

**COMPOSITION AND OCCURRENCE OF ELECTRUM  
AT THE MORNING STAR DEPOSIT,  
SAN BERNARDINO COUNTY, CALIFORNIA:  
EVIDENCE FOR REMOBILIZATION OF GOLD AND SILVER**

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ABSTRACT

Electrum, acanthite and uytenbogaardtite have been examined from six depths within the tabular quartz  $\pm$  calcite stockwork and breccia-filled veins in the fault-zone-hosted Morning Star deposit of the northeastern Mojave Desert, California. Six distinct types of electrum have been identified on the basis of mineral association, grain morphology and composition. Two types, (1) pyrite-hosted and (2) quartz-hosted electrum, occur with acanthite after argentite and base-metal sulfide minerals in unoxidized portions of the orebody; the remaining four types, (3) goethite-hosted electrum, (4) electrum cores, (5) electrum rims and (6) wire electrum, are associated with assemblages of supergene minerals in its oxidized portions. Pyrite-hosted, quartz-hosted and goethite-hosted electrum range in composition from 61 to 75 wt.% Au and have uniform textures and no zoning. In lower portions of the oxidized ore zone, electrum seems to replace goethite and occurs as small grains on surfaces of the goethite. Textural evidence favors supergene remobilization of Au and Ag, which were deposited as electrum on or replacing goethite. This type of electrum is identical in appearance and composition to primary electrum. In the upper portions of the oxidized zone, secondary electrum occurs as a gold-rich rim on a core of electrum and as wire-like grains, both with acanthite and uytenbogaardtite. Such secondary electrum contains from 78 to 93 wt.% Au. Textural relations and associated minerals suggest that the primary electrum was hydrothermally deposited and partially remobilized by supergene processes.

*Keywords:* electrum, gold (Au), silver (Ag), uytenbogaardtite, supergene, remobilization, Morning Star deposit, California.

SOMMAIRE

Nous avons examiné l'électrum, l'acanthite et l'uytenbogaardtite provenant de six niveaux dans le stockwerk à quartz  $\pm$  calcite et le système de brèches en veines du gisement de Morning Star, mis en place dans une zone faillée dans le secteur nord-est du désert de Mojave, en Californie. Il s'y trouve six types d'électrum, identifiables par l'association de minéraux, la morphologie des grains et leur composition: (1) électrum piégé dans la pyrite, (2) électrum piégé dans le quartz, ces deux types associés à l'acanthite remplaçant l'argentite et aux sulfures des métaux de base dans les parties non oxydées du gisement, (3) électrum associé à la goéthite, (4) noyau des grains, (5) bordure des grains et (6) électrum en filament, ces quatre derniers associés aux assemblages de minéraux supergènes dans les parties oxydées du gisement. L'électrum dans la pyrite, le quartz ou la goéthite a une teneur en Au comprise entre 61 et 75% (poids) et une texture uniforme, sans zonation chimique. Dans les parties inférieures de la zone oxydée, l'électrum semble remplacer la goéthite, et est disposée en petits grains sur les surfaces de celle-ci. D'après l'évidence texturale, il semble y avoir eu remobilisation supergène de Au et Ag, et déposition sous forme d'électrum sur (ou en remplacement de) la goéthite. Cette génération secondaire d'électrum possède une apparence et une composition identiques à l'électrum primaire. Dans les parties supérieures de la zone oxydée, l'électrum secondaire se présente sous forme d'un liseré de bordure sur un cœur d'électrum, ou bien en filaments, les deux en association avec acanthite et uytenbogaardtite. L'électrum secondaire a une teneur en Au entre 78 et 93% (poids). D'après les relations texturales et les minéraux associés, l'électrum primaire a été déposé dans un milieu hydrothermal et a été partiellement remobilisé par processus supergènes.

(Traduit par la Rédaction)

*Mots-clés:* électrum, or (Au), argent (Ag), uytenbogaardtite, supergène, remobilisation, gisement de Morning Star, Californie.

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## INTRODUCTION

Chemical models used to describe the distribution of gold and silver minerals between oxidized and unoxidized portions of gold deposits remain equivocal for many deposits. Gold and silver remobilization by low-temperature oxidizing groundwater is suggested as an important supergene process leading to secondary enrichment of some precious-metal deposits (Emmons 1912, Boyle 1968, 1978, Larkin *et al.* 1974). Also, waning-stage hydrothermal activity may remobilize gold and silver (Barton *et al.* 1978). Increased fineness of electrum during mineralization is commonly cited as evidence for remobilization of gold and silver (Emmons 1912, MacKay 1944, Koshman & Yugay 1972), but recent studies (Mann 1984, Stoffregen 1986) convincingly argue for remobilization of gold and silver without an increased fineness of the deposited electrum in certain chemical environments. Other investigators have suggested that supergene remobilization of gold and silver may actually lead to a decrease in fineness of the electrum in specific circumstances (Webster & Mann 1984).

Other minerals of gold and silver may be produced during late-stage hydrothermal or supergene oxidation of precious-metal deposits. For example, uyttenbogaardtite ( $\text{Ag}_3\text{AuS}_2$ ), a rare silver-gold sulfide, has been reported in a small number of deposits, where it occurs as a late-stage hydrothermal or supergene phase (Barton *et al.* 1978, Dunn *et al.* 1985, Castor & Sjöberg 1993). Uyttenbogaardtite has recently been identified in the upper levels of the Morning Star deposit (Sheets *et al.* 1988, 1989). Stability relationships for uyttenbogaardtite, acanthite and electrum in the supergene environment are not currently available, but low-temperature (100°C) hydrothermal equilibria predict the formation of uyttenbogaardtite and acanthite by sulfidation of electrum (Barton 1980).

This paper describes the distribution and chemistry of precious-metal mineralization in the vicinity of the Morning Star deposit and places constraints on conditions attending gold and silver remobilization. As previously stated, the remobilization of gold and silver may occur either with an increase in fineness of electrum (Mann 1984) or with a constant or slightly decreasing fineness (Webster & Mann 1984, Stoffregen 1986). The Morning Star deposit is unusual in that textural and chemical evidence support both trends in the composition of electrum, at different levels within the oxidized horizon.

## LOCATION AND HISTORY

The Morning Star deposit is located on the southeastern flank of the Ivanpah Mountains, northeastern Mojave Desert, California, approximately 100 km southwest of Las Vegas, Nevada (Fig. 1A). Proven reserves at the Morning Star mine, in 1987, were

approximately 7.3 million metric tonnes of ore averaging 2.057 g/tonne (Ausburn 1988). The mine was operated intermittently in this century, with the last episode of mining occurring from 1987 to mid-1991; heap-leach extraction of gold and silver continues today. Additional subeconomic precious-metal mineralization occurs throughout a series of prospect pits in the Kewanee Hills area, south of the mine, and along the Sunnyside fault, to the west of the mine (Fig. 1B).

The Ivanpah Mountains are underlain by Jurassic to Cretaceous weakly peraluminous, magnetite-series granitic plutons of the Teutonia batholith, which constitutes part of the Mesozoic magmatic arc that intruded the southern portion of the Mesozoic foreland fold-and-thrust belt (Burchfiel & Davis 1972, 1975, 1988, Beckerman *et al.* 1982, Barton *et al.* 1988). Subeconomic porphyry copper-molybdenum and related skarn mineralization is associated with portions of the batholith in the adjacent mountains (Ntiamoah-Agyakwa 1987), and tin, tungsten and copper skarn-type mineralization surrounds the Ivanpah Mountains (Hewett 1956, Thompson 1978). Detailed description of the regional geological setting and associated mineralization is given in Sheets (1995).

