

Sulvanite from Thorpe Hills, Utah¹

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Abstract

Sulvanite, Cu_3VS_4 , has been identified from a prospect in Thorpe Hills, Utah. This is the fourth world occurrence and the second in the United States. The sulvanite forms cubic crystals up to 2.5 cm in size, with a definite bronze sheen on fresh fractures. Except where fractured, all samples are coated with a yellowish-green alteration product of volborthite.

The unit cell parameter determined by a least squares method is a_0 Å 5.3915. X-ray powder diffraction data agree very well with those listed for sulvanite from the Mercur District, Utah. Chemical analysis determined the unit cell content to be $\text{Cu}_{2.00}\text{V}_{0.99}\text{S}_{3.99}$. This is in excellent agreement with the theoretical unit cell content of $\text{Cu}_{3.00}\text{V}_{1.00}\text{S}_{4.00}$. The chemical analysis of the sulvanite is Cu 31.90, S 21.36, V 8.50. Samples from Thorpe Hills were compared with specimens from the type locality at the Edelweiss Mine, near Burra, South Australia. The vanadate alteration product of sulvanite at the Edelweiss Mine is vesignieite.

Sulvanite elements for both deposits are probably derived from underlying carbonaceous shales within the negative oxidation-potential zone below the water table. Migration of vanadium and copper ions occurred when faulting released confining pressure in the shale beds.

Introduction

In 1970 a new occurrence of sulvanite was noted by the author in Thorpe Hills, Utah. This is the fourth reported world occurrence of sulvanite and the second in the United States of America.

Sulvanite, a primary vanadium-copper sulfide, was originally identified and described from the Edelweiss Mine near Burra in South Australia by Goyder (1900). In 1931 it was found at Mercur, Utah, and described by Schempp and Schaller (1931). Smirnov and Premysler (1967) described a third occurrence at Pay Hoy (*sic*), Russia.

Occurrence and Geological Setting

The new occurrence of sulvanite is at a prospect on the west side of Thorpe Hills in section 35, T.7S, R.3W, of the Fivemile Pass Quadrangle. The copper and vanadium mineralization occurs in a brecciated black limestone within the Cedar Fort Member of the Oquirrh Formation of Pennsylvanian age, described by Bissell *et al* (1959). The brecciated zone is parallel to, and is about 1 km west of, the Thorpe Hills Fault. The breccia is characterized by a cement of white calcite and euhedral quartz.

Copper and vanadium alteration minerals impart a green to greenish-yellow color to the sulvanite. The sulvanite is found as intergrowths of crystals up to 3 cm across. Some individual crystals up to 2.5 cm were noted, but these are rare. All the sulvanite found occurred with quartz in a white calcite and black limestone breccia.

Physical and Optical Properties

In all occurrences, sulvanite is coated with alteration minerals consisting of malachite, volborthite, and azurite. Fresh fractures reveal a dark gray-to-black metallic surface with a bronze sheen. A gray color is imparted by the reticulated network of quartz veinlets along cleavage planes and fracture zones in the sulvanite (Fig. 1). These veinlets also make it extremely difficult to obtain an accurate specific gravity. However, the results obtained (Table 2) are in close agreement with values listed in Palache, Berman, and Frondel (1944). The sulvanite may appear harder than 3.5 because of the reticulate quartz that it contains. Reflectivity measurements are listed in Table 1.

In polished section it can be seen that quartz veinlets along cleavage planes tend to protect the crystal faces from alteration. Prominent alteration occurs along fracture surfaces and exposed crystal faces and is discernible proceeding along some reticu-

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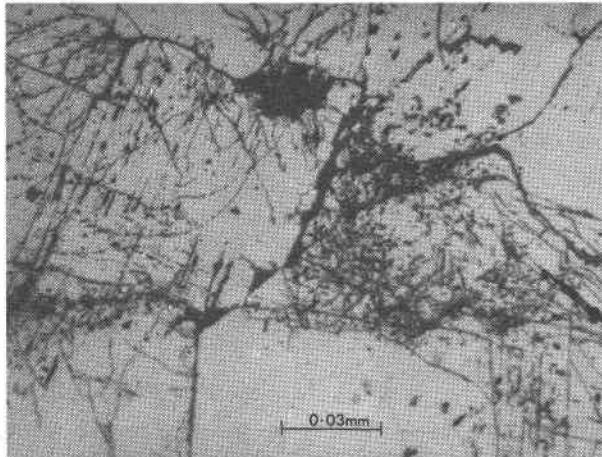


