res* 7:2219–2224
- Shannon RD (1976) Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Crystallogr* A32:751–767
- Sheldrick GM (2008) A short history of SHELX. *Acta Crystallogr* A64:112–122
- Suh I-K, Ohta H, Waseda Y (1988) High-temperature thermal expansion of six metallic elements measured by dilatation method and X-ray diffraction. *J Mat Sci* 23:757–760.
- Spry PG, Thieben SE (1996) Two new occurrences of benleonardite, a rare silver tellurium sulphosalt, and a possible new occurrence of cervelleite. *Miner Mag* 60:871–876
- Spry PG, Tombros SF, Seymour KSt, Williams-Jones AE, Zouzias DP (2006) Geology, mineralogy and geochemistry of granite-hosted gold telluride mineralization at Panormos Bay, Tinos Island, Greece. *Geol Soc Am Abstr* 38:55
- Tombros S, Seymour KSt, Spry PG (2004) Description and conditions of formation of new unnamed Ag-Cu and Ag-Cu-Au sulfotellurides in epithermal polymetallic Ag-Au-Te mineralization, Tinos Island, Hellas. *N Jb Miner Abh* 179:295–310
- Tombros SF, Seymour KSt, Williams-Jones AE (2010) Controls on tellurium in base, precious, and telluride minerals in the Panormos Bay Ag-Au-Te deposits, Tinos Island, Cyclades, Greece. *Econ Geol* 105:1097–1111

- 1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65
- Van der Lee A, de Boer JL (1993) Redetermination of the structure of hessite, Ag_2Te -
III. *Acta Crystallogr C* 49:1444–1446
- Voudouris P, Spry PG (2008) A new occurrence of cervelleite-like phases and Te-
polybasite from gold-bearing veins in metamorphic rocks of the Cycladic
Blueschist Unit, Greece. 33rd International Geological Congress, MRD-09 Au-Ag
tellurideselenide deposits, CD-ROM, Abstract
- Voudouris P, Spry PG, Sakellaris GA, Mavrogonatos C (2011) A cervelleite-like
mineral and other Ag-Cu-Te-S minerals [Ag_2CuTeS and $(\text{Ag,Cu})_2\text{TeS}$] in gold-
bearing veins in metamorphic rocks of the Cycladic Blueschist Unit, Kallianou,
Evia Island, Greece. *Miner Petrol* 101:169–183
- Wiegers GA (1971) The crystal structure of the low-temperature form of silver
selenide. *Am Mineral* 56:1882–1888
- Williams SA (1982) Cuzticitic and eztlite, two new tellurium minerals from Moctezuma,
Mexico. *Mineral Mag* 46:257–259

Figure Captions

1
2
3
4 Figure 1 – Reflected plane polarized light digital image (in oil immersion) illustrating
5
6 pale greenish cervelleite overgrowths on acanthite rosettes (with intergrown
7
8 unknown phase) and coarser acanthite (near scale bar) and quartz (middle
9
10 left). Creamy white hessite forms the infill. The sample (catalogue number
11
12 E.1161 BM 1985, 354) is the type specimen for both cervelleite and
13
14 benleonardite.
15
16
17

18
19 Figure 2 – The crystal structure of cervelleite projected down [100]. The horizontal
20
21 direction is the *c* axis. Ag and X (S and Te) are given as white and black
22
23 spheres, respectively. The unit cell is outlined.
24
25
26

27 Figure 3 – The unit-cell volume (\AA^3) plotted against the Se content (a.p.f.u.). Filled
28
29 symbol represents the cervelleite crystal (this study), whereas empty symbols
30
31 are data from synthetic compounds (Pingitore et al. 1992).
32
33
34

35 Figure 4 – SEM-BSE image showing the coexistence of two phases (brighter:
36
37 cervelleite, darker: unnamed Ag_2FeS_2) in the crystal used for the structural
38
39 investigation.
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

