

# **Ag-Cu-Pb-Bi SULFOSALTS NEW TO DARWIN, INYO COUNTY, CALIFORNIA**

**Gail E. Dunning**

773 Durshire Way

Sunnyvale, California 94087-4709

**Yves Moëlo**

Institut des Matériaux, Laboratoire de Chimie des Solides, UMR 110

(CNRS - Université de Nantes), B.P. 32229

44322 Nantes Cedex 03, France

**Andrew C. Roberts**

Geological Survey of Canada

601 Booth Street

Ottawa, Ontario K1A 0E8

**Joseph F. Cooper, Jr.**

430 Van Ness Avenue

Santa Cruz, California 95060

***Several rare Ag-Cu-Pb-Bi sulfosalts occur sparingly in dump material from three small mines in the Darwin mining district. These sulfosalts include cupropavonite, friedrichite, gustavite, heyrovskyite, junoite, krupkaite, pavonite and vikingite.***

## INTRODUCTION

The Darwin mining district, Inyo County, California, located at 36° 17' N., 117° 35' W., has long been known for its deposits of lead-silver-zinc ore, including several rare sulfosalts; in addition, ores of tungsten, antimony, copper and gold have been produced. Complete descriptions of the Darwin Quadrangle geology and ore-related deposits are given by Hall and MacKevett (1958), Czamanske and Hall (1975), Hall (1962,1971), and Hall *et al.* (1971).

The sulfosalts described in this study were identified following a quantitative electron microprobe and X-ray powder-diffraction examination of specimens collected during the winters of 1961 and 1962 from the dumps of the abandoned St. Charles, Lucky Lucy and Silver Spoon mines. These sulfosalts include cupropavonite, fried-richite, gustavite, heyrovskyite, junosite, krupkaite, pavonite and vikingite and are represented by the  $\text{Cu}_2\text{S-Ag}_2\text{S-PbS-Bi}_2(\text{S,Se})_3$  system with no discernible Sb or As substitution. The complexity of the sulfosalt mineralogy at Darwin, noted first by Czamanske and Hall (1975), is confirmed by the discovery of these additional rare sulfosalts.

## GEOLOGICAL SETTING

The geology of the Darwin area has been described by Hall and MacKevett (1958) and Hall (1962). Lead-zinc-copper ores occur in a sequence of upper Paleozoic sedimentary rocks ranging in age from early Ordovician to Permian. These sedimentary rocks were intruded by a biotite-hornblende quartz monzonite stock of Jurassic (?) age and were altered to calc-silicate minerals. Ore deposits are correlated with the lower member of the Keeler Canyon formation, which is of Pennsylvanian and Permian age. Overturned bedding in the meta-sedimentary rocks strikes N. 30° W. and dips 50° SW, with many faults cutting these rocks at steep angles.

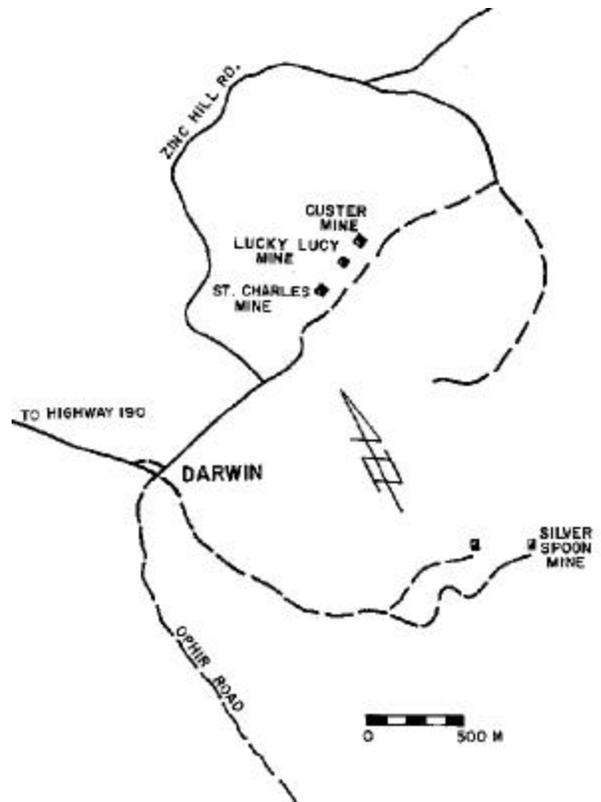
Most of the ore mined in the Darwin district is massive and occurs in veins, bedded deposits and steep, irregular replacement-type bodies. The sulfide ore consisted of galena, sphalerite and pyrite, with lesser amounts of bismuthinite, chalcopyrite, pyrrhotite, arsenopyrite, stibnite, tetrahedrite and rare Ag-Cu-Pb-Bi sulfosalts, some of which contain appreciable Se substituted for S. Oxidation of the sulfide ore has produced massive cerussite in addition to lesser amounts of malachite, azurite, aurichalcite, chrysocolla, smithsonite, hemimorphite and hydrozincite.

## MINE AND SPECIMEN DESCRIPTIONS

### St. Charles mine

The St. Charles tungsten mine is located near the head of a narrow, steep canyon 18 km east of Darwin at an elevation of about 1500 meters. Rocks in the mine area are interbedded calc-hornfels and pure limestone beds that are in part recrystallized to marble and altered to tactite.

This tactite is composed of andradite and calcite with minor pyrite, fluorite and vesuvianite. The mine workings include an incline shaft and two adits that have exposed veins of scheelite associated with small amounts of sphalerite and pyrite.



**Figure 1.** Location map for the Darwin mining district, Inyo County, California.

The single discovery specimen recovered from the dump measured about 3 x 5 cm and was composed of a thin sulfosalt vein, as determined by EDS, replacing calcite in tactite. The steel gray sulfosalt vein has a feathery habit with a metallic luster. When broken, the sulfosalt possesses a conchoidal fracture. Megascopically, several small, flat crystal sections were visible along the sulfosalt margin with the calcite and are heavily striated along the direction of elongation. This specimen contained less than three grams of sulfosalt material, most of which is now contained in two polished sections and several small specimens. Extensive searching of the dump area failed to yield additional sulfosalt-containing material.