FIG. 1. Reticulate quartz veinlets along crystal cleavages and fracture zones in sulvanite appear as dark gray-to-black lines.

late quartz veinlets. Figure 2 shows massive light gray sulvanite with black seams of volborthite replacing the sulvanite along cleavage planes filled with quartz.

The sulvanite in polished section is creamy-white with areas of triangular pits similar to those exhibited by galena. However, the pits appear to be restricted to rhombic and triangular zones that are limited by cleavage planes (Fig. 3). The texture is a random intergrowth of coarse cubic crystals that tend to fracture in the (111) planes. A random cutting of the sample will occasionally intersect a crystal axis and produce triangular pits (as in Fig. 3) or facets (Fig. 6) when polished. Studies by Trojer (1966) indicate that there is a tetrahedral coordination of V and Cu to S, and that the tetrahedron about V is a regular one with the angle S-V-S = $109^{\circ} 28'$. The Cu however is somewhat distorted so that the S-Cu-S angle is $\approx 103^{\circ} 51'$ and $112^{\circ} 21'$. This S-Cu-S distortion could explain the peculiar pattern areas of triangular pits. A twenty

TABLE 1. Reflectivity Measurements with E.E.L. Photometer R Percent (Air)

Wave Length nm	Std. SiC	Range of Values		Wave Length nm	Uytenbogaardt & Burk (1971)
		Thorpe Hills, Utah	Edelweiss Mine, S.A.		
470	20.5	24.1-24.7	24.1-24.7	480	25.8-27.9
546 Hg _e	20.0	28.1-28.4	27.9-28.4	540	19.2-31.2
589 Na _D	19.5	27.3-27.3	27.3-28.3	580	29.1-30.4
650	18.5	27.3-28.2	28.2-29.9	640	33.0-34.8

TABLE 2. Chemical Analysis Wt Percent, Unit Cell Content, Sp. Gr.

	Previous Data				Present Data	
	(1)	(2)	(3)	(4)	(5)	(6)
Cu	51.55	51.57	52.96	50.0	52.62	51.65
V	13.78	13.46	13.72	14.5	13.51	13.76
S	34.67	34.97	33.32	30.0	33.85	34.58
Total	100.00	100.00	100.00	94.5	99.98	99.99
UNIT CELL CONTENT (based on 8 atoms)						
Cu	3.000	2.997	3.112	3.136	3.081	3.008
V	1.000	0.975	1.005	1.134	0.986	0.999
S	3.999	4.027	3.881	3.729	3.928	3.991
Specific Gravities						
	3.94	4.00	4.00	3.86	3.82	3.86

- (1) Calculated composition for Cu_3VS_4 (1938) C.A. Schempp and W.T. Schaller.
 (2) (3) (1900) Goyder (Burra, S.A.).
 (4) Schempp, et al (1938) C.A. Schempp, analyst (Mercur, Utah).
 (5) Edelweiss Mine, S.A.
 (6) Thorpe Hills, Utah, U.S.A. } T.D. Rice, Analyst, N.S.W. Dept. of Mines.

second etch with 55 percent hydriodic acid accented cleavage planes and triangular pits. Some wedge-shaped triangular surfaces indicate the cubic crystals are cut close to their (111) plane (Fig. 4).

Most of the sulvanite grains are idioblastic in calcite or unequally granular when in a mass. Very little perpendicular cleavage was noted except as seen in Figure 5.

Volborthite, a hydrated vanadate of copper, is mixed with malachite and some azurite. These minerals form a yellowish-green to blue encrustation along exposed surfaces of the sulvanite.

