

UYTENBOGAARDTITE, A NEW SILVER-GOLD SULFIDE

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ABSTRACT

Uytenbogaardtite, Ag_3AuS_2 , occurs with acanthite, electrum and quartz in specimens from Tambang Sawah, Benkoelen district, Sumatra, Indonesia, the Comstock lode, Storey County, Nevada, U.S.A. and Smeinogorski (Schlangenberg), Altai, U.S.S.R. The mineral is tetragonal, $P4_122$ or $P4_1$, a 9.76, c 9.78 Å (Comstock lode), a 9.68, c 9.81 Å (Tambang Sawah), $Z = 8$; $D(\text{calc}) = 8.34 \text{ g/cm}^3$ (Comstock lode), 8.45 g/cm^3 (Tambang Sawah). The strongest X-ray powder diffraction lines are $2.71(10)$ (203), $2.60(9)$ (321), $2.12\text{Å}(7)$ (421). Measured compositions lie close to Ag_3AuS_2 , although uytenbogaardtite from the Comstock lode contains up to 4 wt. % Cu. These data indicate that uytenbogaardtite is identical with synthetic low-temperature Ag_3AuS_2 . Pleochroism in reflected light is: grey-white to grey-white with a brownish tint (air), brownish grey-white to brownish pink (oil). Measured reflectivities ($R\%$ at specific wavelengths) are: 33.2–34.6 (470 nm), 30.3–34.6 (546 nm), 31.1–35.2 (589 nm), 30.5–33.3 (650 nm). The polishing hardness is slightly below that for acanthite; VHN_{15} is about 20. The name is in honor of Willem Uytenbogaardt, Professor of geology at the Technical University, Delft, The Netherlands.

SOMMAIRE

On trouve l'uytenbogaardtite, Ag_3AuS_2 , accompagnée d'acanthite, électrum et quartz, dans des échantillons de Tambang Sawah, district de Benkoelen, Sumatra (Indonésie), dans la veine Comstock, comté de Storey, Nevada (E.U.), et à Smeinogorsk (Schlan-

genberg), Altaï (U.R.S.S.). C'est un minéral tétragonal, $P4_122$ ou $P4_1$, a 9.76, c 9.78 Å (Comstock); a 9.68, c 9.81 Å (Tambang Sawah); $Z = 8$; $D(\text{calc})$ 8.34 (Comstock), 8.45 (Tambang Sawah). Les raies de diffraction-X les plus intenses sont 2.71(10) (203), 2.60(9) (321) et 2.12Å(7) (421). Les compositions obtenues par analyse sont proches de Ag_3AuS_2 , quoique l'uytenbogaardtite de Comstock contient jusqu'à 4% (poids) de cuivre. Ces données montrent que l'uytenbogaardtite et la forme basse-température de Ag_3AuS_2 sont identiques. En lumière réfléchie, le minéral est pléochroïque, de gris-blanc à gris-blanc teinté de brun dans l'air, et d'un gris-blanc brunâtre au rose brunâtre dans l'huile. Les réflectivités mesurées (en % R à certaines longueurs d'onde données) sont les suivantes: 33.2–34.6 (470 nm), 30.3–34.6 (546 nm), 31.1–35.2 (589 nm), 30.5–33.3 (650 nm). La dureté au polissage, VHN_{15} , est approximativement 20, soit un peu moins que pour l'acanthite. Ce minéral est dédié au Professeur Willem Uytenbogaardt, de l'Université Technique de Delft (Pays Bas).

(Traduit par la Rédaction)

INTRODUCTION

Two ternary compounds, Ag_3AuS_2 and AgAuS , are known at low temperatures in the system Ag–Au–S. Neither phase has been reported to occur in nature, although they might be expected in certain gold–silver deposits. Examination of several acanthite (Ag_2S) + electrum (Au,Ag) assemblages has led to the discovery of natural Ag_3AuS_2 , uytenbogaardtite, from the Comstock lode, Storey County, Nevada, U.S.A. and Smeinogorski (Schlangenberg), Altai, U.S.S.R. Simultaneously, in the course of an investigation of the gold–silver ores from the Tertiary volcanic belt of Sumatra, Indonesia,

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uytenbogaardtite was found in a sample from Tambang Sawah, Benkoelen district. At all three localities, uytenbogaardtite occurs as small blebs up to 100 μm across and as rims intimately associated with acanthite, electrum, quartz and other minerals.

