Canadian Mineralogist
Vol. 18, pp. 519-523 (1980)

GEERITE, $Cu_{1.60}S$, A NEW COPPER SULFIDE FROM DEKALB TOWNSHIP, NEW YORK

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ABSTRACT

Geerite is a new mineral from Dekalb Township, St. Lawrence County, New York. It occurs as thin black plates and iridescent epitactic (?) overgrowths on {110} of sphalerite. In reflected light, geerite is bluish-white and weakly bireflectant with moderate anisotropism in yellow. Geerite has a well-developed cubic subcell, similar to the cell of sphalerite, with $a = 5.410$ Å; space group $F\bar{4}3m$. The true cell has not been identified. The ideal composition for geerite is $Cu_{1.60}S$ with $Z = 4$ (cubic subcell); $D_{calc} = 5.61$ g cm^{-3}. The strongest reflections in the geerite powder pattern [$d_{hkl}(I)$ (hkl)] are: 3.128 (100)(111), 1.918 (50)(220), 1.637(30)(311), 1.109(20)(422); the indices refer to the cubic subcell.

Keywords: geerite, sphalerite, copper sulfide, Dekalb Township, New York.

SOMMAIRE

On a découvert la geerite, nouveau sulfure de cuivre, dans le canton de Dekalb (comté St.-Lawrence, New-York, E.U.A.) en minces plaquettes noires et surcroissances iridescentes (épitactiques?) sur {110} de la sphalérite. En lumière réfléchie, la geerite est d'un blanc-bleuâtre et légèrement biréflectante, avec un peu d'anisotropie dans le jaune. Elle possède une maille sous-multiple cubique bien développée, analogue à la maille de la sphalérite: a 5.410 Å, groupe spatial $F\bar{4}3m$; la vraie maille n'a pas été déterminée. La composition idéale est $Cu_{1.60}S$ ($Z = 4$ pour la sous-maille); $D_{calc} = 5.61$. Les réflexions les plus intenses du cliché de poudre [d_{hkl} (I) (hkl)] sont: 3.128(100)(111), 1.918(50)(220), 1.637(30)(311), 1.109(20)(422), où les indices se rapportent à la maille sous-multiple.

(Traduit par la Rédaction)

Mots-clés: geerite, sphalérite, sulfure de cuivre, canton de Dekalb, New-York.

INTRODUCTION

Shortly before the leaching experiments on anilite outlined by Goble (1977, in prep.) were performed, an unidentified copper sulfide from Dekalb Township, (specific locality not known), New York State, was analyzed on the electron microprobe. A composition of $Cu_{1.55}S$ was obtained (energy-dispersive analysis), and the mineral was tentatively identified as a copper-deficient anilite, although only sphalerite-like X-ray patterns could be obtained. Upon completion of the leaching experiments on anilite and the identification of a $Cu_{1.60}S$ structure, the Dekalb mineral was re-examined. It was identified as a new mineral, geerite, named for Adam Geer (deceased) of Utica, New York, who originally collected the material studied. Both the mineral and name have been approved by the I.M.A. Commission on New Minerals and Mineral Names (May 1978).

PHYSICAL AND OPTICAL PROPERTIES

Geerite occurs as a thin, iridescent coating or as platelets up to approximately 15 μm thick, oriented along {110} cleavage planes of sphalerite, as shown in Figure 1. In some specimens geerite is partly or completely replaced by spionkopite, a new copper sulfide described by Goble (1980). Other associated minerals include calcite, malachite, azurite, brochantite, chrysocolla, stibiconite, cervantite, hemimorphite, tetrahedrite and chalcopyrite.

Geerite is opaque and appears bluish-white and weakly bireflectant in reflected light. It is moderately anisotropic in yellow, with no internal reflections. Its polishing hardness is less than that of sphalerite, and it undercuts with respect to that mineral. Small grain size did not permit reflectivity and microhardness measurements to be made.