X-ray powder diffraction data on the sulvanite and its alteration minerals are consistent with those

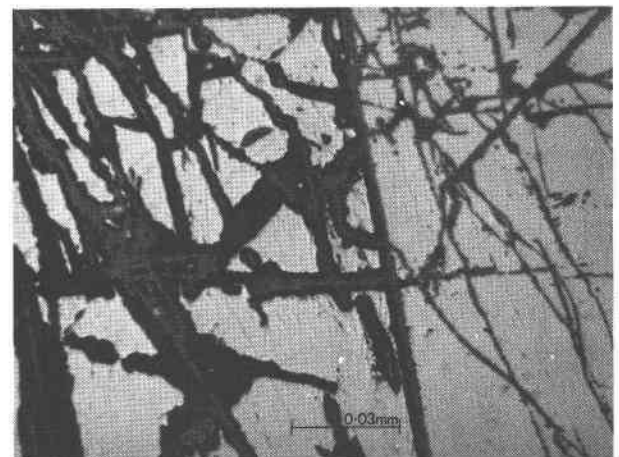


FIG. 2. Sulvanite (light grey) with cleavage planes filled by quartz (medium grey) in rhombic and irregular patterns. Volborthite which forms low refracting black lines is replacing the sulvanite. The reticulate quartz is outlined by alteration products of the adjacent sulvanite.

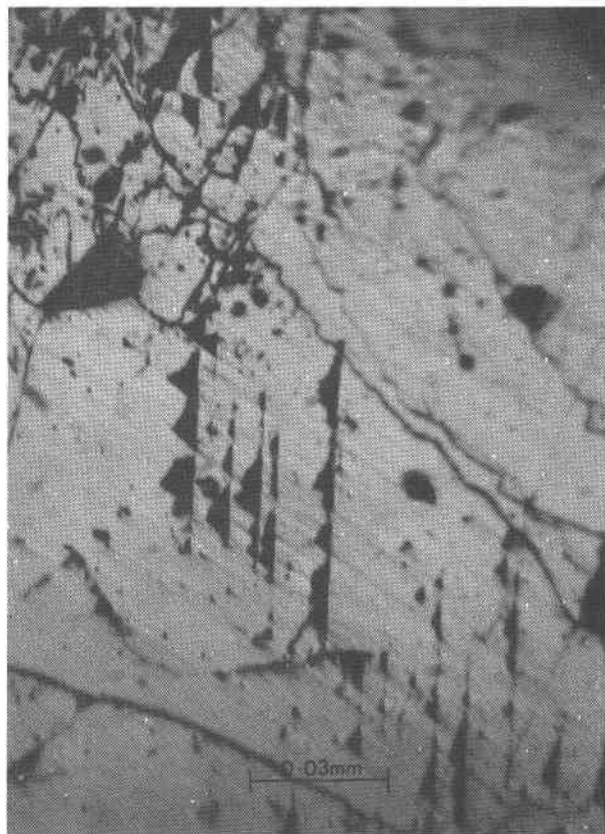
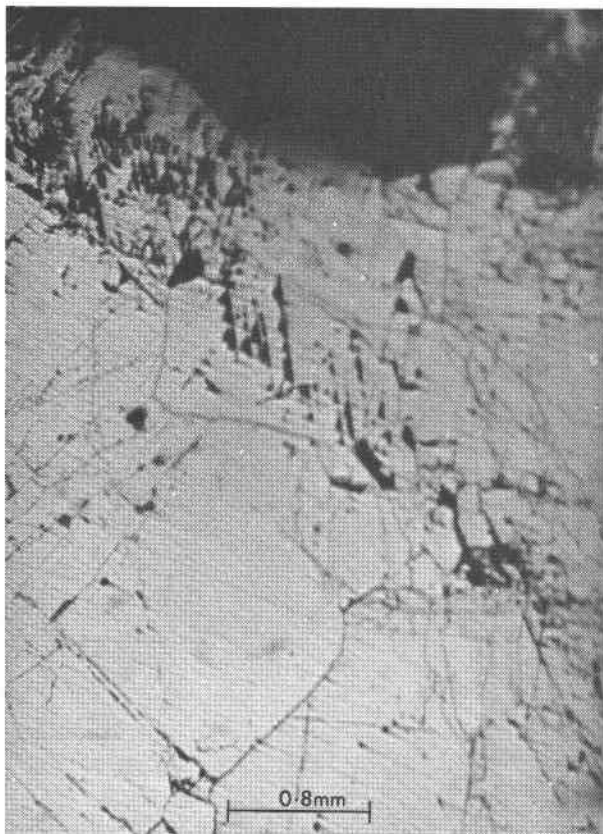


FIG. 3. Triangular pits (or facets as in Fig. 6) in rhombic and triangular zones limited by cleavage planes. Two magnifications of the same area show the patterns.

listed in the X-ray Powder Data File. Those for sylvanite are listed in Table 5.