The name (pronounced YÜTENBO•GARDAIT) is for Willem Uytenbogaardt, Professor of mineralogy and petrology at the Free University in Amsterdam from 1960 to 1976, dedicated promoter of quantitative ore microscopy in his function as chairman of the I.M.A. Commission on Ore Microscopy from 1962 to 1970, and now Professor of geology at the Technical University in Delft, The Netherlands.

Both the mineral and the name have been approved by the Commission on New Minerals and Mineral Names of the International Mineralogical Association. Type material will be preserved in the collections of the Free University in Amsterdam, the University of Amsterdam and the United States National Museum [N.M.N.H. 105328 (Comstock lode) and N.M.N.H. B239 (Smeinogorski)].

PHYSICAL AND OPTICAL PROPERTIES

In polished section uytenbogaardtite shows weak to distinct reflection pleochroism. In air the color varies from grey-white to grey-white with a brownish tint. In oil immersion the pleochroism is more distinct: brownish grey-white to brownish pink; in contrast, acanthite is distinctly blue. The anisotropy is strong in both air and in oil, but without distinct colors. The reflectance is slightly higher than that for acanthite and was measured with a Leitz MPV microscope photometer at four standard wavelengths. The instrument was equipped with a Knott 9592A photomultiplier tube, a Veril B-200 continuous-band interference filter and a 16:1 objective of 0.40 N.A. A tungsten carbide, WC-6, provided by Messrs. Carl Zeiss (Oberdochen), was used as a standard. The reflectance values, measured on a grain with maximum birefractance, are given in Table 1.

Light (*i.e.*, heat) etching is extremely strong, even stronger than for acanthite. The Comstock-

TABLE 1. REFLECTANCE VALUES FOR UYTENBOGAARDTITE*

λ	R_{max}	R_{min}
470 nm	34.6%	33.2%
546	34.6	30.3
589	35.2	31.1
650	33.3	30.5

* measured on material from Tambang Sawah

TABLE 2. REPRESENTATIVE ANALYSES OF UYTENBOGAARDTITE*

LOCALITY	Ag	Au	Cu	S	TOTAL
Ag_3AuS_2 (ideal)	55.34	33.69	-	10.97	100.00
Comstock lode	56.1	29.8	2.2	11.2	99.3
"	55.8	27.3	3.0	12.3	98.4
"	56.5	27.4	3.6	12.4	99.9
Smeinogorski	56.0	32.4	-	10.4	98.8
"	57.1	32.7	-	10.3	100.1
"	54.6	35.3	-	10.8	100.7
Tambang Sawah	54.5	33.4	-	11.3	99.2
"	53.2	35.1	-	11.7	100.0
"	56.7	32.6	-	11.0	100.3

* in weight per cent

lode material develops a completely different surface in several tens of seconds under moderate illumination. This surface suggests photo-induced decomposition; it requires a fresh polish for its removal. Tambang Sawah and Smeinogorski uytenbogaardites, in contrast, seem to be relatively stable.

Microindentation hardness (VHN), measured with a Leitz Durimet-Pol hardness tester applying the minimum load of 15 g and an indentation time of 15 seconds, is about 20, which corresponds to a Mohs hardness of about 2. Because of the small grain-size and the low hardness only one indentation could be made. The polishing hardness is lower than that for acanthite. Uytenbogaardtite is considerably more