### Lucky Lucy mine

The Lucky Lucy mine is located about 100 meters to the east of the St. Charles mine along the north side of the same steep canyon. Rocks in the area

are consistent with those of the St. Charles mine except that most are heavily iron stained and silicified. The mine consists of a single surface pit about 4 meters deep that extends into the steep canyon slope. Oxidation of the primary minerals (chalcopyrite, sphalerite, pyrite) has produced several secondary Cu and Zn-bearing minerals, which include brochantite, serpierite, rosasite, aurichalcite, hemimorphite, bismutite and iron oxides. The serpierite and brochantite are very attractive and typically occur as delicate, well-formed acicular crystals attached to cavity and fracture surfaces in the silicified tactite.

Two sulfosalt-bearing specimens, each about 4 x 6 cm, were recovered from the small dump and constitute the entire material known. Megascopically, the first specimen consisted of small, irregular, elongate masses of a dark gray sulfosalt with a conchoidal fracture in a coarse calcite-rich tactite. No evidence of crystallization was observed. The specimen contained less than one gram of material that is contained a single polished section and several very small specimens.

The second specimen was similar to the first but contained a dark gray sulfosalt vein with a definite fibrous habit and partially altered to a yellowish-green, fine-grained copper-stained bismutite. Further searching of the limited dump area during subsequent years failed to yield additional specimens.

### **Silver Spoon mine**

The Silver Spoon mine is located about 2 km south of Darwin along the southwest flank of the Darwin Hills and is developed by a single inclined shaft about 25 meters deep. Rocks exposed in the mine area consist of fine-grained wollastonite-bearing limestone that has been partially replaced by tactite.

Specimens from the mine dump show disseminated masses of a silvery sulfosalt that occur as replacement bands in the limestone. The sulfosalt appears as minute flattened grains that are somewhat tarnished yellowish-blue upon exposure. When specimens are treated with warm, dilute acetic acid, the individual sulfosalt grains show rough crystalline outlines. No secondary alteration or weathering products were observed.

### **MINERALOGY**

Initially, a small, unaltered portion of each specimen was examined by energy-dispersive spectrometry (EDS) which indicated significant levels of Ag, Cu, Pb, Bi, Se and S. Following this initial examination, a small representative unaltered portion from each specimen was submitted for routine X-ray powder-diffraction identification. The resulting patterns contained diffraction lines that were not readily identified with any known mineral, which can often be characteristic of a complex mixture of several phases. To resolve this problem, polished sections were carefully prepared, using standard methods, from the remaining

portions of the bulk specimens for optical, electron microprobe and X-ray power-diffraction study.

Optical microscopy, using bright field and polarized light, resulted in the detection of several phases in the polished sections, including bright inclusions within the sulfosalt matrix and along some grain boundaries of one of the primary matrix phases. All the matrix phases observed are moderately to strongly anisotropic under cross nicols. Backscattered electron (BSE) imaging and EDS of these polished sections also confirmed that more phases were present within these specimens than originally suspected.

To further characterize these phases, the polished sulfosalt sections were analyzed by electron-probe microanalysis using a CAMECA SX-50 microprobe (BRGM-CNRS-University common laboratory, Orléans; programming by O. Rouer, CNRS). Operating conditions were 20 kV, 20 nA, 10 s/spot counting time; standards (element, emission line) used were Cu (Cu K $\alpha$ ), FeS<sub>2</sub> (S K $\alpha$ ), PbS (Pb M $\alpha$ ), Bi (Bi M $\alpha$ ), Se (Se L $\alpha$ ), Cd (Cd L $\alpha$ ), Ag (Ag L $\alpha$ ), Te (Te L $\alpha$ ); undetected were Fe, Sb, As, Mn, Hg, Sn at less than 0.01%. The electron microprobe analyses (Table 1) resulted in the probable identification of cupropavonite, friedrichite, gustavite, heyrovskyite, junote, krupkaite, pavonite and vikingite. All these sulfosalts are members of well known homologous series, according to the modular classification of Makovicky (1989).

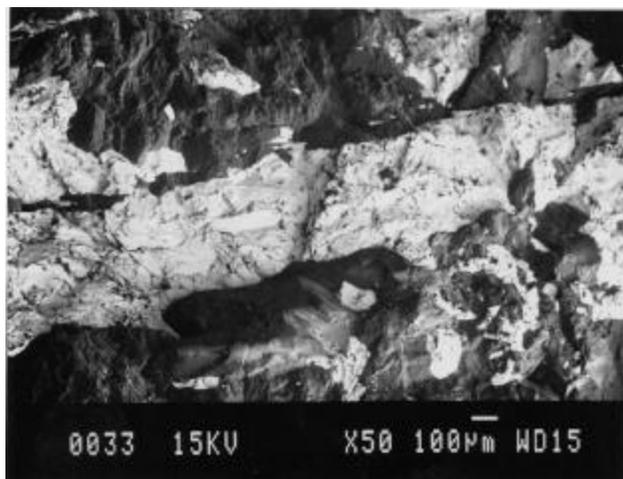
Following the microprobe analyses, small amounts of material were extracted from the polished sections using photomicrographs and microhardness indents as guides and subjected to X-ray powder-diffraction using modified 57.3 mm Debye-Scherrer powder cameras with Ni-filtered Cu radiation. Friedrichite, gustavite, krupkaite, junote, pavonite and vikingite were confirmed. Heyrovskyite, cupropavonite, junote and gustavite from the Lucky Lucy mine could not be confirmed by X-ray powder-diffraction because of their minute grain size. Specific descriptions of these eight sulfosalts and their associations are presented below.

