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On the symmetry and crystal structure of aguilarite, Ag_4SeS

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ABSTRACT

An examination of a specimen of aguilarite from the type locality provides new data on the chemistry and structure of this mineral. The chemical formula of the crystal used for the structural study is $(Ag_{3.98}Cu_{0.02})(Se_{0.98}S_{0.84}Te_{0.18})$, on the basis of 6 atoms. The mineral was found to be monoclinic, crystallizing in space group $P2_1/n$, with $a = 4.2478(2)$, $b = 6.9432(3)$, $c = 8.0042(5)$ Å, $\beta = 100.103(2)^\circ$, $V = 232.41(2)$ Å^3 and $Z = 4$. The crystal structure [refined to $R_1 = 0.0139$ for 958 reflections with $I > 2\sigma(I)$] is topologically identical to that of acanthite, Ag_2S. It can be described as a body-centred array of tetrahedrally coordinated X atoms (X = S, Se and Te) with $Ag2X_3$ triangles in planes nearly parallel to (010); the sheets are linked by the Ag1 silver site, which has twofold coordination.

Aguilarite is definitively proved to be isostructural with acanthite; it does not have a naumannite-like structure, as previously supposed. Our data support the hypothesis that there are two solid solution series in the system: a monoclinic 'acanthite-like' series (from $Ag_2S-Ag_2S_{0.4}Se_{0.6}$), and an orthorhombic 'naumannite-like' series (from $Ag_2S_{0.3}Se_{0.7}-Ag_2Se$). This is supported by data gathered on synthetic counterparts. Aguilarite remains as a valid as a mineral species, but it should be described as the Se-analogue of acanthite.

In this study we also (1) review the history of the aguilarite; (2) compare properties of synthetic and natural aguilarite; and (3) demonstrate how earlier researchers erred in describing aguilarite as orthorhombic.

The Te-bearing composition of the studied aguilarite crystal suggests the possibility of a solid solution with cervelleite (Ag_4TeS).

Keywords: aguilarite, crystal structure, Ag-sulfides, acanthite, naumannite, cervelleite, Mexico.

Introduction

The system Ag_2S-Ag_2Se has recently attracted significant attention in materials research due to its optical, electrical and thermoelectric properties (e.g. Xiao *et al.*, 2012); it has been of considerable interest in mineral sciences for many years due to the importance of the minerals involved. At ambient conditions these are: acanthite, Ag_2S, which is monoclinic, space group $P2_1/n$ according to Frueh (1958); naumannite, Ag_2Se, which is orthorhombic, space group $P2_12_12_1$ according to Wiegers (1971); and the intermediate member aguilarite (Genth, 1891, 1892), Ag_4SeS, which is orthorhombic according to Petruk *et al.* (1974) and is listed as such in several mineralogical databases (e.g. www.webmineral.com; www.mindat.org), although there are no detailed structural studies. According to Pingitore *et al.* (1992, 1993), these three semiconductor phases undergo structural transitions to a cubic high-temperature conductive form in the temperature range 70–178ºC, depending on their composition.

The possible solid solution between Ag_2S and Ag_2Se has been debated for a long time. Indeed, chemical analyses reported in the scientific literature for acanthite and naumannite support

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the solid-solution argument. Moreover, cervelleite, Ag_4TeS (Criddle *et al.*, 1989) was reported to contain selenium (Spry and Thieben, 1996) thus suggesting the possibility of solid solution with aguilarite (Ag_4SeS).

To examine the extent of solid solution in the system Ag_2S-Ag_2Se at ambient conditions, Pingitore *et al.* (1992) carried out a careful experimental study of 80 experimental charges with compositions ranging from Ag_2S to Ag_2Se by optical microscopy, electron-probe microanalysis and X-ray diffraction. The main conclusions were that the intermediate member, aguilarite, could be considered to be Se-rich acanthite, with the same monoclinic crystal structure, and that at ambient conditions there are two solid solutions [i.e. the Ag_2S–$Ag_2S_{0.4}Se_{0.6}$ monoclinic series and $Ag_2S_{0.3}Se_{0.7}-Ag_2Se$ orthorhombic series]. Pingitore *et al.* (1992) also pointed out that the status of aguilarite as a mineral species could be called into question as it was erroneously thought to be orthorhombic by Petruk *et al.* (1974). The conclusions drawn by Pingitore *et al.* (1992), however, have not been demonstrated for natural samples.

To resolve concerns relating to the *status* of aguilarite, structural, physical and chemical data for the mineral from the type locality, San Carlos mine, Guanajuato, Mexico, are reported herein.

Aguilarite review

Early studies of aguilarite

Aguilarite was described by Genth (1891, 1892) and named after Mr P. Aguilar, who was the superintendent of San Carlos Mine, Guanajuato, Mexico, which is the type locality. The initial description predates both X-ray diffraction and electron-probe microanalysis.

X-ray powder diffraction data, consisting of ten *d*-spacings with their relative intensities, were first reported for aguilarite from Guanajuato, Mexico by Harcourt (1942). A systematic investigation of selenide minerals, which includes X-ray powder diffraction photographs of both aguilarite and synthetic Ag_4SeS, along with a table of intensities, peak angles and lattice spacings for the latter was subsequently reported by Earley (1950). Earley commented on the similarities between the peaks of aguilarite, those of synthetic Ag_4SeS and those reported by Harcourt (1942). He concluded that because the X-ray powder patterns of aguilarite and synthetic Ag_4SeS showed only "faint resemblances" to those of naumannite and acanthite, aguilarite was a distinct mineral species. In particular, he specifically rejected the suggestion of Schneiderhöhn and Ramdohr (1931), that aguilarite was a member of the acanthite–naumannite series.