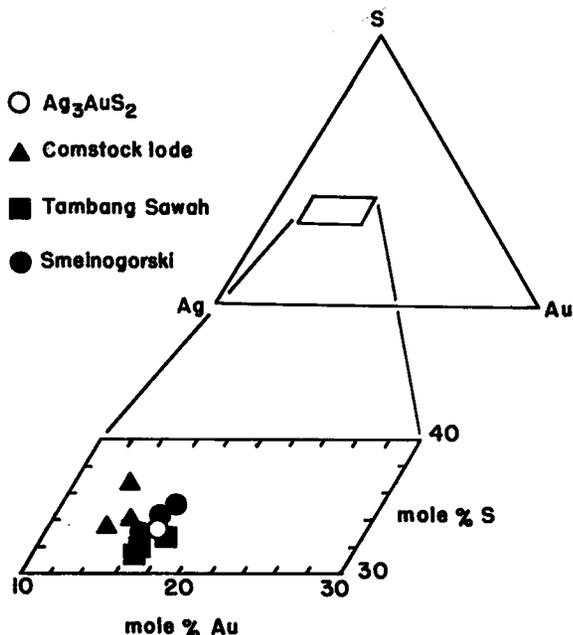


FIG. 1. Selected analyses from the Comstock lode, Tambang Sawah, and Smeinogorski specimens plotted in the triangular diagram Ag-Au-S.

brittle than acanthite. On probing with a sharpened steel needle uytenbogaardtite broke up into small pieces, whereas associated acanthite tended to smear. Synthetic Ag_3AuS_2 is reasonably easy to grind to a powder.

CHEMICAL COMPOSITION

Electron-microprobe analyses were obtained independently in three laboratories. Despite the use of different operating conditions, different standards and different correction schemes, the results obtained are comparable.

Analyses of material from the three localities demonstrate that uytenbogaardtite is close to ideal Ag_3AuS_2 . Neither the Ag/Au nor the (Ag + Au)/S ratios (atomic) show any systematic departure from the expected values of 3/1 and 2/1. Analyses selected from the more than 70 done are given in Table 2 and plotted in Figure 1. The only additional elements detected occur in the Comstock-lode material, where up to 4 wt. % copper is present along with traces of selenium and tellurium.

In spite of inaccuracies introduced by the small grain-size and instability under the electron beam, possibly due to diffusion processes similar to those described by Rucklidge & Stumpfl (1968) for petzite, Ag_3AuTe_2 , analyses were reproducible. During long exposures of a single spot to the beam a detectable shift of the gold to silver ratio occurs in which the excited area of sulfide becomes more silver-rich.

CRYSTALLOGRAPHY

Owing to the small grain-size and the multi-granular nature of uytenbogaardtite, neither powder smear-mounts nor single-crystal methods could be used. X-ray powder data obtained using a Straumanis-type Debye-Scherrer camera (Tambang Sawah specimen; Mn-filtered $\text{FeK}\alpha$ radiation) and a Gandolfi camera (Comstock lode specimen; Ni-filtered $\text{CuK}\alpha$ radiation) indicate that the new mineral is identical with the tetragonal low-temperature form of synthetic Ag_3AuS_2 (Graf 1968; PDF 20-461). The X-ray data and cell edges (calculated by least-squares methods) are given in Table 3.

For the Debye-Scherrer camera exposure, uytenbogaardtite was powdered under the microscope with a tungsten carbide microdrill and taken into droplets of rubber solution. For the Gandolfi camera exposure, it was gouged from a polished section with a sharpened steel needle and picked up on a glass fibre coated with sili-