## GEOLOGY OF THE MORNING STAR DEPOSIT

The area around the Morning Star deposit is underlain by coarse-grained, equigranular Ivanpah granite of Jurassic age (Fig. 1B). Mineralization occurs in foliated to mylonitic Ivanpah granite situated between the Morning Star and Sunnyside thrust faults, both oriented roughly N20°W/35°SW. Each fault is marked by a zone of ductile deformation (mylonite and protomylonite) overprinted by brittle deformation.

Precious-metal mineralization at the Morning Star deposit is hosted by the Ivanpah granite in the upper plate of the Morning Star thrust fault (Figs. 1B, C). The fault crops out at the mine site as a zone of fault gouge consisting of bleached and rounded granite fragments of variable size surrounded by anastomosing foliated, clay-rich selvages. Very rare galena and chalcocopyrite have been found in fault-gouge samples, but gold and silver mineralization is truncated at the gouge layer. The upper edge of the Morning Star diorite dike, which underlies the thrust fault, is truncated by the Morning Star fault, and fragments of altered diorite are found in samples of fault gouge. A series of gouge-filled E-W- to ENE-WSW-trending vertical to steeply north-dipping unmineralized structures cut the orebody, Morning Star fault and Morning Star diorite. Displacement on the E-W structures appears to be left-lateral normal oblique-slip, with maximum throw of 5 meters on each E-W structure.

Disseminated base- and precious-metal mineralization at the Morning Star deposit is structurally controlled within a tabular zone of quartz  $\pm$  calcite stockwork vein system and silica-flooded breccia units

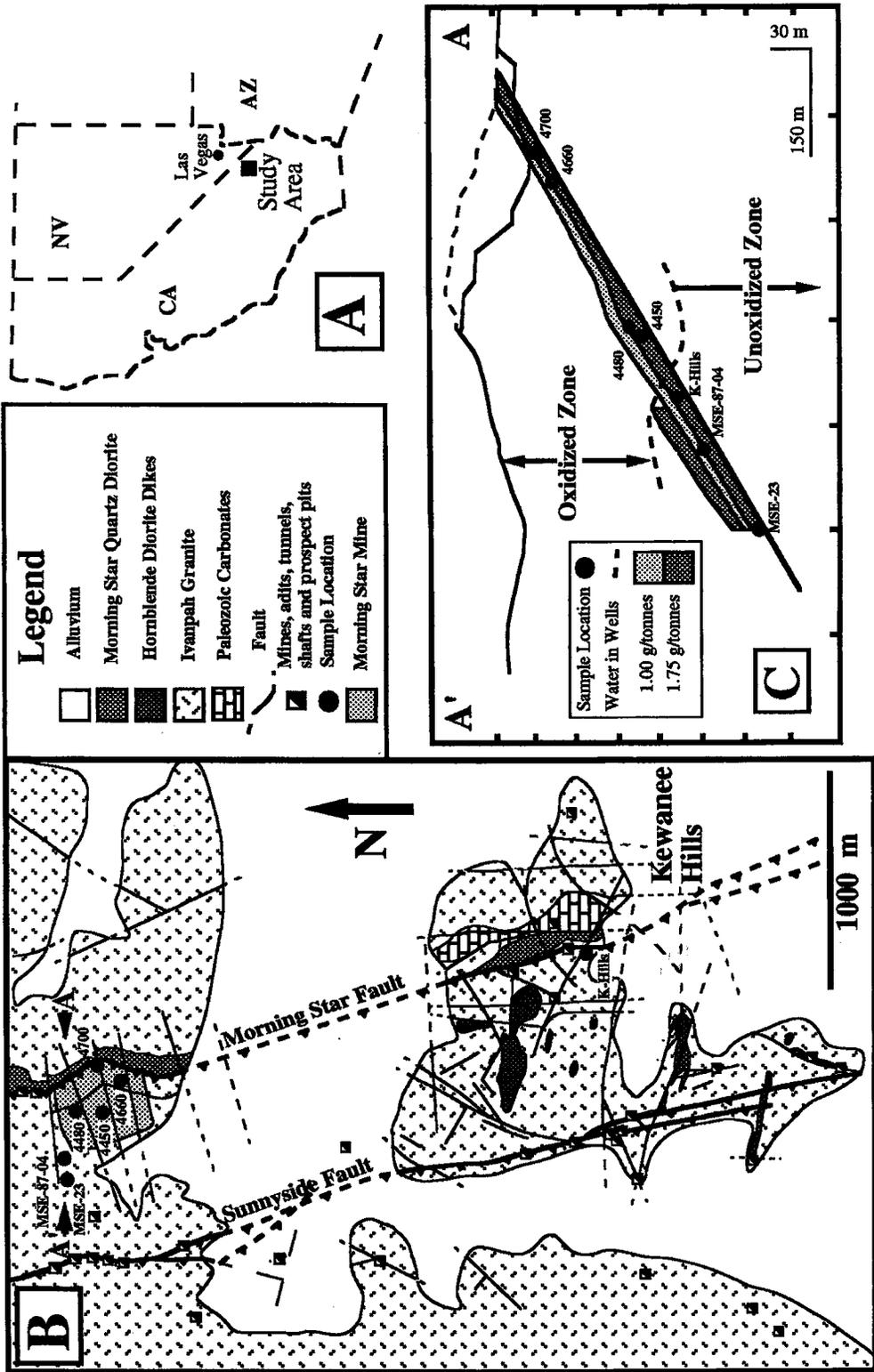


FIG. 1. Generalized geology and mineralization of the Morning Star mine area. A. Location map. B. Geological map of the southeastern Ivavpah Mountains and Kewanee Hills areas, showing the location of the seven gold-bearing samples analyzed in this study. C. Schematic cross-section of the northern portion of the Morning Star orebody. This east-west cross-section contains drill holes MSE-23 and MSE-87-04. All other sample locations are plotted as points projected along the Morning Star fault at the appropriate elevations. Sample K-Hills is from a surface sample from the Kewanee Hills incline, south of the Morning Star mine, and is plotted on the cross-section according to its elevation and distance from the Morning Star fault. See text for further discussion of the geology and sample descriptions.

subparallel to the Morning Star thrust fault (Fig. 1C). The tabular orebody is truncated to the north and south by unmineralized clay-gouge-filled E–W high-angle structures, and to the east by the Morning Star fault. Horizontal thickness of the ore horizon increases below the zone of intense oxidation, which occurs down to the 1340 and 1370 m elevation, and corresponds to the present-day water table. Standing water in abandoned mines and perched water tables are near neutral to slightly acidic (pH ranges from 6.5 to 8.0). The coincidence of oxidation with the present-day groundwater table has been noted in other gold deposits of the northeastern Mojave Desert (pers. comm., J. Cline, 1992).

Two stages of mineralization have been identified on the basis of petrographic studies and results of electron-microprobe analyses (Sheets 1995). An early stage of hypogene quartz, calcite, barite, fluorite, pyrite, chalcopyrite, galena, sphalerite, tetrahedrite, acanthite after argentite and electrum occurs below the zone of oxidation, and a later stage of calcite, covellite, digenite ( $\pm$  chalcocite), goethite, acanthite, uytenbogaardtite, native bismuth, electrum, Pb, Zn and Cu carbonates and Cu oxides occur within the zone of oxidation. Partially oxidized remnants of assemblages of primary minerals are present in most of the oxidized ore. Mineralization is confined to quartz  $\pm$  carbonate veins, stockwork zones and brecciated units. Early-formed quartz and pyrite veins are commonly deformed. A second episode of quartz and pyrite was precipitated as open-space fillings, and base- and precious-metal mineralization typically fills small openings in this second episode of quartz. Cavities and vugs are typically lined by euhedral crystals of quartz and filled with coprecipitated pyrite, galena, sphalerite, chalcopyrite, tetrahedrite, acanthite and electrum. Quartz-absent calcite veins occur later than main-stage precious-metal mineralization and only contain galena and chalcopyrite. Carbonate veins are more abundant in upper levels of the deposit, where mafic dikes or mafic-mineral-bearing fault gouge were encountered. Factors controlling the intensity of precious-metal mineralization include fracture density, presence of pyrite with galena, sphalerite and chalcopyrite (or the oxidized equivalents), and silicification.

