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CALVERTITE, $\text{Cu}_5\text{Ge}_{0.5}\text{S}_4$, A NEW MINERAL SPECIES FROM TSUMEB, NAMIBIA

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ABSTRACT

The sulfide-rich matrix of a partly oxidized specimen from the Tsumeb mine, Tsumeb, Namibia, consists mainly of renierite, tennantite, gallite, chalcocite, and the new mineral calvertite, simplified as $\text{Cu}_5\text{Ge}_{0.5}\text{S}_4$, which is named after Lauriston D. Calvert (1924–1993) of the National Research Council, Ottawa, Canada. Calvertite occurs as anhedral grains, up to 100 μm across, that are outlined by a network of chalcocite veinlets of micrometric width. In reflected light, calvertite is opaque, pale bluish grey, and isotropic. Reflectance percentages in air are 26.3 (470 nm), 23.1 (546), 22.2 (589), and 21.5% (650). The mineral is brittle, macroscopically black with a black streak, and has a hardness of 4 to 5, a conchoidal to uneven fracture, and no cleavage. Single-crystal X-ray study indicated *F*-centered cubic symmetry, *a* 5.337(3) Å; the structure has not been solved, and the powder-diffraction pattern has only four lines [*d* in Å(*I*)(*hkl*)]: 3.053(100)(111), 2.639(10)(200), 1.869(90)(220), and 1.595(30)(311). An electron-microprobe analysis gave Cu 63.10, Fe 1.66, Zn 0.55, Ge 5.76, As 1.50, Ga 0.36, V 0.05, S 26.63, total 99.60 wt.%, corresponding to $(\text{Cu}_{4.782}\text{Fe}_{0.143}\text{Zn}_{0.041}\text{Ga}_{0.025}\text{V}_{0.005})_{\Sigma 4.996}(\text{Ge}_{0.382}\text{As}_{0.096})_{\Sigma 0.478}\text{S}_4$ on the basis of *S* = 4 atoms and *Z* = 1. It is likely that the structure is disordered, and the measured unit-cell is the subcell of a compound whose ordered equivalent has the simplified formula $\text{Cu}_{10}\text{GeS}_8$.

Keywords: calvertite, new mineral species, Cu–Ge sulfide, electron-microprobe analysis, reflectance data, Tsumeb mine, Namibia.

SOMMAIRE

La matrice riche en sulfures d'un échantillon partiellement oxydé provenant de la mine Tsumeb, à Tsumeb, en Namibie, contient surtout renierite, tennantite, gallite, chalcocite, et la nouvelle espèce minérale calvertite, ayant la formule simplifiée $\text{Cu}_5\text{Ge}_{0.5}\text{S}_4$. Le nom honore Lauriston D. Calvert (1924–1993), du Conseil National de la Recherche à Ottawa, Canada. La calvertite se présente en grains xénomorphes atteignant un diamètre de 100 μm ; leur pourtour est décoré par un réseau de veinules micrométriques de chalcocite. En lumière réfléchie, la calvertite est opaque, gris bleuâtre pâle, et isotrope. Nous en avons mesuré la réflectance dans l'air: 26.3 (470 nm), 23.1 (546), 22.2 (589), et 21.5% (650). Le minéral est cassant, et macroscopiquement noir avec une rayure noire. Sa dureté est entre 4 et 5, elle possède une fracture conchoïdale à inégale, et semble dépourvue de clivage. Les données de diffraction obtenues sur monocristal indiquent une symétrie cubique, un réseau avec *F* centré, et un paramètre réticulaire égal à *a* 5.337(3) Å; nous n'avons pas résolu la structure, et le spectre de diffraction (méthode des poudres) ne montre que quatre raies [*d* en Å(*I*)(*hkl*)]: 3.053(100)(111), 2.639(10)(200), 1.869(90)(220), et 1.595(30)(311). Une analyse