Chemical Composition

Wet chemical analyses of carefully separated sylvanite material are listed in Tables 2 and 3.

The analyses have been calculated after deducting 37.83 and 14.39 percent silica from the Thorpe Hills Prospect and Edelweiss Mine samples respectively. The high silica content is the result of cleavage plane and fracture filling of quartz noted in Figure 1.

Analytical Procedure

The procedure described here was developed by T. D. Rice of the Chemical Laboratory, New South Wales Department of Mines.

Grains chosen for analysis were ground to -100 mesh and carbonate minerals were removed by treating a 0.4-gram portion twice with dilute acetic acid in a covered beaker for 1 hour on a steam bath. The sample was then washed well with de-ionized water and dried at 50°C for 3 days. The

filtrate from the second acid treatment was a much paler blue than the first, indicating that a single treatment with hot dilute acetic acid removed the bulk of copper-bearing minerals decomposable by

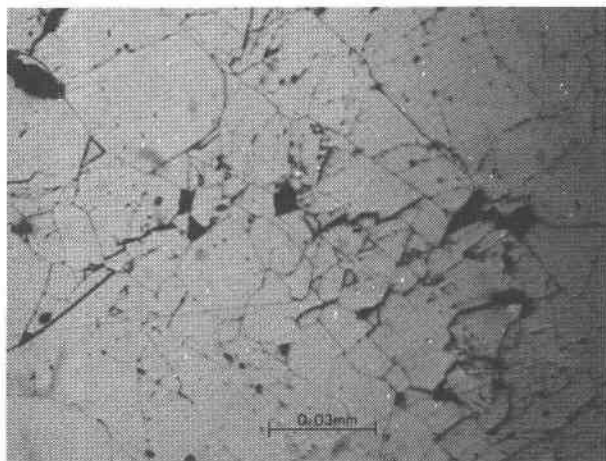


FIG. 4. Texture of sylvanite mass after polished section was etched twenty seconds by 55 percent HI.

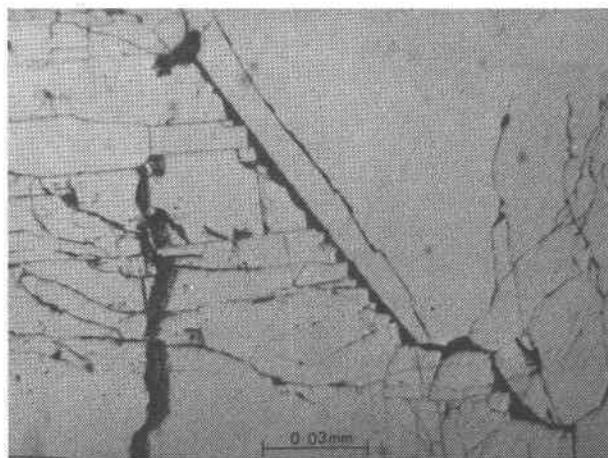


FIG. 5. Cubic cleavages of sulvanite filled by quartz.

acetic acid. Goyder (1900) found a slight excess of copper in a sample treated in a similar way with acetic acid but did not note whether he used more than one treatment with acetic acid.

It was hoped that the whole chemical analysis could be done on the sample solution from a fusion with lithium metaborate in the presence of potassium nitrate. This was found impracticable because of partial volatilization of sulfur during fusion.

An acid dissolution procedure using bromine, carbon tetrachloride, and nitric acid, similar to that

of Allen and Bishop as described by Hillebrand *et al* (1953), was used for determination of sulfur. Copper and vanadium were also determined in aliquots of this sample solution with results identical to those obtained by fusion. Silica was sufficiently separated by digesting the residue, after evaporating with nitric acid to dryness, with a mixture of hydrogen peroxide and dilute nitric acid.

