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UYTENBOGAARDTITE, Ag_3AuS_2, IN THE BULLFROG MINING DISTRICT, NEVADA

STEPHEN B. CASTOR
Nevada Bureau of Mines and Geology, University of Nevada, Reno, Nevada 89557, U.S.A.

JAMES J. SJOBERG
U.S. Bureau of Mines, Reno Research Center, 1605 Evans Avenue, Reno, Nevada 89507, U.S.A.

ABSTRACT

The rare mineral uytenbogaardtite, Ag_3AuS_2, has been identified in specimens from two mines in the Bullfrog district of southern Nevada. The mines exploit gold–silver vein deposits of the low-sulfur type that are hosted by volcanic rocks of middle Miocene age. At both mines, uytenbogaardtite occurs in local masses of high-grade ore within shallowly to moderately dipping systems of quartz–carbonate veins emplaced during late Miocene volcanism and extensional tectonism. Uytenbogaardtite from the Bullfrog district is chemically and structurally identical to previously described synthetic and natural Ag_3AuS_2. It occurs in association with two types of electrum: relatively coarse, early electrum, with approximately equal molar amounts of gold and silver, and late gold-rich electrum. It is also associated with acanthite, copper-bearing sulfides, and products of oxidation such as limonite and chrysocolla. Textural evidence indicates that the uytenbogaardtite replaced early electrum, formed contemporaneously with late electrum and acanthite, and that its deposition may have overlapped, in part, with that of minerals formed in an oxidizing environment. Equilibrium relationships among electrum, acanthite, and uytenbogaardtite in specimens from the Bullfrog district seem to be consistent with those predicted experimentally. On the basis of experimental work by others, the uytenbogaardtite + acanthite + electrum assemblage in the Bullfrog district is considered to have formed at a low temperature (<113°C). A late-stage hypogene or supergene origin, following early, higher-temperature deposition of electrum and sulfide, is proposed for the assemblage uytenbogaardtite + acanthite + gold-rich electrum.

Keywords: uytenbogaardtite, electrum, gold–silver vein deposits, Bullfrog district, Nevada.

SOMMAIRE

Nous avons identifié l'uytenbogaardtite, Ag_3AuS_2, espèce rare, dans des échantillons provenant de deux mines du district de Bullfrog, dans le sud du Nevada. Ces mines exploitent des gisements fissuraux d'or et d'argent à faible teneur en soufre, localisées dans des roches htes volcaniques d'ge miocène moyen. Aux deux endroits, l'uytenbogaardtite se trouve dans des amas localisés de minerai enrichi dans des systèmes de veines à quartz + carbonate à pendage faible ou moyen, mis en place lors du volcanisme miocène tardif et d'un épisode d'extension. L'uytenbogaardtite est identique, tant du point de vue chimique que structural, aux exemples naturels et au composé Ag_3AuS_2 décrits antérieurement. Elle est associée à deux types d'électrum: une première, précoce et à grains relativement grossiers, contient une proportion à peu près équivalente d'or et d'argent; l'électrum tardif est riche en or. Elle est aussi associée à l'acanthite, des sulfures cuprifères, et des produits d'oxydation comme limonite et chrysocolle. D'après l'évidence texturale, l'uytenbogaardtite aurait remplacé l'électrum précoce et serait contemporaine de l'électrum tardif et de l'acanthite; elle pourrait l'tre aussi par rapport aux minéraux caractéristiques du milieu oxydant. Les relations d'équilibre parmi électrum, acanthite et uytenbogaardtite dans le district de Bullfrog semblent concorder avec celles qui sont prédites à partir des expériences. A la lumière des travaux expérimentaux publiés, l'assemblage uytenbogaardtite + acanthite + électrum dans ces échantillons se serait formé à une faible température (<113°C). Une origine hypogénétique tardive ou supergénétique semble indiquée pour l'assemblage uytenbogaardtite + acanthite + électrum riche en or suite à la déposition antérieure, à température plus élevée, d'électrum et de sulfure.

(Traduit par la Rédaction)

Mots-clés: uytenbogaardtite, électrum, gisements fissuraux, or argent, district de Bullfrog, Nevada.

INTRODUCTION

Uytenbogaardtite, Ag_3AuS_2, is a rare mineral. We are aware of only eight occurrences in the world: in Sumatra, Indonesia, the Altai Mountains of Russia, and the Comstock lode, Nevada (Barton *et al.* 1978), at three sites in China (Chen *et al.* 1979, as reported in Fleischer *et al.* 1980), at the Morning Star mine, California (Sheets

et al. 1988), and at an unspecified gold prospect in Montana (W. Fuchs, pers. comm., 1992). Recently, we identified the mineral in high-grade gold–silver ore from two mines in the Bullfrog district of Nye County, Nevada.

Following the discovery of the Original Bullfrog mine in 1904, gold and silver were produced from several mines in the Bullfrog district until 1940, most notably from the Montgomery–Shoshone mine. Renewed exploration since the mid-1970s resulted in the discovery and development of the Lac Bullfrog mine (originally the Bond Gold Bullfrog mine), a deposit with gold production and reserves in excess of 61×10^6 g (D. McClure, pers. comm., 1992). Uytenbogaardtite has been identified in specimens from both the Original Bullfrog and Lac Bullfrog mines.

