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Cervelleite, Ag_4TeS, a new mineral from the Bambolla mine, Mexico, and a description of a photo-chemical reaction involving cervelleite, acanthite and hessite

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Abstract : Cervelleite, Ag_4TeS, is a new mineral from the Bambolla mine, Moctezuma, Sonora, Mexico. It occurs as thin, 30 μm rims surrounding acanthite in hessite and as vermiform inclusions in the latter. Isotropic and opaque ; in plane-polarized light, it is slightly bluish to slightly greenish white. Colour values (for CIE illuminant *C*) are : x 0.302, y 0.311, $Y\%$ 37.8, λ_d 482, $P_e\%$ 3.5. A Vickers microhardness value (VHN_{10}) is 26. The strongest reflections in the X-ray powder pattern are [d_{hkl} in Å (I) (hkl)] : 6.29 (s) (012), 5.00 (vvs) (022), 4.64 (m) (122,003), 4.24 (vs) (113), 3.766 (ms) (123). The reflections are indexable in terms of a primitive cubic cell with a 14.03(1) Å and probable contents 24[Ag_4TeS], giving a calculated density of 8.53 $g.cm^{-3}$. Averaged electron microprobe analyses gave : Ag 73.0, Cu 0.1, Te 22.2, S 5.3, total 100.6 wt%.

Cervelleite, acanthite and hessite are altered rapidly and profoundly by light, in a surface reaction interpreted as photo-chemical in origin.

Key-words : cervelleite - new mineral, Bambolla mine - Moctezuma - Mexico, reflectance data, X-ray data, photo-chemical reaction.

Introduction

Cervelleite, a new mineral with the composition Ag_4TeS, was found in the same polished section as the recently described new mineral benleonardite (Stanley *et al.*, 1986). This section is one of a number cut from specimens collected (by AJC) from the spoil tips of the abandoned Bambolla mine, Moctezuma, Sonora, Mexico (29°41′ N, 109°43′ W), The deposit, in which tellurium minerals are abundant, was described by Gaines (1970). Cervelleite and its associated minerals, native silver, acanthite, hessite, benleonardite, pyrite and sphalerite, occur with dolomite and quartz as thin (1-2 mm) black and crumbly fracture fillings in an highly altered silicified 'rhyolite vitrophyre' (Williams, 1982).

The identification of cervelleite as a species distinct from acanthite was, initially, hampered by its unusual optical behaviour : in freshly polished section the minerals were clearly different in appearance, yet, in a relatively short period of time, when exposed to light, cervelleite altered to adopt the appearance of freshly polished acanthite (while acanthite, which in this assemblage is strongly light-sensitive, turned black). Thus, when the same section was examined independently and at different times by CJS and AJC after it had been exposed to light, there was a difference of opinion as to what was what. This is mentioned to emphasise the difficulty in identifying the mineral in any but the most freshly polished surfaces. The problem was resolved with a series of carefully controlled reflectance measurements, allied to a check on compositional changes in the polished surface by electron microprobe. The results of these experiments are described in detail as they clearly demonstrate an alteration

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phenomenon involving surface migration or diffusion which is interpreted as photo-chemical in origin.

Cervelleite is named to honour Dr Bernard Cervelle (1940-) of the Laboratoire de Minéralogie et Cristallographie, Université Pierre et Marie Curie, Paris, currently Chairman of the Commission on Ore Mineralogy of the International Mineralogical Association, for contributions to ore mineralogy, microscope-photometry, and the development of quantitative ore microscopy.

The mineral was approved by the Commission on New Minerals and Mineral Names of the I.M.A. and the type specimen, BM 1985,354 ; E.1161, is preserved at the British Museum (Natural History).

Mineral description

Cervelleite occurs as thin (30 μm) rims surrounding irregular inclusions of finely granular acanthite in hessite. The acanthite may be homogeneous, or intergrown with a much lower reflecting phase which, because of its minute grain size, remains unidentified. 'Bridges' of cervelleite sometimes connect the discrete acanthite inclusions (Fig. 1a). Cervelleite also forms vermiform inclusions in hessite (Fig. 1b) and is finely intergrown with benleonardite.