Copper was separated from sulfur and vanadium by passing an aliquot of sample solution through a cation exchange column. Vanadium was then totally removed from the column with 0.01 M nitric acid containing 2.5 ml of 100 volumes hydrogen peroxide per 100 ml. Copper was subsequently obtained by elution with 3.5 M hydrochloric acid. After adding 4 ml of 18 M sulfuric acid to the copper-bearing eluate, the whole was evaporated to dryness, and copper was determined by the iodometric method of Meites (1952).

Vanadium was determined in the presence of sulfate by atomic absorption spectroscopy using a nitrous oxide-acetylene flame. Measurement solutions were buffered with 400 ppm of cesium and 720 ppm of aluminum. Each 50 g of sample measurement solution also contained 12 g of potassium sulfate solution containing 3.00 mg of sulfur per gram. Standard measurement solutions matched the sample measurement solutions by containing 16.5 g of the above potassium sulfate solution per 50 g as well as 400 ppm of cesium and 720 ppm of aluminum. Addition of 400 ppm of cesium and 720 ppm of aluminum was found to increase the sensitivity by slightly more than 100 percent while addition of 400 ppm of cesium without any aluminum increased the sensitivity by only 20 percent. Further addition of cesium and aluminum gave no further enhancement of sensitivity. This agrees with Sachdev *et al.* (1967) who observed a considerable sensitivity enhancement for vanadium on adding aluminum or titanium.

Sulfur was determined (in an aliquot of the vanadium plus sulfur fraction from the ion exchange separation of copper) gravimetrically as barium sulfate. Before precipitation of barium sulfate, vanadium was reduced to the quadrivalent state and, after adjusting acidity to 0.05 M, separated from sulfur by passing through the same cation exchange column as used for separation of copper. This procedure was similar to that recommended by Samuelson (1952) for determining sulfur in pyrites. In the present work, quadrivalent vanadium was

TABLE 3. Wet Chemical Analysis in Wt Percent of Samples Previously Treated with 30 Percent Acetic Acid**

	Thorpe Hills, Utah	Edelweiss, S.A.
Cu	31.90	42.75
S	21.36	27.50
V	8.50	10.98
SiO ₂	37.59	13.66
Total Fe as Fe ₂ O ₃	0.04	1.27
Na ₂ O	0.02	0.02
Acid Sol. K ₂ O	<0.01	0.03
MgO	0.01	0.42
CaO	0.02	0.02
SrO	<0.003	0.006
BaO	0.02	0.91
H ₂ O (105°C)	<0.1	<0.1
Total	99.46	97.56*

* The low total for the Edelweiss sample is partly due to the presence of vesignieite, BaCu₂(VO₄)₂(OH)₂. Assuming that all the barium is in this mineral, the vesignieite content is 3.50 per cent. If this were decomposed by acid dissolution, barium would have taken some of the sulphur into the insoluble residue and the corrected sulphur figure would be 27.69. Assuming that vesignieite is the only other copper and vanadium-bearing mineral in the sample submitted for analysis, the results for copper and vanadium combined as sulvanite become 41.62 and 10.38 per cent respectively. O.E. (table 4) revealed the presence of about 0.3% Al. in the Thorpe Hills sample, and 0.6% Al. in the Edelweiss sample. Kaolinite was identified in the Edelweiss sample.

** (Analyst, T.D. Rice)

found to behave like ferric iron in being completely retained by the cation exchange resin.

X-ray Diffraction Data

X-ray powder diffraction data is listed in Table 5. Results were obtained from Debye-Scherrer powder photographs. The film was mounted in the Straumanis manner and, except where indicated, $\text{CoK}\alpha$ radiation was used to lessen the effect of fluorescence. Intensities are by visual estimation.