### **Bismuthinite-Aikinite series**

#### **Friedrichite** Pb<sub>5</sub>Cu<sub>5</sub>Bi<sub>7</sub>S<sub>18</sub>

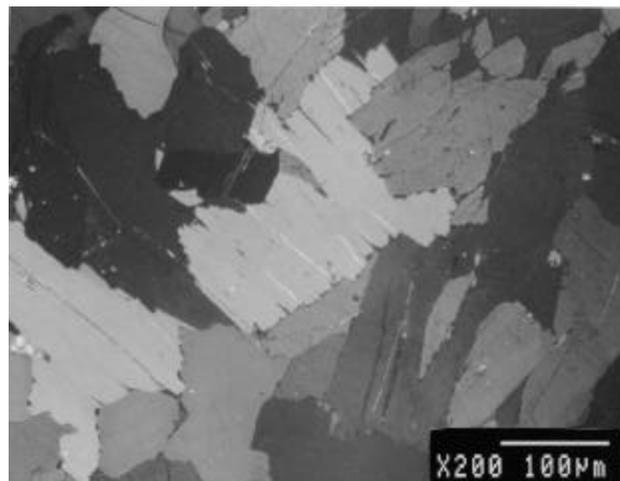
Friedrichite was originally found in the "Sedl" region, Habach Valley, Salzburg, Austria (Chen *et al.*, 1978). At Darwin the mineral occurs associated with gustavite in the specimen from the St. Charles mine. In polished section, both friedrichite and gustavite grains are visible under BSE imaging, with friedrichite being slightly darker. Under cross nicols, both minerals can be distinguished by their polarization colors. The friedrichite grains are irregular (200 x 300

microns) and compose about 25% of the polished section area. The average of four microprobe analyses gives the formula  $\text{Cu}_{4.95}\text{Pb}_{5.15}\text{Bi}_{6.95}(\text{S}_{17.88}\text{Se}_{0.12})_{\Sigma=18}$ . Also observed in the polished section are small grains of galena, chalcocopyrite and sphalerite.

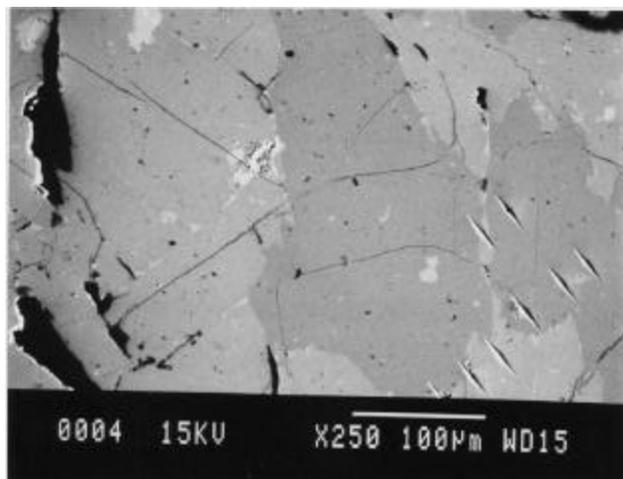


**Figure 2.** Thin vein containing a mixture of friedrichite and gustavite in calcite from the St. Charles mine. BSE image.

grains associated with junote and inclusions of Se-rich tetradymite and pyrite as a vein constituent of the limestone-tactite rock. In polished section the krupkaite can be distinguished from the junote by its polarization colors. The two minerals also can be distinguished by the difference in the Cu-(Pb,Bi) ratio using BSE imaging. The average of two microprobe analyses gives the formula  $\text{Cu}_{0.99}\text{Pb}_{1.02}\text{Bi}_{3.00}(\text{S}_{5.60}\text{Se}_{0.40})_{\Sigma=6}$ .



**Figure 4.** Typical mixture of gustavite and friedrichite (St. Charles mine) under polarized light. 200X.



**Figure 3.** Polished section showing dark friedrichite grains in gustavite. Lighter phase is Ag-rich galena. St. Charles mine. BSE image.

#### Krupkaite $\text{CuPbBi}_3\text{S}_6$

Krupkaite was described from Krupka, northeast Bohemia, Czech Republic (Žák *et al.*, 1974; Mumme, 1975a). At the Silver Spoon mine it occurs as minute

#### Lillianite series

##### Gustavite $\text{Pb}_3\text{Bi}_2\text{S}_6$ to $\text{AgPbBi}_3\text{S}_6$

Gustavite, originally found with berryite in the cryolite deposit at Ivigtut, southwest Greenland (Karup-Møller, 1970) occurs as rare grains associated with heyrovskyite and vikingite in the second specimen from the Lucky Lucy mine. Microprobe analysis of a single grain gives  $\text{Ag}_{0.67}\text{Pb}_{1.81}\text{Bi}_{2.69}(\text{S}_{5.45}\text{Se}_{0.50}\text{Te}_{0.05})_{\Sigma=6}$  and places this gustavite at  $\text{Gus}_{65}$  between the solid solution compositional range of  $\text{Pb}_3\text{Bi}_2\text{S}_6$  to  $\text{AgPbBi}_3\text{S}_6$  and illustrates the coupled substitution of  $\text{Ag}^+ + \text{Bi}^{3+} \leftrightarrow 2\text{Pb}^{2+}$  found in several of the sulfosalt series. Due to the small grain size, it was not confirmed by X-ray powder-diffraction.

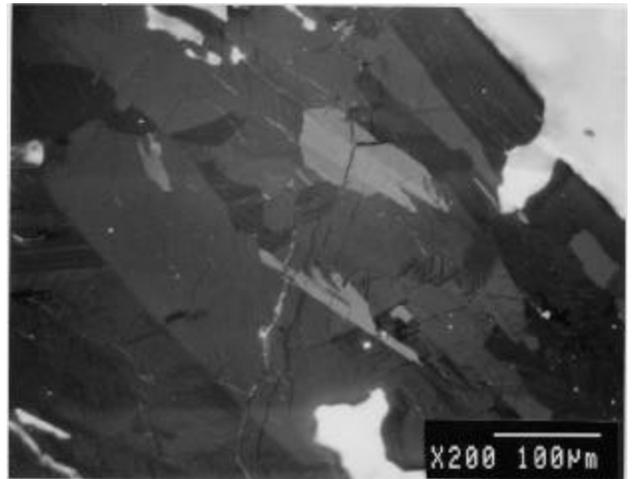
Gustavite, containing appreciable copper, also occurs with friedrichite from the adjacent St. Charles mine. In polished section the grains are irregular and strongly anisotropic. Under BSE the gustavite and friedrichite can be distinguished. The average microprobe analysis of five spots gives  $\text{Cu}_{0.12}\text{Ag}_{0.79}\text{Pb}_{1.39}\text{Bi}_{2.78}(\text{S}_{5.73}\text{Se}_{0.26}\text{Te}_{0.01})_{\Sigma=6}$ . Also present is rare Ag-bearing galena seen as a thin exsolution (?) phase along some of the gustavite grains. Previously at Darwin, gustavite was reported

as small exsolution inclusions in Ag-Bi-rich galena (Czamanske and Hall, 1975). Moëlo *et al.* (1987) discusses the Ag and Bi-rich chemistry of several members of the lillianite series, including gustavite, vikingite and heyrovskyite.