TABLE 3. X-RAY POWDER DIFFRACTION DATA FOR UYTENBOGAARDTITE AND SYNTHETIC Ag_3AuS_2

hkl	Synthetic $\text{Ag}_3\text{AuS}_2^*$				Uytenbogaardtite				
	d_{obs}	d_{calc}	I	I	Tambang Sawah		Comstock lode		
					d_{obs}	d_{calc}	d_{obs}	d_{calc}	
110	6.98	6.894	8	6.94	6.845	4	-	-	
210	4.38	4.360	6	4.33	4.329	3	4.40	4.365	
220	3.46	3.447	2	3.47	3.422	1	-	-	
300	3.24	3.250	3	-	-	-	3.24	3.253	
310	3.09	3.053	3	-	-	-	3.09	3.086	
222	2.809	2.825	6	2.802	2.807	3	2.82	2.819	
203	2.731	2.724	10	2.712	2.710	10	2.71	2.711	
321	2.609	2.609	9	2.591	2.590	9	2.60	2.609	
331	2.236	2.238	3	2.226	2.222	1	-	-	
421	2.124	2.129	8	2.112	2.114	4	2.13	2.130	
422	1.992	1.994	5	1.980	1.980	2	-	-	
520	1.807	1.811	5	1.798	1.798	1	1.81	1.812	
521	1.780	1.781	4	1.788	1.768	1	-	-	
a (Å)	9.75			9.68		1	9.76		
c (Å)	9.85			9.81			9.78		
densities	8.29 g/cm ³			8.45 g/cm ³			8.34 g/cm ³		

* Powder data and cell edges from Graf (1968); only those data that correspond to observed lines in the natural material are given here. Graf's intensities are ten times those given here.

cone grease. In both cases, owing to small grain size and intimate intergrowth with acanthite or electrum (or both), all patterns contained lines of acanthite or electrum. The small amounts of material used yielded rather diffuse diffraction lines. For d_{hkl} greater than 3Å , background from the rubber solution was significant. In neither case could a correction for film shrinkage be made because of the absence of back reflections.

Messien *et al.* (1966) reported low-temperature Ag_3AuS_2 to be cubic, a 9.72Å, but Graf (1968) later demonstrated that the symmetry is actually tetragonal. Observed reflections show that the space group is primitive and that the only possible non-unit translational symmetry elements are a 4_1 - or a 4_3 -axis. As there are no observed reflections of the type $00l$ it is not possible to ascertain if a four-fold screw axis is present; however, as Messien *et al.* (1966) indicate the presence of a 4_1 axis, the probable space group is either $P4_122$ or $P4_1$.

OCCURRENCE AND PARAGENESIS

Uytenbogaardtite occurs with acanthite, electrum and quartz at the three localities, all hydrothermal precious-metal deposits. The Tambang Sawah and Comstock lode deposits closely resemble each other and the late-stage uytenbogaardtite parageneses are similar. The Smejnogorski deposit is of a different type; there, uytenbogaardtite may be supergene. All three assemblages, however, contain typical low-temperature gold-silver parageneses.

Hydrothermally-altered Tertiary andesitic rocks are the hosts for the gold- and silver-bearing quartz veins of Tambang Sawah and

the Comstock lode. Hypogene minerals common to both deposits include quartz, chalcedony, kaolinite, calcite, rhodochrosite, adularia, sphalerite, galena, acanthite, pyrrargyrite and electrum; opal, inesite and rhodonite occur only at Tambang Sawah, and pyrite, chalcopyrite and Ag-

bearing sulfosalts (besides pyrrargyrite) are reported only from the Comstock lode. The oxidation zone at Tambang Sawah consists of a mass of quartz and manganese oxides, whereas the cementation zone is enriched in acanthite. A variety of supergene sulfides and sulfosalts are