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avec une microsonde électronique a donné Cu 63.10, Fe 1.66, Zn 0.55, Ge 5.76, As 1.50, Ga 0.36, V 0.05, S 26.63, total 99.60% (poids), ce qui correspond à $(\text{Cu}_{4.782}\text{Fe}_{0.143}\text{Zn}_{0.041}\text{Ga}_{0.025}\text{V}_{0.005})_{\Sigma 4.996}(\text{Ge}_{0.382}\text{As}_{0.096})_{\Sigma 0.478}\text{S}_4$ sur une base de S = 4 atomes et Z = 1. Il semble probable que la structure est désordonnée, et que la maille élémentaire mesurée est une sous-maille d'un composé dont l'équivalent ordonné possède la formule simplifiée $\text{Cu}_{10}\text{GeS}_8$.

Mots-clés: calvertite, nouvelle espèce minérale, sulfure de Cu–Ge, données de microsonde électronique, données de réflectance, mine Tsumeb, Namibie.

INTRODUCTION

The Tsumeb mine at Tsumeb, Namibia, is one of the world's most famous mineral localities. The deposit, which formed a vertically zoned, discordant pipe-like structure in fractured and brecciated Precambrian dolomite and sandstone (Lombaard *et al.* 1986), has been the source of many museum-quality oxidation-induced minerals and is the type locality for more than 50 mineral species. Mining of the Tsumeb deposit occurred intermittently for decades at a small scale, and the subsequent main exploitation period was from 1948 to nominal closure in 1996. Total production was about 30 Mt grading 10% Pb, mainly as galena, 3.5% Zn, mainly as sphalerite, and 4.3% Cu, principally as chalcocite, bornite, tennantite, and enargite (Lombaard *et al.* 1986, Melcher 2003). However, the Tsumeb ores also contained notably high concentrations of various other elements, such as Ag, Cd, As, Sb, and Ga, and the mine also represents the world's largest occurrence of Ge in sulfide minerals (Melcher 2003). Within the orebody were pockets, some attaining several tens of tonnes, that contained high-grade ores of germanite $[\text{Cu}_{26}\text{Fe}_4\text{Ge}_4\text{S}_{32}]$ and renierite $[(\text{Cu},\text{Zn})_{11}(\text{Ge},\text{As})_2\text{Fe}_4\text{S}_{16}]$ (Lombaard *et al.* 1986).

During the examination of the specimen that hosts holotype gallobeudantite, $\text{PbGa}_3[(\text{AsO}_4)(\text{SO}_4)]_2(\text{OH},\text{H}_2\text{O})_6$, from the Tsumeb mine (Jambor *et al.* 1996), the matrix of the specimen was observed to consist largely of partly oxidized Cu-rich massive sulfides, among which was a sulfide mineral that remained unidentified. Further study of the unidentified mineral has led to the definition of a new species of simplified composition $\text{Cu}_5\text{Ge}_{0.5}\text{S}_4$. The mineral is named calvertite in honor of Lauriston (Larry) Derwent Calvert (1924–1993) of the National Research Council, Ottawa, Canada, in recognition of his numerous studies of metallic phases and his important contributions to the Powder Diffraction File produced by the International Centre for Diffraction Data. The new mineral and name have been approved by the Commission on New Minerals, Nomenclature and Classification, IMA (2006–30). Cotype polished sections of calvertite are in the Canadian Museum of Nature, Ottawa (CMNMC 85731), and the Natural History Museum, London, U.K. (BM 2004, 78).