Optical properties

In freshly polished section, in plane-polarised light (at colour temperature of ~ 3300 K), cervelleite is a bluish to greenish white in comparison with hessite and has a lower reflectance. In turn, acanthite has a lower reflectance than cervelleite and appears darker blue. Cervelleite is isotropic, opaque and does not possess internal reflections.

Reliable micro-indentation hardness measurements could not be obtained because of the small grain size of cervelleite. A single measurement on the largest grain gave VHN_{10} 26. The indentation was slightly fractured and concave. There was no other evidence for fracturing in cervelleite.

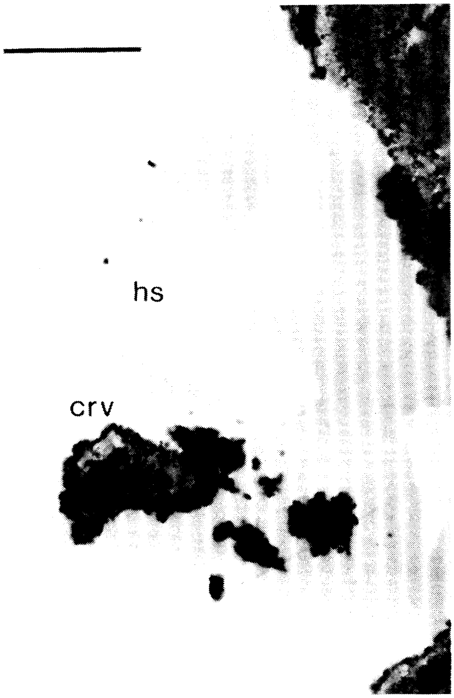

Fig. 1a. Reflected-light photomicrograph illustrating cervelleite (crv) as thin rims around altered acanthite in hessite (hs). Scale bar = 20 μm.

Fig. 1b. Reflected-light photomicrograph of vermiform cervelleite in hessite with cervelleite selvedges at hessite grain boundaries. The dark areas are altered acanthite. Scale bar = 20 μm.

The polishing technique (for reflectance measurements) was as described in Criddle *et al.* (1983) but the final buffing was with 0.25 μm diamond rather than with MgO. Measurements, both for freshly polished and altered surfaces of cervelleite, were made using the equipment and procedures described by Criddle *et al.* (1983). A Zeiss WTiC standard (no.314) was used ; the numerical apertures of the x40 air and oil objectives were adjusted to 0.28, and a plane-glass reflector was employed.

The reflectance spectra in air (Fig. 2) and in oil for freshly polished cervelleite are gently curved ; peaking at 420-440 nm, R and ^{im}R descend monotonically to 700 nm (Table 1), thus conforming with the visual impression of the mineral. This is further confirmed by the colour values calculated from the R and ^{im}R data (Table 2, column 1).

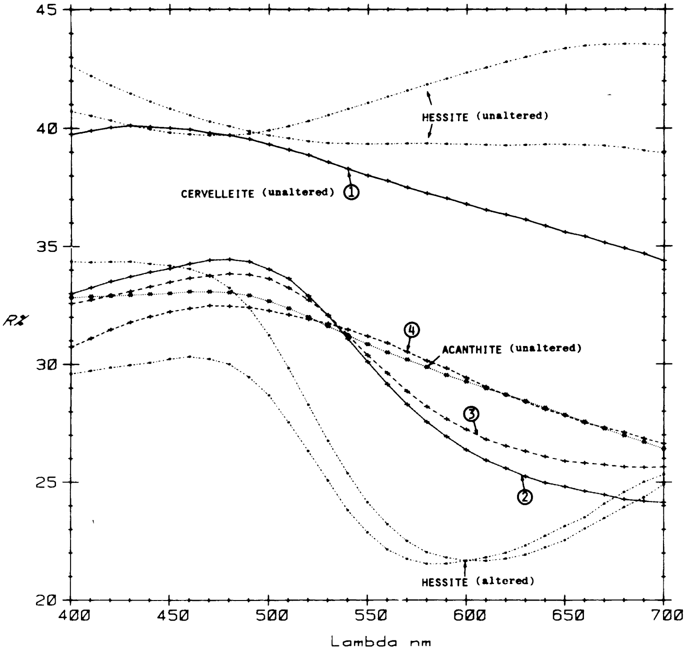

Fig. 2. Reflectance spectra for cervelleite, hessite and acanthite, and for altered hessite and cervelleite. The numbers attached to the cervelleite spectra correspond to the alteration sequence shown in Fig. 3 and described in detail in the text.