Pervasive propylitic alteration occurs in both the upper and lower plates of the Morning Star fault and envelops the area of mineralization. The intensity of the propylitic alteration decreases markedly away from the deposit and is truncated to the north by an E–W high-angle structure. Argillic  $\pm$  sericitic alteration occurs only adjacent to mineralization in the upper plate. Alteration of the Morning Star fault gouge and unmineralized E–W structures is also considered to be related to the episode of argillic  $\pm$  sericitic alteration (Sheets 1995). Quartz veins and veinlets are prevalent throughout the tabular ore horizon and at structurally higher levels of the upper plate at the

intersection of principal sets of fractures.

Although the ore horizon forms a continuous regularly shaped tabular body (Fig. 1C), concentrations of gold within the ore horizon have a complex distribution owing to the structurally controlled nature of the deposit. Silver concentrations, where data are available, generally mirror gold concentrations. The relationship between gold and silver assay values is consistent for both oxidized portions and unoxidized portions of the deposit, but gold and silver concentrations are depleted in the zone of oxidation compared to the unoxidized zone. Also, a slight difference in Au/Ag exists between the oxidized ore and the unoxidized ore. Au/Ag values for the oxidized portions of the ore body range from 0.005 to 1.150 and have an average ( $\pm 1\sigma$ ) of  $0.143 \pm 0.169$  ( $N = 116$ ), whereas Au/Ag values for unoxidized portions of the orebody range from 0.010 to 5.000 and average  $0.340 \pm 0.540$  ( $N = 164$ ). Rock-chip-based geochemical surveys around the Kewanee Hills historic workings exhibit similar relationships between gold and silver as oxidized surface-samples within the mine. Concentrations of gold in the Morning Star mine have a strong geochemical correlation with concentrations of Ag, As, Cu, Mo, Pb and Bi, and a moderate correlation with levels of Zn and Cd (Sheets 1995). Similar correlations were seen in rock-chip and soil samples around the Kewanee Hills area (Forgerson 1974, Byington 1988). With the exception of the As and Sb anomalies, all trace-element correlations have been accounted for by minerals associated with gold and silver (discussed below). For a more detailed description of the geology, mineralization and geochemistry of the Morning Star deposit, see Sheets (1995).

#### OCURRENCE AND COMPOSITION OF PRECIOUS-METAL MINERALS

Electrum and silver–gold sulfide minerals have been examined petrographically and analytically at seven locations in the vicinity of the Morning Star deposit (Figs. 1B, C). Four samples were taken from the high-grade ore horizon within the open-pit mine (4700, 4660, 4480 and 4450 bench samples), and two samples represent high-grade ore from drill core (MSE–23 and MSE–87–04) beyond the current extent of the mine workings. Another sample with microscopic gold (K–Hills) was taken from an incline in the southern Kewanee Hills area. Although this latter sample has been plotted on Figure 1C by its elevation and distance from the Morning Star fault, it is a surface sample and has been completely oxidized. Sample descriptions are given in Sheets (1995).

The chemical composition of electrum, silver sulfides and uytenbogaardtite was determined using Cameca SX50 and ARL–SEMQ electron microprobes. Details of analytical procedures and standards are given in Sheets (1995). Grains smaller than three

TABLE 1. COMPOSITION OF TYPES OF ELECTRUM AT THE MORNING STAR DEPOSIT

TYPE OF ELECTRUM	TYPE OF ORE	GOLD CONTENT (wt.%)	
		RANGE	MEAN $\pm 1\sigma$
pyrite-hosted	unoxidized	63 - 75	68.3 $\pm$ 3.4
quartz-hosted	unoxidized	65 - 72	68.7 $\pm$ 2.2
goethite-hosted	oxidized	62 - 76	68.7 $\pm$ 2.8
core	oxidized	61 - 73	66.1 $\pm$ 2.5
rim	oxidized	73 - 93	83.4 $\pm$ 5.3
wire	oxidized	81 - 90	85.4 $\pm$ 2.7

micrometers in the long dimension were analyzed as a grain composite. Larger grains of electrum were analyzed in multiple spots using various beam-sizes. Every attempt was made to analyze larger grains in at least two places in the central portion of the grain and at least two spots near the margin. The chemical composition of electrum is summarized in Table 1 and shown on Figure 2. Representative compositions of acanthite and uytenbogaardtite are summarized in Table 2. The complete data-set is given in Sheets (1995), and a copy is available from the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ontario K1A 0S2.

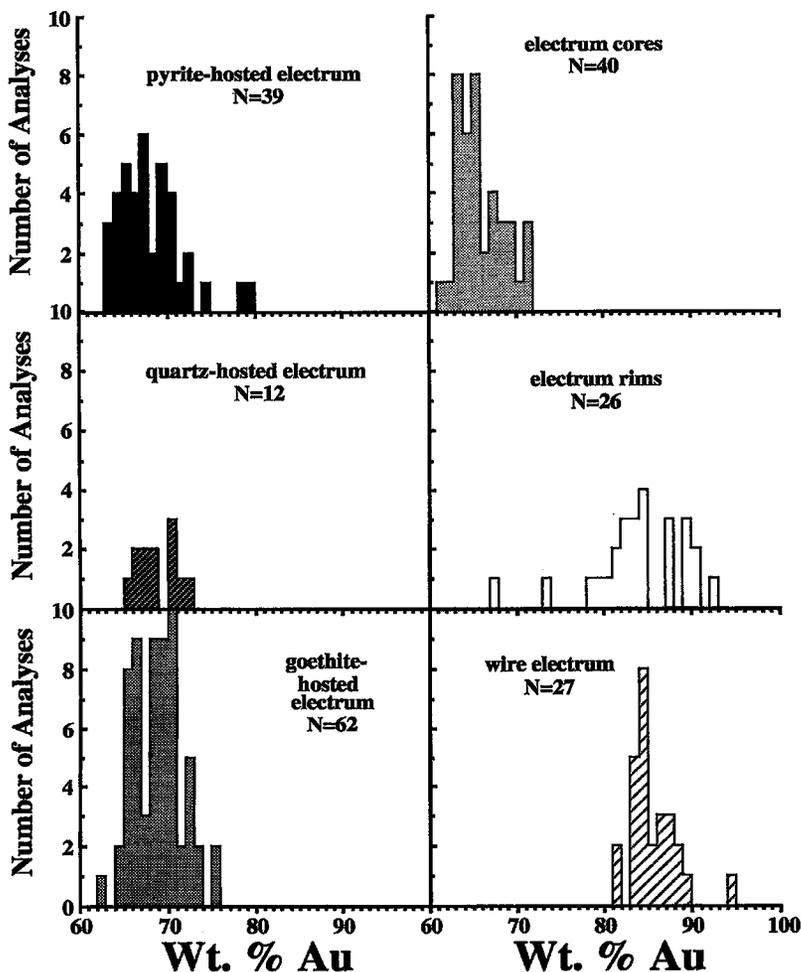


FIG. 2. Composition of the six types of electrum. Each datum represents the average composition for a given grain, core, rim or wire structures. N is the number of grains, rims or wires analyzed.