Geological Setting

The Bullfrog district, which is about 175 km northwest of Las Vegas, contains low-sulfur type (*cf.* Bonham 1989) epithermal gold–silver vein deposits that are scattered over an area of nearly 100 km^2. The veins cut rhyolitic ash-flow tuffs and associated rocks erupted between about 15 and 10 Ma. They are associated with secondary K-feldspar that yielded K–Ar ages of 8.7 ± 0.3 and 9.5 ± 0.2 Ma (Jackson 1988, Morton *et al.* 1977), and with extensional faulting that was mainly active between 11.3 and 7.6 Ma (Weiss *et al.* 1990).

The Original Bullfrog mine exploits a complex, shallowly north-dipping system of veins that underlies an area of about 0.1 km^2 and appears to be truncated at its base by post-mineralization displacement along a regional low-angle fault (Ransome *et al.* 1910, Maldonado 1990). The best exposures of the vein system are in a small area of open cuts that expose a complex mass of veins and silicified breccia up to about 10 m thick, as well as stockwork veins that extend upward from this mass into altered ash-flow tuff. At the Lac Bullfrog mine, gold–silver mineralization occurs in a moderately west-dipping system of veins that lies along a normal fault. Ore comprises a central zone up to 70 m thick within the vein system. The ore zone contains altered volcanic rock, hydrothermal breccia, and abundant veins in stockworks and sheeted swarms. The ore zone is generally bounded by faults that separate it from sparse vein stockworks above and below (Jorgensen *et al.* 1989). High-grade gold ore is mainly composed of hydrothermal breccia lying along the bounding faults (B. Claybourne, pers. comm., 1991). This breccia consists of vein and wallrock fragments in matrices of crustiform to spongy quartz ± calcite.

Alteration assemblages near the veins at both mines consist of K-feldspar + albite ± illite. This alteration grades outward into illite + calcite ± quartz ± albite ± sericite alteration (Castor & Weiss 1992). Pyrite (or limonite pseudomorphs) comprises 1–2 vol.% of altered wallrock in and near the veins. At the Lac Bullfrog mine, chlorite- and carbonate-bearing assemblages have been reported in sedimentary and metamorphic rocks at depth (Jorgensen *et al.* 1989).

Veins and breccias at the two mines are similar. Types of vein quartz include crustiform, fine granular to chalcedonic quartz, and fine- to medium-grained comb quartz that is locally amethystine. The veins also contain coarse to finely bladed calcite. Rare crustiform layers of very fine-grained K-feldspar are present in veins at the Lac Bullfrog mine, and fluorite and barite also have been reported (Jorgensen *et al.* 1989) but are rare (B. Claybourn, pers. comm., 1991).

The paragenesis of individual veins appears to follow the same sequence from place to place within the Original Bullfrog vein system: early calcite deposited along vein walls, followed by delicately banded chalcedonic to fine comb quartz (± gold, silver, and copper minerals), followed by late comb quartz. Many veins contain only a portion of this sequence, but high-grade veins typically contain all three stages. In places, fragments that consist of part or all of this sequence are caught up in fenestral breccia cemented by fine quartz ± calcite. Vein paragenesis at the Lac Bullfrog mine is similar except that bladed calcite, which is mostly replaced by fine-grained granular quartz, occurs in the first two stages.

Ransome *et al.* (1910) reported that gold in the Bullfrog district characteristically occurs as electrum in limonite after pyrite. We found electrum of this type at the Lac Bullfrog mine, but also found electrum in other forms. Electrum of composition $Au_{44}Ag_{56}$ (mole %, SEM–EDX analysis) occurs in quartz veins as contorted flakes between quartz grains, and late-stage electrum of composition $Au_{59}Ag_{41}$ occurs as irregular grains up to 2 mm in diameter in the matrix of hydrothermal breccia at the Lac Bullfrog mine. Specimens of high-grade ore

TABLE 1. TRACE ELEMENT CONTENTS OF SAMPLES FROM THE ORIGINAL BULLFROG AND LAC BULLFROG MINES

	Lac Bullfrog Mine				Original Bullfrog Mine		
SAMPLE	BGBH	449	457A	SF1	BH20	OBM2	BH16
Ag	21000	26	4.6	1.6	1100	16.7	1.8
As	50.2	2.8	5.1	12.1	355	1.6	7.7
Au	9223	45.2	4.2	3.4	117	1.9	0.1
Cu	4413	61.4	37.6	38.4	5160	60.8	121
Hg	<0.10	0.17	<0.10	<0.10	<0.10	<0.10	<0.10
Mo	8.8	2.3	2.1	3.2	8.1	2.2	4.5
Pb	381	8	8	8	91	3	8
Sb	296	0.4	0.5	0.4	494	16.6	2.0
Tl	4.5	<0.25	<0.25	<0.25	<0.25	<0.25	0.8
Zn	179	9	6	3	27	2	17
Bi	0.4	<0.25	<0.25	<0.25	19.1	<0.25	1.3
Cd	0.42	<0.10	<0.10	<0.10	1.42	<0.10	<0.10
Ga	<0.5	0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Se	173	<1	<1	<1	<1	<1	<1
Te	12	0.7	<0.5	<0.5	<0.5	<0.5	<0.5
Type	1	2	3	4	1	3	4

Concentrations expressed in ppm. Analyses by ICP emission spectroscopy. Rock types: 1 = High-grade ore containing electrum, uytenbogaardtite, and copper minerals; 2 = Quartz vein with macroscopic electrum, no sulfide or copper minerals; 3 = Quartz vein without visible electrum, sulfide, or copper minerals; 4 = Altered volcanic rock with quartz veins.