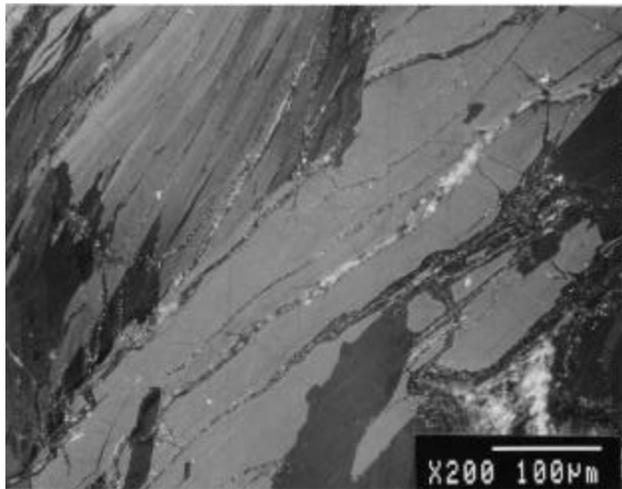
**Heyrovskyite**  $Pb_6Bi_2S_9$  to  $Ag_{2.5}PbBi_{4.5}S_9$

Heyrovskyite, originally described from Hürky, Czech Republic (Klomínský *et al.*, 1971) occurs as elongated rare grains associated with gustavite and vikingite in the second specimen from the Lucky Lucy mine. These sulfosalts cannot be distinguished by either optical or BSE imaging. Microprobe analyses of a single grain gives  $Cu_{0.08}Ag_{0.83}Pb_{4.38}Bi_{2.97}(S_{8.18}Se_{0.74}Te_{0.08})_{\Sigma=9}$ . Relative to the Ag-free end member (Hey<sub>100</sub>), its composition is close to Hey<sub>65</sub>, between  $Pb_6Bi_2S_9$  and  $Ag_{2.5}PbBi_{4.5}S_9$ .

Foord and Shawe (1989) give microprobe data for exsolved phases in galena from the Jackass mine, Darwin which they consider to be either eskimoite (?) or Ag-bearing heyrovskyite (?).



**Figure 6.** Polished section of Lucky Lucy mine specimen showing isolated thin grains of junosite (light gray) in pavonite. 200X.



**Figure 5.** Polished section of Lucky Lucy mine specimen showing mixture of thin, parallel grains of vikingite and heyrovskyite. 200X.

**Vikingite**  $Pb_{18}Bi_8S_{30}$  to  $Ag_7Pb_4Bi_{15}S_{30}$

Vikingite, initially described from the cryolite deposits, Ivigtut, Greenland (Makovicky and Karup-Møller, 1977) occurs associated with heyrovskyite and gustavite in the second specimen from the Lucky Lucy mine. These minerals are not distinguishable by either optical or BSE imaging. The microprobe analysis of four grains gives  $Cu_{0.13}Ag_{3.14}Pb_{11.92}Bi_{11.00}(S_{27.12}Se_{2.62}Te_{0.26})_{\Sigma=30}$  and places this vikingite at about Vik<sub>43</sub> between the compositional end members  $Pb_{18}Bi_8S_{30}$  and  $Ag_7Pb_4Bi_{15}S_{30}$ . Vikingite from Ivigtut corresponds to Vik<sub>60</sub>-Vik<sub>67</sub>.

**Junosite series**

**Junosite**  $Pb_3Cu_2Bi_8(S,Se)_{16}$

Junosite was first described from the Juno mine, Tennant Creek, Australia (Mumme, 1975b). Later it was identified from the Kidd Creek mine, Timmins, Ontario (Pringle and Thorpe, 1980) and the Linka mine, Lander County, Nevada (Williams, 1988).

At Darwin it occurs as elongated grains with krupkaite and inclusions of Se-rich tetradymite in limestone-tactite rock at the Silver Spoon mine. When this rock is treated with dilute acetic acid, abundant grains with striations parallel to the elongated direction are observed. The junosite can be distinguished from krupkaite by its polarization colors and BSE imaging effect. Microprobe analysis of two grains gives  $Cu_{1.95}Ag_{0.16}Pb_{2.67}Bi_{8.08}(S_{13.97}Se_{1.95}Te_{0.08})_{\Sigma=16}$ .

Junosite also occurs rarely as elongated grains in the first specimen from the Lucky Lucy mine associated with Cu-rich pavonite, cupropavonite and Se-rich tetradymite. Microprobe of two grains gives  $Cu_{1.95}Ag_{0.22}Pb_{2.56}Bi_{8.22}(S_{14.24}Se_{1.70}Te_{0.06})_{\Sigma=16}$ .