TABLE 2. REPRESENTATIVE ELECTRON-MICROPROBE DATA FOR ACANTHITE AND UYTENBOGAARDTITE AT THE MORNING STAR DEPOSIT

	Normalized wt. %				Mole %				Formula
	Au	Ag	Cu	S	Au	Ag	Cu	S	
<b>ACANTHITE</b>									
K-Hills-5	0.00	83.37	3.45	13.19	0.00	62.41	4.38	33.21	Ag <sub>1.88</sub> Cu <sub>0.13</sub> S
K-Hills-22	0.00	85.65	1.09	13.26	0.00	64.83	1.40	33.77	Ag <sub>1.92</sub> Cu <sub>0.04</sub> S
4700-1	6.75	78.96	1.44	12.86	2.88	61.52	1.90	33.70	Au <sub>0.09</sub> Ag <sub>1.83</sub> Cu <sub>0.06</sub> S
4700-12	4.97	78.20	3.88	12.96	2.08	59.66	5.03	33.23	Au <sub>0.06</sub> Ag <sub>1.80</sub> Cu <sub>0.15</sub> S
<b>UYTENBOGAARDTITE</b>									
4700-3	29.26	57.23	1.99	11.52	13.89	49.6	2.93	33.58	Au <sub>0.83</sub> Ag <sub>2.95</sub> Cu <sub>0.17</sub> S <sub>2</sub>
4700-11	26.87	56.57	4.57	11.99	12.32	47.38	6.50	33.79	Au <sub>0.74</sub> Ag <sub>2.82</sub> Cu <sub>0.39</sub> S <sub>2</sub>

Electrum has been divided into six distinct types based on grain morphology, association with primary and secondary minerals, and composition. These types of electrum are listed in Table 1.

#### *Electrum in unoxidized ore*

Primary hypogene electrum occurs with quartz and pyrite in unoxidized portions of the orebody below the 1340 to 1370 meter elevation. Rare grains of electrum were found in pyrite remnants in partially oxidized upper portions of the deposit. Precious-metal mineralization is restricted to quartz ( $\pm$  carbonate) veins with abundant pyrite and galena, lesser chalcopyrite and sphalerite, and minor acanthite and tetrahedrite. Early pyrite-bearing quartz veins consist of fine-grained bands of pyrite deposited at the vein-host rock contact. The early-deposited pyrite and quartz exhibit abundant evidence of deformation, manifest as brittle fracturing of pyrite and undulatory extinction, subgrain structures and grain-size reduction of the enveloping quartz. Some early pyrite-bearing veins contain pyrite fragments cataclastically sheared into

bands subparallel to the mylonitic foliation. The main stage of pyrite deposition formed euhedral isolated crystals or interpenetrating aggregates of cataclastically deformed subhedral grains of pyrite. It is the main-stage pyrite that is spatially and temporally associated with precipitation of base-metal sulfides. In samples from drill hole MSE-23, main-stage pyrite is cut by 0.1- to 1.0-cm-wide fine-grained quartz veinlets free of base- and precious-metal minerals. Individual grains of pyrite can be correlated across these late veinlets of quartz with little or no lateral displacement. In other samples, vein edges consist of fine-grained quartz that grades inward into open vugs encrusted by later euhedral quartz. The vugs commonly contain base-metal sulfides with pyrite, electrum and acanthite.

#### *Pyrite-hosted electrum*

Electrum in the unoxidized ore commonly occurs with galena in inclusions and fracture fillings in main-stage pyrite (Figs. 3A, B). Pyrite-hosted grains of electrum range from less than 1 to approximately

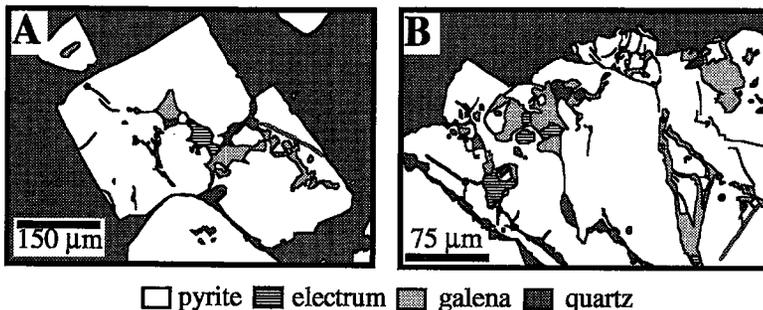


FIG. 3. Line drawings from photomicrographs illustrating the typical occurrence of pyrite-hosted electrum with galena in main-stage pyrite. A. Electrum and galena inclusions in pyrite. B. Electrum and galena along fractures in cataclastically deformed pyrite.

70  $\mu\text{m}$  in the long dimension, with the vast majority of grains being about 10  $\mu\text{m}$  long. Grain shape is largely controlled by the host pyrite and its fracture geometry. Pyrite-hosted electrum in polished sections has a uniform silvery white color across individual grains. Minor acanthite was found with pyrite-hosted electrum only in the case of pyrite surrounded by abundant base-metal sulfides. No silver was detected in any galena associated with electrum and acanthite. Silver sulfide in the primary mineral assemblage was originally deposited as argentite and has converted to the low-temperature polymorph, acanthite, upon cooling, as inferred on the basis of abundant twinning in the acanthite pseudomorphs. Although twinning in acanthite has been interpreted as being indicative of inversion from the high-temperature polymorph argentite, Taylor (1969) showed that acanthite grown at low temperatures also can be twinned; hence, twinning alone is not definitive of temperature of formation. Gold-to-silver ratios throughout the unoxidized portions of the tabular orebody suggest the presence of additional silver-bearing minerals, but no other argentiferous minerals were found. The only other silver-bearing mineral found was a single grain of Ag-bearing tetrahedrite.

#### *Quartz-hosted electrum*

Electrum also occurs in unoxidized portions of the orebody in quartz surrounding pyrite from main-stage pyrite-bearing veins. Quartz-hosted electrum is slightly later in the paragenesis and occurs interstitially between euhedral crystals of quartz and along healed microfractures in quartz. Quartz-hosted electrum and electrum at the pyrite-quartz interface are generally finer grained (less than 5  $\mu\text{m}$  across) than electrum in pyrite, but exhibits the same uniform texture and appearance as observed in pyrite-hosted electrum. Also, electrum in quartz and on the surfaces of pyrite is not as common as pyrite-hosted electrum.

#### *Electrum in oxidized ore*

The oxidized portions of the orebody consist mainly of goethite, digenite ( $\pm$  chalcocite), covellite, cerussite, smithsonite, malachite and azurite in quartz  $\pm$  carbonate veins. Goethite occurs as a pseudomorph after pyrite and with digenite surrounding chalcopyrite. Typically, oxidation is not complete, so that remnants of pyrite and chalcopyrite persist within these pseudomorphs. Heavy-metal carbonates either