Chemical composition

Electron microprobe analyses of freshly polished cervelleite are summarised in Table 3 together with details of the instrumentation, operating conditions, and standards used. Cervelleite is not sensitive to the electron beam and normal counting times of 10 seconds on peak and background were employed. The formula calculated to a sum of 6 atoms (from the average of eight analyses) is :

$Ag_{3.99}Cu_{0.01}Te_{1.02}S_{0.97}$, or, ideally, Ag_4TeS.

X-ray data

Barely sufficient material could be extracted from the polished section to make a small mount for X-ray powder photography and this included some adhering acanthite. The resulting powder diffraction pattern was too weak for measurement by microdensitometer, therefore, only estimated intensities are given (Table 4). If, in future, more material should become available providing a stronger pattern, that pattern may contain lines too weak to have been observed here. The precision with which the lines were located was checked by repeated film measurement. Indexing, in terms of the

Table 1. R and ${}^{im}R$ data for cervelleite.

λnm	R	${}^{im}R$	λnm	R	${}^{im}R$
400	39.75	24.0	550	38.0	22.0
410	39.9	24.1	560	37.8	21.8
420	40.0	24.2	570	37.5	21.5
430	40.1	24.2	580	37.2	21.3
440	40.1	24.1	*590*	37.0	21.1
450	40.0	24.05	600	36.8	20.9
460	39.95	23.9	610	36.5	20.7
470	39.8	23.8	620	36.3	20.5
480	39.7	23.6	630	36.1	20.3
490	39.6	23.4	640	35.85	20.1
500	39.3	23.2	*650*	35.6	19.9
510	39.1	23.0	660	35.4	19.7
520	38.9	22.8	670	35.15	19.5
530	38.6	22.5	680	34.9	19.3
540	38.3	22.3	690	34.7	19.1
546	38.15	22.15	700	34.4	18.9

cubic cell, and the convergence of the refinement of the cell edge, provided further checks on the reliability of the *d*-spacings.

The primitive cubic cell edge is *a* 14.03(1) Å, derived from least-squares refinement of 13 indexed reflections. Four other indexed lines in Table 4 are close to strong lines of acanthite and are omitted from the refinement. Including these lines does not significantly alter *a* and slightly improves the agreement between observed and calculated *d*-values. It is, therefore, uncertain whether or not the four lines occur in the powder pattern of cervelleite but if any do, their intensities will be lower than shown in Table 4.

Two of the unindexed lines correspond to acanthite ; the remaining two, at 2.530 and 1.8174 Å, are presumed to come from an unidentified impurity, and do not match acanthite or hessite.

Table 2. Colour values in air relative to the CIE illuminant *C*.

	1	2	3	4	5	6		7	
						R_1	R_2	R_1	R_2
x	0.302	0.286	0.290	0.301	0.298	0.307	0.316	0.283	0.273
y	0.311	0.303	0.306	0.313	0.309	0.312	0.320	0.280	0.279
Y%	37.8	29.6	30.0	30.8	30.6	39.4	41.3	23.7	24.9
λ_d	482	484	485	487	483	464	587	477	478
P_e%	3.5	10.2	8.3	3.8	5.1	1.6	2.5	13.2	17.7

1. cervelleite
2-4. altered cervelleite
5. acanthite (data of Criddle & Stanley in QDF II, 1986)
6. hessite (data of Criddle & Stanley in QDF II, 1986)
7. altered hessite

Table 3. Electron microprobe data for cervelleite.

wt%:	Ag	Cu	Te	S	Total
1	73.0	---	21.8	5.2	100.0
2	73.9	0.1	21.8	5.4	101.2
3	73.1	0.1	22.1	5.2	100.5
4	73.0	0.1	21.9	5.5	100.5
5	72.6	0.1	22.8	5.1	100.6
6	73.2	0.2	22.4	5.2	101.0
7	72.6	0.1	22.7	5.1	100.5
8	72.8	0.1	22.2	5.3	100.4
9	73.0	0.1	22.2	5.3	100.6