In a review of selenium in epithermal deposits, Davidson (1960) repeated the suggestion that there was a solid solution from acanthite to naumannite. This was based on the similarity in the radii of Se^{2-} and S^{2-} anions, and on the substitution of these anions in solid solutions of related minerals. Main *et al.* (1972) examined aguilarite from a hydrothermal vein deposit in New Zealand, a sample from Guanajuato (Mexico), and synthetic Ag_4SeS. On the basis of X-ray powder diffraction studies of the last two of these, they suggested that some of the diffraction peaks reported by Earley (1950) were in error. They also reported the elemental composition of a single grain of the New Zealand material by electron-probe microanalysis. Differential thermal analysis of a galena-aguilarite concentrate and of their synthetic material each yielded an endotherm with a maximum at 122ºC. This endotherm represents the transition to a high-temperature solid phase, which corresponds to those reported for acanthite (176ºC) and naumannite (133ºC). Main *et al.* (1971) concluded that the available X-ray data were insufficient to permit confident indexing of the aguilarite powder pattern.

The cornerstone investigation of Petruk et al. (1974)

For the past four decades, the data, literature review and phase diagram presented by Petruk *et al.* (1974) have served as the foundation for studies of the mineralogy and behaviour of the silver–sulfur–selenium system. These authors examined aguilarite and acanthite from Guanajuato, Mexico, and naumannite from Silver City, Idaho, USA, by ore microscopy (with etching), electron-probe microanalysis and X-ray powder diffraction. The X-ray diffraction pattern of aguilarite was indexed on a naumannite-type orthorhombic cell. On the basis of these data, previously published elemental analyses, and their interpretation of the parageneses of their mineral suites, Petruk *et al.* (1974) made the assertion that acanthite, aguilarite and naumannite are distinct mineral species. They suggested molar compositional limits for sulfur–selenium substitutions of up to 0.15 Se in acanthite, 0.025 Se or

0.05 S in aguilarite (converted here to an Ag_2X-type formula for comparative purposes), and 0.12 S in naumannite. They also suggested that these compositional ranges are separated by two fields where a presumed high-temperature cubic solid solution destabilizes between 176 and 115ºC to form intergrowths of the two appropriate minerals (acanthite–aguilarite or aguilarite–naumannite).

Further studies

Shikazono (1978) documented various compositions between acanthite and aguilarite outside the substitutional limits suggested by Petruk *et al.* (1974). Shikazono concluded that if those limits were correct, his materials must be intergrowths of acanthite and aguilarite. Morales and Borodayev (1982) reported microprobe analyses of a range of compositions between acanthite and aguilarite from a segment of the Veta Madre (Las Torres area) in Guanajuato. Backscattered-electron images and X-ray mapping showed that the small (10–100 μm) grains they examined were monomineralic, rather than intergrowths of acanthite and aguilarite. They concluded that a continuous isomorphic solid solution must exist between acanthite and aguilarite, suggesting that Petruk *et al.* (1974) had been misled by their reliance on etching and broad-beam (15–80 μm) probe analyses. These investigators did not, however, address the structural problem: acanthite is monoclinic, whereas aguilarite was supposed to be orthorhombic. The isomorphous solid solution that they proposed is, therefore, logically impossible.

Samples studied

The San Carlos sample containing aguilarite used for the structural study reported herein is from the Gem and Mineral Collection of the Department of Geosciences at Princeton University, which consists of approximately 6000 catalogued mineral specimens and several hundred cut gemstones that were collected from the 1820s to the 1970s, together with historic documents and rare specimen labels from early mineral dealers, recording the growth and development of mineral collecting and its interaction with the scientific community.

The label associated with the sample used for the structural study reads: "*aguilarite, Ag_4SeS, San Carlos mine, Mexico*" (catalogue number I/53a/2312). Unfortunately, we are unable to provide additional information about the sample, but, based on the writing style on the index card, it was probably catalogued in the 1920s. On the small vial containing the sample there is a tiny price tag "*$1.00*" in the style of Ward's old labels. This makes sense as, shortly after the formal establishment of the Department of Geology (as it was known then) in 1904, Professor Alexander Phillips, who occupied the chair in mineralogy in the period 1905–1936, led an effort to greatly expand the collection through purchases, assembling a comprehensive teaching and reference collection consisting of nearly all the minerals known at the time with an emphasis on specimens from type localities.

The sample mainly consists of aguilarite associated with a very small amount of acanthite. The aguilarite exhibits a subhedral to anhedral grain morphology, and does not show any inclusions of, or intergrowths with, other minerals. The maximum aguilarite grain size is ~250 μm.

Aguilarite samples 48a.2 and 48a.6 from the 'Pennsylvania Genth San Carlos collection' of Pennsylvania State University were examined independently in the laboratory of the Department of Geological Sciences of the University of Texas. It is possible that these are cotype specimens and they may be from the original (presumed lost) type specimen, given the provenance, and in the absence of other claims as to the whereabouts of the type specimen. Specimens from the National Museum of Natural History (Washington D.C.), with registration numbers USNMNH C 380 (Canfield Collection, pre-1927, from the San Carlos mine) and 93436 were also examined.

Physical and optical properties

Aguilarite is black with a dark brown-black streak. The mineral is opaque in transmitted light and has a metallic lustre. No cleavage is present and the fracture is uneven. Microindentation hardness measurements carried out on the specimen used in the structural study with a load (VHN) of 25 g give a mean value of 21 kg mm^{-2} (range: 19–23) corresponding to a Mohs hardness of 1–1½.

In plane-polarized incident light, aguilarite is dark grey in colour, moderately bireflectant and not pleochroic. Between crossed polars, aguilarite is very weakly anisotropic with greyish to light-green rotation tints. Internal reflections are absent

and there is no optical evidence of growth zonation.