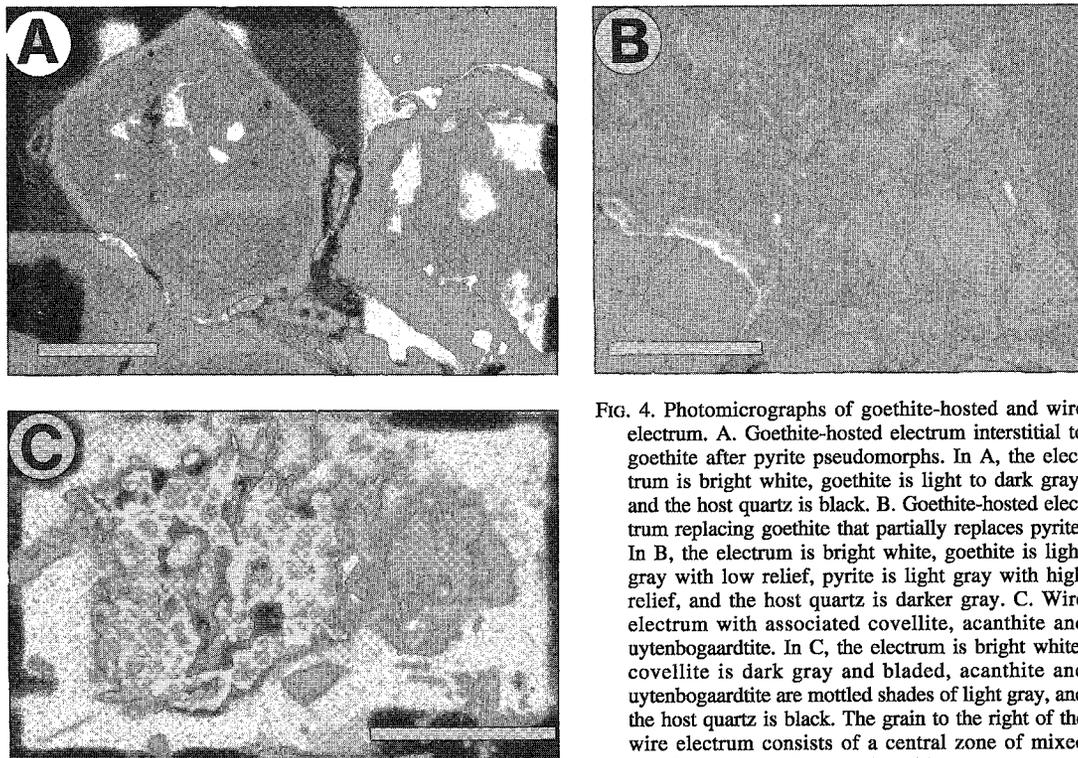


FIG. 4. Photomicrographs of goethite-hosted and wire electrum. A. Goethite-hosted electrum interstitial to goethite after pyrite pseudomorphs. In A, the electrum is bright white, goethite is light to dark gray, and the host quartz is black. B. Goethite-hosted electrum replacing goethite that partially replaces pyrite. In B, the electrum is bright white, goethite is light gray with low relief, pyrite is light gray with high relief, and the host quartz is darker gray. C. Wire electrum with associated covellite, acanthite and uyttenbogaardtite. In C, the electrum is bright white, covellite is dark gray and bladed, acanthite and uyttenbogaardtite are mottled shades of light gray, and the host quartz is black. The grain to the right of the wire electrum consists of a central zone of mixed acanthite and uyttenbogaardtite with an outer zone of acanthite and bladed covellite. Scale bars are 150  $\mu\text{m}$  long for both A and B, and 50  $\mu\text{m}$  long for C.

form pseudomorphs after their perspective sulfide minerals or occur as fracture coatings and fillings. Goethite and malachite are the most common coatings along open fractures and joints. Covellite also forms surface coatings along open fractures in quartz. These fractures typically cross-cut the tabular ore horizon. All covellite is *blaubleibender* (blue-remaining) covellite, on the basis of optical identification.

#### *Goethite-hosted electrum*

Electrum occurs in the oxidized zone as fracture fillings and inclusions in goethite pseudomorphs after pyrite, interstitially between goethite pseudomorphs (Fig. 4A) and embaying goethite or finely disseminated on goethite surfaces (Fig. 4B). Electrum that embays goethite may result from either replacement of goethite by electrum or electrum sorption onto goethite surfaces during goethite precipitation. Schoonen *et al.* (1992) have shown that disseminated gold on goethite surfaces is probably not a result of sorption processes because of the low efficiency of sorption on goethite, owing to either the lack of oxidizable surface-groups on goethite or the low stability of Au-O surface complexes. Schoonen *et al.* (1992) argued that gold sorption is more likely on pre-existing electrum than on goethite. Regardless of the mechanism of electrum formation, the textural evidence suggests remobilization of at least some gold and silver during oxidation. Both textures of goethite-hosted electrum have the same silvery white appearance and uniform texture seen in pyrite-hosted and quartz-hosted electrum. Grains of goethite-hosted electrum also have a range in size similar to that of pyrite-hosted electrum (<1 to 80  $\mu\text{m}$ ), but the size distribution is skewed toward larger grain-sizes. One grain of electrum from the high-grade ore zone in sample 4450 was found with cerussite and enclosed in a goethite pseudomorph of pyrite.

#### *Core and rim electrum*

Electrum also occurs in late cross-cutting fractures and open vugs within quartz from oxidized portions of the orebody. These fractures and vugs contain laths of covellite, Cu-oxide (cuprite  $\pm$  tenorite?) and native bismuth as surface coatings and grains or clusters of electrum with silver  $\pm$  gold sulfides. Acanthite associated with electrum in the oxidized portions of the orebody seems untwinned, which suggests low-temperature deposition as acanthite. This is different than acanthite from the unoxidized ore, which contains abundant twins that suggest higher-temperature deposition as argentite and conversion to acanthite upon cooling. This late electrum commonly has a core-rim morphology (Figs. 5A) or a wire-like morphology (Fig. 4C). Core and rim electrum were found in the highest level of the Morning Star orebody (sample

4700), but have not been found in surface exposures in the Keweenaw Hills. One grain of electrum with a rim less than 2  $\mu\text{m}$  thick also was found in drillhole MSE-87-04 in the relatively unoxidized portion of the orebody. Electrum cores, which range from 6 to 140  $\mu\text{m}$  long, are composed of homogeneous silvery white silver-rich electrum, similar to pyrite-hosted, quartz-hosted and goethite-hosted electrum. Grain-size distribution of electrum cores also is skewed toward coarser sizes, with an average grain-size larger than either pyrite- or goethite-hosted electrum. Electrum rims, which range in average thickness from <1 to 41  $\mu\text{m}$ , have a brilliant yellow-gold color in polished section compared to other types of electrum. Rim thickness has a bimodal distribution between thin rims, <1 to 5  $\mu\text{m}$ , and thick rims, >10  $\mu\text{m}$ , with thin rims being encountered twice as often as thick rims. Electrum rims and cores also are texturally different, with the rims having an irregular angular morphology, and the cores being massive. Electrum rims are also not uniformly developed around individual cores. Thin rims may occur on one side of a core or between adjacent cores and not occur on other parts of the same core. The extent of rim development appears to have been controlled by the location of the electrum cores within a fracture or vug (*e.g.*, Fig. 5A). Also, thin rims generally do not contain mineral inclusions and are surrounded by fine-grained bladed covellite, whereas thick rims typically form angular morphologies encapsulating bladed covellite and irregular grains of acanthite and uyttenbogaardite.

#### *Wire electrum*

Wire electrum (Fig. 4C) exhibits characteristics identical to thick rims, but contains no vestiges of an electrum core. The wire electrum morphology has been designated separately, but may actually represent sections cut through thick rims that did not intersect the associated core-zone. Individual wire structures have rounded edges and smooth surface features compared to the thick rims, which have sharp angular edges (*cf.* Fig. 5A). Wire electrum was found exclusively in covellite-bearing pockets, which also contain Cu-oxides, silver  $\pm$  gold sulfides and native bismuth. The size distribution of wire electrum is similar to that of goethite-hosted electrum, but the wire texture is sponge-like, and therefore contains considerably less metal within individual wire grains, compared to other types of electrum.