OCCURRENCE

The calvertite-bearing specimen was originally about $3 \times 5 \times 1.5$ cm and is now smaller because of offcuts for the two polished sections of the sulfide-rich matrix. The unoxidized portion of the matrix consists largely of renierite and calvertite, with local tennantite and inclusions of gallite $[\text{CuGaS}_2]$. The major sulfides, *i.e.*, renierite and calvertite, are concentrated in bands rather than uniformly intergrown, and calvertite locally cuts renierite and inclusions of tennantite in renierite (Fig. 1). Brittle fracturing apparently led to the deposition of numerous late-stage chalcocite-filled veinlets of micrometric width. In calvertite-rich portions, the chalcocite forms a network that has produced a granular texture in which the calvertite is anhedral and commonly elongate to elliptical (Fig. 1a); the largest homogeneous grains rarely attain 100 μm across. Along the contact between calvertite and the network of veinlets of chalcocite is another Cu sulfide, or possibly a mixture of digenite and djurleite. Among the associated non-sulfide minerals in the specimen are goethite, hematite, quartz, veinlets of Hg-rich native silver, stolzite $[\text{PbWO}_4]$, otjissimeite $[\text{PbGe}_4\text{O}_9]$, and vugs that contain various members of the alunite supergroup. The principal sulfide minerals are of hypogene origin, and the oxide minerals are supergene. However, this assemblage does not necessarily indicate that the calvertite-bearing specimen was collected near the surface of the Tsumeb deposit; the pipe was mined to a depth of about 1700 m below surface, and within the orebody were large but discontinuous zones of oxidation that extended to a depth of >1300 m (Lombaard *et al.* 1986, Melcher 2003).

PROPERTIES AND COMPOSITION

Calvertite is macroscopically black and has a metallic luster, a black streak, brittle tenacity, an irregular to conchoidal fracture, and no cleavage, parting, or fluorescence. The Mohs hardness is 4 to 5, and VHN_{25} is 283 (268–307) kg/mm^2 . The mineral is opaque, and in reflected light is pale bluish grey and without internal reflections, pleochroism or birefractance. The veining by chalcocite suggests an anhedral morphology, and the chalcocite-enclosed grains of calvertite are opti-

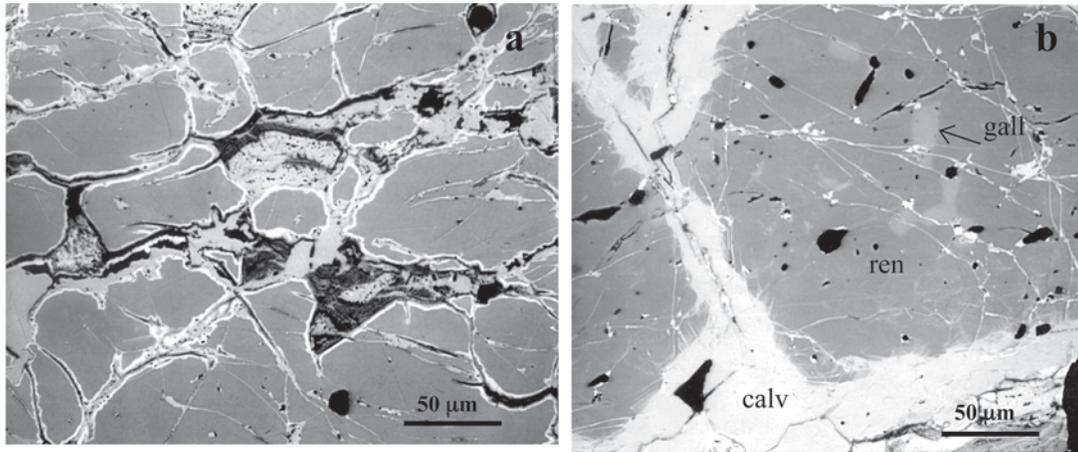


FIG. 1. SEM images of (a) the typical appearance of massive calvertite, which makes up the bulk of the image. The granular texture is made apparent by the presence of a thin rind of chalcocite (white) on the calvertite grains. The interstitial material consists of pits and heterogeneous oxidation-derived products. (b) Renierite (ren) with inclusions of gallite (gall) cut by calvertite (calv); all are cut by thread-like veinlets of chalcocite (white).