TABLE 2. COMPOSITION OF UYTENBOGAARDTITE AND ELECTRUM FROM THE BULLFROG DISTRICT

	Weight %			Formula (with 2S)		Molar ratio	
	S	Ag	Au	Ag	Au	Ag	Au
LAC BULLFROG MINE							
Uytenbogaardtite							
BGB 1D	12.9	51.9	35.2	2.4	0.9	72.9	27.1
BGB 5D	12.5	53.0	34.6	2.5	0.9	73.7	26.3
BGB 1	13.5	54.0	32.4	2.4	0.8	75.3	24.7
BGB A1 (average of 19) †	12.6	50.8	36.6	2.4	0.9	71.7	28.3
BGB 2	12.3	54.2	33.5	2.6	0.9	74.7	25.3
BGB A2 (average of 10) †	12.2	53.9	33.9	2.6	0.9	74.4	25.6
BGB 5	12.2	56.6	31.2	2.8	0.8	76.8	23.2
BGP 1B	11.7	53.2	35.1	2.7	1.0	73.5	26.5
BGP 3E	11.8	53.5	34.7	2.7	1.0	73.7	26.3
Coarse electrum							
BGB 1A		34.7	65.3			49.2	50.8
BGB 5A		33.1	66.9			47.4	52.6
BGB 3		33.0	67.0			47.3	52.7
BGB A3 (average of 35) †		33.7	66.3			48.1	51.9
BGB A4 (average of 23) †		35.0	65.0			49.6	50.4
BGP 1A		31.3	61.7			48.1	51.9
BGP 3A		30.5	69.5			44.5	55.5
BGP 3C		29.1	70.9			42.8	57.2
BGB A		34.0	66.0			48.5	51.5
Rim, coarse electrum							
BGB 1B		17.3	82.7			27.7	72.3
BGBP 49 †		11.4	88.6			19.0	81.0
BGBP 50 †		20.8	79.2			32.4	67.6
Small electrum grains in uytenbogaardtite							
BGB 1C		17.1	82.9			27.4	72.6
BGB 5B		15.8	84.2			25.5	74.5
BGB 4		16.7	83.4			26.7	73.3
BGP 3B		14.2	85.8			23.2	76.8
BGBA 5 (average of 7) †		17.1	82.9			27.4	72.6
"Webby" electrum in chalcocite							
BGBA 10 #		17.0	79.3			28.1	71.9
ORIGINAL BULLFROG MINE							
Uytenbogaardtite							
20 20A	10.9	57.4	31.7	3.1	0.9	76.8	23.2
20 20A †	10.7	57.6	31.7	3.2	1.0	76.8	23.2
20 20B	11.4	54.5	34.1	2.8	1.0	74.5	25.5
20 20C	11.0	54.6	34.4	3.0	1.0	74.4	25.6
20 20C †	12.2	53.6	34.3	2.6	0.9	74.0	26.0
BH 20H	11.9	54.7	33.4	2.7	0.9	74.9	25.1
Coarse electrum							
BH 20N		39.2	60.8			54.1	45.9
BH 20T		43.0	57.0			58.0	42.0
BH 20A		33.2	66.8			47.6	52.4
BH 20F		42.5	57.5			57.4	42.6
BH 20I		40.9	59.1			55.8	44.2
BH 20F (average of 9) †		37.4	62.6			52.2	47.8
Small electrum grain in uytenbogaardtite							
BH 20U		11.7	88.3			19.5	80.5
Electrum veinlet							
BH 20M		22.2	77.9			34.2	65.8
BH 20M †		21.3	78.7			33.1	67.0

Mostly SEM-EDX data; wt. % normalized to 100%; † denotes microprobe analyses; # includes 3.7 wt. % Cu.

found in a small areas at the Lac Bullfrog and Original Bullfrog mines contain irregular grains of electrum associated with limonite, malachite, chrysocolla, and sulfide in crustiform quartz. At the Lac Bullfrog mine, such ore contains irregular masses of electrum up to 3 mm in diameter disseminated in pillow-shaped masses of quartz, limonite, chrysocolla, and sulfide.

In addition to high concentrations of gold and silver, ore from the Original Bullfrog mine with visible electrum and copper minerals has high copper and antimony contents, along with moderately elevated bismuth, arsenic, lead and cadmium (Table 1). Vein quartz without visible electrum and copper minerals has relatively low contents of these elements.

Ore from the Lac Bullfrog mine has relatively low contents of trace metals if compared with epithermal precious-metal deposits elsewhere in Nevada (Castor & Weiss 1992). A sample of unusually rich ore containing 0.9 wt.% gold and 2.1 wt.% silver from the Lac Bullfrog

mine is an exception, containing high levels of copper, lead, antimony, zinc, selenium and tellurium (Table 1).