Reflectance measurements were performed in air by means of a MPM-200 Zeiss microphotometer equipped with a MSP-20 system processor on a Zeiss Axioplan ore microscope. The filament temperature was approximately 3350 K. An interference filter was adjusted, in turn, to select four wavelengths for measurement (471.1, 548.3, 586.6, and 652.3 nm). Measurements were made on an area of the specimen 0.1 mm in diameter and on a silicon carbide standard under the same focussing conditions. Reflectance percentages, R_{min} and R_{max}, are: 34.2, 34.7 (471.1 nm); 33.9, 34.5 (548.3 nm); 32.7, 33.9 (586.6 nm); and 30.8, 31.3 (652.3 nm), respectively, in excellent agreement with the values reported by Stanley and Gooday in Criddle and Stanley (1993).

X-ray crystallography and crystal-structure refinement

A small crystal fragment ($80 \times 65 \times 55$ μm) was selected from specimen I/53a/2312 for a single-crystal X-ray diffraction study using an Oxford Diffraction Xcalibur 3 CCD single-crystal diffractometer (Table 1). Surprisingly, the unit-cell parameters determined for the selected crystal indicated monoclinic symmetry, with $a \sim 4.25$, $b \sim 6.94$, $c \sim 8.00$ Å and $\beta \sim 110^{o}$, which are very

TABLE 1. Crystallographic data and refinement parameters for aguilarite (sample # I/53a/2312).

Crystal data	
Ideal formula	Ag_4SeS
Crystal system	monoclinic
Space group	$P2_1/n$
Unit-cell parameters (Å, º)	4.2478(2) 6.9432(3) 8.0042(5) 90.00 100.103(2) 90.00
Unit-cell volume (Å^3)	232.41(2)
Z	4
Crystal size (mm)	$0.080 \times 0.065 \times 0.055$
Data collection	
Diffractometer	Oxford Xcalibur 3
Temperature (K)	298(3)
Radiation, wavelength (Å)	Mo$K\alpha$, 0.71073
2θ max for data collection (º)	69.94
Crystal–detector dist. (mm)	50
h, k, l ranges	$-6 \leqslant h \leqslant 6$, $-11 \leqslant k \leqslant 11$, $-12 \leqslant l \leqslant 12$
Axis, frames, width (º), time per frame (s)	ω–φ, 1152, 1.00, 25
Total reflections collected	3832
Unique reflections (R_{int})	958 (0.066)
Unique reflections $I > 2\sigma(I)$	520
Data completeness to θ_{max} (%)	99.6
Absorption correction method	*ABSPACK* (Oxford Diffraction, 2006)
Structure refinement	
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	958/0/29
R_1 [$I > 2\sigma(I)$], wR_2 [$I > 2\sigma(I)$]	0.0139, 0.0305
R_1 all, wR_2 all	0.0152, 0.0306
Goodness-of-fit on F^2	0.223
Largest diff. peak and hole (e$^-$ Å^{-3})	1.26, −1.41

$R_{int} = (n/n - 1)^{1/2}[F_o^2 - F_o\,(\text{mean})^2]/\Sigma F_o^2$
$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$;
$w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = (\max(F_o^2,0) + 2F_c^2)/3$;
$\text{GooF} = \{\Sigma[w(F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$
where n is the number of reflections and p is the number of refined parameters.

TABLE 2. Atoms, Wyckoff letter, site occupancy, fractional atom coordinates, and isotropic atomic displacement parameters (Å^2) for aguilarite (sample # I/53a/2312).

Atom	Wyckoff	Site occupancy	*x*/*a*	*y*/*b*	*z*/*c*	U_{eq}
Ag1	4*e*	$Ag_{1.00}$	0.75442(6)	0.01378(4)	0.30116(2)	0.01762(6)
Ag2	4*e*	$Ag_{1.00}$	0.28840(6)	0.31874(4)	0.43144(2)	0.01803(6)
X	4*e*	$S_{0.333(3)}Se_{0.667}$	0.3603(1)	0.24110(7)	0.13054(4)	0.0216(1)

close to those of acanthite (Frueh, 1958). Systematic absences (*h*0*l*: $h + l = 2n$; *h*00: $h = 2n$; 0*k*0: $k = 2n$; 00*l*: $l = 2n$) are consistent with space group $P2_1/n$ ($P2_1/c$ as standard). Statistical tests on the distribution of $|E|$ values strongly indicate the presence of an inversion centre ($|E^2 - 1| = 0.893$), supporting the choice of space group $P2_1/n$. It was therefore decided to refine the aguilarite structure in the non-standard space group $P2_1/n$ in order to have the same orientation reported for acanthite. The program *SHELXL* (Sheldrick, 2008) was used to refine the structure, starting from the atom coordinates listed by Frueh (1958) for acanthite. The occupancy of all the sites was left free to vary (Ag *vs*. vacancy; S *vs*. Se) and then fixed to the resulting value. The refined values are listed in Table 2. Neutral scattering curves for Ag, S and Se were taken from the *International Tables for X-ray Crystallography* (Ibers and Hamilton, 1974). At the last stage of refinement, with anisotropic atomic-displacement parameters for all atoms and no constraints, the residual value settled at $R = 0.0139$ for 520 observed reflections [$2\sigma(I)$ level] and 29 parameters and at $R = 0.0152$ for all 958 independent reflections. Experimental details and *R* indices are listed in Table 1. Fractional atom coordinates and isotropic-displacement parameters are reported in Table 2 (anisotropic ADPs can be found in the accompanying CIF). Selected bond distances are listed in Table 3. The calculated powder-diffraction pattern, based on the atom coordinates and occupancies reported in Table 2, is provided in Table 4. A table of structure factors has been deposited with the Principal Editor of *Mineralogical Magazine* and is available at http://www.minersoc.org/pages/e_journals/dep_mat_mm.htm