TABLE 1 – Crystallographic data and refinement parameters for cervelleite

Crystal data			
Ideal formula	Ag ₄ TeS		
Crystal system	monoclinic		
Space group	<i>P2₁/n</i>		
Unit-cell parameters (Å, °)	4.2696(4)	6.9761(5)	8.0423(7)
Unit-cell volume (Å ³)	90.00	100.332(6)	90.00
Z	4		
Crystal size (mm)	0.060×0.055×0.040		
Data collection			
Diffractometer	Oxford Xcalibur 3		
Temperature (K)	293(2)		
Radiation, wavelength (Å)	MoKα 0.71073		
2θ max for data collection (°)	69.96		
Crystal-detector dist. (mm)	50		
<i>h, k, l</i> ranges	-6 – 6, -11 – 11, -12 – 12		
Axis, frames, width (°), time per frame (s)	ω/φ, 1211, 1.00, 70		
Total reflections collected	3911		
Unique reflections (<i>R</i> _{int})	956 (0.041)		
Unique reflections <i>I</i> > 2σ(<i>I</i>)	418		
Data completeness to θ _{max} (%)	99.6		
Absorption correction method	ABSPACK (Oxford Diffraction 2006)		
Structure refinement			
Refinement method	Full-matrix least-squares on <i>F</i> ²		
Data/restraints/parameters	956/0/29		
<i>R</i> ₁ [<i>I</i> > 2σ(<i>I</i>)], <i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)]	0.0298, 0.0560		
<i>R</i> ₁ all, <i>wR</i> ₂ all	0.0329, 0.0562		
Goodness-of-fit on <i>F</i> ²	0.975		
Largest diff. peak and hole (e ⁻ /Å ³)	0.76, -0.45		

$$R_{\text{int}} = (n/n-1)^{1/2} [F_o^2 - F_o(\text{mean})^2] / \sum F_o^2$$

$$R_1 = \sum || F_o | - | F_c || / \sum | F_o | \quad wR_2 = \left\{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \right\}^{1/2}$$

$$GooF = \left\{ \sum [w(F_o^2 - F_c^2)^2] / (n-p) \right\}^{1/2} \quad \text{where } n = \text{no. of reflections, } p = \text{no. of refined parameters}$$

TABLE 2 – Atoms, Wyckoff letter, site occupancy, fractional atom coordinates (Å), and isotropic atomic displacement parameters (Å²) for cervelleite

atom	Wyckoff	site occupancy	x	y	z	U_{eq}
Ag1	4e	Ag _{1.00}	0.7542(3)	0.0339(1)	0.34094(8)	0.0244(2)
Ag2	4e	Ag _{1.00}	0.2887(2)	0.3487(1)	0.41168(8)	0.0261(2)
X	4e	Te _{0.527(3)} S _{0.473}	0.3608(2)	0.2417(2)	0.13068(9)	0.0296(3)

TABLE 3 – Selected bond distances (Å) for cervelleite

Ag1 - X	2.600(1)	Ag2 - X	2.451(1)	Ag1 -Ag2	3.041(1)
- X	2.603(1)	- X	2.815(1)	-Ag2	3.079(1)
- X	2.776(1)	- X	2.821(1)	-Ag2	3.083(1)
<Ag1-X>	2.660	- X	2.827(1)	-Ag2	3.145(1)
		<Ag2-X>	2.729	-Ag2	3.321(1)
				Ag2 -Ag2	2.968(1)

TABLE 4 – Calculated powder diffraction pattern for cervelleite

<i>h</i>	<i>k</i>	<i>l</i>	<i>I</i> _{calc}	<i>d</i> (Å)
1	1	1	21	3.1009
-1	1	2	100	2.8923
1	2	0	61	2.6834
-1	2	1	43	2.6347
0	2	2	8	2.6163
1	1	2	56	2.4791
0	1	3	23	2.4669
1	2	1	71	2.4571
-1	0	3	33	2.4392
0	3	1	39	2.2310
0	2	3	13	2.1037
2	0	0	37	2.1002
1	0	3	6	2.0724
-1	3	1	6	2.0129
2	1	0	19	2.0110
0	3	2	36	2.0047
-1	2	3	19	1.9989
1	1	3	17	1.9866
0	0	4	29	1.9780
-2	1	2	10	1.9317
0	3	3	9	1.7442
-2	2	2	12	1.7417
0	4	1	7	1.7031
-1	2	4	8	1.6872
-1	4	1	8	1.6000
-2	0	4	11	1.5892
-2	3	1	7	1.5693
-2	3	2	6	1.5208
2	3	1	11	1.4920
-1	3	4	9	1.4841
2	1	3	7	1.4812
-1	2	5	5	1.4370
-2	3	3	8	1.4276
-3	1	2	8	1.3739
1	3	4	8	1.3603
-2	4	1	6	1.3486
-1	5	1	12	1.3181
3	1	1	7	1.3142
2	1	4	7	1.3028
1	2	5	7	1.2995
1	5	1	7	1.2941
2	4	2	7	1.2285
-2	2	6	7	1.1513
-3	4	1	7	1.1026