The temperature of the low-salinity fluids associated with the main stage of mineralization at the Lac Bullfrog and Montgomery–Shoshone mines, during which electrum and sulfide were deposited, was slightly above 200°C, according to fluid inclusion data (Jorgenson *et al.* 1989). The maximum depth of mineralization was about 2000 m, judging from the total thickness of volcanic units that predate mineralization and occur stratigraphically above host units for both the Lac Bullfrog and Original Bullfrog mines. Mineralization overlapped temporally with extensional displacement within the Bullfrog district, as suggested by radiometric dates on secondary K-feldspar, stratigraphic and structural relations in the district, mineralization control by normal faults, and evidence for fracturing and brecciation concurrent with vein deposition (Noble *et al.* 1991, Castor & Weiss 1992). The depth of mineralization would be lowered from the maximum indicated by stratigraphy if extensional thinning took place prior to, or during, mineralization.

Properties of Uytenbogaardtite from the Bullfrog District

In the Bullfrog district, uytenbogaardtite has been found only in ore specimens that contain macroscopic electrum; it is generally intergrown with electrum and acanthite. On freshly polished surfaces, it is bright gray with a faint pink tint, and tarnishes over a period of days to a brassy color. Freshly polished surfaces of uytenbogaardtite are very similar to those of acanthite (which is bright gray with a faint blue tint), but the two minerals can be distinguished with difficulty when compared in the same field of view. Anisotropy is very weak for both sulfides. The hardness of uytenbogaardtite seems to lie between that of acanthite and electrum (*ca.* 2.5 on the Mohs scale) based on polishing hardness. Uytenbogaardtite from the Bullfrog district is relatively brittle if compared with acanthite, as noted by Barton *et al.* (1978) for specimens from other occurrences. X-ray-diffraction data obtained on uytenbogaardtite from the Lac Bullfrog mine are identical to those for synthetic Ag_3AuS_2, which is tetragonal (Graf 1968), and to uytenbogaardtite from other natural occurrences (Barton *et al.* 1978).

On the basis of SEM–EDX and results of electron-microprobe analyses, the composition of uytenbogaardtite from the Bullfrog district is consistent with microprobe data reported by Barton *et al.* (1978); it contains between 50.8 and 57.6 wt.% silver, 31.2 and 36.6 wt.% gold, and 10.7 and 13.5 wt.% sulfur (Table 2). Copper, which is reported to occur in minor amounts in some examples of uytenbogaardtite (Barton *et al.* 1978, Chen *et al.* 1979, as reported in Fleischer *et al.* 1980), was not noted. Normalized compositions of uytenbogaardtite and electrum from the Bullfrog district are reported in Table 2.

TABLE 3. COMPARISON OF COMPOSITIONAL DATA OBTAINED BY SEM AND ELECTRON MICROPROBE

	SEM/EDX			MICROPROBE		
	Au	Ag	S	Au	Ag	S
E, LBM	66.69	32.83	--	66.95	33.48	0.01
E, LBM	81.14	16.21	--	82.66	16.61	0.03
U, LBM	33.40	54.00	12.20	35.26	51.77	12.92
U, OBM	34.79	55.34	11.15	32.10	58.32	10.87
U, OBM	33.01	59.76	11.34	35.65	55.71	12.60

Concentrations in wt. %. Compared analyses are of adjacent sites in the same mineral grain. E, electrum; U, uytenbogaardtite; LBM, Lac Bullfrog mine; OBM, Original Bullfrog mine.

The SEM–EDX analyses were performed at the Reno Research Center of the U. S. Bureau of Mines using a JEOL T–300 scanning electron microscope equipped with a Princeton Gamma-Tech System 4 X-ray analyzer. Electron-microprobe (ARL) analyses were performed at the Twin Cities Research Center of the U. S. Bureau of Mines using a JEOL Model 733 electron microprobe. In both cases, pure metals and analyzed sulfide samples prepared in the same manner as the ore specimens were used as standards. Compositions of adjacent sites in grains of uytenbogaardtite and electrum, obtained using both methods, are compared in Table 3. Replicate analyses performed at the same site using either method resulted in consistently lower sulfur and higher silver values for successive analyses because of volatilization of sulfur in the electron beam. In the following discussions, mineral compositions are given in mole %, except as noted.

Textures and Mineral Assemblages of Uytenbogaardtite-Bearing Ore

Specimens of high-grade ore from the Original Bullfrog mine contain irregular grains of uytenbogaardtite up to 200 μm across and acanthite grains up to 0.5 cm in diameter associated with coarse electrum ($Au_{52}Ag_{48}$ to $Au_{42}Ag_{58}$, Table 1) up to 2 mm in maximum dimension. Uytenbogaardtite, acanthite, and coarse electrum comprise irregular masses rimmed by chrysocolla, malachite, unidentified antimony – bismuth – copper oxide phases, and limonite. Irregular grains of gold-rich electrum ($Au_{80}Ag_{20}$) up to 30 μm across are sparsely to abundantly scattered in uytenbogaardtite adjacent to electrum in some masses, and gold-rich electrum of similar composition forms a rim up to 3 μm thick on coarse electrum adjacent to uytenbogaardtite in places (Fig. 1A). In addition, veinlets of electrum ($Au_{66}Ag_{34}$) up to 2 μm across were found cutting both acanthite and uytenbogaardtite (Fig. 1B). Acanthite, along with traces of electrum, also occurs in cavities lined with quartz crystals and in late-stage veinlets with chrysocolla. In addition, acanthite, limonite, malachite,