X-RAY AND CHEMICAL DATA

Samples for X-ray analysis were plucked

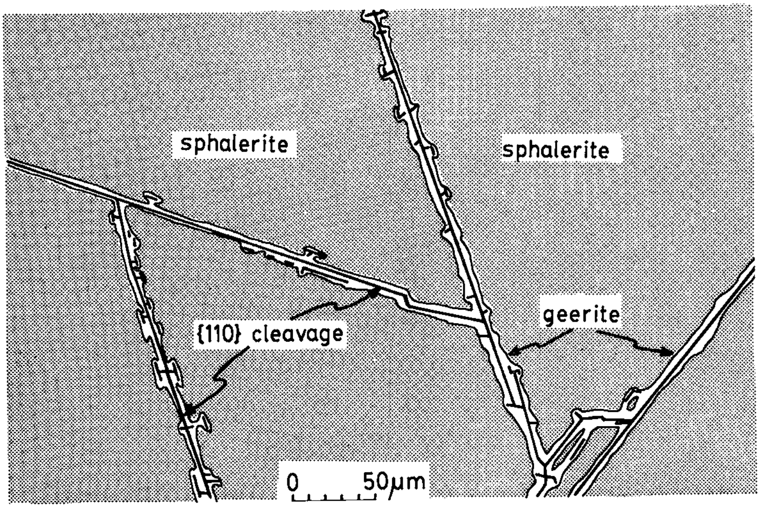

FIG. 1. Replacement of sphalerite along {110} cleavage planes by geerite. Maximum thickness of geerite platelets is approximately 15 μm. Drawing after photomicrograph.

from polished sections, cleaned in acetone and mounted on glass fibres. The largest sample was 72 x 64 x 16 μm, resulting in long exposures and low intensity lines on X-ray films. The X-ray powder data given in Table 1 were obtained using a 114.6 mm Gandolfi camera with Cu *K*α radiation; the intensities were estimated by visual comparison with standard-scale films. The pattern was indexed as cubic with a = 5.410 Å (precession data), space group $F\bar{4}3m$. With the "ideal" composition $Cu_{1.60}S$ in this cubic cell, the formula $Cu_{1.60}S$ with $Z = 4$ is obtained. D_{calc} is 5.61 g cm^{-3}. However, the optical data indicate that the mineral is only pseudocubic (probably orthorhombic).

TABLE 1. X-RAY SIMULATED POWDER DATA (GANDOLFI CAMERA) FOR GEERITE AND THE ASSOCIATED SPHALERITE IN COMPARISON WITH A STANDARD SPHALERITE

geerite		associated sphalerite	JCPDS Standard Number 5-566		
d (Å)	I/I1	d (Å)	d (Å)	I/I1	hkℓ
3.128	100	3.121	3.123	100	111
2.712	10	2.706	2.705	10	200
1.918	50	1.914	1.912	51	220
1.870*	10				
1.683*	10				
1.637	30	1.633	1.633	30	311
1.576	10	1.567	1.561	2	222
		1.355	1.351	6	400
1.247	10	1.243	1.240	9	331
			1.209	2	420
1.109	20	1.105	1.103	9	422

* reflection not noted on zero-level precession photographs. For geerite, a = 5.410 Å; for the associated sphalerite, a = 5.398 Å; for JCPDS 5-566, a = 5.406 Å. The a parameters for geerite and the associated sphalerite were determined from precession data corrected for film shrinkage; the Gandolfi powder data were not corrected for film shrinkage, but the spacings of the (220) reflections were in agreement with precession data.

The very strong pseudocubic subcell has an a parameter approximately equal to that of the associated sphalerite. The X-ray patterns of these minerals are very similar; they could easily be confused on the basis of powder patterns, where the small size of the sample and resulting low intensity reflections make film-shrinkage corrections difficult. However, there is a distinguishable difference in the a parameter between the 5.410 Å of geerite and the 5.398 Å of the associated sphalerite, reflected most strongly in an increase in the (200) spacing for geerite relative to the intergrown sphalerite on precession photographs. There is also a very noticeable weakening of the (200) intensity [relative to the (111) intensity] for geerite compared with the associated sphalerite when a direct comparison of precession and Gandolfi films is made.