Discussion and Comparison

Sulvanite from the Thorpe Hills prospect in Utah occurs in a brecciated black limestone cemented with white calcite and quartz. The brecciated zone is between the lower Cedar Fort Member and upper Meadow Canyon Member of the Oquirrh Formation of Pennsylvanian age. The underlying beds consist of shales and limestones. The breccia zone is related to the Thorpe Hills Fault. Alteration minerals of the sulvanite consist of volborthite mixed with malachite and some azurite. No copper sulfides were detected in specimens examined. In polished sections sulvanite from both sites are nearly identical, except for the degree of weathering and quartz displayed in the Edelweiss samples.

Sulvanite from the Edelweiss Mine in South Australia occurs in a ruptured zone related to the Koorunga Fault within the Torrensian Formation which is of Proterozoic age. The general sequence of sedimentary beds in this formation consists of interbedded dolomites and slates underlain by carbonaceous shales. The sulvanite is anhedral and occurs in quartz veins and breccias. Some pink calcite is present in the breccia zone in minor amounts. However, the alteration products and associated minerals differ to a marked degree from the Thorpe Hill deposit. The yellow-green ochres on the sulvanite from the Edelweiss Mine are composed of malachite intergrown with vesignieite.

To the author's knowledge vesignieite has not previously been reported from Australia. Barium was detected in the Edelweiss samples (see Tables 3 and 4). X-ray diffraction data on vesignieite correlates with that listed in the ASTM X-ray Powder Data File. Other related minerals are chalcopyrite, chalcocite, digenite, covellite, chrysocolla, and azurite. A further study of the alteration minerals is anticipated in a future work. Most of the copper, other than that in sulvanite, is concentrated as supergene chalcocite, digenite, and covellite (Fig.

TABLE 4. Optical Emission Spectrographic Analysis in PPM for Heavier Elements on Samples Previously Treated with 30 Percent Acetic Acid, and Untreated

	Thorpe Hills, Utah		Edelweiss, S. A.	
	Treated	Untreated	Treated	Untreated
Ni	20	20	<10	<10
Co	<25	<25	<25	<25
Mn	< 5	<5	<5	<5
Ti	150	130	150	100
Zr	<10	<10	<10	<10
Ag	5	10	70	60
Au	<250	<250	<250	<250
Cr	10	10	10	10
Sn	<250	<250	<250	<250
Mo	<100	<100	<100	<100
Zn	<250	5,000	<250	<250
Cd	<500	<500	500	<500
Bi	<100	<100	<100	<100
Sb	1,000	1,000	1,000	<1,000
Pb	<250	<250	<250	<250
B	<250	<250	<250	<250
Ba	160	210	7,900	6,300
Sr	10	100	50	50
Nb	<50	<50	<50	<50
* U	-	4.4	-	2.8

Where not detected, the element is given as less than the detection limit.

* Determined by fluorimetric methods.

6). The black rim around the supergene copper minerals is quartz. The wedge shaped sulvanite sections are cut near the (111) plane. In a group of crystals their intergrowth tends to give an impression of massive sulvanite.

Conclusions

Primary vanadium minerals are rare because of their susceptibility to weathering, and the tendency of vanadium to combine readily with other elements. In each of the present cases, the sulvanite occurs in a brecciated zone that has been exposed to oxidation after the sulvanite formed. The age of the sulvanite may be approximated by the dating of the orogenies that produced the breccia zone in which it occurs.

Both occurrences of sulvanite are in areas that have been underlain by carbonaceous shales, which provided the source elements and fluids for the formation of sulvanite. Hawkes and Webb (1962) show that carbonaceous shales may carry up to 2000 ppm vanadium and up to 300 ppm copper. These elements, in a low pH, reducing environment, can be mobilized once confining pressure is released by faulting. The subsequent compaction of the shale beds would cause hydrogen sulfide or humic acid fluids, carrying the vanadium and copper ions, to migrate into the brecciated zone and react. The fluids within this zone would have to be at a pH of less than 4.5 for sulvanite to form, or else volborthite or vesignieite would form (according to