Chemical composition

Qualitative chemical analysis, using energy-dispersive spectrometry, on the crystal fragment used for the structural study (sample no. I/53a/2312), showed that the only elements present (with $Z > 9$) were Ag, S, Se, Te and minor Cu. Quantitative chemical compositions were determined by wavelength-dispersive spectrometry (WDS) on a JEOL JXA-8600 electron microprobe. Major and minor elements were determined at 20 kV accelerating voltage and 15 nA beam current with a 2 μm beam diameter and 15 s counting times. The following lines were used: Ag*L*α, Cu*K*α, S*K*α, Se*L*α and Te*L*α. The standards were Ag metal (Ag), Cu metal (Cu), pyrite (S), synthetic $PtSe_2$ (Se) and synthetic Sb_2Te_3 (Te). The crystal fragment was found to be homogeneous to within analytical errors. The mean composition (8 analyses of different spots) together with wt.% ranges of elements are reported in Table 5. On the basis of 6 atoms, the empirical formula of this specimen of aguilarite is $(Ag_{3.98}Cu_{0.02})(Se_{0.98}S_{0.84}Te_{0.18})$.

Chemical analyses of the four other samples reported in Table 5 were carried out at the University of Texas at El Paso using a Cameca

TABLE 3. Selected bond distances (Å) for aguilarite (sample # I/53a/2312).

Ag1–*X*	2.4996(5)	Ag2–*X*	2.5382(4)	Ag1–Ag2	3.0184(3)
Ag1–*X*	2.5213(5)	Ag2–*X*	2.6526(5)	Ag1–Ag2	3.1442(4)
<Ag1–*X*>	**2.5105**	Ag2–*X*	2.6936(5)	Ag1–Ag2	3.1748(5)
		<Ag2–*X*>	**2.6281**	Ag1–Ag2	3.1750(3)

TABLE 4. Calculated X-ray powder-diffraction data for aguilarite (sample # I/53a/2312).

I	d_{calc}	h	k	l
5	3.9956	$\bar{1}$	0	1
5	3.4631	$\bar{1}$	1	1
52	3.0909	1	1	1
58	2.8742	$\bar{1}$	1	2
37	2.6711	1	2	0
95	2.6206	$\bar{1}$	2	1
63	2.6047	0	2	2
31	2.4721	1	1	2
32	2.4568	0	1	3
100	2.4477	1	2	1
86	2.4241	$\bar{1}$	0	3
43	2.2206	0	3	1
7	2.1042	1	2	2
14	2.0947	0	2	3
45	2.0910	2	0	0
22	2.0670	1	0	3
20	2.0021	2	1	0
5	1.9956	0	3	2
8	1.9875	$\bar{1}$	2	3
23	1.9811	1	1	3
11	1.9199	$\bar{2}$	1	2
13	1.8952	0	1	4
6	1.7394	$\bar{2}$	1	3
11	1.7358	0	4	0
27	1.7315	$\bar{2}$	2	2
10	1.7134	0	2	4
5	1.5957	$\bar{2}$	2	3
7	1.5921	$\bar{1}$	4	1
7	1.5885	0	4	2
7	1.5613	$\bar{2}$	3	1
12	1.5369	0	1	5
10	1.4861	2	3	1
8	1.4772	2	1	3
22	1.4761	$\bar{1}$	3	4
8	1.4513	1	4	2
5	1.4113	$\bar{1}$	4	3
15	1.3557	1	3	4
9	1.3538	$\bar{2}$	1	5
6	1.3418	$\bar{2}$	4	1
7	1.3319	$\bar{3}$	0	3
5	1.3117	$\bar{1}$	5	1
8	1.3092	3	1	1
7	1.2994	2	1	4
7	1.2711	$\bar{1}$	5	2
6	1.2239	2	4	2
5	1.1443	$\bar{2}$	2	6
5	1.0972	$\bar{3}$	4	1
5	1.0968	$\bar{3}$	3	4

The calculated X-ray powder pattern was computed on the basis of $a = 4.2478(2)$, $b = 6.9432(3)$, $c = 8.0042(5)$ Å, $\beta = 100.103(2)^{\circ}$, and with the atom coordinates and site occupancies reported in Table 2. Intensities calculated using *XPOW* software version 2.0 (Downs *et al.*, 1993). Only those reflections with $I_{calc} > 5$ are listed.

SX-50 electron microprobe, operating at 15 kV, 15 nA with a 10 μm beam diameter and 20 s counting times. The analytical standards were pure Ag and Se, and marcasite for S.

Results and discussion

Description of the crystal structure

The crystal structure of aguilarite (Fig. 1) is topologically identical to that of acanthite (Frueh, 1958). It can be described as a body-centred array of tetrahedrally coordinated X atoms (X = S, Se and Te) with $Ag2X_3$ triangles in planes nearly parallel to (010); the sheets are linked by the Ag1 silver site, which has twofold coordination. The mean bond distances for the two silver sites [i.e. <Ag1–X> = 2.511 Å and <Ag2–X> = 2.628 Å] are slightly longer than those in acanthite [<Ag1–S> = 2.503 Å and <Ag2–S> = 2.602 Å; Frueh (1958)], as a result of the larger radii of Se and Te (Shannon, 1976). The shortest Ag–Ag distance in aguilarite (Ag1–Ag2 = 3.0184 Å) is nearly identical to the corresponding value in acanthite [Ag1–Ag2 = 3.036 Å, Frueh (1958)]. In naumannite the shortest Ag–Ag distance is 2.93 Å, a value very similar to those in *fcc* silver [$r_{(Ag-Ag)}$ = 2.89 Å; Suh *et al.*, 1988] and *hcp* silver [$r_{(Ag-Ag)}$ = 2.93 Å; Petruk *et al.*, 1970]. The mean electron number refined for the X position [0.333(3)S + 0.667Se = 28.01] is in excellent agreement with the value calculated from chemical data (0.49Se + 0.42S + 0.09Te = 28.06).