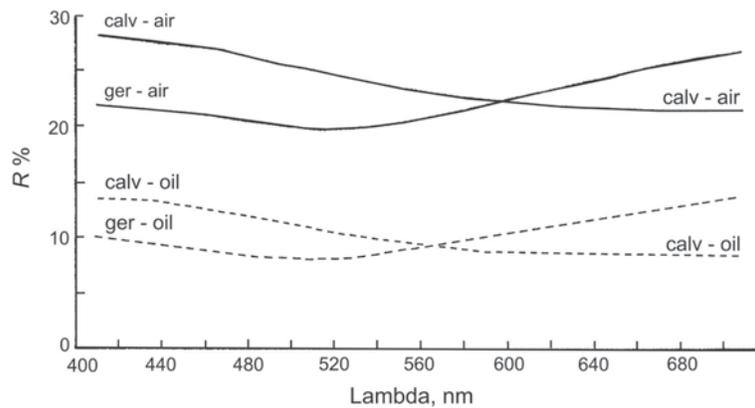


FIG. 2. Plots showing the distinct differences in the reflectances of calvertite (calv) and germanite (ger) in air and in oil. Data for germanite are by R. Caye and J. Padeloup (Criddle & Stanley 1993).

cally uniform and isotropic. Reflectance percentages measured in air and in oil are given in Table 1. The data were obtained using a SiC standard, an oil with an index of refraction of 1.515, and the methodology of Stanley *et al.* (2002). The optical properties of calvertite do not match those of germanite or any mineral in the COM data file (Fig. 2).

Electron-microprobe analysis of eight grains of calvertite gave the composition listed in Table 2. The microprobe, a JEOL 8900 instrument at CANMET, Ottawa, was operated in the wavelength-dispersion

mode at 20 kV and 20 nA, with a nominal beam-diameter of 1 μm . We used CuS as a standard for Cu ($K\alpha$), chalcopyrite for Fe ($K\alpha$) and S ($K\alpha$), sphalerite for Zn ($K\alpha$), InAs for As ($L\alpha$), GaS for Ga ($K\alpha$), and Ge and V metals for Ge ($K\alpha$) and V ($K\alpha$), respectively. Counting times were 40 s except for Cu (10 s) and S (30 s). Minimum detection-limits ranged from 180 ppm for Zn to 560 ppm for As. The results of the analyses, on the basis of four atoms of S per formula unit, correspond to the general formula $(\text{Cu,Fe,Zn,Ga,V})_{\Sigma 5.00}(\text{Ge,As})_{\Sigma 0.48}\text{S}_4$, simplified as $\text{Cu}_5\text{Ge}_{0.5}\text{S}_4$. The

simplified formula requires Cu 65.88, Ge 7.53, S 26.59 wt.%. The data in Table 2, and results of other analyses, indicate that there is little compositional variation from grain to grain. The electron-microprobe composition of the associated renierite corresponds to $(\text{Cu}_{10.55}\text{Zn}_{0.49})_{\Sigma 11.04}(\text{Fe}_{3.80}\text{Ga}_{0.10})_{\Sigma 3.90}(\text{Ge}_{1.65}\text{As}_{0.39})_{\Sigma 2.04}\text{S}_{16}$, and that of tennantite approximates $\text{Cu}_6\text{Cu}_4(\text{Zn}_{1.7}\text{Cu}_{0.1}\text{Fe}_{0.1}\text{Ga}_{0.1})_{\Sigma 2.0}(\text{As}_{3.9}\text{Ge}_{0.1})_{\Sigma 4.0}\text{S}_{13}$.

The empirical formula for calvertite and the single-crystal unit cell give a D_{calc} of 5.239 g/cm³ for $Z = 1$. The composition of calvertite differs substantially from that of germanite (Table 3), and calvertite does not seem to be related to any other Cu or Cu-Ge sulfide, either natural or synthetic. In terms of compositional similarity, a phase synthesized by Wang (1976) was reported to be $\text{Cu}_{4.33}\text{Ge}_{0.67}\text{S}_5$, which for $S = 4$ atoms per formula unit corresponds to $\text{Cu}_{3.47}\text{Ge}_{0.54}\text{S}_4$. The phase is hexagonal, and the X-ray powder-diffraction pattern is unlike that for calvertite. An orthorhombic compound synthesized by Onoda *et al.* (1999), given as $\text{Cu}_5\text{GeS}_{4.5}$ in PDF 89-6686, likewise has little similarity to the X-ray character of calvertite.