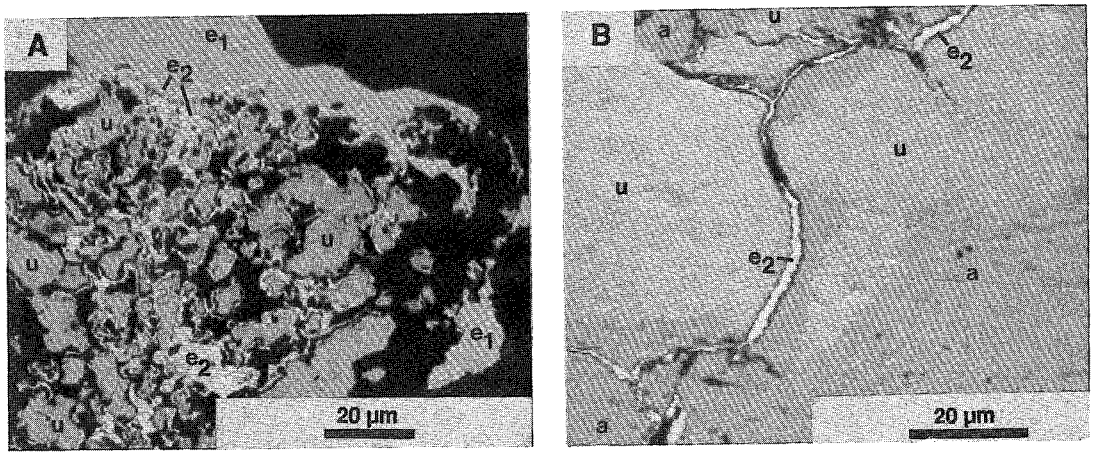


FIG. 1. Back-scattered SEM images of specimens from the Original Bullfrog mine. A. Coarse electrum (e_1) with gold-rich electrum (e_2) rim, uytenbogaardtite (u) with included gold-rich electrum grains. Chrysocolla (c) is intermixed with uytenbogaardtite and gold-rich electrum. B. Uytenbogaardtite and acanthite (a) cut by gold-rich electrum vein (e_2).

and traces of electrum fill thin tabular cavities that are considered to have formed by the dissolution of calcite blades.

Some vein specimens from the Original Bullfrog mine contain stromeyerite ± chalcocite that is generally rimmed and partially replaced by platy covellite and surrounded by chrysocolla ± malachite ± copper sulfate. Tiny corroded grains of electrum ($Au_{56}Ag_{44}$) were found included in covellite in one specimen, but uytenbogaardtite was not found adjacent to copper-bearing sulfide. Grains entirely composed of stromeyerite that are encapsulated by quartz also are present.

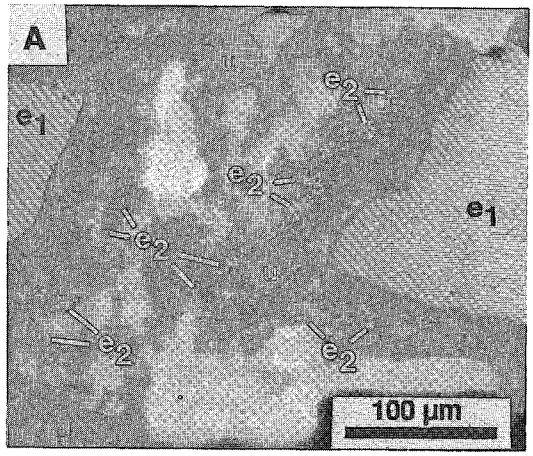
In addition to copper and iron, products of oxidation in Original Bullfrog ore contain arsenic, bismuth, lead, antimony, and zinc. These elements were detected by SEM-EDX techniques in extremely fine-grained mixtures of oxide and silicate minerals that could not be identified.

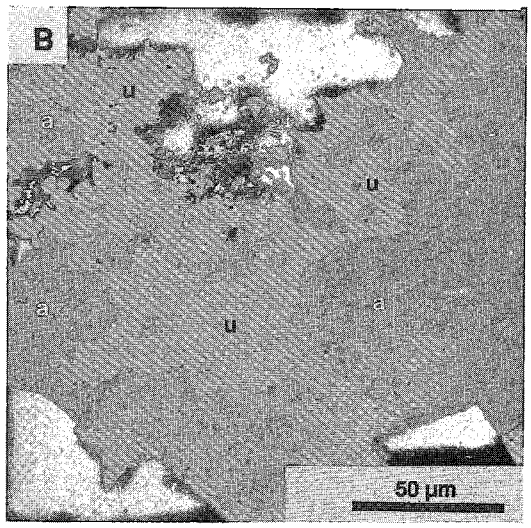
In specimens from the Lac Bullfrog mine, coarse electrum ($Au_{57}Ag_{43}$ to $Au_{50}Ag_{50}$, Table 1) occurs in grains up to 3 mm across, and is associated with uytenbogaardtite in grains up to 300 μm across. The uytenbogaardtite rims and seems to replace the coarse electrum, which has a thin gold-rich rim ($Au_{72}Ag_{28}$) in many places along contacts with uytenbogaardtite. In addition, the uytenbogaardtite commonly is studded with tiny gold-rich grains of electrum ($Au_{77}Ag_{23}$ to $Au_{73}Ag_{27}$) that in some cases form a halo around included coarse electrum (Fig. 2A).