1-4 analyses of single grains
5-8 analyses for grain measured for reflectance
9 average of analyses 1-8

Instrument: Cambridge Instruments Microscan IX
Accelerating voltage: 20 kV
Beam current: 25 nA on Faraday cage
Standards: Ag, Cu, Te and FeS
Radiations: AgLα, CuKα, TeLα, SKα

Because of the overlap of some lines in the powder pattern and the limited number of lines observed, not all the extinction conditions could be tested. Possible diffraction symbols are *P*---, *P*2_1--, *P*4_2--, *P*4_1--, *Pa*-- in the cubic system and these lead to the following space groups : *P*23, *Pm*3, *P*432, *P*43*m*, *Pm*3*m*, *P*$2_1$3, *P*$4_2$32, *P*$4_1$32, *P*$4_3$32, *Pa*3.

To derive the unit-cell contents, the densities of acanthite, Ag_2S (7.04) and aguilarite, Ag_4SeS (7.59) were scaled up in proportion to the formula weight to obtain estimates (8.40 and 8.26) for the density of cervelleite and these correspond to Z = 23.7 and 23.3. Z is therefore taken as 24, which is reasonable for a cubic cell, and the calculated density is then 8.53(2) g.cm^{-3}.

Table 4. X-ray powder diffraction data for cervelleite (Philips 11.46 cm diameter camera, Cu*K*α radiation : λ = 1.541838 Å).

h k l	$d_{obs.}$	$d_{calc.}$	*I*	
0 1 2	6.29	6.275	s	
1 1 2	5.74	5.729	w	
0 2 2	5.00	4.962	vvs	
122,003	4.64	4.678	m	
1 1 3	4.24	4.231	vs	
1 2 3	3.766	3.751	ms	
014,223	3.421	3.404	vw	
1 2 4	3.074	3.062	vw	ac
n.i.	2.842	-	m	ac
134,015	2.753	2.752	vw	
234,025	2.596	2.606	w	ac
n.i.	2.530	-	vw	
225,144	2.447	2.443	w	ac
0 1 6	2.304	2.307	w	
126,045,344	2.197	2.192	w	ac
3 3 5	2.137	2.140	vw	
n.i.	2.084	-	w	ac
4 4 4	2.026	2.026	vw	
117,155	1.9659	1.9651	vw	
146,027	1.9247	1.9276	vw	
n.i.	1.8174	-	vw	

n.i. = not indexed
ac = lines affected by acanthite impurity

Relationship of cervelleite to other minerals

Compositionally, cervelleite is the tellurium analogue of aguilarite. In addition, several unnamed minerals have been described which may be closely related to cervelleite. Mineral Z of Aksenov *et al.* (1969) is of similar composition, is isotropic, and has a very similar reflectance spectrum to cervelleite. An intriguing feature of this mineral, which was found in the Zyranov deposit in the Altai, U.S.S.R., is its association with hessite and a mineral with a composition similar to that of benleonardite from Bambolla. Other unnamed minerals with compositions not dissimilar to cervelleite were observed by Karup-Møller (1976) and Gadzheva (1985). Compositional data for these, and for mineral Z, are compared with those of cervelleite in Table 5. Mineral B of Karup-Møller (1976), described as distinctly anisotropic, was found, at Ivigtut, southern Greenland, in a sulphosalt assemblage which is quite different from the assemblage at Bambolla, the only similarity being an association with acanthite. Gadzheva's unnamed $(Ag,Cu)_4TeS$ mineral, from the Shadiitsa deposit, central Rhodopes, Bulgaria, is also described as anisotropic but, because it was microgranular, *R* values were measured on composite grains. The two spectra listed bracket those of cervelleite. At Shadiitsa, the mineral was found in association with hessite as irregular grains and myrmekitic intergrowths. VHN measurements for mineral Z (load not specified) gave values of 84-87, while those for the unnamed $(Ag,Cu)_4TeS$ mineral gave VHN_{10-25} 74-86, both appreciably harder than our single value for cervelleite.