#### COMPOSITION OF THE ELECTRUM

The chemical composition of pyrite-hosted, quartz-hosted and goethite-hosted electrum and electrum cores is essentially the same (Table 1, Fig. 2). The gold content of pyrite-hosted electrum forms a nearly bell-shaped distribution, which is slightly skewed

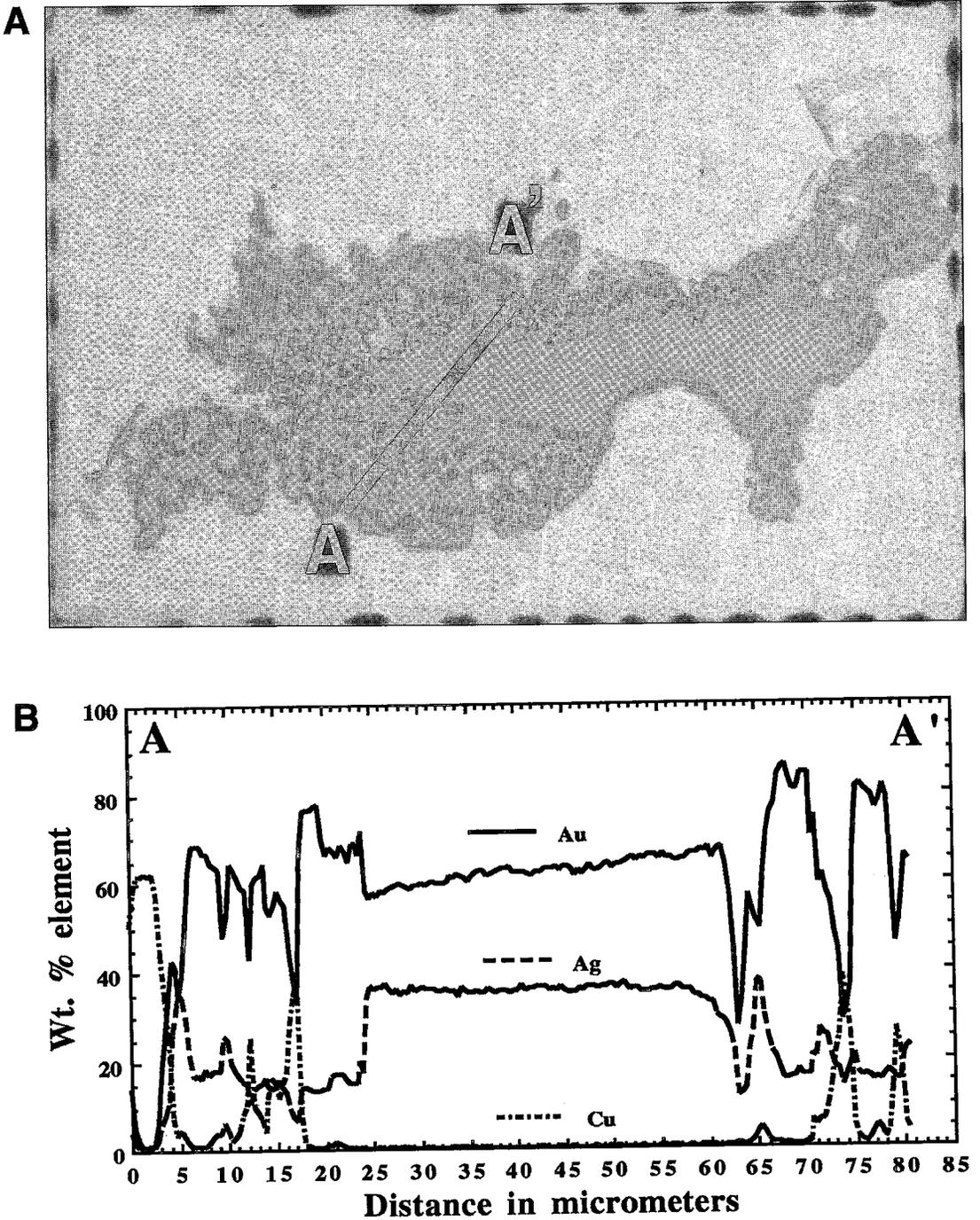


FIG. 5. Typical example of the occurrence and composition of a thick rim of electrum on a core grain. A. Photomicrograph of the thick rim of electrum and the core zone. The electrum rim has an irregular bright white appearance and contains inclusions of covellite, dark gray and bladed. The core zone has a uniform bright white appearance. The entire grain is encapsulated in quartz (black). B. Electron-microprobe traverse for Au, Ag and Cu across the electrum core and thick rim shown in A. Individual analyses were performed with a 1- $\mu\text{m}$  beam size, and the traverse was conducted with a 0.4- $\mu\text{m}$  step size.

toward gold-rich compositions (Fig. 2). No difference in chemical composition was detected for electrum that occurs on the surface of pyrite or which formed inclusions and fracture fillings in pyrite. Also, pyrite-hosted electrum shows a uniform appearance and chemical composition across individual grains. Quartz-hosted and goethite-hosted electrum have the same range and mean composition as pyrite-hosted electrum (Table 1, Fig. 2). No chemical distinction exists between electrum found as inclusions or fracture fillings in goethite, interstitial to goethite pseudomorphs, or embaying goethite. Goethite-hosted electrum also has a uniform chemical composition for individual grains. In core zones, the range and median composition of electrum are similar to those found in pyrite-hosted, quartz-hosted and goethite-hosted electrum, but core zones are skewed toward slightly lower Au content. Electrum rims are more Au-rich than electrum cores, with rim composition generally greater than 78 wt.% Au. Electrum rims are skewed toward Ag-enriched compositions (Fig. 2). Two rims have a composition less than 74 wt.% Au (Fig. 2). Both of these rims are less than 2  $\mu\text{m}$  thick and formed around large core-type grains. Thin rims generally have gold contents at or below the median composition of rim electrum, which may reflect difficulty in analyzing the thin rims without obtaining X-ray scattering from the electrum core. Alternatively, the difference may be real and reflect diffusion of Ag between cores and rims or precipitation of subsequently more gold-rich electrum as the rims precipitated. These latter hypotheses are not likely correct, because no correlation exists between electrum composition in core grains and corresponding rims. Also, elemental X-ray maps show no zoning of gold and silver between electrum cores and rims across the sharp core-rim boundaries (Sheets 1995). Thus, the slight enrichment in Ag of thin rims relative to thick rims is likely a result of analytical difficulties. An example of the analytical difficulties can be seen in the thick rim traverse of Figure 5B, where analyses of electrum rims and enclosed covellite laths reveal intermediate compositions of electrum. The one grain of electrum in the unoxidized ore-zone that developed a rim (sample MSE-87-04) has the same distribution of Ag-rich core (71 wt.% Au) and Au-rich rim (84 wt.% Au) described above for oxidized samples from the higher levels within the Morning Star deposit. Electrum cores for any given core-rim pair are compositionally homogeneous (e.g., Fig. 5B). Thin rims also appear to be compositionally homogeneous, but fewer analyses of each thin rim were performed. Thick rims, on the other hand, are compositionally heterogeneous, with individual segments varying by up to 12 wt.% Au (Fig. 5B). However, no consistent change in composition was noticed along traverses away from the core zone.

Wire electrum has a distribution of compositions

similar to that of electrum rims, in the range between 81 and 90 wt.% Au, with one wire grain being 94 wt.% Au. The composition of wire electrum is skewed toward Au-depleted values below the mean composition. The mean value of wire electrum is essentially identical to the mean value for rim electrum. Electrum composition is generally uniform throughout individual wire structures, compared to the irregular distribution observed in thick rims.

#### *Silver and silver-gold sulfides*

Coexisting acanthite and uytenbogaardtite have been found only within thick rims of electrum or associated with wire electrum. Acanthite was found in sample K-Hills, which contains goethite-hosted electrum and no uytenbogaardtite. A typical occurrence for silver  $\pm$  gold sulfide minerals includes anhedral masses of intergrown acanthite and uytenbogaardtite, which commonly contain laths and rosettes of covellite. These clusters of silver  $\pm$  gold sulfide and individual grains of acanthite or uytenbogaardtite are surrounded by wire electrum (Fig. 4C) or thick rims of electrum. Secondary acanthite is untwinned, and so probably formed at a low temperature.