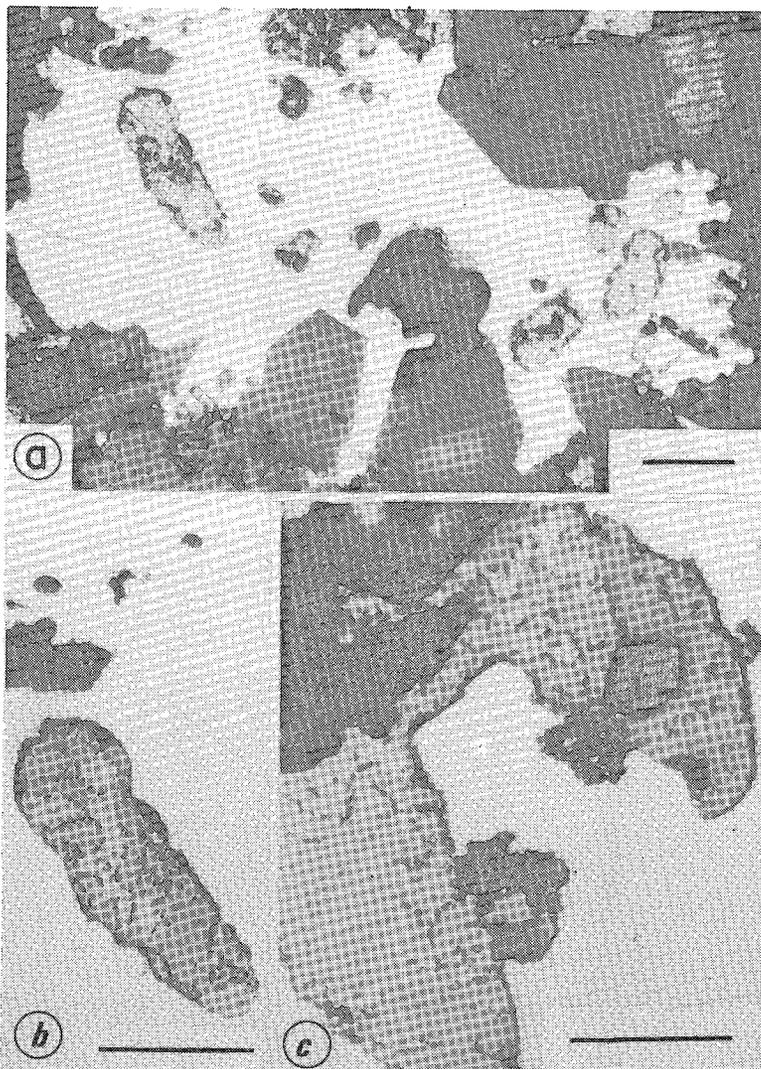


FIG. 2. (a) Vug-filling electrum (white) enclosing corroded acanthite which shows replacement by uytenbogaardtite (see b); euhedral quartz crystals protruding into vug. (b) Detail of a: acanthite (grey) recrystallized into granular aggregate and partly replaced by uytenbogaardtite (lighter grey); black spots lining grain boundaries are effects of light etching; enclosing material (white) is electrum. (c) Acanthite (darker grey) showing replacement by irregular, locally vein-like spots of uytenbogaardtite (lighter grey); black spots lining acanthite-uytenbogaardtite boundaries are due to light etching; white is electrum and black is quartz. The bars are 100 μm long.

reported from the Comstock lode (Bastin 1922, van Bemmelen 1949, Bonham 1969).

The uyttenbogaardtite-bearing samples from Tambang Sawah and the Comstock lode are similar in texture and paragenesis. The sample from Tambang Sawah is composed of an inequigranular quartz aggregate enclosing small vugs partly filled either with manganese oxides and a chloritic mineral or with acanthite and a chloritic mineral. Locally there is brecciation and recementation with chloritic-sericitic material. The sample shows the usual black coating of manganese-bearing rocks exposed at the surface, but not the expected veining with manganese oxides or acanthite.

Textural relations in the acanthite-filled vugs suggest an overlapping order of deposition of quartz, galena, sphalerite, acanthite, electrum and uyttenbogaardtite. There is a gradation inward from anhedral quartz to prismatic quartz crystals that protrude into the vugs. Inclusions of acanthite in the prismatic quartz crystals demonstrate the overlapping deposition of acanthite and vug-filling quartz. The acanthite aggregates in the vugs enclose and partly replace a few corroded and veined grains of galena and sphalerite. Electrum generally occurs as very fine grains, partly interstitial to and partly enclosed in the acanthite grains. Occasionally, aggregates of electrum form the central filling of a vug and enclose corroded and rounded grains of acanthite. The acanthite adjoining such aggregates of late electrum shows replacement by irregular, locally vein-like spots of uyttenbogaardtite less than 100 μm across (Fig. 2a, b). In places the acanthite has apparently recrystallized into a fine-grained aggregate of acanthite with interstitial uyttenbogaardtite grains (Fig. 2c). The dispersed fine-grained electrum is locally associated with a few small grains of uyttenbogaardtite in the surrounding acanthite. Microprobe analyses indicate that the silver content of the electrum (about 43 wt. %) is similar to that in the hypogene electrum from the Salida and Mangani deposits in the same Au-Ag ore province (Kieft & Oen 1973, 1977).