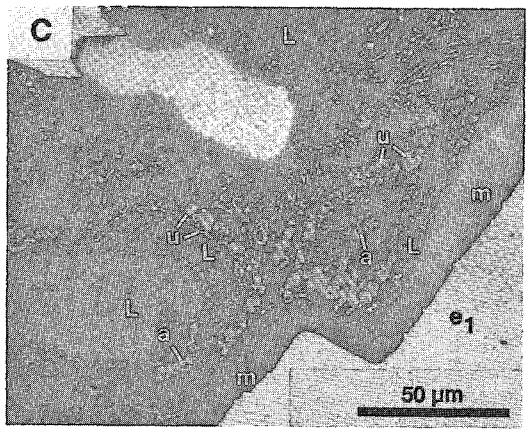
Specimens of high-grade ore from the Lac Bullfrog mine contain acanthite in irregular masses up to 400 μm across, as mixed grains with uytenbogaardtite (Fig. 2B), and in late cross-cutting veins with chrysocolla. Uytenbogaardtite does not accompany acanthite that is more than 1 mm away from coarse electrum, although small amounts of high-gold electrum is found replacing or rimming such acanthite. Copper-bearing sulfide consists of chalcopyrite and stromeyerite partially replaced by chalcocite, covellite, limonite, malachite, chrysocolla, and brochanthite. The relationship between chalcopyrite and stromeyerite is ambiguous; in places, chalcopyrite rims stromeyerite, and in other cases, stromeyerite rims and veins chalcopyrite. Covellite partially replaces both phases. Filiform veins of high-gold electrum ($Au_{72}Ag_{28}$) accompanied by tiny blebs of naumannite (Ag_2Se with minor Cu) were found in one case in chalcocite replacing stromeyerite. Products of oxidation generally rim uytenbogaardtite and acanthite; however, uytenbogaardtite and acanthite are interlayered with limonite in places (Fig. 2C). As in Original Bullfrog ore, very fine-grained products of oxidation in uytenbogaardtite-bearing ore at the Lac Bullfrog mine carry trace metals including lead, antimony, and zinc.

PARAGENESIS AND PHASE EQUILIBRIA

On the basis of textural evidence from reflected-light microscopy and SEM imagery, the sequence of mineral deposition in high-grade ore at both occurrences of uytenbogaardtite in the Bullfrog district is the same. Early-formed electrum, with compositions approximating $Au_{50}Ag_{50}$, was deposited during or between episodes of deposition of comb quartz ± calcite. Stromeyerite (+ chalcopyrite at the Lac Bullfrog mine) seems to have been deposited at approximately the same time as this electrum. Uytenbogaardtite and acanthite then crystal-







lized, uytenbogaardtite forming, at least in part, as a result of replacement of early electrum. Late, relatively gold-rich electrum ($Au_{80}Ag_{20}$–$Au_{73}Ag_{27}$) formed contemporaneously with uytenbogaardtite as a rim on early electrum adjacent to uytenbogaardtite and as tiny irregular grains in the uytenbogaardtite. Contemporaneous deposition of these phases is consistent with stability relations reported by Barton *et al.* (1978), which indicate that uytenbogaardtite and acanthite form together in equilibrium with electrum that contains 20 – 30 mole % silver. An isothermal section for the system Ag–Au–S at 100°C shows electrum with approximately $Au_{75}Ag_{25}$ to be in equilibrium with acanthite and uytenbogaardtite (Barton 1980), and the small grains of gold-rich electrum in uytenbogaardtite from the Bullfrog district cluster around this composition (Fig. 3). The occurrence of grains of gold-rich electrum in halos about partially replaced early electrum (Fig. 2A) suggests that the gold-rich electrum grains are relics of earlier rims left behind as replacement of early electrum by uytenbogaardtite advanced. Acanthite and uytenbogaardtite seem to have cocrystallized (Fig. 2B), but late cross-cutting veins carrying acanthite with a little gold-rich electrum but no uytenbogaardtite may postdate the period of deposition of uytenbogaardtite.

The reaction of $Au_{50}Ag_{50}$ electrum with sulfur to form uytenbogaardtite, acanthite, and gold-rich electrum ($Au_{75}Ag_{25}$) is predictable from the phase diagram for the system Au–Ag–S at 100°C, as determined by Barton (1980); Figure 3 shows the phase relationships along with compositions of the minerals in the Bullfrog district. The reactions that take place when sulfur is added to $Au_{50}Ag_{50}$ electrum can be predicted from Figure 3 along a straight line connecting the sulfur corner and $Au_{50}Ag_{50}$. Initial addition of sulfur would move the bulk composition into the acanthite + electrum field. Extraction of silver from electrum to form acanthite would cause the composition of electrum to move toward the gold corner. When sufficient sulfur is added, the bulk composition can be expected to reach the

FIG. 2. Photomicrographs of uytenbogaardtite from the Lac Bullfrog mine. A. Reflected-light image of coarse electrum (e_1) rimmed by uytenbogaardtite (u) containing small grains of gold-rich electrum (e_2) arranged in zones that are roughly parallel to uytenbogaardtite – coarse electrum contacts. B. Back-scattered SEM image of intergrown uytenbogaardtite (u) and acanthite (a) with minor gold-rich electrum. C. Back-scattered SEM image of coarse electrum (e_1) partially rimmed by uytenbogaardtite (u) and malachite (m). Thin bands of uytenbogaardtite (u) and acanthite (a) are interlayered with limonite (L).