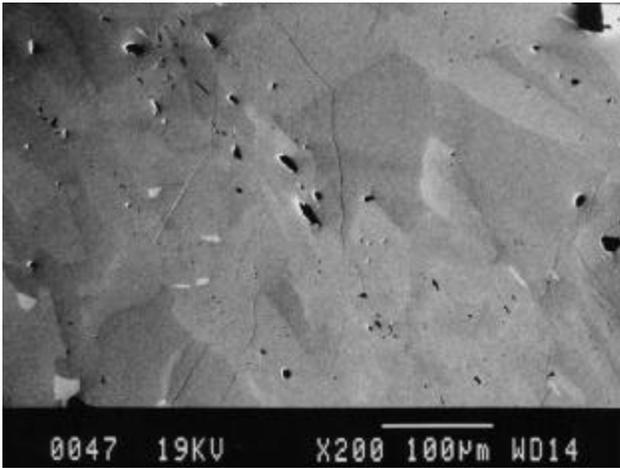
**Pavonite series**

**Pavonite**  $(Ag,Cu)(Bi,Pb)_3S_5$

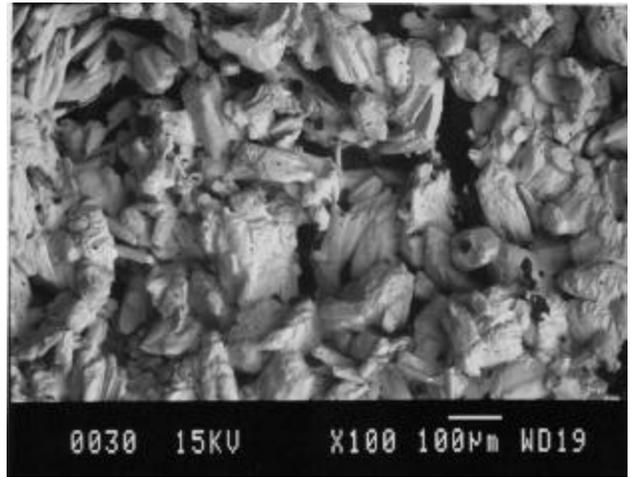
Pavonite, originally named alaskaite (benjaminite) from the Porvenir mine, Cerro Bonete, Bolivia (Nuffield, 1954), occurs as the Cu-Se-rich variety associated with exsolved cupropavonite, junosite and Se-rich tetradymite in the first specimen from the Lucky Lucy mine. The pavonite constitutes most of the specimen. It is moderately anisotropic and the grains are generally elongated parallel to the vein direction.

Microprobe analysis of two grains gives  $\text{Cu}_{0.43}\text{Ag}_{0.67}\text{Pb}_{0.33}\text{Bi}_{2.74}(\text{S}_{4.34}\text{Se}_{0.64}\text{Te}_{0.02})_{\Sigma=5}$ .

them in the pavonite region of the pavonite-cupropavonite compositional range.



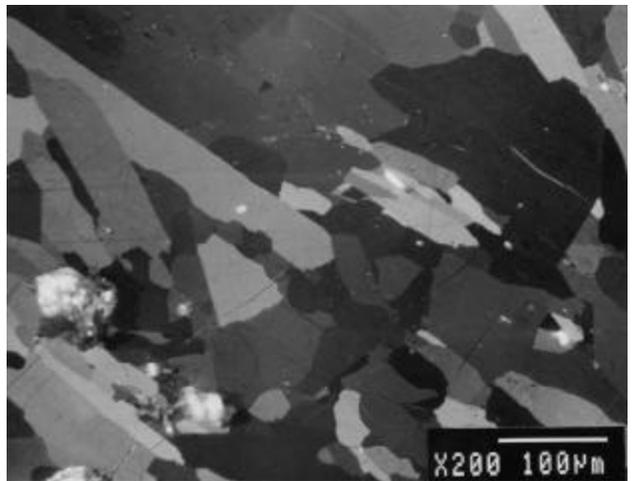
**Figure 7.** Polished section of Silver Spoon mine specimen showing mixture of junosite (light massive phase) and krupkaite (dark massive phase) with isolated bright grains of Se-rich tetradymite. BSE image.



**Figure 9.** Typical combination of junosite and krupkaite grains exposed by etching from limestone. SEM image.



**Figure 8.** Isolated elongated grains of junosite exposed by etching from limestone (Silver Spoon mine). SEM image.

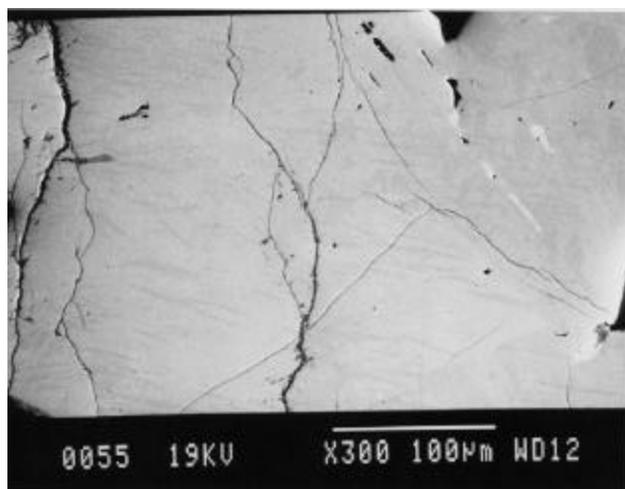


**Figure 10.** Polished section of Silver Spoon specimen showing elongated junosite grains in krupkaite under polarized light. 200X.

**Cupropavonite**  $\text{Cu}_{0.9}\text{Ag}_{0.5}\text{Bi}_{2.5}\text{Pb}_{0.6}\text{S}_5$

Cupropavonite was first noted from the Alaska mine, Colorado (Karup-Møller and Makovicky, 1979) as exsolved lamellae in pavonite associated with interstitial gustavite.

Two of the nine microprobe analyses of the pavonite-rich specimen from the Lucky Lucy mine gave Cu/(Cu+Ag) atom ratios of 0.52 and 0.56, indicating the possibility that cupropavonite exists as an exsolved phase within the pavonite. The seven other microprobe analyses gave Cu/(Cu+Ag) atom ratios from 0.31 to 0.46, which places



**Figure 11.** Pavonite matrix showing thin exsolution lamellae of cupropavonite (Lucky Lucy mine). BSE image. 300X.

An optical examination of the microprobed area containing high copper revealed abundant, exsolution lamellae within the pavonite grains. The strong anisotropism and habit of these lamellae are comparable with the exsolved lamellae observed in the Cu-rich pavonite from the Alaska mine, Colorado cited by Karup-Møller and Makovicky (1979). SEM/BSE imaging of the pavonite grains revealed that the lamellae observed optically all are indeed Cu-rich with respect to the host pavonite grains. These lamellae average 5 microns x 50 microns and are oriented parallel along the crystallographic planes of the pavonite. The X-ray powder-diffraction of the area rich in Cu was of a mixture of pavonite (confirmed) and cupropavonite (suspected). The calculated microprobe analysis gives  $\text{Cu}_{0.72}\text{Ag}_{0.67}\text{Pb}_{0.36}\text{Bi}_{2.63}(\text{S}_{4.34}\text{Se}_{0.63}\text{Te}_{0.03})_{\Sigma=5}$ , which probably consists of a mixture of pavonite and cupropavonite.