Cervelleite : alteration phenomena

The changes in the appearance of cervelleite and its associated minerals during the routine examination of the polished section were not, at first, regarded as exceptional or remarkable. These examinations were performed, as usual, using almost the full numerical apertures of the objectives. In the relatively short periods (rarely more than 10 minutes) in which observations were made the only significant change was to acanthite, which blackened. Repeated examination over several days revealed, however, appreciable changes in the appearance of

Table 5. Comparison of the compositional data for cervelleite and cervelleite-like phases.

	cervelleite	min. Z 1	min. B 2		Unnamed phase 3	
Ag	73.0	68.0	68.6	65.5	68.12	
Cu	0.1	-	2.5	1.5	3.36	
Bi	-	-	0.3	1.0	-	
Pb	-	-	0.8	1.5	-	
Te	22.2	22.0	23.0	25.4	22.54	
Se	-	-	-	-	0.10	
S	5.3	7.0	5.8	5.2	5.62	
Total	100.6	97.0	101.0	100.1	99.74	wt%

References: 1: Aksenov <u>et al.</u>, 1969; 2: Karup-Møller, 1976; 3: Gadzheva, 1985.

cervelleite and hessite. These changes were, at first, ascribed to tarnishing or oxidation of the polished surface. It was only when reflectance measurements were made on cervelleite that it was appreciated that alteration was occurring very rapidly because repeated measurements of the same grain (not re-buffed), within a two-hour period, were not reproducible. As time passed, the reflectance of the mineral was dropping and its dispersion was changing. The logical conclusion was that cervelleite, like many other silver minerals (including acanthite) is light-sensitive. In itself, however, this would not explain an associated phenomenon – a progressive, and time-related, change in the appearance of the surrounding hessite. It was decided, therefore, to conduct a series of reflectance measurements on cervelleite and hessite under controlled conditions. Before doing so, the freshly polished specimen was briefly examined and then stored in a light-tight box. Upon re-examination, 24 hours later, its appearance was unchanged, *i.e.,* the effect of oxidation on cervelleite, or on any of the associated minerals, if such had occurred, was imperceptible.

The first series of measurements was on freshly polished surfaces of cervelleite which were illuminated in isolation. Selection and levelling of the areas for measurement was made within less than three minutes of exposure to the microscope lamp (under conditions of reduced illumination). Immediately upon levelling, a ×40 measuring-objective was introduced ; its numerical aperture (NA) was reduced by means of the illuminator-aperture-diaphragm (IAD) to 0.28, and the illuminated field was restricted to a diameter of 15 μm by the illuminator-field-stop (IFS). Thus cervelleite, and cervelleite alone, was illuminated. The effective diameter of the photometer-stop (PhS) was 8 μm. Illumination was increased to the full output of the 100 W, 12 V, quartz-halogen bulb, and reflectance measurements were made by the wavelength-scanning procedure (Galopin and Henry, 1972) from 400 to 700 nm at an interval of 10 nm. To minimise the period during which cervelleite was illuminated, results were taken from a single scan (duration 90 seconds). Repetition of this procedure on other (freshly polished) areas of cervelleite produced reflectance spectra which varied by less than the generally accepted measurement error for a single grain of ± 0.5 % (relative). A representative reflectance spectrum (spectrum 1) is shown in Fig. 2. At the completion of these measurements, one of the measuring areas was kept illuminated for 12 hours, during which time it was measured several times. The dispersion of the reflectance remained constant, but the luminance (*Y*%) dropped by 1-2 % absolute. This reduction may indicate that cervelleite is very weakly photo-sensitive ; equally it may be in response to surface oxidation (but see introductory remarks).

The second series of measurements was made on an area of the specimen centred on cervelleite but including, in the illuminated field, acanthite and hessite. The IFS was removed, providing an illuminated field of 180 μm diameter (the NA was kept at 0.28), which was lit continuously for 8 hours. Within 45 minutes, the reflectance of the cervelleite appeared to have dropped dramatically. Measurement (on re-insertion of the IFS, and using the same procedure as described above) confirmed this, and revealed a remarkable change in the dispersion of the reflectance (spectrum 2, Fig. 2) : at 400 nm *R* had dropped by 6 % and at 700 nm by more than 10 %. Comparison of this curve with one for acanthite (QDF II, Acanthite 1, Criddle and Stanley, 1986) revealed significant differences in their dispersion (Fig. 2). There was little difference in a reflectance spectrum measured 60 minutes later, and only a moderate change at the end of 8 hours of continuous illumination (spectrum 3, Fig. 2).