Comparison of natural and synthetic 'aguilarite' specimens

A comparison of the d-spacings (Table 6) of historic aguilarite specimens with those of synthetic samples (taken from Pingitore *et al.*, 1992) indicates an acanthite-type structure with a composition close to Ag_4SeS for samples Genth 48a.2 and USNMNH C 380. Electron-probe microanalysis (Table 5) yielded normalized (to an ideal total of 2) anion fractions of $S_{0.95}Se_{1.08}$ and $S_{1.03}Se_{0.93}$, respectively; these are consistent with the X-ray data. The second studied sample from the NMNH collection (no. 93436) is also from Mexico but there is no further locality information. Its X-ray diffraction pattern is similar to that of naumannite, with some substitution of S for Se. Electron-probe microanalysis (Table 5) indicates anion fractions of $S_{0.19}Se_{1.73}$, and therefore this sample is naumannite with ~10%

TABLE 5. Electron microprobe data [means in wt.% of elements with standard deviations (σ)] together with the crystal-chemical formulae on the basis of 6 atoms for aguilarite crystals.

	I/53a/2312 8	Genth 48a.2 13	Genth 48a.6 12	USNMNH C 380 13	USNMNH 93436 6
Ag	76.5(2)	79.0(3)	78.3(8)	80.1(3)	74.9(1)
Cu	0.23(4)	n.d.	n.d.	n.d.	n.d.
S	4.80(7)	5.6(4)	7.1(1.8)	6.1(2)	1.0(1.0)
Se	13.79(8)	15.8(4)	13.4(1.1)	13.5(2)	23.2(9)
Te	4.10(6)	n.d.	n.d.	n.d.	n.d.
Total	99.42(2)	100.4(3)	98.8(1.0)	99.6(1.0)	99.1(7)
Ag	3.98	3.97	3.90	4.04	4.08
Cu	0.02	–	–	–	–
S	0.84	0.95	1.19	1.03	0.19
Se	0.98	1.08	0.91	0.93	1.73
Te	0.18	–	–	–	–

The second row is the number of analyses; n.d. = not determined.

substitution of S for Se. The Genth 48a.6 specimen produced an X-ray powder pattern similar to those of USNMNH C 380 and Genth 48a.2, with idealized anion fractions of $S_{1.19}Se_{0.91}$.

A comparison of the *d*-spacings determined for one of the synthetic compounds described by Pingitore *et al.* (1992) of composition Ag_4SeS, with the Genth 48a.2 and USNMNH C 380 specimens, and the aguilarite studied by Petruk *et al.* (1974) is given in Table 6. Note the close correspondence between the values listed for synthetic Ag_4SeS (Pingitore *et al.*, 1992) and those measured for the two museum specimens from San Carlos mine. All three of these are also a credible match to the *d*-spacings listed for aguilarite by Petruk *et al.* (1974).

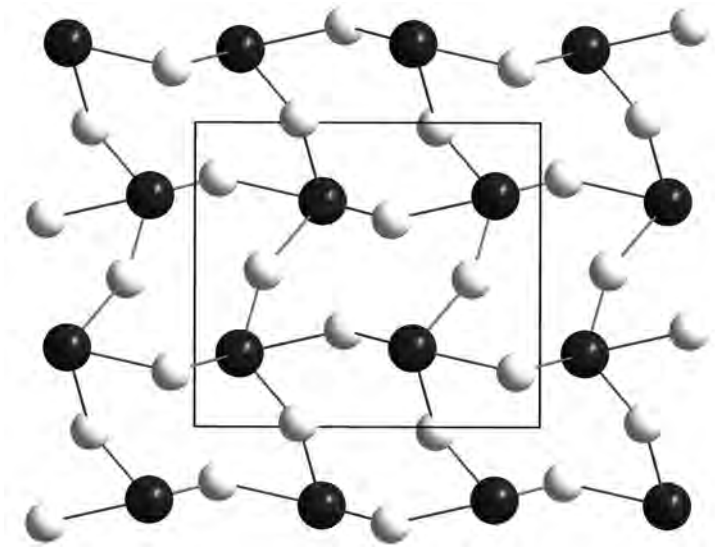

FIG. 1. The crystal structure of aguilarite projected down [100]. The horizontal direction is the *c* axis. The Ag and *X* (S, Se and Te) atoms are shown as white and black spheres, respectively. The unit cell is outlined.

TABLE 6. Comparison of X-ray powder diffraction data and indexing of synthetic Ag_4SeS and aguilarite*.