TABLE 5. X-ray Diffraction Powder Data for Sulvanite

Thompson and Berry (1962) CuK α /Ni		Present Paper Measured, Co α /Fe				calculated	
I/I ₁	d(\AA)	Utah****		South Australia		d(\AA)	hkl
100	5.4	100	5.39	100	5.38	5.391	100
50	3.12	80	3.11	80	3.10	3.113	111
20	2.70	30	2.69	20	2.69	2.696	200
40	2.40	50	2.40	50	2.40	2.111	210
80	1.910	80	1.895	80	1.903	1.906	220
30	1.804	40	1.793	30	1.793	1.797	300, 221
40	1.634	50	1.622	40	1.622	1.626	311
20	1.501	30	1.492	15	1.493	1.495	320
30	1.349	20	1.346	20	1.346	1.348	400
20	1.308	20	1.307	10	1.307	1.308	410, 322
20	1.236		*(1.237)		** -	1.237	331
5	1.206		(1.206)		-	1.206	420
10	1.177	10	1.1755	10	1.1755	1.177	421
40	1.101	50	1.1000	40	1.002	1.101	422
20	1.037	20	1.0372	20	1.0373	1.038	511, 333
20	1.002	20	1.0009	20	1.0010	1.001	520, 432
20	0.953	20	0.9532	20	0.9535	0.9530	440
10	0.940	15	0.9385	15	0.9390	0.9386	441, 522
10	0.911	10	0.9114	10	0.9115	0.9113	531
10	0.953		(0.8526)		-	0.8524	620
10	0.843		(0.8422)		-	0.84202	621, 443
a_0 \AA ***	5.391	5.3915(5)		5.3940(5)			
ρ_x (g/cm ³)	3.92	3.918(1)		3.912(1)			

* d - spacings shown in bracket were obtained using CuK α radiation.

** d - spacings not listed indicate lines which were either too faint and diffuse to be confidently read or inappropriately placed on the film.

*** The lattice parameter (a_0) was calculated from the CoK α_1 [1.78896(9)] back reflection lines using a Bradley and Jay-type extrapolation of a weighted linear least squares analysis of a_{hkl} versus $\frac{1}{2}(\cos^2 \theta / \sin \theta + \cos^2 \theta / \theta)$.

**** Unit cell dimension and d - spacings determination by C.R. Ailwood of the Chemical Laboratory, N.S.W. Dept. of Mines.

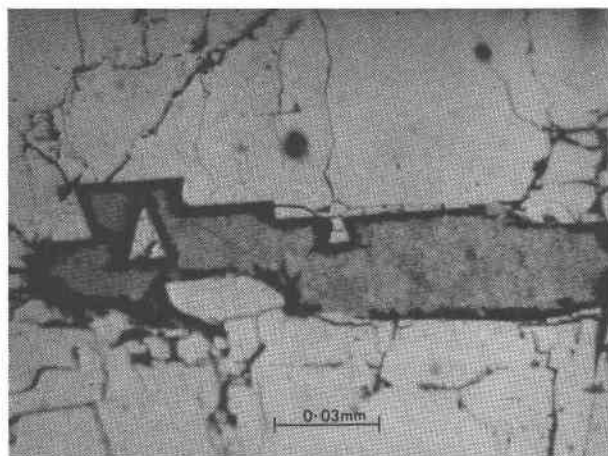


FIG. 6. Light grey is sulvanite; the patchy medium to dark grey area is a mixture of chalcocite, digenite, and covellite and is surrounded by quartz (dark grey).

Guillemin, 1953). The migrating fluids contacting the overlying carbonate beds would increase in alkalinity and form secondary white calcite. This would be followed by a silica gel which would penetrate the cleavage planes of the sulvanite. A second generation of quartz crystals would have formed at a later stage. In samples from the Edelweiss Mine secondary enrichment of copper minerals is found along the cleavage planes. This feature has not been observed in samples from Thorpe Hills. The secondary enrichment is related not only to their respective water table levels, but also to the difference in their ages.

The formation of volborthite and vesignieite must have occurred within the water table as the pH increased. Exposure to atmospheric conditions would have produced far more extensive weathering

than that noted in the samples. Also the Edelweiss Mine specimens display predominately massive sulvanite intergrowths and extensive quartz with very little calcite. These features are more characteristic of an older deposit where the carbonates have been weathered away and silification is in progress.

This study has revealed that much work remains to be done to better understand sulvanite texture, intergrowth patterns, and mode of formation.

Acknowledgments

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