At this stage the lamp was switched off and the specimen was covered and left for 18 hours before re-measurement. The new spectrum (spectrum 4, Fig. 2) was akin to that of acanthite and markedly different from spectra 1 and 2.

During this experiment, the appearance of the hessite surrounding cervelleite had changed rapidly in the first 45 minutes of exposure of the full field to light, and continued to change, although more slowly, for a further 135 minutes. At first, a mauve 'rim' concordant with the cervelleite-hessite boundary appeared. As time passed, this developed gradually and symmetrically away from the boundary into the hessite. As the alteration progressed outwards, it changed in colour, becoming much darker (darker even than the altered cervelleite) and finishing as a somewhat purplish blue. The reflectance spectra of the altered hessite (Fig. 2) confirm these observations and clearly illustrate the enormous reduction in luminance combined with massive changes in the dispersion of the measured spectra and of the bireflectance.

The alteration phenomena observed during this second series of measurements are shown schematically in Fig. 3, and the changes in R are summarised in the calculated colour values (Table 2). The complete reflectance data are available for inspection at the British Museum (Natural History). To summarise :

1. Cervelleite, when illuminated in isolation, undergoes a slight reduction in reflectance, but its dispersion is unaltered. This reduction may be caused by a weak photosensitive reaction, surface oxidation (unrelated to light), or a combination of both phenomena.
2. Rapid and profound changes in the reflectance of cervelleite (and its dispersion) occur when it is illuminated together with acanthite and hessite. In this assocation, hessite undergoes equally profound changes in its reflectance properties, as does acanthite, which blackens.
3. The alteration phenomena are progressive, spreading outwards from a core of severely altered acanthite. They eventually stop, at which time the surface is unaffected by further illumination.

In the simplest terms, these effects may be interpreted as the result of the altered surface acting as an interference layer and, in the case of cervelleite and hessite, as a natural anti-reflection coating. Such layers, or films, are invariably too thin for their composition to be determined directly by electron microprobe (*cf.* Vaughan *et al.*, 1987, on bornite). Given the depth of penetration of the electron beam, the best that can be hoped for is that significant differences might be found between the composition of the unaltered substrate and that of the coating and substrate combined. This proved to be the case for cervelleite and hessite. Acanthite was neglected as unsuitable for micro-analysis because, at the completion of the reflectance measurements, it had become heavily pitted and blackened.

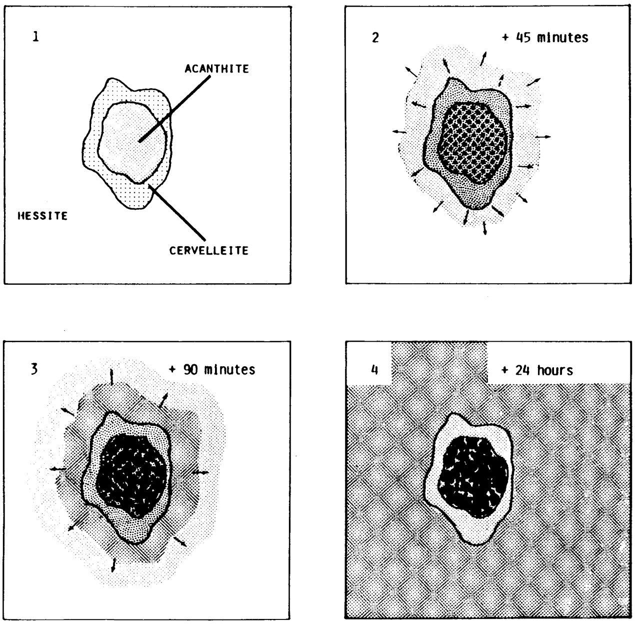

Fig. 3. Schematic representation of the alteration phenomena : 1. a freshly polished surface containing acanthite, cervelleite and hessite. In terms of R, acanthite $<$ cervelleite $<$ hessite ; 2. black spots appear on acanthite, cervelleite's reflectance drops and an alteration zone starts to affect hessite ; 3. acanthite is almost completely blackened, cervelleite is unchanged, but hessite, which is much darker immediately adjacent to cervelleite, continues to alter ; 4. acanthite is unchanged, cervelleite now resembles unaltered acanthite, and hessite is uniformly dark (for a distance up to 2× the diameter of the acanthite/cervelleite inclusion). Each block is about 450 μm across.