Acanthite JCPDS 14-72			Ag_4SeS synthetic		Aguilarite NMNH C 380		Aguilarite Genth 48a.2		Aguilarite Petruk *et al.* (1974)		Naumannite —— JCPDS 24$\bar{1}$041 ——		
3.437	35	$\bar{1}$11	3.461	<10	3.435	<10	3.467	<10					
3.383	20	012											
									3.33	10**	3.333	70	111
3.080	60	111	3.086	20	3.092	30	3.101	20					
					2.973	10							
2.836	70	$\bar{1}$12	2.878	60	2.880	80	2.895	90	2.88	30	2.737	20	120
2.664	45	120	2.670	30	2.674	30	2.680	40	2.67	20	2.673	100	112
2.606	100	$\bar{1}$21	2.619	40	2.622	40	2.632	50	2.59	20	2.581	85	121
2.583	70	022			2.618	20							
2.456	70	112	2.457	60	2.465	50	2.473	100					
2.440	80	121	2.446	60	2.455	100	2.451	80					
2.421	60	013	2.433	100	2.434	80	2.447	80	2.43	100	2.429	31	013
2.383	75	$\bar{1}$03					2.350	<10					
			2.294	10	2.296	<10	2.304	20					
2.213	45	031	2.220	30	2.229	30	2.228	40	2.23	30	2.254	33	031
											2.238	17	122
2.093	16	122									2.119	34	113
2.083	45	200	2.092	30	2.095	40	2.098	40	2.09	10	2.080	35	023,301
2.072	16	023			2.065	10	2.074	10			2.067	12	210,130
2.047	16	103									2.014	25	032
1.995	16	$\bar{1}$31	1.995	20	1.987	20	2.002	40	2.00	10	2.001	15	211,131
1.963	20	$\bar{1}$23	1.984	20	1.969	10	1.986	30					
1.866	16	014	1.897	10	1.896	10	1.905	20	1.88	10	1.881	23	123
											1.872	23	014
											1.827	10	212,132
1.733	12	040	1.735	10	1.739	10	1.741	30	1.73	30	1.719	06	114,041
1.718	20	$\bar{2}$13					1.715	10					
1.587	14	$\bar{1}$41	1.598	<10	1.587	<10	1.591	<10	1.60	20	1.594	06	230
1.579	10	$\bar{2}$23	1.589	<10	1.579	<10	1.567	<10	1.56	20	1.562	06	231
1.513	12	015											
1.483	10	231	1.478	10	1.486	<10	1.483	20	1.48	40	1.475	04	232
1.470	10	213	1.473	10	1.475	10	1.442	10					
1.459	14	$\bar{1}$34											
5 minors, 1.31–1.38			1.356	<10	1.357	<10	1.358	<10	1.35	20 302			

* *d*-spacings are listed in Å, with relative intensities based on 100. The indices, *hkl*, are based on a monoclinic acanthite-type cell for: synthetic Ag_4SeS, USNMNH C 380 aguilarite, and Genth 48a.2 aguilarite; indexing is based on a naumannite-type orthorhombic cell for the Petruk *et al.* (1974) aguilarite. Petruk *et al.* (1974) aguilarite also is listed as JCPDS 27-620. Possible minor peaks (<10) on the Genth 48a.2 pattern, not indexed, are at approximately 3.36 (quartz?) and 1.93 Å.
** This *d*-spacing is likely to be due to contamination by quartz; it is very close to the 3.34 Å spacing of the *I*100 peak for that common mineral.

It is apparent that all four of these specimens have essentially identical structures; only one minor ($I = 1$) aguilarite peak listed by Petruk *et al.* (1974) at 3.33 Å is not matched reasonably in the synthetic, Genth and USNMNH specimens. This peak was not reported by Earley (1950) and may be due to a contaminant phase. The quartz I_{100} peak corresponds closely to this spacing (3.34 Å) and Petruk *et al.* (1974) reported that their Guanajuato material was "disseminated in dark grey quartz".

We have identified a number of peaks that were not documented by Petruk *et al.* (1974). Our diffractometer produces higher resolution data than the powder camera used by Petruk *et al.* (1974). In early analyses using a Gandolfi camera we were unable to resolve some multiple peaks, such as those with *d*-spacings of 2.457, 2.446 and 2.433 Å. We conclude that the structure of aguilarite reported by Petruk *et al.* (1974) is identical to that of compounds with the same stoichiometry which we produced in the laboratory and with the Genth and USNMNH San Carlos mine aguilarite specimens; they are all the same phase.

Natural and synthetic aguilarite form by an unquenchable solid-state transition from a presumably continuous solid solution (ranging in composition from Ag_2S to Ag_2Se) which is stable at elevated temperatures. The commonly observed cubic morphology of 'acanthite pseudomorphs after argentite' document this transition in nature; calorimetry and the similarly cubic morphology of our synthetic phases do the same in the laboratory. For this reason, we do not believe that natural hydrothermal aguilarite differs significantly from synthetic material; both experience the same phase transition. However, the precise boundaries of the two-phase zone between the acanthite- and naumannite-type solid solutions may be affected by the disparity in the rates of cooling in laboratory and natural settings.

Indexing of aguilarite by Petruk et al. (1974) on the naumannite pattern

The seemingly credible indexing of aguilarite on the orthorhombic naumannite cell achieved by Petruk *et al.* (1974) remains disturbing. Most of their indexing (the narrowest spacings have been omitted) is listed in Table 6. Two points are important in this regard.

First, we suspect that Petruk *et al.* (1974) were unable to resolve some closely spaced multiple lines on their films, as discussed above. The extra lines would not correspond to any naumannite-type reflection. Second, there is a major internal inconsistency in the results of the aguilarite indexing by Petruk *et al.* (1974). The individual *d*-spacings (Table 6) and the *a*, *b* and *c* dimensions of their naumannite-indexed aguilarite unit cell are larger, in every case, than the corresponding dimension of the naumannite unit cell (4.33 *vs.* 4.31 Å for *a*, 7.09 *vs.* 7.02 Å for *b*, and 7.76 *vs.* 7.71 Å for *c*). The volume of the naumannite-indexed aguilarite unit cell is thus larger (238.2 *vs.* 237.6 $Å^3$) than that of naumannite; and the naumannite indexed by Petruk *et al.* (1974) yields an even greater difference, as it has a calculated cell volume of 233.3 $Å^3$. Recalling that S^{2-} is 7% smaller in radius than Se^{2-}, that half of the anion sites in aguilarite are occupied by S rather than Se, and that aguilarite and naumannite were assumed by Petruk *et al.* (1974) to have the same structure, it is impossible for the aguilarite unit cell to have a greater volume than that of naumannite. Clearly, in hindsight, the decision to index aguilarite on a naumannite-type cell was inappropriate.