#### Unclassified sulfosalt analyses

Two unclassified microprobe analyses were obtained from one St. Charles mine specimen (UN-1 and UN-2 in Tables 1 and 2). They resemble gustavite, but with an abnormally high Cu content (2.4 wt. %) for UN-1, and a significant Se enrichment in UN-2. Without correlated X-ray data, one cannot definitively assume their identification as gustavite varieties.

#### Metacinnabar HgS

Metacinnabar occurs as a rare constituent of a very fine-grained mineral mixture at the end of the specimen from the St. Charles mine that is rich in friedrichite and Cu-rich gustavite. This is the first recorded occurrence of a mercury mineral in the Darwin ores. Also associated in

this mixture is a Cu-Cd sulfide that has formed very thin replacement veins along the gustavite grain boundaries.

#### Tetradymite $\text{Bi}_2\text{Te}_2(\text{S},\text{Se})$

Se-rich tetradymite occurs as minute inclusions in the sulfosalt assemblage of the Silver Spoon and Lucky Lucy mines. It is easily recognized by its high reflectivity, good polish, EDS spectrum and microprobe analyses. This mineral previously has been reported by Czamanske and Hall (1975) from the Thompson mine, Darwin as inclusions in galena.

#### DISCUSSION

Czamanske and Hall (1975) recognized four different assemblages of sulfide minerals in the Darwin district, two of which are galena-rich. These latter assemblages consist of fine-grained galena-rich ore that contains abundant Ag, Bi and Se (Te) and minor associated pyrite. They reported an exsolved Ag-bearing phase in galena with associated matildite that was considered to be heyrovskite. Foord and Shawe (1989) gave micro-probe data for these exsolved phases in galena that they considered to be either eskimoite (?) or a Ag-bearing heyrovskyite (?).

Pb-sulfosalts previously reported from the Darwin mines were generally considered as minor exsolution products from main galena (Czamanske & Hall, 1975). Those reported herein from the St. Charles, Lucky Lucy and Silver Spoon mines appear to be the result of a complex galena-free Pb-Bi-Cu-Ag co-precipitation event related to the relative high temperature W mineralization. The specimens, which we have examined, consist of a complex intergrowth of members of the lillianite, bismuthinite-aikinite, pavonite and the junioite series, associated with very minor galena and tetradymite.

Galena and associated sulfosalts at Darwin were interpreted to have crystallized at a temperature greater than 350°C (Czamanske & Hall, 1975), while Mumme (1975b) suggests a temperature below 600°C. The Sb:Bi ratio is an indication of formation temperature. Low values are indicative of relatively high temperature and considerable depth. Galena from the Jackass mine, Darwin has a Sb:Bi ratio of <0.07 (Foord & Shawe, 1989). EDS results for the several sulfosalts examined in our study show no discernible Sb at the 0.1 wt.% analytical level. Microprobe analyses of tetradymite specimens from the Lucky Lucy and Silver Spoon mines show an Sb range from 0.02 to 0.22 wt.%.

This new mineralogical data of our study correlates with some of the results obtained by Czamanske & Hall (1975) on the Darwin district, and by Foord *et al.* (1988), who discussed the relationship between

coexisting galena, (Bi, Ag)-enriched galena, and sulfosalts. At the Lucky Lucy mine, the gustavite-vikingite-(Ag,Bi)-rich heyrovskyite trend (or  $\text{Gus}_{65}\text{-Vik}_{47}\text{-Hey}_{65}$  trend) is very close to the Type I – Type II – Type III sulfosalts (+ galena) trend of Czamanske & Hall (1975). This trend has also been described from the following deposits: the Treasure mine, Colorado (Karup-Møller, 1977); the Monteneme W-Sn deposit, Spain, (Gouanvic & Babkine, 1985); the La Roche-Balue, France (Moëlo *et al.* 1987); the Corrie Buie lead veins, Scotland (Patrick, 1984); the Round Mountain and Manhattan gold districts, Nevada (Foord *et al.* 1988) and in the mineralized veins in the Oberprinzgau region, Austria (Paar *et al.* 1980).

Increasing the Ag-Cu-Bi content relative to Pb gives the gustavite-friedrichite association at the St. Charles mine. Ag-Pb impoverishment gives the krupkaite-junoite association at the Silver Spoon mine.

Se partitioning between Bi-sulfosalts is an interesting aspect of our study. In the sulfosalts of the pavonite series, which always have a high Bi/Pb ratio, Mumme (1990) indicates no limit in the Se-for-S substitution in such a crystal structure type. This explains the highest Se content encountered in the pavonite-cupropavonite intergrowth from Lucky Lucy mine. For a lower Bi/Pb ratio, corresponding to junosite and krupkaite, the equilibrium association between these two sulfosalts at the Silver Spoon mine is original and clearly confirms the stabilizing effect of Se for junosite (Se content twice that of krupkaite). Reversibly, the Se-for-S substitution in krupkaite may be considered as a maximum value. On the other hand, the association of junosite and pavonite-cupropavonite at the Lucky Lucy mine represents another phase equilibrium, but with only a weak Se-partitioning in favor of the pavonite-type phase.

Mumme (1975b) reports that junosite was not found during studies of the  $\text{Bi}_2(\text{S,Se})_3\text{-Pb}(\text{S,Se})\text{-Cu}_2(\text{S,Se})$  compositions carried out above 600°C. He suggests that selenium is an essential component of the junosite crystal structure, ordering out during the conditions of relatively slow cooling found in natural systems.

Minerals of the gustavite series have the lowest Bi/Pb ratio, but the limit of the Se-for-S substitution is unknown. Our data shows up to 3.3 wt.% Se, but Czamanske & Hall (1975) indicate up to 10 wt.% Se for the sulfosalt assemblage (probable (Ag, Bi)-rich heyrovskyite) at Darwin, and Large & Mumme (1975) about 7 wt.% Se for pure heyrovskyite at the Juno mine, Australia.

In such a complex district as Darwin, from deposit to deposit, or even within a given deposit, small variations in the ratio between various associated elements (Pb, Bi, Ag, Cu, Se) is sufficient to induce the formation of distinct (and various) Bi-sulfosalts. In the future, one may hope that the collection and examination of new samples at the Darwin district will permit the discovery of other rare sulfosalts.