Microprobe analyses were obtained using an Applied Research Laboratories – AMX electron microprobe equipped with a Tracor Northern NS–880 energy-dispersive spectrometer. Operating conditions were: accelerating voltage 15 kV, sample current about 1.5 nA, and beam diameter about 2 μm. Standards used were: CuS, $Cu_{1.8}S$ for Cu and S, ZnS, Zn metal for Zn and Fe metal for Fe. Apparent concentrations were corrected for absorption, secondary fluorescence and atomic number effects using a general ZAF program, TAPEEMX2 (Department of Geological Sciences, Queen's University). Results of the analyses are presented in

Table 2. To resolve problems caused by the undercutting of the softer geerite and uncertainties about its Zn content owing to its small grain-size relative to the microprobe beam, we plotted the analyses in Table 2 in Figure 2; analysis total is plotted against analyzed % Cu. The analyses are plotted with Zn included in the analysis total (circles) and with stoichiometric ZnS (the amount determined from Zn analyses) deleted from the total (crosses). A least-squares fit of those data in which Zn was not detected gives a formula $Cu_{1.55}S$, but with stoichiometric ZnS subtracted from the analyses the composition is $Cu_{1.53}S$; this may indicate that minor Zn may occasionally substitute for Cu. Traces of Fe were also detected.

To confirm that the specimen used for X-ray analysis was not simply a thin film of copper sulfide coating sphalerite, with the X-ray pattern being that of the latter mineral, we floated the 72 x 64 x 16 μm sample on silver paint and analyzed it on the electron microprobe at 30 kV accelerating voltage in an attempt to include some of a postulated core of sphalerite in the analyzed total. At the 17 points analyzed,

TABLE 2. ELECTRON-MICROPROBE ANALYSES OF GEERITE

Traverse Number	% Cu	% S	% Zn	% Fe	Total %	Cu:S ratio	Zn:S ratio
1	71.75	22.93	nd*		94.68	1.58	-
1	68.23	20.52	2.17*		90.92	1.68	0.50
1	76.05	23.72	nd*		99.77	1.62	-
1	63.50	18.35	2.12*		83.97	1.75	0.06
1	68.78	24.04	4.46*		97.28	1.44	0.09
2	61.44	21.47	nd*		82.91	1.44	-
2	69.33	22.81	nd*		92.14	1.53	-
2	70.43	22.74	nd*		93.17	1.56	-
2	73.90	23.12	nd*		97.02	1.61	-
2	70.43	25.23	2.10*		97.76	1.41	0.04
random	73.36	25.32	nd*		98.68	1.46	-
random	72.70	24.93	nd*		97.63	1.47	-
random	76.94	26.04	nd*		102.98	1.49	-
random	73.48	24.23	nd*		97.71	1.53	-
random	73.54	24.22	5.11*		102.87	1.53	0.10
random	75.28	24.02	5.03*		104.33	1.58	0.10
random	75.2	25.2	1.0	nd	102.4	1.53	0.02
random	74.1	25.0	0.9	nd	100.0	1.49	0.02
random	70.7	25.0	5.6	nd	101.3	1.43	0.11
random	71.7	25.1	4.1	nd	100.9	1.44	0.08
random	72.9	24.5	3.1	nd	100.5	1.50	0.06
random	72.1	23.5	3.8	nd	99.4	1.55	0.08
random	70.3	25.5	3.9	nd	99.7	1.39	0.07
random	65.0	25.7	9.2	nd	99.9	1.28	0.17
random	72.7	26.0	3.8	nd	102.5	1.41	0.07
random	72.1	27.3	2.5	nd	101.9	1.33	0.04
random	66.5	21.5	1.8	0.7	90.5	1.56	0.04
random	nd	33.5	68.5	nd	102.0	-	1.03
random	nd	33.3	67.8	nd	101.1	-	1.03

Standards used are CuS and $Cu_{1.8}S$ for Cu and S, Zn metal for Zn, ZnS for Zn* and Fe metal for Fe. ZAF corrections applied. Analyses represent two traverses across geerite platelets in sphalerite plus 16 random geerite and 2 random sphalerite points; nd designates an element analyzed for but not detected.