Manganese oxides appear only where acanthite is almost completely replaced. Other vugs are filled with chloritic material or aggregates of several manganese oxides, or both, commonly with concentric banded textures. Electron microprobe analyses indicate that the manganese oxides enclosing electrum contain between 4 and 20 wt. % silver. The dissolution of acanthite and replacement by a chloritic mineral and manganese oxides is presumably related to a late change in the physico-chemical environment.

Massive acanthite fills the interstices between euhedral quartz crystals (about 1 mm) at one end of the Comstock lode specimen (*N.M.N.H.* 105328). The remainder of the specimen is composed of an equigranular aggregate of quartz with minor acanthite.

The textural relationships indicate that quartz, the earliest mineral, is followed by sphalerite, chalcopyrite, pearceite, electrum and acanthite. The acanthite encloses irregular masses of chalcopyrite, sphalerite, pearceite and electrum. Covellite replaces some of the chalcopyrite, whereas the electrum blebs are almost universally surrounded by 5–10 μm rims of uyttenbogaardtite (Fig. 3). No other phases are observed in contact with the uyttenbogaardtite apart from acanthite and electrum. The mole fraction of silver in the electrum is about 0.45 adjacent to the uyttenbogaardtite and is up to 0.7 in the centres of the larger grains. The acanthite contains about 0.5 wt. % copper as well as traces of selenium.

The deposits of the Smeinogorski area consist of veins in hydrothermally altered, strongly folded slates, sandstones and carbonates of Devonian and Carboniferous age that have been intruded by Hercynian-age granites. Most of the rich precious-metal ore is thought to be supergene (Emmons 1937).

The uyttenbogaardtite specimen from Smeinogorski (*N.M.N.H.* B239) is a yellow-stained ag-

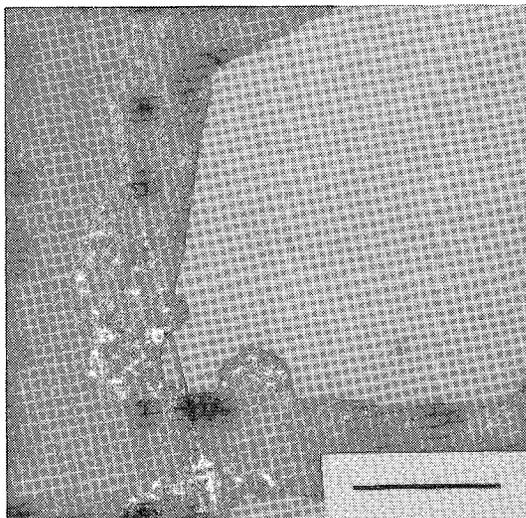


FIG. 3. Uyttenbogaardtite rims (grey with black spots) around electrum (white) and enclosed by acanthite (uniform grey). The spotting of the uyttenbogaardtite is due to the extremely rapid and pronounced photo-etching. The bar is 20 μm long.

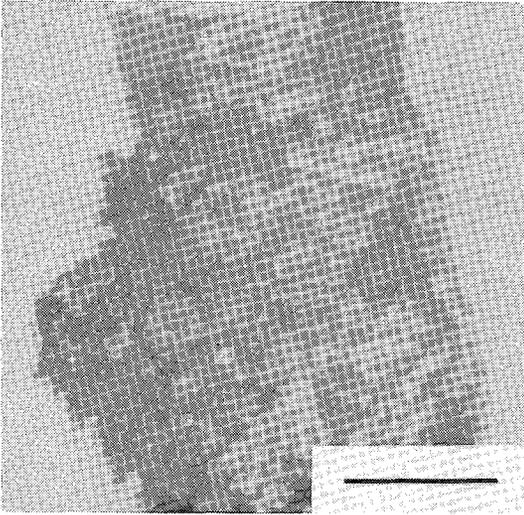


FIG. 4. Intergrowth of acanthite and electrum having a bulk Ag: Au ratio of 3:1 (expanded-beam microprobe analysis). Enclosing material is electrum (white). The bar is 10 μm long. Oil immersion.