## ACKNOWLEDGMENTS

The authors sincerely thank Drs. A. J. Criddle, T. T. Chen, J. Jambor, J. H. G. LaFlamme, and J. Cabri for reviews of this paper.

## REFERENCES

CHEN, T. T., KIRCHNER, E., and PAAR, W. (1978) Friedrichite,  $\text{Cu}_5\text{Pb}_5\text{Bi}_7\text{S}_{18}$ , a new member of the aikinite-bismuthinite series. *Canadian Mineralogist*, **16**, 127-130.

CZAMANSKE, G. K., and HALL, W. E. (1975) The Ag-Bi-Pb-Sb-S-Se-Te mineralogy of the Darwin lead-silver-zinc deposit, southern California. *Economic Geology*, **70**, 1092-1110.

FOORD, E. E., SHAW, D. R., and CONKLIN, N. M. (1988) Coexisting galena,  $\text{PbS}_{ss}$  and sulfosalts: evidence for multiple episodes of mineralization in the Round Mountain and Manhattan gold districts, Nevada. *Canadian Mineralogist*, **26**, 355-376.

FOORD, E. E., and SHAW, D. R. (1989) The Pb-Bi-Ag-Cu-(Hg) chemistry of galena and some associated sulfosalts: a review and some new data from Colorado, California and Pennsylvania. *Canadian Mineralogist*, **27**, 363-382.

GOUANVIC, Y. and BABKINE, J. (1985) Métallogénie du gisement à tunstène-étain de Monteneme (N.W. Galice, Espagne). *Mineralium Deposita*, **20**, 8-15.

HALL, W. E., and MACKEVETT, E. M. (1958) Economic geology of the Darwin Quadrangle, Inyo County, California. *California Division of Mines Special Report*, **51**, 73 p.

HALL, W. E. (1962) Geology and ore deposits of the Darwin Quadrangle, Inyo County, California. *U. S. Geological Survey Professional Paper*, **368**, 87p.

HALL, W. E. (1971) Minor-element contents of the sulfide minerals, Darwin lead-silver-zinc mine, Inyo County, California. *Society of Mining Geologists, Japan, Special Issue 2*, 119-126.

HALL, W. E., ROSE, H. J., JR., and SIMON, F. O. (1971) Fractionation of minor elements between galena and sphalerite, Darwin lead-silver-zinc mine, Inyo County, California and its significance in geothermometry. *Economic Geology*, **66**, 602-606.

- KARUP-MØLLER, S. (1970) Gustavite, a new sulfosalt from Greenland. *Canadian Mineralogist*, **10**, 173-190.
- KARUP-MØLLER, S. (1977) Mineralogy of some Ag-(Cu)-Pb-Bi sulphide associations. *Bulletin Geological Society Denmark*, **26**, 41-68.
- KARUP-MØLLER, S., and MAKOVICKY, E. (1979) On pavonite, cupropavonite, benjaminite, and "oversubstituted" gustavite. *Bulletin de la Société française Minéralogie et Cristallographie*, **102**, 351-367.
- KLOMÍNSKÝ, J., RIEDER, M., KIEFT, C., and MRAZ, L. (1971) Heyrovskyite,  $6(\text{Pb}_{0.86}\text{Bi}_{0.08}(\text{Ag,Cu})_{0.04}\text{S}\cdot\text{Bi}_2\text{S}_3)$  from Hürky, Czechoslovakia, a new mineral of genetic interest. *Mineralium Deposita*, **6**, 133-147.
- LARGE, R.R. and MUMME, W.G. (1975) Junoite, "wittite" and related seleniferous bismuth sulfosalts from Juno Mine, Northern Territory, Australia. *Economic Geology*, **70**, 369-383.
- MAKOVICKY, E., and KARUP-MØLLER, S. (1977) Chemistry and crystallography of the lillianite homologous series II. Definition of new minerals: eskimoite, vikingite, ourayite, and treasureite. Re-definition of schirmerite and new data on the lillianite-gustavite solid-solution series. *Neues Jahrbuch für Mineralogie Abhandlungen*, **131**, 56-82.
- MAKOVICKY, E. (1989) Modular classification of sulphosalts--current status: Definition and Application of homologous series. *Neues Jahrbuch für Mineralogie Abhandlungen*, **160**, 269-297.
- MOËLO, Y., MARCOUX, E., MAKOVICKY, E., KARUP-MØLLER, S., AND LEGENDRE, O. (1987) Homologues de la lillianite (gustavite, vikingite, heyrovskyite riche en Ag et Bi...) de l'indice à W-As-(Pb, Bi, Ag) de La Roche-Baloue (Loire-Atlantique, France). *Bulletin de Minéralogie*, **110**, 43-64.
- MUMME, W. G. (1975a) The crystal structure of krupkaite,  $\text{CuPbBi}_3\text{S}_6$ , from the Juno mine at Tennant Creek, Northern Territory, Australia. *American Mineralogist*, **60**, 300-308.
- MUMME, W. G. (1975b) Junoite,  $\text{Cu}_2\text{Pb}_3\text{Bi}_8(\text{S,Se})_{16}$ , a new sulfosalt from Tennant Creek, Australia: its crystal structure and relationship with other bismuth sulfosalts. *American Mineralogist*, **60**, 548-558.
- MUMME, W.G. (1990) A note on the occurrence, composition and crystal structures of pavonite homologous series members  $^4\text{P}$ ,  $^6\text{P}$ , and  $^8\text{P}$ . *Neues Jahrbuch für Mineralogie, Monatshefte*, 193-204.
- NUFFIELD, E. W. (1954) Studies of mineral sulphosalts: XVIII-pavonite, a new mineral. *American Mineralogist*, **39**, 409-415.
- PAAR, W.H., CHEN, T.T. and MEIXNER, H. (1980) Pb-Bi-(Cu)-sulfosalts in Paleozoic gneisses and schists from Oberpinzgau, Salzburg Province, Austria. *Tschermaks Mineralogische und Petrographische Mitteilungen*, **27**, 1-16.
- PATTRICK, R. A. D. (1984) Sulphide mineralogy of the Tomnadashan copper deposit and the Corrie Buie lead veins, south Loch Tayside, Scotland. *Mineralogical Magazine*, **48**, 85-91.
- PRINGLE, G. J., and THORPE, R. I. (1980) Bohdanowiczite, junoite and laitakarite from the Kidd Creek mine, Timmins, Ontario. *Canadian Mineralogist*, **18**, 353-360.
- WILLIAMS, S. A. (1988) Potts site, a new vanadate from Lander County, Nevada. *Mineralogical Magazine*, **52**, 389-390.
- ŽÁK, L., SYNECEK, V., and HYBLER, J. (1974) Krupkaite,  $\text{CuPbBi}_3\text{S}_6$ , a new mineral of the bismuthinite-aikinite group. *Neues Jahrbuch für Mineralogie, Monatshefte*, 533-541.