The analyses were made with pure metal and troilite standards and were repeated using hessite as the Ag and Te standard (without significant difference in the results). A cursory examination of the analyses (Table 6) suggests that the altered surfaces of cervelleite and hessite had gained Ag and S and lost Te. When these figures are recalculated to (Ag+Cu) = 4 for cervelleite and (Ag+Cu) = 2 for hessite (Table 7), a slightly different picture emerges : sulphur is increased and tellurium is lost, but there is little, if any, change in the proportions of (Ag+Cu) to (Te+S).

Table 6. Summary of the compositional differences between freshly polished and altered hessite and cervelleite (electron microprobe operating conditions and standards as for Table 3).

wt%	Ag	Cu	Te	S	Total
cervelleite					
fresh	72.8	0.1	22.5	5.2	100.6
altered	74.1	0.1	20.1	5.9	100.2
difference	+1.3	-	-2.4	+0.7	
hessite					
fresh	62.4	0.1	37.8	0.1	100.4
altered	63.0	-	36.9	0.4	100.3
difference	+0.6	-0.1	-0.9	+0.3	

A tentative explanation that would accord with these data (and would account for the optical phenomena) is that exposure to light reduced the acanthite core, releasing sulphur which migrated into the surrounding cervelleite and hessite. Tellurium must also have migrated, either into the altered acanthite core, or into the hessite. The latter possibility is eliminated as there is no change in the (Te+S) : (Ag+Cu) ratio in hessite. Counter-migration of Te into the altered acanthite core is favoured but, unfortunately, given the nature of the damaged acanthite surface, cannot be confirmed. This mechanism satisfactorily explains the continued change in the reflectance spectrum of the altered cervelleite during the 18 hour period when it was not illuminated : the counter-migration of S and Te could continue for some time once the initial release of sulphur had occurred.

Table 7. Summary of the compositional differences in atomic % between freshly polished and altered surfaces of cervelleite and hessite.

	fresh		altered		difference	
cervelleite (calculated to Ag+Cu = 4):						
Ag	3.990		3.991			
Cu	0.010		0.009			
Te	1.043	)2.002	0.915	)1.984	-0.128	)-0.018
S	0.959		1.069		+0.110	
hessite (calculated to Ag+Cu = 2):						
Ag	1.995		2.000			
Cu	0.005		-			
Te	1.021	)1.032	0.990	)1.033	-0.031	)+0.001
S	0.011		0.043		+0.110	

Partial and indirect support for this hypothesis was supplied by the observed response to light of an acanthite-free intergrowth of cervelleite and hessite : the appearance of a freshly polished intergrowth of these minerals was unchanged after illumination for 8 hours, indicating that the alteration phenomena described above do not take place in the absence of acanthite. This observation prompted a final experiment : a test of the effect of a beam of light restricted to a small area of acanthite in an acanthite-cervelleite-hessite intergrowth. The illuminated area, 15 μm in diameter was restricted to acanthite by the IFS, and its centre was situated 100 μm from the nearest boundary with cervelleite. It was lit continuously for 8 hours. Within one minute of exposure to the light, the first black spots appeared in the illuminated field. At half-hourly intervals, the IFS was removed and the full-field (180 μm in diameter) was briefly examined. For four hours, no change was detected outside the illuminated field (within, the acanthite had almost completely blackened). At this time, although the acanthite between the illuminated field and the cervelleite boundary appeared to be unaltered, a few black spots had started to appear at the boundary. As time passed, these spots became more numerous, finally merging into a thin, less than 2 μm, black line defining the boundary. Immediately adjacent to the boundary, the cervelleite appeared to have changed colour, and 'whitened' or 'bleached'. This effect may be real, or it may result from the eye being misled by the large difference between the luminance of the cervelleite and the blackened acanthite.