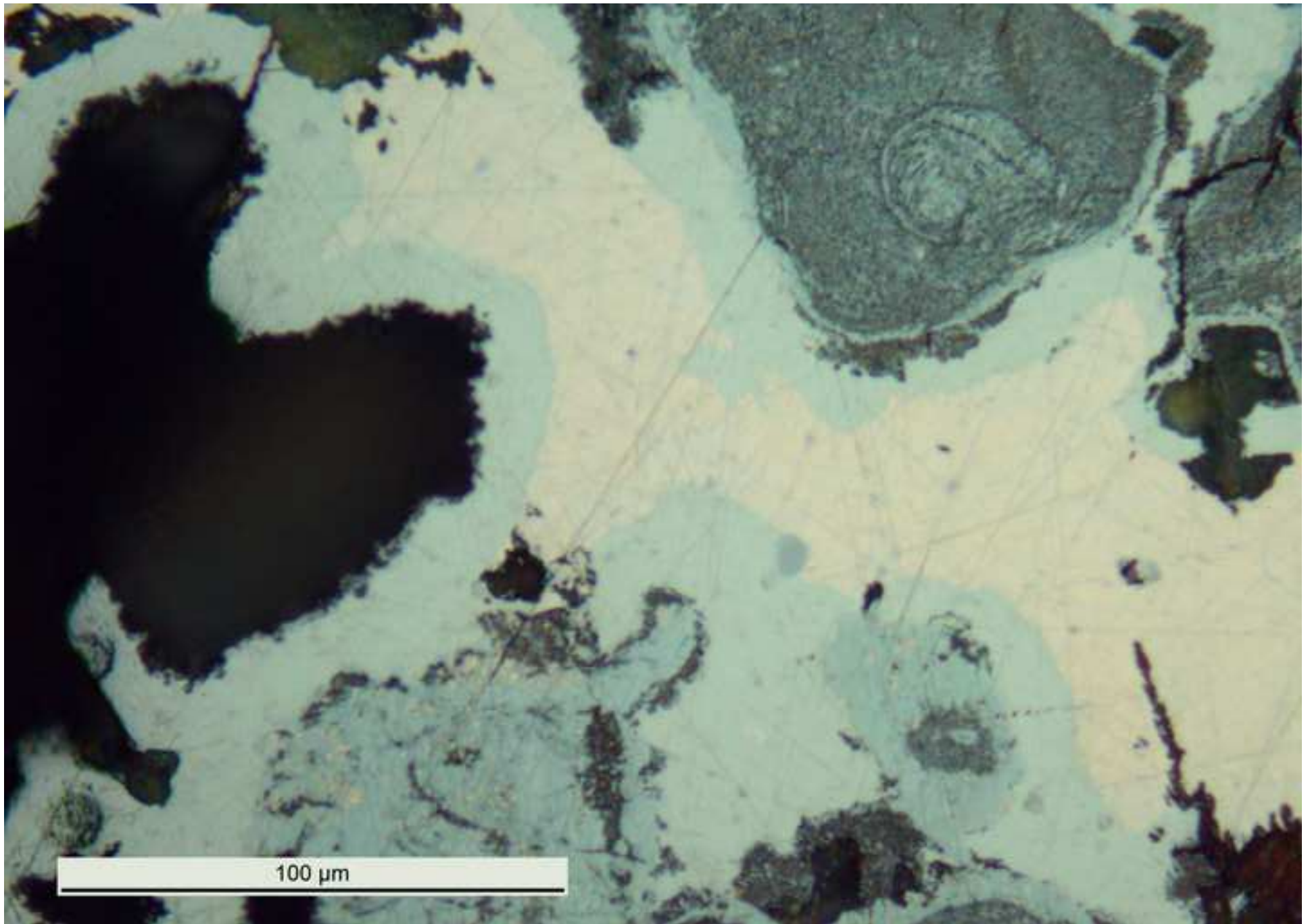
d values calculated on the basis of $a = 4.2694(4)$, $b = 6.9761(5)$, $c = 8.0423(7)$ Å, $\beta = 100.332(6)^\circ$, and with the atomic coordinates and occupancies reported in Table 2.

Intensities calculated using XPOW software version 2.0 (Downs et al. 1993). Only $I > 5\sigma(I)$ are reported.