The composition of the electrum is slightly depleted in gold for wire and rims intergrown with both acanthite and uytenbogaardtite, as opposed to wire or rims without visible silver  $\pm$  gold sulfides. The composition of electrum ranges from 80.0 to 85.3 wt.% Au in the presence of silver  $\pm$  gold sulfides and ranges from 81.0 to 91.8 wt.% Au where no silver-gold sulfides are present. Acanthite composition ranges from 78.5 to 79.5 wt.% Ag in the presence of electrum and uytenbogaardtite (Table 2). For acanthite coexisting with electrum but not uytenbogaardtite, the composition of acanthite ranges from 82.5 to 86.5 wt.% Ag (Table 2). Goethite-hosted electrum coexisting with acanthite is slightly Au-rich compared to the mean value for goethite-hosted electrum. The silver  $\pm$  gold sulfides seem to be sulfur-rich, but all silver  $\pm$  gold sulfides and wire or thick-rim electrum are found in open vugs and fractures containing covellite. Because Cu appears in all analyses, the sulfur enrichment is likely due to intergrowths of covellite. The composition of uytenbogaardtite is consistent with those reported by Barton *et al.* (1978), who noted sulfur enrichment in supergene or Cu-rich uytenbogaardtite.

Acanthite after argentite that occurs in quartz vugs with electrum and base-metal sulfides is essentially pure (containing 86 to 87 wt.% Ag), with less than 0.05 wt.% combined Au and Cu. No sulfur enrichment was observed in acanthite after argentite.

Thus, the chemical compositions of goethite-hosted, quartz-hosted and pyrite-hosted electrum and electrum cores are essentially identical. Also, no chemical distinction exists for Ag-rich electrum (pyrite-hosted, quartz-hosted, goethite-hosted and core

electrum types) with depth along the tabular ore horizon. With the exception of electrum rims (discussed above), there is no relationship between grain size of electrum and chemical composition. Electrum rims and wire electrum morphologies have similar chemical compositions, and are considerably more Au-rich compared to cores, pyrite-hosted, quartz-hosted and goethite-hosted electrum.

#### DISCUSSION

Two distinct stages of electrum mineralization occur in the Morning Star deposit. The principal stages of electrum deposition are primary hypogene and secondary, either supergene or late-stage, low-temperature hydrothermal. Within these two stages of deposition, multiple episodes of electrum precipitation probably occurred. Temperature estimates for primary electrum mineralization range from 280 to 315°C from fluid inclusions and electrum – argentite – pyrite – sphalerite thermometry (Sheets 1995). Primary hypogene electrum was deposited in two stages from fluids moving up along the Morning Star fault (Sheets 1995), both stages spatially and temporally related to pyrite and galena precipitation. The earliest electrum and argentite (now acanthite) were deposited contemporaneously with main-stage pyrite and base-metal sulfides. Silver-bearing tetrahedrite may also be part of this assemblage, as one grain of tetrahedrite was found. Trace-element geochemistry also suggests a strong correlation among As, Sb, Ag and Au in the unoxidized ore (Sheets 1995). No other As and Sb minerals have been identified in the primary ore. The second episode of primary electrum occurs with galena in cataclastically deformed pyrite and quartz vugs. The two episodes of primary electrum are texturally distinct but are chemically and mineralogically similar, and may form one continuous episode of electrum deposition.

Textural evidence from the oxidized portions of the orebody support the late-stage remobilization of at least some of the gold and silver. In the uppermost portions of the orebody, electrum is present as a higher-fineness rim around a lower-fineness core. The core zone is chemically similar to all stages of primary hypogene electrum. Lower in the oxidized orebody, the electrum also is chemically similar to primary electrum, but occurs in various textural relationships with goethite. Much of the goethite-hosted electrum is probably primary electrum that was not remobilized. Evidence for oxidation without remobilization includes electrum with cerussite as inclusions in goethite after pyrite pseudomorphs and electrum in pyrite remnants within goethite. These grains of goethite-hosted electrum are texturally and chemically identical to electrum with galena that occurs as inclusions in pyrite (pyrite-hosted electrum). Replacement of these sulfide minerals may have occurred without

dissolution of the enclosed electrum. Additional goethite-hosted electrum occurs as large grains embaying goethite or as fine grains deposited on the surface of goethite. These latter textures suggest that remobilization of Au and Ag and precipitation of electrum during late-stage hydrothermal or supergene oxidation occurred with little or no change in the composition of electrum. Thus in the highest levels of the deposit, remobilization of Au and Ag caused increased fineness of electrum (rim and wire morphologies) and is associated with silver ± gold sulfide minerals, but in lower levels of the deposit, the remobilization of Au and Ag was essentially isochemical.

Uytenbogaardtite can form in equilibrium with acanthite up to 113°C (Graf 1968, Barton 1980). Thus, the assemblage Au-rich electrum + acanthite + uytenbogaardtite must have formed during the waning stage of hydrothermal processes or by supergene processes. A supergene origin is favored because of the textural overlap with mineralization formed during oxidation of the Morning Star deposit. For example, wire and rim electrum occur with intergrown acanthite, uytenbogaardtite and bladed *blaubleibender* covellite. This assemblage, and especially the presence of *blaubleibender* covellite, is consistent with a supergene origin. Furthermore, the zone of oxidation corresponds to the present-day water table at the deposit, which argues for fairly recent supergene oxidation. In addition, only one Au-rich rim and no uytenbogaardtite were found below the zone of oxidation, suggesting that remobilization of gold and silver occurred owing to descending fluids from the surface instead of fluids rising from below. Late-stage hydrothermal fluids would rise along the Morning Star fault and should have remobilized or oxidized significant quantities of the deep ore. No evidence of this deep oxidation was found. Although mineralogical and textural evidence supports the supergene formation of silver ± gold sulfide minerals and the remobilization of Au and Ag, a late-stage hydrothermal origin cannot be completely ruled out at this time.

Present-day waters at the Morning Star mine, Sunnyside decline and rain water at the minesite have a pH between 6.5 and 8.0. The mineral assemblage malachite + cerussite + smithsonite, common in extensively altered samples, is consistent with these pH values (Mann & Deutscher 1984). Thus if recent supergene solutions are responsible for oxidation and remobilization of precious metals at the Morning Star deposit, these solutions should have been near-neutral to alkaline. Locally, acidic conditions may have prevailed owing to the breakdown of pyrite and other sulfide minerals, but the abundance of carbonate minerals, especially in the upper portions of the deposit, probably reacted to neutralize the acidic solutions. At depth within the tabular ore horizon, where the abundance of sulfide minerals increases and that of

the carbonate minerals decreases, acidic conditions may prevail locally.

Gold and silver are soluble and transported in oxygenated aqueous solutions by organic complexes (Boyle *et al.* 1975, Baker 1979, Vlassopoulos *et al.* 1990), halogen complexes (Krauskopf 1951, Cloke & Kelly 1964, Seward 1976, Mann 1984, Zotov *et al.* 1986), hydroxide complexes (Zotov *et al.* 1982, Vlassopoulos & Wood 1990) and S-donor ligand complexes such as  $\text{HSO}_3^-$  and  $\text{S}_2\text{O}_3^{2-}$  (Goleva *et al.* 1970, Plyusnin *et al.* 1981, Webster 1986, Gammons & Barnes 1989, Renders & Seward 1989). If precious-metal mobilization took place at the Morning Star mine under conditions similar to present-day conditions, organic complexes are probably of no consequence, because vegetation is sparse and only occurs in alluvial valleys. Chloride complexes are only significant at pH values less than 5 (Cloke & Kelly 1964, Seward 1976), and hydroxide complexes are not significant if other dissolved species, particularly sulfur-bearing species, are present (Zotov *et al.* 1982, Vlassopoulos & Wood 1990). For these reasons, neither halogen or hydroxide complexes are considered to be important mechanisms of transport at the Morning Star deposit.