Indexing of synthetic Ag_4SeS by Pingitore et al. (1992) on the acanthite pattern

The indexing of synthetic Ag_4SeS on an acanthite-type monoclinic unit cell is based on our observation of a gradual and systematic shift in the X-ray diffraction peaks of samples with increasing Se content (see Pingitore *et al.*, 1992). These shifts correspond to an expansion of the lattice dimensions as the larger Se^{2-} anion replaces S^{2-}, following Vegard's law for solid solutions. Table 6 shows our indexing of both Ag_4SeS and the aguilarite of Petruk *et al.* (1974) on an acanthite-type structure. Compare the *d*-spacings of these two phases with those of acanthite, in the far left position. Note that the *d*-spacings in both Ag_4SeS and aguilarite are typically larger than those of acanthite, as expected for Se substitution. The fit for both phases, given the anticipated shifts, is quite reasonable.

Status of aguilarite as a mineral species

The foregoing discussion definitively demonstrates that aguilarite is monoclinic, crystallizing in space group $P2_1/n$, and is therefore isostructural with monoclinic acanthite, rather than

orthorhombic $P2_12_12_1$, naumannite, as previously supposed. Aguilarite remains as a valid mineral species, but it should be described as the Se-analogue of acanthite rather than S-rich naumannite. The crystal structure determination revealed no cation ordering at room temperature. Our conclusions support the hypothesis of Pingitore *et al.* (1992, 1993) that there are two distinct solid solution series: a monoclinic 'acanthite-like' $Ag_2S-Ag_2S_{0.4}Se_{0.6}$ series; and an orthorhombic 'naumannite-like' $Ag_2S_{0.3}Se_{0.7}$–Ag_2Se series; and is supported by data gathered on synthetic analogues. Moreover, if unit-cell volumes are plotted against selenium content (Fig. 2) for natural aguilarite (this study) and synthetic compounds of both the series (Pingitore *et al.*, 1992), a clear linear trend is observed, which includes neotype specimen 1/53a/2312, despite its enrichment in tellurium.

In the Ag_2S–Ag_2Se solid solution at room temperature there is a transition from monoclinic to orthorhombic symmetry between 60 and 70 at.% Se (i.e. between $Ag_2S_{0.4}Se_{0.6}$ and $Ag_2S_{0.3}Se_{0.7}$). As structural studies do not indicate site-specific substitutions, the name aguilarite should be applied to the monoclinic phase with more than 50 at.% Se. Aguilarite is therefore monoclinic with an ideal formula Ag_4SeS and a composition field that extends from 50 at.% Se to the monoclinic–orthorhombic transition.

Possible solid-solution with cervelleite, Ag_4TeS

Cervelleite, Ag_4TeS, is a rare mineral first described by Criddle *et al.* (1989) from Moctezuma mine, Mexico. Spry and Thieben (1996) subsequently reported a cervelleite-like mineral at the Mayflower epithermal gold-silver telluride deposit in Montana, USA, with an unusual Se-rich composition. The two chemical analyses reported by these authors correspond to a formula $(Ag_{3.74-3.76}Cu_{0.08-0.09}As_{0.00-0.10})_{\Sigma\approx 4}(Te_{1.11-1.20}S_{0.66-0.91}Se_{0.14-0.21})_{\Sigma\approx 2}$, which indicates the possibility of a solid solution, or at least a limited solid solution, between cervelleite and the Se-analogue of cervelleite, aguilarite (Ag_4SeS). Such a feature is strongly corroborated by the chemistry of one of the aguilarite crystals in the present study. Unfortunately, no structural data have been reported either for cervelleite or for synthetic cervelleite-like compounds, the only information being that the mineral may be cubic, with a = 14.03 Å and a primitive lattice (Criddle *et al.*, 1989). As discussed above, members of the Ag_2S-Ag_2Se system undergo structural transitions to a cubic high-temperature conductive form in the temperature range 70–178ºC, depending on composition. Full structural data are not available for the high-temperature forms but they are described as cubic with I lattices and unit-cell parameters a = 4.88(2) and 4.98(2) Å for Ag_2S and Ag_2Se, respectively (Pingitore *et al.*, 1993). In the light of these data, the unit-cell parameter reported for cervelleite (a = 14.03 Å; Criddle *et al.*, 1989), might represent a superstructure with $a_{\text{cervelleite}} = 3a$, the tripling of the cell parameter possibly being due to cation ordering. Such a hypothesis, however, seems unlikely for two reasons: (1) the value of 14.03 Å is too small with respect to the tripled basic cell parameters observed for the high-temperature cubic forms of Ag_2S and Ag_2Se; and (2) the high-temperature cubic forms are usually disordered structures (the conductive allotropes) and it would seem unlikely that the superstructure in cervelleite was the result of cation ordering.