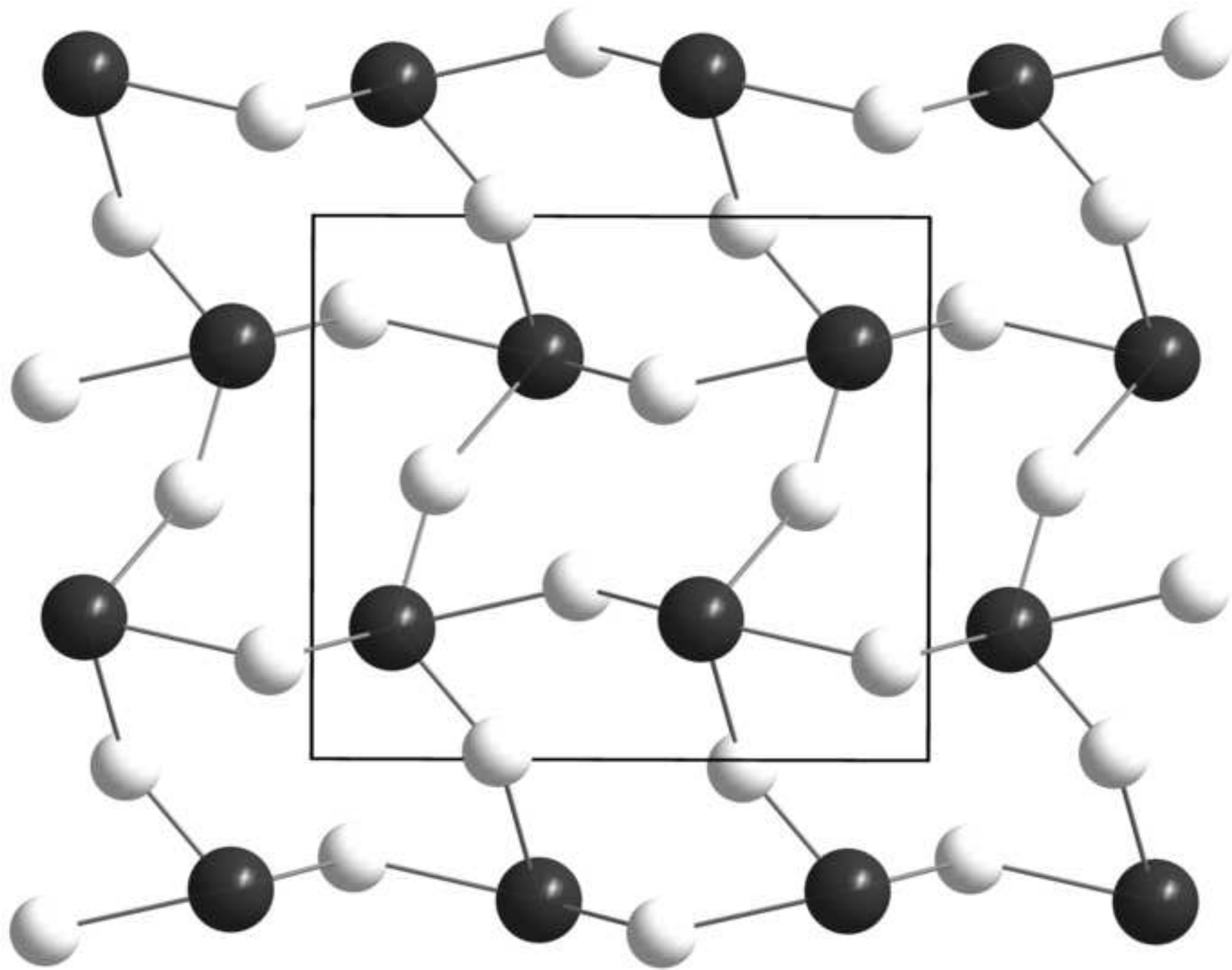
TABLE 5 – X-ray powder diffraction patterns for the unnamed Ag_2FeS_2 phase intergrown with cervelleite