Thus, for the proposed supergene conditions at the Morning Star deposit, thiosulfate would form metastable sulfur species that could remain in solution in high concentrations (Goldhaber 1983, Williamson & Rimstidt 1992) and could account for the remo-

bilization of Au and Ag. Bisulfide species could only be responsible for transporting Au and Ag in lower portions of the deposit, where reducing conditions prevail and total dissolved sulfur in solution is higher (Webster 1986, Gammons & Barnes 1989, Vlassopoulos & Wood 1990, Benedetti & Boulègue 1991).

Webster (1986) experimentally showed that the solubility of electrum is a function of composition. Electrum containing 50 at.% Ag (64.6 wt.% Au) has a lower solubility as thiosulfate complexes than gold-rich electrum or pure gold. Webster (1986) interpreted these results in terms of the formation of a mixed-metal complex  $[(\text{Au},\text{Ag})(\text{S}_2\text{O}_3)_2]^-$ . Whether a mixed-metal complex actually forms is beyond the scope of this paper. However, when Au and Ag are dissolved from electrum with a composition containing between 60 and 70 wt.% Au, the resulting electrum should be deposited with little or no chemical separation between Au and Ag. Thus, precipitation of secondary electrum should occur with a composition similar to that of the initial primary electrum. Primary electrum (pyrite-hosted and quartz-hosted electrum and electrum cores) at the Morning Star deposit has a median composition of 68 wt.% Au, which is identical to goethite-hosted electrum. Goethite-hosted electrum occurs in various textural relationships that resemble both primary electrum and electrum deposited from the remobilization of Au and Ag. Solubility and transport of Au and Ag by thiosulfate complexes are

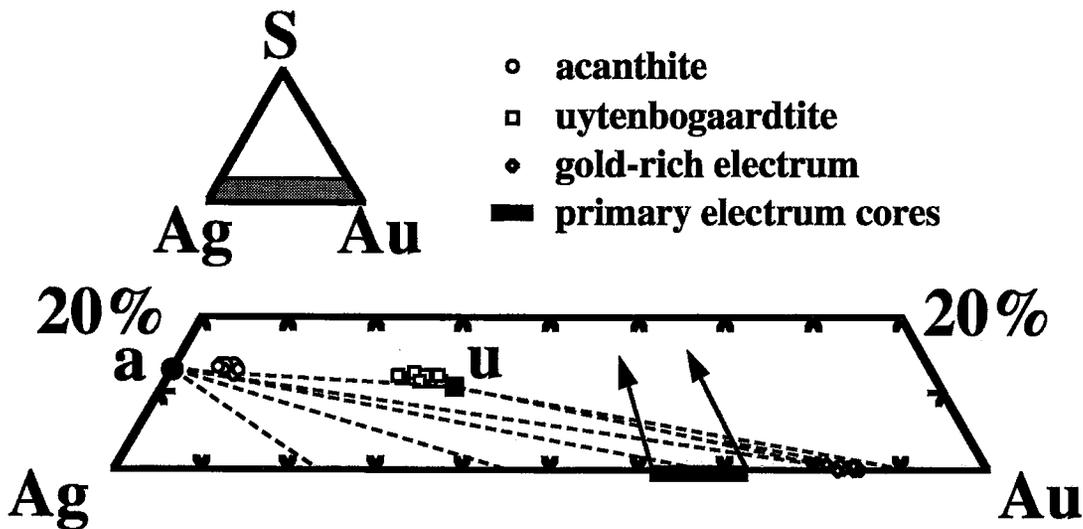


FIG. 6. Chemistry of coexisting electrum (diamonds), acanthite (circles) and uytenbogaardtite (squares) plotted on the 100°C isothermal section showing Au-Ag-S in weight %, after Barton (1980), whose plot is given in molar units, which have been converted to units of weight in this paper. Dashed line represents the equilibrium mineral assemblages at 100°C. The black rectangle represents the composition of the primary electrum, and the arrows indicate compositional changes due to sulfidation of electrum. The black circle (a) and square (u) show the ideal compositions of acanthite and uytenbogaardtite, respectively.

consistent with both textures. Precipitation of secondary goethite-hosted electrum may have occurred by reduction of thiosulfate complexes, local decreases in pH or sorption onto goethite and electrum surfaces (Webster 1986, Schoonen *et al.* 1992).

In the highest levels of the Morning Star deposit, electrum occurs as gold-rich rims on core zones and wire structures with silver  $\pm$  gold sulfide minerals. In light of the phase relationships determined by Barton (1980), the higher fineness of the electrum can be accounted for by sulfidation of original compositions of electrum (Fig. 6). Reaction of primary electrum with sulfur produces the assemblage acanthite + electrum, and further sulfidation would eventually produce the assemblage acanthite + uyttenbogaardtite + electrum (Fig. 6). Each addition of sulfur and change in mineral assemblage form electrum with high concentrations of Au, driving the composition of the electrum to 84.0 wt.% Au in equilibrium with ideal acanthite and uyttenbogaardtite compositions (Barton 1980). Goethite-hosted electrum coexisting with acanthite is richer in Au than the mean for goethite-hosted electrum, which is consistent with the sulfidation theory and the phase relationship determined by Barton (1980). Equilibrium is commonly not maintained during supergene processes, and no attempt is made to imply that equilibrium conditions prevailed during supergene oxidation of the Morning Star deposit, but compositions for rim and wire electrum have a mean value of 84.4 wt.% Au, which is consistent with experimental phase-equilibria. Castor & Sjöberg (1993) also found compositions of electrum in the assemblage acanthite + uyttenbogaardtite + electrum, in the Bullfrog deposit of Nevada, that agree with the phase equilibria of Barton (1980). Transport by thiosulfate complexes may also produce gold-rich electrum in rim and wire morphologies (Webster & Mann 1984, Webster 1986). As silver reacted to form acanthite, and silver and gold reacted to form uyttenbogaardtite, the thiosulfate complexes would be destabilized and precipitate gold-rich electrum owing to the preferential loss of silver. Further data regarding the stability of acanthite and uyttenbogaardtite during supergene processes, especially processes related to thiosulfate solutions, are required to verify this final hypothesis.

#### CONCLUSIONS

Within the structurally controlled high-grade ore horizon at the Morning Star deposit, electrum grains have been divided into six types based on associated minerals and grain morphology. These include (1) pyrite-hosted and (2) quartz-hosted electrum occurring with base-metal sulfide minerals in unoxidized portions of the orebody, and (3) goethite-hosted electrum, (4) electrum cores, (5) electrum rims, and (6) wire electrum associated with supergene mineral assem-

blages in the oxidized portions of the orebody. Pyrite-hosted and quartz-hosted electrum represent primary electrum deposited by hydrothermal processes. Electrum cores and much of the goethite-hosted electrum have chemical compositions similar to that of primary electrum, and are considered to represent primary electrum that remained unaltered by oxidation. Goethite-hosted electrum that embays goethite or was deposited on goethite surfaces has textures indicative of supergene remobilization of Au and Ag, but exhibits chemical compositions similar to that of primary electrum. Remobilization of Au and Ag by thiosulfate complexes can produce secondary goethite-hosted electrum with no chemical separation of Au and Ag, and should form abundant metastable complexes for the inferred supergene fluids at the Morning Star deposit. Electrum cores with rims of higher-fineness electrum and wire electrum occur in the uppermost levels of the Morning Star deposit with acanthite and uyttenbogaardtite. Rims of gold-rich electrum and wire structures are consistent with sulfidation of primary electrum to form silver  $\pm$  gold sulfide minerals. Thus, within the Morning Star deposit, remobilization of Au and Ag occurs isochemically and with gold enrichment, each occurring at different levels within this one deposit.

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