GEERITE, Cu$_{1.00}$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 $F\overline{4}3m$. The true cell has not been identified. The ideal composition for geerite is Cu$_{1.66}$S with $Z = 4$ (cubic subcell); $D_{\text{calc}} = 5.61$ 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.

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.

X-RAY AND CHEMICAL DATA
Samples for X-ray analysis were plucked...
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 Kα 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 \( Fd3m \). With the "ideal" composition \( \text{Cu}_4\text{S}_8 \) in this cubic cell, the formula \( \text{Cu}_4\text{S}_8 \) with \( Z = 4 \) is obtained. \( \rho_{\text{calc}} \) is 5.61 g cm\(^{-3}\). However, the optical data indicate that the mineral is only pseudocubic (probably orthorhombic).

![Fig. 1. Replacement of sphalerite along \{110\} cleavage planes by geerite. Maximum thickness of geerite platelets is approximately 15 µm. Drawing after photomicrograph.](image)

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, \( \text{Cu}_4\text{S}_8 \) 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

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**Table 1.** X-ray simulated powder data (Gandolfi camera) for geerite and the associated sphalerite in comparison with a standard sphalerite

<table>
<thead>
<tr>
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<th>geerite</th>
<th>associated sphalerite</th>
<th>JCPDS Standard Number 5-566</th>
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</thead>
<tbody>
<tr>
<td>( d (\bar\lambda) )</td>
<td>( 2\theta (\text{CuK}\alpha) )</td>
<td>( d (\bar\lambda) )</td>
<td>( 2\theta (\text{CuK}\alpha) )</td>
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<tr>
<td>3.128</td>
<td>100</td>
<td>3.128</td>
<td>2.705</td>
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<tr>
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<tr>
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<tr>
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<td>1.109</td>
<td>1.109</td>
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<tr>
<td>1*</td>
<td>5*</td>
<td>1*</td>
<td>1*</td>
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</table>

* 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, \( a = 5.468 \) 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 (200) reflections were in agreement with precession data.
GEERITE, Cu₁₄₀S, A NEW COPPER SULFIDE FROM

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 Cu₁₄₁S, but with stoichiometric ZnS subtracted from the analyses the composition is Cu₁₄₂S; 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,

![Fig. 2. Microprobe analyses of geerite, with % Cu measured plotted as a function of analysis total. For analyses with detectable Zn (O), total % ZnS (+) is also plotted. Predicted lines for compositions Cu₁₄₂S, Cu₁₄₆S, and Cu₁₄₉S are shown, as is the line fitted to the Zn-free data (●) by least-squares analysis.](image-url)
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.

**Discussion**

With the (110)_{covellite} and (006)_{covellite} spacings from precession photographs and Figure 3, reproduced from Goble (1977, in prep.), an "ideal" composition of Cu_{1.5}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 covellite. 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+0.1}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 \( \{110\}_{\text{sphalerite}} \approx \{110\}_{\text{geerite}} \) (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.).

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**References**


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