**Table 1.** Average microprobe analysis (wt. %) of Darwin sulfosalts (this study).

<b>Mineral (#)</b>	<b>Mine</b>	<b>Cu</b>	<b>Ag</b>	<b>Cd</b>	<b>Pb</b>	<b>Bi</b>	<b>Te</b>	<b>Se</b>	<b>S</b>	<b>Total</b>
Friedrichite (4)	St. Charles	9.18	n.d.	n.d.	31.12	42.39	n.d.	0.54	16.61	99.84
Gustavite (5)	St. Charles	0.62	7.24	0.03	24.58	49.68	0.09	1.8	15.64	99.68
Krupkaite (2)	Silver Spoon	5.68	n.d.	n.d.	19.16	56.78	n.d.	2.80	16.29	100.69
Junoite (2)	Silver Spoon	4.28	0.50	n.d.	18.54	56.14	0.32	5.12	14.92	99.67
Junoite (2)	Lucky Lucy	4.08	0.78	0.01	17.49	57.06	0.25	4.46	15.22	99.31
Heyrovskyite (1)	Lucky Lucy	0.17	4.77	0.0	46.90	31.47	0.36	3.13	13.52	100.33
Vikingite (4)	Lucky Lucy	0.10	5.58	0.03	40.38	37.24	0.36	3.32	14.16	101.13
Gustavite (1)	Lucky Lucy	0.08	6.03	0.0	30.21	45.73	0.45	3.33	14.69	100.51
Pavonite (7)	Lucky Lucy	2.92	7.76	0.10	7.25	61.83	0.37	5.37	14.85	100.44
Cupropavonite (2)	Lucky Lucy	4.93	7.05	0.10	8.02	58.94	0.35	5.38	14.96	99.71
Unclassified (1)	St. Charles	2.42	7.23	0.14	24.27	48.57	0.13	1.79	15.78	100.33
Unclassified (1)	St. Charles	1.01	8.10	0.0	18.74	52.60	0.09	2.98	15.22	98.83

(#) = number of microprobe analyses.

**Table 2.** Average chemical formulas for Darwin sulfosalts (this study).

<b>Mineral</b>	<b>Mine</b>	<b>Chemical formula</b>
<b>Friedrichite</b>	St. Charles	$\text{Cu}_{4.95}\text{Pb}_{5.15}\text{Bi}_{6.95}(\text{S}_{17.88}\text{Se}_{0.12})_{\Sigma=18}$
<b>Gustavite</b>	St. Charles	$\text{Cu}_{0.12}\text{Ag}_{0.79}\text{Pb}_{1.39}\text{Bi}_{2.78}(\text{S}_{5.73}\text{Se}_{0.26}\text{Te}_{0.01})_{\Sigma=6}$
<b>Krupkaite</b>	Silver Spoon	$\text{Cu}_{0.99}\text{Pb}_{1.02}\text{Bi}_{3.00}(\text{S}_{5.60}\text{Se}_{0.40})_{\Sigma=6}$
<b>Junoite</b>	Silver Spoon	$\text{Cu}_{1.95}\text{Ag}_{0.16}\text{Pb}_{2.67}\text{Bi}_{8.08}(\text{S}_{13.97}\text{Se}_{1.95}\text{Te}_{0.08})_{\Sigma=16}$
Junoite	Lucky Lucy	$\text{Cu}_{1.95}\text{Ag}_{0.22}\text{Pb}_{2.56}\text{Bi}_{8.22}(\text{S}_{14.24}\text{Se}_{1.70}\text{Te}_{0.06})_{\Sigma=16}$
Heyrovskyite	Lucky Lucy	$\text{Cu}_{0.08}\text{Ag}_{0.83}\text{Pb}_{4.38}\text{Bi}_{2.97}(\text{S}_{8.18}\text{Se}_{0.74}\text{Te}_{0.08})_{\Sigma=9}$
<b>Vikingite</b>	Lucky Lucy	$\text{Cu}_{0.13}\text{Ag}_{3.14}\text{Pb}_{11.92}\text{Bi}_{11.00}(\text{S}_{27.12}\text{Se}_{2.62}\text{Te}_{0.26})_{\Sigma=30}$
Gustavite	Lucky Lucy	$\text{Ag}_{0.67}\text{Pb}_{1.81}\text{Bi}_{2.69}(\text{S}_{5.45}\text{Se}_{0.50}\text{Te}_{0.05})_{\Sigma=6}$
<b>Pavonite</b>	Lucky Lucy	$\text{Cu}_{0.43}\text{Ag}_{0.67}\text{Pb}_{0.33}\text{Bi}_{2.74}(\text{S}_{4.34}\text{Se}_{0.64}\text{Te}_{0.02})_{\Sigma=5}$
Cupropavonite	Lucky Lucy	$\text{Cu}_{0.72}\text{Ag}_{0.67}\text{Pb}_{0.36}\text{Bi}_{2.63}(\text{S}_{4.34}\text{Se}_{0.63}\text{Te}_{0.03})_{\Sigma=5}$
Unclassified	St. Charles	$\text{Cu}_{0.44}\text{Ag}_{0.78}\text{Pb}_{1.37}\text{Bi}_{2.70}(\text{S}_{5.73}\text{Se}_{0.26}\text{Te}_{0.01})_{\Sigma=6}$
Unclassified	St. Charles	$\text{Cu}_{0.20}\text{Ag}_{0.88}\text{Pb}_{1.06}\text{Bi}_{2.94}(\text{S}_{5.55}\text{Se}_{0.44}\text{Te}_{0.01})_{\Sigma=6}$

Minerals in bold verified by X-ray powder diffraction.