Discussion and conclusions

It is somewhat surprising, given the current interest in the surface properties of semiconducting minerals, that photo-conducting minerals have received scant attention. Little original work has been published in this field since the observations of Guild (1917), Whitehead (1917) and Stephens (1931). Stephens, who used very intense and unfiltered arc lamps and 1000 W filament lamps, observed that acanthite blackened within one minute's exposure to the lamps and that a yellow-brown sublimate coated his microscope objectives. He attributed the blackening and the sublimate to the production of free silver and sulphur respectively. Undoubtedly, heat from the lamps contributed to these reactions, since chalcosine recrystallised under these conditions and its inversion point is approximately 103 °C. Such extreme temperatures are not realised with modern microscope-photometers : the instrument used in the current investigation was tested under the 0.28 effective numerical aperture operating conditions employed for all measurements : the temperature rose gradually from ambient (22 °C) to 22.7 °C within three minutes and then stabilised. However, accepting the limitations of Stephens' apparatus, there is no reason to doubt his conclusions that the rate and nature of the surface alteration are dependent on the intensity and wavelength of the incident radiation and on the crystallographic orientation of the mineral.

Acanthite and hessite are extrinsic semiconductors (Deren *et al.,* 1958) as, it is reasonable to suppose, is cervelleite. Hence, the photo-sensitivity of acanthite, at least, may be accounted for by electromagnetic radiation providing : 1. the energy required to transfer electrons from the valence to the conduction band (assuming that the photon-energy is larger than the band gap), or 2. where the energy of the incident photon falls below the threshold for the production of pairs of holes and electrons, it may still cause ionisation of donor and acceptor impurity atoms and produce mobile electrons or holes depending on the nature of the impurity (Kittel, 1966). The second mechanism is plausible given the low activation energy (0.45 eV, Allen and Moore, 1959) for ionic mobility in acanthite, $Ag+$ and $Cu+$ being the most mobile ions known. Indeed, acanthite is the only known example of a mineral in which ionic conductivity may exceed electronic conductivity (Shuey, 1975). Either mechanism would, however, increase the number of electrons in the conduction band available for trapping by donor atoms, thus producing free silver.

Two other factors are pertinent when dealing with n-type semi-conductors such as acanthite and hessite, these are that free electrons/charge carriers may be derived from trace impurity atoms in solid solution, or from vacancies, *i.e.* non-stoichiometry, and that impurities and imperfections may dramatically affect the electronic properties of semi-conductors (Shuey, 1975). Indeed, conductivity may be increased a thousandfold by the presence of as little as 10 ppm impurity (Kittel, 1966). This latter factor may well explain the extreme variation in photosensitivity observed for acanthite from different localities (*cf.* Barton *et al.,* 1978, on uytenbogaardtite).

Singly, or in combination, these mechanisms plausibly account for conductivity in acanthite, the most photo-responsive ore mineral ; they also accord with the observations of Stephens (1931). However, they fall short of explaining our observations on the assemblage, acanthite-cervelleite-hessite. Here, we have shown that the surface alteration of cervelleite and hessite requires the photo-activation of acanthite. Sulphur, rather than subliming, apparently diffused through the surface film from acanthite to cervelleite to hessite. At the same time it appears that counter-migration of tellurium occurred. This is in direct contrast to diffusion within the crystal structure of ionic compounds, where it is the smaller cations which diffuse through a fixed framework of large anions. The difference must rest, at least in part, on the less cohesive nature of the surface film. The simplest interpretation of the blackening of the boundary between acanthite and cervelleite, when only the centre of the acanthite grain was illuminated, is that silver migrated. If we accept that an atom as large as Ag can migrate within the surface, it is not unreasonable to suppose that Te and S may also migrate.

Clearly, there is much more to be learned about the photo-chemistry of surface films in the silver ore minerals. Their absorption spectra may readily be determined from reflectance measurements in two media but, for this to be useful, it will be necessary to cover the spectrum from the ultra-violet to the near infra-red. The chief limiting factor is that to illuminate these minerals is to change them. As serious a limitation, in the case of cervelleite, is the paucity of the naturally occurring material. With fast-reading electronics available for modern microscope-photometers, the first problem can be overcome ; synthesis of Ag_4TeS is proving more difficult.

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