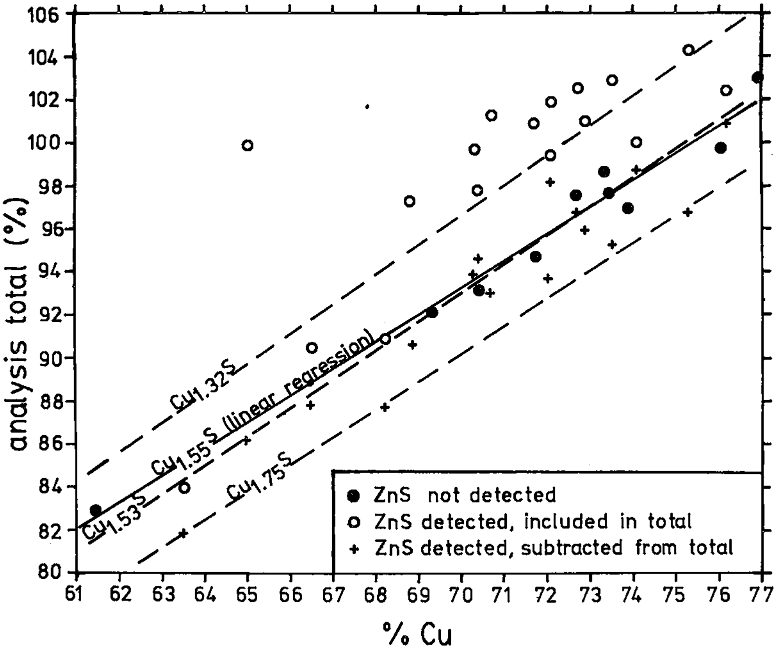

FIG. 2. Microprobe analyses of geerite, with % Cu measured plotted as a function of analysis total. For analyses with detectable Zn (○), total % ZnS (+) is also plotted. Predicted lines for compositions $Cu_{1.32}S$, $Cu_{1.53}S$ and $Cu_{1.75}S$ are shown, as is the line fitted to the Zn-free data (●) by least-squares analysis.

the average amount of Zn was 1.27%, corresponding to 1.9% incorporated stoichiometric ZnS; the maximum amount of Zn was 4.45%, or 6.6% incorporated stoichiometric ZnS. These quantities could easily be due to small amounts of sphalerite intermixed with the geerite platelets, as shown in Figure 1. The theoretical depth-of-generation data compiled in Tables 2 and 3 of Beaman & Isasi (1972) can be used to calculate the minimum volume percentage of copper sulfide present in the sample. The minimum and maximum electron penetrations for Zn in geerite would be 1.15 μm (Reed 1966) and 3.75 μm (Castaing 1960), respectively. Correcting for the 1.9% stoichiometric ZnS detected in microprobe analyses, these correspond to minimum volume percentage of copper sulfide present in the sample of 19.1% (1.15 μm penetration) and 49.3% (3.75 μm penetration). The data of Shinoda *et al.* (1968), adjusted for the difference in geerite and copper densities, show that the depth of maximum X-ray production is 0.48 μm at 30 kV, corresponding to a minimum volume percentage of 11.5% copper sulfide in the sample analyzed. In test sphalerite–anilite mixtures, as little as 10% anilite was readily detectable on Gandolfi X-ray powder patterns. No such mixture was detected in the sample studied, indicating that the specimen consists of a single mineral, geerite.