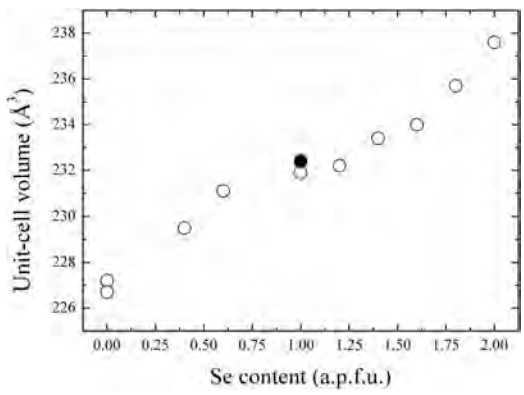

FIG. 2. The unit-cell volume (Å^3) plotted against the Se content (a.p.f.u.). The filled symbol represents the aguilarite crystal (this study); empty symbols are data from synthetic compounds (Pingitore *et al.*, 1992).

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University to the attention of one of the authors (LB). Deane K. Smith lent two of the 6 original aguilarite specimens from Genth's collection at The Pennsylvania State University for analysis. Pete J. Dunn of the National Museum of Natural History, Washington, D.C., provided two samples of aguilarite. Part of this report is based upon work supported by the US National Science Foundation under grants RII-8922191 and HRD-9450412. The assistance of Benjamin Ponce and Letty Estrada at UTEP is appreciated.

References

Criddle, A.J. and Stanley, C.J. (editors) (1993) *Quantitative Data File for Ore Minerals*, third edition. Chapman & Hall, London.

Criddle, A.J., Chisholm, J.E. and Stanley, C.J. (1989) Cervelleite, Ag_4TeS, a new mineral from the Bambolla mine, Mexico, and a description of photo-chemical reaction involving cervelleite, acanthite and hessite. *European Journal of Mineralogy*, **1**, 371–380.

Davidson, F. (1960) Selenium in some epithermal deposits of antimony, mercury and silver and gold. *U.S. Geological Survey Bulletin*, **1112-A**, 152–164.

Downs, R.T., Bartelmehs, K.L., Gibbs, G.V. and Boisen, M.B. Jr (1993) Interactive software for calculating and displaying X-ray or neutron powder diffractometer patterns of crystalline materials. *American Mineralogist*, **78**, 1104–1107.

Earley, J.W. (1950) Description and synthesis of the selenide minerals. *American Mineralogist*, **35**, 337–364.

Frueh, A.J. Jr (1958) The crystallography of silver sulfide, Ag_2S. *Zeitschrift für Kristallographie*, **110**, 136–144.

Genth, F.A. (1891) Aguilarite, a new species. *American Journal of Science*, **41**, 401–403.

Genth, F.A. (1892) Aguilarite. *American Journal of Science*, **44**, 381–383.

Harcourt, G.A. (1942) Tables for the identification of ore minerals by X-ray powder patterns. *American Mineralogist*, **27**, 63–113.

Ibers, J.A. and Hamilton, W.C. (editors) (1974) *International Tables for X-ray Crystallography*, vol. IV. Kynock Press, Birmingham, UK, 366 pp.

Main, J.V., Rodgers, K.A., Kobe, H.W. and Woods, C.P. (1972) Aguilarite from the Camoola Reef, Maratoto Valley, New Zealand. *Mineralogical Magazine*, **38**, 961–964.

Morales, L.F.V. and Borodayev, Y.S. (1982) New data on minerals of the acanthite–aguilarite–naumannite series. *Doklady Akademi Nauk SSSR*, **264**, 685–688.

Oxford Diffraction (2006). *CrysAlis RED (Version 1.171.31.2) and ABSPACK in CrysAlis RED.* Oxford Diffraction Ltd, Abingdon, Oxfordshire, UK.

Petruk, W., Cabri, L.J., Harris, D.C., Stewart, J.M. and Clark, L.A. (1970) Allargentum, redefined. *The Canadian Mineralogist*, **10**, 163–172.

Petruk, W., Owens, D.R., Stewart, J.M. and Murray, E.J. (1974) Observations on acanthite, aguilarite and naumannite. *The Canadian Mineralogist*, **12**, 365–369.

Pingitore, N.E., Ponce, B.F., Moreno, F. and Podpora, C. (1992) Solid solutions in the system Ag_2S–Ag_2Se. *Journal of Material Research*, **7**, 2219–2224.

Pingitore, N.E., Ponce, B.F., Estrada, L., Eastman, M.P., Yuan, H.L., Porter, L.C. and Estrada, G. (1993) Calorimetric analysis of the system Ag_2S–Ag_2Se between 25 and 250ºC. *Journal of Material Research*, **8**, 3126–3130.

Schneiderhöhn, H. and Ramdohr, P. (1931) *Lehrbuch der Erzmikroskopie*, Volume 2. Gebruder Borntraeger, Berlin, 222 pp.

Shannon, R.D. (1976) Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Crystallographica*, **A32**, 751–767.

Sheldrick, G.M. (2008) A short history of *SHELX*. *Acta Crystallographica*, **A64**, 112–122.

Shikazono, N. (1978) Selenium content of acanthite and the chemical environments of Japanese vein-type deposits. *Economic Geology*, **73**, 524–533.

Spry, P.G. and Thieben, S.E. (1996) Two new occurrences of benleonardite, a rare silver-tellurium sulphosalt, and a possible new occurrence of cervelleite. *Mineralogical Magazine*, **60**, 871–876.

Suh, I-K., Ohta, H. and Waseda, Y. (1988) High-temperature thermal expansion of six metallic elements measured by dilatation method and X-ray diffraction. *Journal of Materials Science*, **23**, 757–760.

Wiegers, G.A. (1971) The crystal structure of the low-temperature form of silver selenide. *American Mineralogist*, **56**, 1882–1888.

Xiao, C., Xu, J., Li, K., Feng, J., Yang, J. and Xie, Y. (2012) Superionic phase transition in silver chalcogenide nanocrystals realizing optimized thermoelectric performance. *Journal of the American Chemical Society*, **134**, 4287–4293.

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