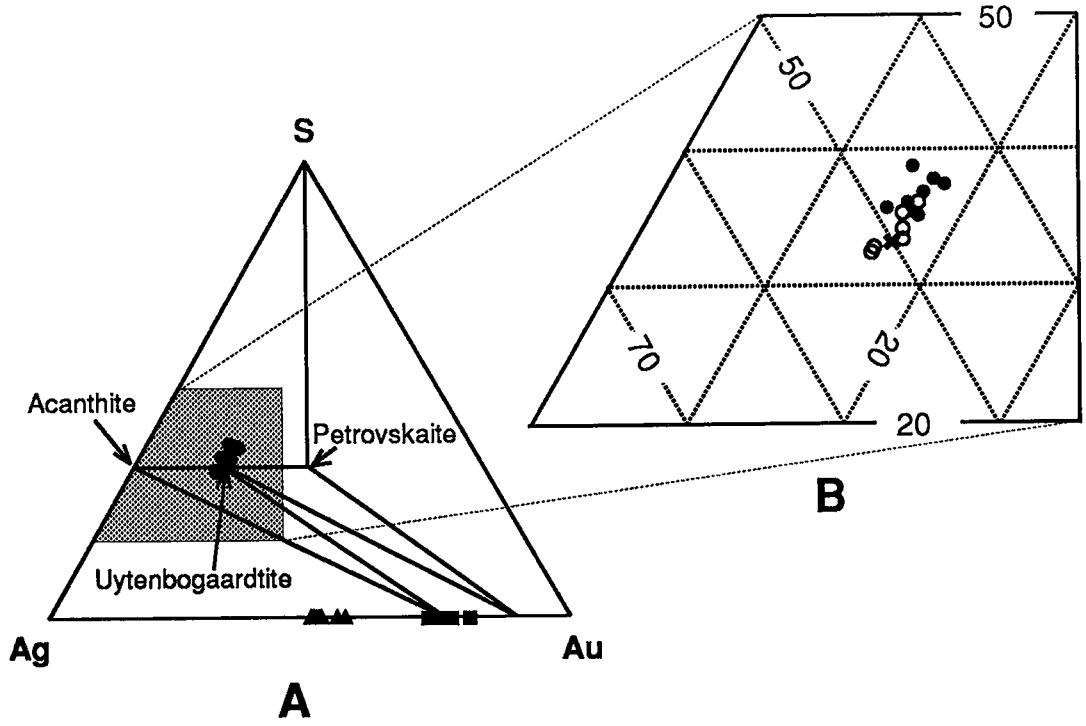


FIG. 3. A. Compositions of uytenbogaardtite and electrum from the Bullfrog district (Table 2) plotted on the isothermal section for the system Ag–Au–S at 100°C, adapted from Barton (1980): uytenbogaardtite (●); coarse electrum (▲); small electrum grains in uytenbogaardtite (■). B. Compositions of uytenbogaardtite from the Lac Bullfrog mine (○) and the Original Bullfrog mine (●) plotted on a portion of Figure 3A. Theoretical uytenbogaardtite composition: ×.

acanthite–electrum join, and uytenbogaardtite would begin to form, in equilibrium with acanthite and electrum ($Au_{75}Ag_{25}$). Continued addition of sulfur would cause the bulk composition to enter the three-phase field acanthite + uytenbogaardtite + electrum ($Au_{75}Ag_{25}$), with the proportion of the phases changing. Eventually, acanthite would disappear, and other phases could form. Evidence from natural assemblages in the Bullfrog district indicate that the amount of sulfur remained sufficiently low for acanthite to persist, or that silver was added along with sulfur. The agreement between phase relationships observed in Bullfrog district ore and predictions from phase studies is remarkable, but may be fortuitous considering uncertainties inherent in such predictions.

Mass-balance calculations show that the conversion of early electrum to uytenbogaardtite and gold-rich electrum in ore from the Bullfrog district was accompanied by the introduction of both silver and sulfur. The expected volume-ratio of a mixture of gold-rich electrum (at $Au_{75}Ag_{25}$) and uytenbogaardtite produced from early electrum (at $Au_{50}Ag_{50}$), following $8Au_{0.5}Ag_{0.5} + S_2 = 4Au_{0.75}Ag_{0.25} + Ag_3AuS_2$ and conserving both gold and silver, is approximately 40:60 (using a density of uytenbogaardtite of 8.3 g/cm^3: Barton *et al.* 1978). In a few cases, the amount of gold-rich electrum in uytenbogaardtite seems to approach this amount (Fig. 1A), but our examinations indicate that most uytenbogaardtite grains contain much lower amounts of gold-rich electrum (Fig. 2A) and, in some cases, none at all. The formation of variable mixtures of uytenbogaardtite ± acanthite ± gold-rich electrum is consistent with the addition of variable amounts of silver and sulfur to $Au_{50}Ag_{50}$.

Equations can also be written for the reaction of electrum, acanthite, and sulfur that will produce relatively large volumes of uytenbogaardtite (*e.g.*, $10Ag_2S + 36Au_{0.5}Ag_{0.5} + 7S_2 = 12Ag_3AuS_2 + 8Au_{0.75}Ag_{0.25}$, producing about 70 vol.% uytenbogaardtite and 30 vol.% gold-rich electrum). However, we did not find early-formed acanthite in ore from the Bullfrog district, such as that reported by Barton *et al.* (1978) in uyten-

bogaardtite-bearing specimens from Indonesia and the Comstock lode.