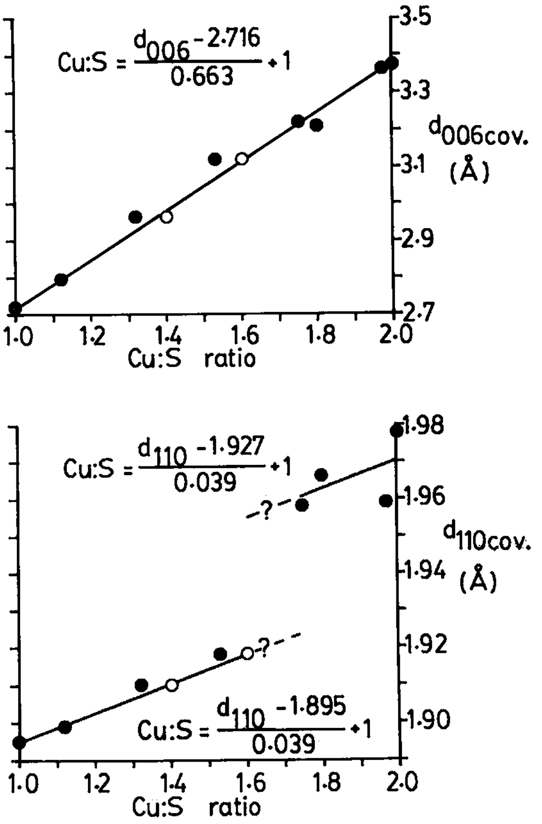

FIG. 3. Correlation of composition with spacing of planes corresponding to $d_{110\ \mathrm{covelline}}$ and $d_{006\ \mathrm{covelline}}$ for minerals in the system copper–sulfur. The spacing $d_{110\ \mathrm{covelline}}$ corresponds to one-half the sulfur-to-sulfur distance measured in the plane of the sulfur atoms in any copper sulfide (*i.e.*, it does not include covalently bonded sulfur atoms); $d_{006\ \mathrm{covelline}}$ corresponds to the average spacing between these sulfur planes and may include covalently bonded sulfur atoms (after Goble 1977). The *d* values for geerite are from Table 1; *d* values for other copper sulfides are from the data of Craig & Scott (1974), Potter & Evans (1976) and Goble (1980). Open circles (○) indicate theoretical compositions for spionkopite and geerite; closed circles (●) indicate measured compositions and *d* values.

DISCUSSION

With the $(110)_{\mathrm{covelline}}$ and $(006)_{\mathrm{covelline}}$ spacings from precession photographs and Figure 3, reproduced from Goble (1977, in prep.), an "ideal" composition of $Cu_{1.60}S$ is indicated. This composition was predicted from the data of Goble (1977, in prep.) and corresponds to that composition in the system copper–sulfur having the lowest copper-to-sulfur ratio but still retaining cubic close-packing of the sulfur atoms. As described by Goble (1977, in prep.), precession photographs of artificially leached anilite show that with removal of copper, a structure similar to that of geerite is developed, and the material remains in this structure state metastably until the composition approaches that of covelline. This is presumably a result of the kinetics of the structural changes.

Potter (1977) did not detect geerite as a stable phase in the system copper–sulfur. He did, however, report a metastable phase with the composition $Cu_{1.4\pm0.1}S$. As noted above, material synthesized by the leaching of anilite develops and retains a pseudocubic structure similar to that of geerite until compositions approach CuS. The leached material is distinguishable from spionkopite only on single-crystal patterns; this is probably what was synthesized by Potter (1977). If in fact Potter was looking at materials with a related structure but with the wrong composition for geerite to be stable, the presence of geerite as a stable phase in the system copper–sulfur cannot be precluded.

Geerite is probably not uncommon, but has likely gone unnoticed owing to its structural similarity to sphalerite and its intimate association with that mineral. Geerite probably forms epitactically upon sphalerite with $\{110\}_{\text{sphalerite}} \simeq \{110\}_{\text{geerite}}$ (cubic subcell used), and should be looked for as coatings on iridescent and altered sphalerites.

PRESERVATION OF TYPE MATERIAL

Polished sections and a typical hand specimen of geerite are preserved in the collection of Queen's University, Kingston, Ontario, in the U.S.N.M.N.H. Smithsonian Institution, Washington, D.C., and in the New York State Museum, Albany, New York. The fragment used in the X-ray examination is preserved, mounted on a glass fibre, by one of the authors (R.J.G.).

ACKNOWLEDGEMENTS

The authors acknowledge the helpful discussions with Dr. J.D. Scott (Eldorado Nuclear) concerning the single crystal patterns and possible structure of geerite, and Dr. M.I. Corlett (Queen's University) for her invaluable assistance in proving that the material used was indeed a new mineral. Special thanks are also given to Dr. M. Raymond Buyce (New York State Museum) for making the material available for this study.

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Received April 1980, revised manuscript accepted August 1980.