gregate of anhedral to euhedral quartz crystals, partly coated on one surface by acanthite, electrum, chlorargyrite and minor naumannite. The acanthite, naumannite and chlorargyrite surround masses of electrum up to 1 cm in maximum dimension. Euhedral quartz crystals are interspersed. Uyttenbogaardtite occurs in contact with the outer edge of the electrum and as inclusions in the electrum. Extremely fine-grained intergrowths of acanthite and electrum having a bulk Ag/ Au ratio of 3/1 (determined by expanded-beam electron-microprobe analysis) are interpreted to be breakdown products of uyttenbogaardtite (Fig. 4). The presence of chlorargyrite supports a supergene origin for at least part of the observed assemblage.

STABILITY

Experimental work on the system $\text{Ag}_3\text{AuS}_2 - \text{Ag}_2\text{S}$ by Graf (1968) indicates that only below 113°C can Ag_3AuS_2 (uyttenbogaardtite) coexist with Ag_2S (acanthite). Low Ag_3AuS_2 is stable with gold-bearing argentite solid solution from 113° to 185°C where it inverts to high Ag_3AuS_2 , part of the solid solution. Figure 5 (Barton 1978) shows some of the electrum compositions coexisting with uyttenbogaardtite and acanthite. Observed electrum compositions are not compatible with these experimentally determined tie-lines. One possible explanation is that the uyttenbogaardtite-bearing assemblages reflect dis-

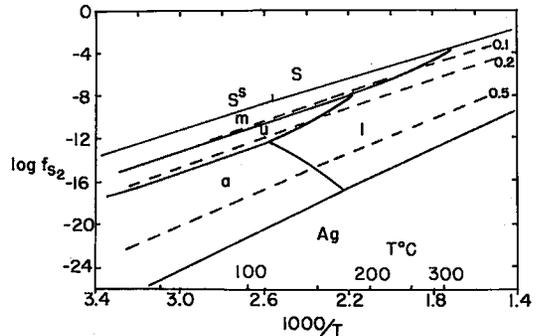


FIG. 5. Log fugacity of sulfur versus $1000/T$ ($^{\circ}\text{K}$) plot (Barton 1978) showing stability of the metal-saturated phases in the system Ag-Au-S. Abbreviations: low-temperature AgAuS *m*, uyttenbogaardtite *u*, $(\text{Ag},\text{Au})_2\text{S}$ solid solution *I*, acanthite *a*, solid sulfur S^s , liquid sulfur *S*, silver *Ag*. The dashed lines are isopleths showing mole fraction Ag in coexisting electrum.

equilibrium during cooling of a high-temperature, gold-bearing argentite + electrum assemblage. On cooling the argentite would have exsolved uyttenbogaardtite leaving the original silver-rich electrum with acanthite + uyttenbogaardtite.

The variation in Ag/ Au ratio in the electrum from the Comstock lode suggests that the uyttenbogaardtite is breaking down to acanthite + gold-rich electrum or that it is reacting with silver-rich electrum to yield assemblages more compatible with the phase diagram. Although the occurrence of uyttenbogaardtite as rims around the electrum blebs in the Comstock-lode specimen might suggest that acanthite and electrum reacted to give uyttenbogaardtite, this is unlikely given the electrum composition(s) and the experimentally determined phase relations.

Barton (1978) has estimated the standard free energy of formation of low-temperature Ag_3AuS_2 as a linear function of temperature: $\Delta G^{\circ} = -40750 + 22.0T$ (calories; $T = ^{\circ}\text{K}$). The estimated error is ± 1500 calories.

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