As shown by Barton (1980), addition of sulfur to gold-rich electrum at 100°C would result in the formation of uytenbogaardtite and AuAgS (Fig. 3). The latter phase, recently discovered in Kazakhstan as a rim on native gold and named petrovskaite (Nesterenko *et al.* 1984, as reported in Dunn *et al.* 1985), has subsequently been found with uytenbogaardtite in gold ore from Montana (W. Fuchs, pers. comm., 1992). Measured compositions of silver–gold sulfide from the Bullfrog district do not deviate significantly from the theoretical composition of uytenbogaardtite (Fig. 3), and a sulfide with a composition approaching that of petrovskaite was not found.

Replacement of stromeyerite ± chalcopyrite by chalcocite ± naumannite and by covellite may have taken place concurrently with deposition of uytenbogaardtite and acanthite. Electrum veinlets that cut acanthite + uytenbogaardtite (Fig. 1B) or chalcocite have gold contents similar to those of the inclusions of high-gold electrum in uytenbogaardtite (Table 2) but must postdate sulfide deposition (at least in the enclosing grains). Minerals that formed under oxidizing conditions (limonite, chrysocolla, malachite, and brochanthite) generally appear to have postdated sulfide deposition, forming rims around sulfide electrum. However, intimate intermixtures of uytenbogaardtite with products of oxidation, including gold-rich electrum that seems to have been deposited on uytenbogaardtite with chrysocolla (Fig. 1A) and crustiform interlayers of acanthite and uytenbogaardtite with limonite (Fig. 2C), suggest that the deposition of uytenbogaardtite, acanthite, and gold-rich electrum overlapped with oxidizing conditions. Deposition of late silica, calcite, and electrum as components of hydrothermal breccia matrix clearly followed the deposition of early electrum and copper-bearing sulfides, but the temporal relationship between the formation of hydrothermal breccia and uytenbogaardtite is unknown.

Discussion

Data on fluid inclusions in quartz veins from the Lac Bullfrog mine suggest formation at temperatures of about 200°C (Jorgenson *et al.* 1989). However, the work of Graf (1968) indicates that uytenbogaardtite can form in equilibrium with acanthite only below 113°C. In addition, the lack of polysynthetic twinning in acanthite suggests formation at temperatures below 140°C (Taylor 1969). On the basis of this information and the textural data presented above, the assemblage uytenbogaardtite + acanthite + gold-rich electrum in the Bullfrog district represents a relatively late and low-temperature stage of mineralization. Mass-balance considerations, along with the presence of significant amounts of acanthite that seem to have been deposited, at least in part, contemporaneously with uytenbogaardtite, indicate that both silver and sulfur were added during the formation of uytenbogaardtite. Other elements that seem to have been enriched in uytenbogaardtite-bearing ore include lead, antimony, and bismuth (Table 1), which mainly occur in products of oxidation, as shown by SEM–EDX scans.

Hypogene fluids were undoubtedly responsible for the initial deposition of electrum and stromeyerite (chalcopyrite) in the Bullfrog district, possibly at temperatures similar to those indicated for quartz deposition (*ca.* 200°C). Uytenbogaardtite may have formed during the waning stages of hydrothermal activity, when deposition of acanthite and chalcocite was taking place. The formation of gold-rich electrum (70–80 mole % Au) in the Bullfrog district would be due to the partial equilibration of early-formed electrum (*ca.* 50 mole % Au) with uytenbogaardtite and acanthite (*cf.* Barton *et al.* 1978). A similar relationship between early electrum, late-stage electrum with high gold contents, acanthite, and covellite in ore that may contain uytenbogaardtite is ascribed to hydrothermal processes at the Morning Star deposit in southern California (Sheets *et al.* 1988). The products of oxidation in ore from the Bullfrog district, such as limonite and chrysocolla, could have formed as a result of *in situ* leaching of sulfide or transport from higher levels.

An alternative supergene origin for the uytenbogaardtite + acanthite + gold-rich electrum assemblage is suggested by textural relationships that indicate overlap with mineralization produced under oxidizing conditions in the Bullfrog district. In addition, the presence of chalcocite and covellite is consistent with supergene deposition of sulfide, although typical supergene forms (sooty chalcocite and blaubleibender covellite) are absent. Since proposed by Emmons (1912) for the Bullfrog district and other areas, supergene enrichment of precious-metal deposits has been supported by others (*e.g.*, McKay 1944, Webster & Mann 1984, Stoffregen 1986, Moeller 1988). An uytenbogaardtite-bearing assemblage in a specimen from Russia is considered to have been, at least in part, of supergene origin (Barton *et al.* 1978). Mobilization of gold during supergene processes is ascribed to the presence of complexing ions, particularly thiosulfate (Webster & Mann 1984), which is formed by the breakdown of pyrite in environments in which pH of the fluid is maintained at relatively high levels by the presence of calcite (Lakin *et al.* 1974). Such conditions are met in vein systems of the Bullfrog district, which contain vein calcite as well as pyrite in altered wallrock. However, thiosulfate complexes are relatively unstable, and Stoffregen (1986) proposed redeposition of gold at Summitville, Colorado, within meters or centimeters of the initial site of gold dissolution. In the Bullfrog district, redeposition of gold as uytenbogaardtite apparently occurred within millimeters or micrometers of the site of dissolution from early electrum.

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