X-RAY RESULTS

One of the concerns in defining calvertite as a new species was that its X-ray powder pattern has only four measurable diffraction lines (Table 4), and the lines are not definitive in identifying the mineral. For example,

TABLE 1. REFLECTANCE DATA FOR CALVERTITE

λ	R_{air} %	R_{oil} %	λ	R_{sp} %	R_{cal} %
400 nm	28.0	13.5	560 nm	22.8	9.1
420	27.6	13.3	580	22.3	8.8
440	27.1	12.8	589	22.2	8.7
460	26.7	12.3	600	22.1	8.6
470	26.3	11.9	620	21.8	8.5
480	25.9	11.5	640	21.6	8.5
500	25.0	10.8	650	21.5	8.5
520	24.2	10.1	660	21.5	8.5
540	23.5	9.6	680	21.5	8.4
546	23.1	9.4	700	21.5	8.4

TABLE 2. THE COMPOSITION OF CALVERTITE*

	wt.%	range	s.d.	formula ratio, S = 4
Cu	63.10	62.55 - 63.70	0.41	Cu 4.782
Fe	1.66	1.49 - 1.84	0.13	Fe 0.143
Zn	0.55	0.22 - 0.92	0.24	Zn 0.041
Ge	5.76	5.58 - 5.98	0.12	Ga 0.025
As	1.50	1.35 - 1.56	0.08	V 0.005
Ga	0.36	0.31 - 0.39	0.03	Σ 4.996
V	0.05	0.04 - 0.05	0.01	
S	26.63	26.40 - 26.78	0.12	Ge 0.382
				As 0.096
Sum	99.60	99.15 - 99.75		Σ 0.478

s.d.: standard deviation. * Electron-microprobe data.

the compound Cu_3GeS_4 synthesized by Naiding Wang (PDF 41-1032), although not compositionally close to calvertite, also has only four powder-diffraction lines, all of which agree moderately well with those of calvertite. Moreover, the powder pattern of calvertite also agrees well with the strongest diffraction lines of renierite (tetragonal), germanocolusite (cubic), and germanite (cubic).

Single-crystal X-ray precession data for an analyzed grain of calvertite removed from a polished section were obtained with Zr-filtered Mo X-radiation. The results confirmed the optical indication that the mineral is cubic. The precession and powder data indicate an a of 5.29(1) Å. The observed systematic extinctions for hkl are $h + k = 2n$, $k + l = 2n$, and $l = 2n$; for hhl , $h + l = 2n$; for $0kl$, $k = 2n$, $l = 2n$; and for $00l$, $l = 2n$. Thus, the allowed space-groups are $Fm\bar{3}m$, $F432$, and $F43m$, and the diffraction aspect is F^*3^* . The same crystal on the same mount from which the precession results were obtained in 1998 no longer yielded diffraction spots when examined with a CCD unit in 1999 at the University of Manitoba, nor when re-examined in 2005 with an up-to-date CCD unit at the University of British Columbia. Despite this indication that calvertite might be unstable, a re-run of the original powder-diffraction mount showed that the X-ray pattern of the mineral had not changed after 11 years.

Single-crystal data from a second analyzed grain were collected by J.F. Britten in 2000 at McMaster University. The collection, which was done with a Siemens/Bruker instrument with a rotating-anode generator and a CCD detector, yielded 317 reflections