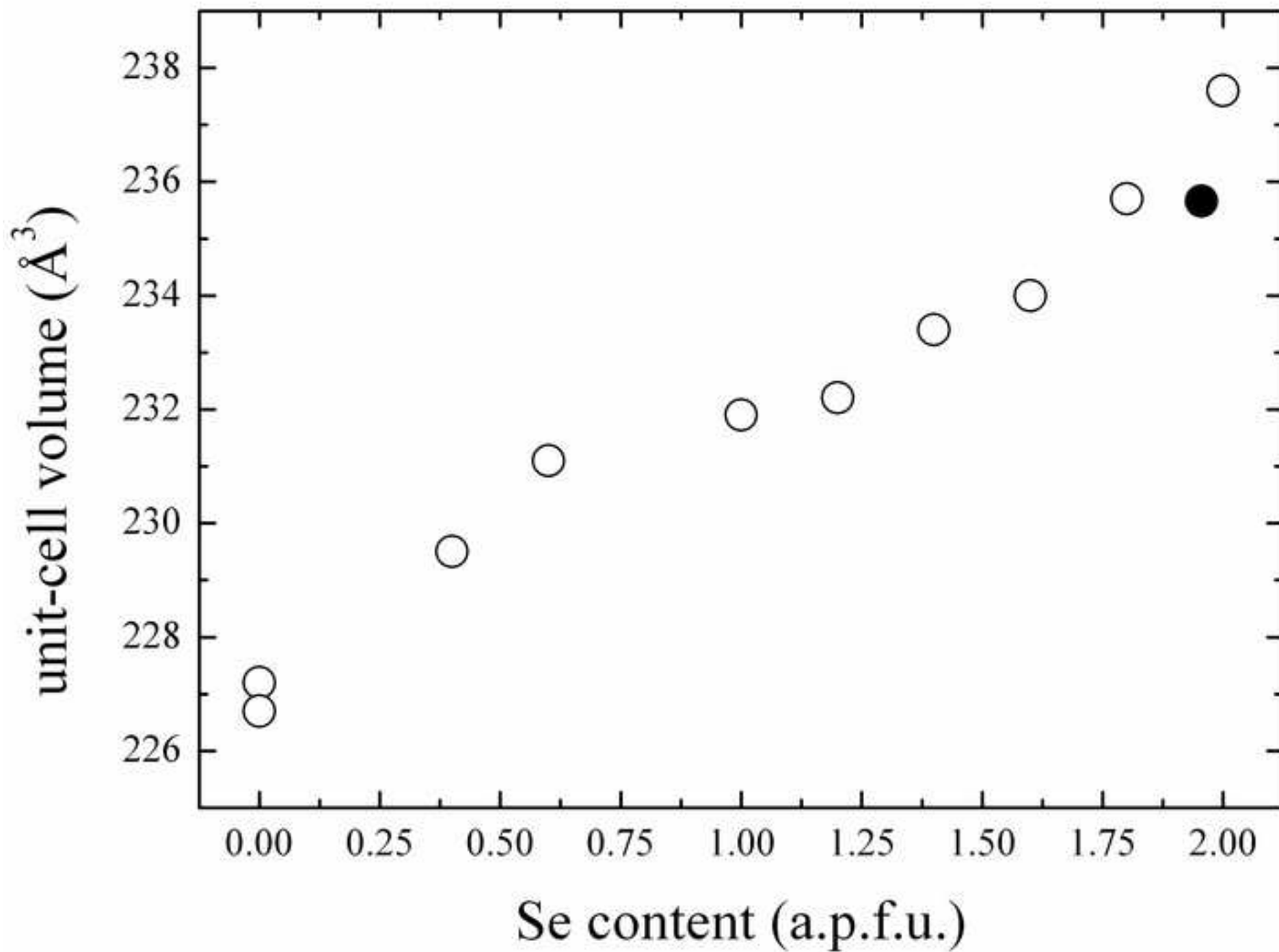
<i>hkl</i>	1		2		
	d_{obs} (Å)	I_{obs}	I_{obs}	d_{obs} (Å)	I_{obs}
020	6.28	60	012	6.29	s
001	5.75	10	112	5.74	w
-101	5.00	100	022	5.00	vvs
-111	4.643	35	122,003	4.64	m
021	4.240	80	113	4.24	vs
121	3.761	35	123	3.766	ms
201	3.425	5	014,223	3.421	vw
230	3.061	5	–	–	–
-231	2.755	2	134,015	2.753	vw
311	2.529	5	n.i.	2.530	vw
212	2.308	10	016	2.304	w
-401	2.140	5	335	2.137	vw
-251	2.071	5	–	–	–
251	2.026	5	444	2.026	vw
061	1.9670	10	117,155	1.9659	vw
350	1.9242	5	146,027	1.9247	vw
-261	1.8170	5	n.i.	1.8174	vw

Note: 1 = observed powder pattern of the unnamed Ag_2FeS_2 phase of this study. 2 = observed powder pattern and indexing originally reported by Criddle et al. (1989) for 'cervelleite'.



Line Figure
[Click here to download high resolution image](#)





Line Figure

[Click here to download high resolution image](#)