TABLE 3. COMPARATIVE COMPOSITIONS OF Cu-Ge SULFIDE MINERALS*

Mineral	Formula	System	Me:S
briartite	$\text{Cu}_{16}\text{Zn}_9\text{Ge}_9\text{S}_{32}$	tetragonal	32:32
catamarcaite [†]	$\text{Cu}_{24}\text{Ge}_6\text{W}_4\text{S}_{32}$	hexagonal	32:32
germanite	$\text{Cu}_{28}\text{Fe}_6\text{Ge}_6\text{S}_{32}$	cubic	34:32
renierite	$(\text{Cu,Zn})_{22}\text{Fe}_6(\text{Ge,As})_2\text{S}_{32}$	tetragonal, pseudocubic	34:32
germanocolusite	$\text{Cu}_{28}\text{V}_2(\text{Ge,As})_2\text{S}_{32}$	cubic	34:32
maikainite	$\text{Cu}_{20}(\text{Fe,Cu})_2\text{Mo}_2\text{Ge}_6\text{S}_{32}$	cubic	34:32
ovamboite	$\text{Cu}_{20}(\text{Fe,Cu,Zn})_6\text{W}_2\text{Ge}_6\text{S}_{32}$	cubic	34:32
calvertite	$\text{Cu}_{20}\text{Ge}_6\text{S}_{32}$	cubic	44:32
putzite	$\text{Cu}_{42}\text{Ge}_6\text{S}_{32}$	cubic	48:32

* for S = 32 or normalized to 32 atoms per formula unit. [†] Putz *et al.* (2006).

TABLE 4. X-RAY POWDER-DIFFRACTION DATA FOR CALVERTITE

l_{est}	$d_{\text{obs}}(\text{Å})$	$d_{\text{calc}}(\text{Å})$	hkl
100	3.053	3.053	111
10	2.639	2.643	200
90	1.869	1.869	220
30	1.595	1.594	311

114.6 mm Debye-Scherrer camera, CuK α X-radiation; the intensities are visually estimated.

TABLE 5. POSSIBLE PARTITIONING OF ELEMENTS IN CALVERTITE

	(1)		(2)		
	apfu	charges	apfu	charges	
Cu ¹⁺	4.025	4.025	Cu ¹⁺	4.183	4.183
Cu ²⁺	0.757	1.514	Cu ²⁺	0.599	1.198
Fe ²⁺	0.143	0.286	Fe ²⁺	0.143	0.429
Zn ²⁺	0.041	0.082	Zn ²⁺	0.041	0.082
Ga ³⁺	0.025	0.075	Σ _a	4.966	5.892
V ²⁺	0.005	0.010			
Σ _a	4.996	5.992	Ge ⁴⁺	0.382	1.528
			As ⁵⁺	0.096	0.480
Ge ⁴⁺	0.382	1.528	Ga ³⁺	0.025	0.075
As ⁵⁺	0.096	0.480	V ⁵⁺	0.005	0.025
Σ _b	0.478	2.008	Σ _b	0.508	2.108
Σ _a + Σ _b		8.000	Σ _a + Σ _b		8.000
S ²⁻	4.000	-8.000	S ²⁻	4.000	-8.000

(29 unique in $F\bar{4}3m$) and a cubic cell with a 5.3365(6) Å, thus confirming the original precession-based results. However, a structure model satisfactorily commensurate with the microprobe composition of calvertite could not be established.

In accordance with the structure description of putzite [(Cu,Ag)₈GeS₆] (Paar *et al.* 2004), wherein Ge is represented as a stoichiometric entity in the formula, a separate position has likewise been allocated to the Ge in calvertite. The small unit-cell of calvertite, and the possibly unstable character, suggest that calvertite is a metastable, highly disordered mineral whose ordered equivalent would be generalized as Cu₁₀GeS₈ with $a = 2a'_{\text{calvertite}} = 2 \times 5.337$ Å and $Z = 4$. Thus, part of the difficulty in solving the structure of calvertite is that only a subcell rather than the true cell is detectable.

Charge balance for these types of sulfides (*e.g.*, germanite: Spiridonov 1987) is commonly obtained by using heterovalent states for the metals. For calvertite, only the Cu needs be partitioned (Table 5). However, if Ga is assigned to the Ge position, as has been done by Spiridonov *et al.* (1992) for germanocolusite, and if the valences of the minor elements are changed (Table 5), the Cu...:Ge...:S proportions of calvertite are still reasonable in terms of charge balance and the proposed general formula.

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