UNITED STATES DEPARTMENT OF THE INTERIOR

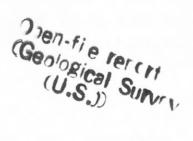
GEOLOGICAL SURVEY

GEOLOGY AND MINERALOGY OF THE APEX MINE,
WASHINGTON COUNTY, UTAH



by

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Abstract

The Apex mine, in Washington County, Utah about 22.5 km west of St. George, is the first mine in the world to be operated primarily for germanium and gallium. The ore, consisting of goethite, limonite, hematite, plumbian jarosite, azurite, malachite, conichalcite, and several other metallic oxides, carbonates, arsenates, and sulfates, is thoroughly oxidized down to at least 425 m below the surface. Most of the copper-rich ore was removed during previous mining operations, leaving behind the iron-rich minerals that contain most of the germanium and gallium. Germanium is concentrated chiefly in goethite (as much as 0.5%), hematite (as much as 0.7%), and limonite (as much as 0.5%), while gallium is concentrated mostly in plumbian jarosite (as much as 0.7%) and in some limonite (as much as 2%). Copper minerals are concentrated in and adjacent to carbonate rock, apparently replacing it. The ore at the Apex mine forms an irregular, branching, chimney-like body (or bodies) in fault breccia, gouge, and fissures associated with steeply-dipping subparallel fault zones in the Pennsylvanian Callville Limestone. Within and immediately adjacent to the fault zones, limestone has been dolomitized and locally silicified. Only a few small pieces of unreplaced primary sulfide ore have been found; these contain pyrite, galena, sphalerite, chalcopyrite, quartz, and traces of barite. The abundance of Cu, Ge, Ga, and As in the supergene ore implies the former presence of sulfides and sulfosalts containing these metals in the primary ore, which would make it similar to dolomite-hosted ores at Kipushi, Zaire; Tsumeb, Namibia; and Ruby Creek, Alaska. High concentrations of germanium and gallium should be looked for in gossans and other oxidized zones of copper-rich, arsenicbearing sulfide deposits, particularly those in carbonate host rocks.

Introduction

The Apex mine (also called the Dixie mine) is located on the east flank of the Beaver Dam Mountains in Washington County, Utah, about 22.5 km west of St. George and 9 km north of the Arizona border (Figure 1). The main adit is at an elevation of 1656 m (5434 feet), at 37°4'11"N latitude and 113°48'14"W longitude (NE-SW-SW Sec. 6, T43S, R17W). Before it was reopened in May, 1985 for germanium and gallium, the mine was operated intermittently from 1884 to 1962, producing over 7000 metric tons of copper, 400 metric tons of lead, 180,000 troy ounces of silver, and minor zinc and gold (Perry and McCarthy, 1976, p.516-525). The ore at the Apex mine consists of goethite, limonite, hematite, azurite, malachite, conichalcite, plumbian jarosite, and minor amounts of other metallic carbonates, oxides, sulfates, and arsenates. These occur in dolomitized and silicified breccia, gouge, and fissures in steeply dipping fault zones within the gently dipping Pennsylvanian Callville Limestone. Germanium is concentrated mostly in the goethite, hematite, and limonite, whereas gallium is concentrated chiefly in plumbian jarosite and in some limonite. These iron-rich minerals were generally rejected as waste during previous mining operations. The Apex mine is the first in the world to be operated primarily for Ge and Ga and is the first to mine supergene ore for these metals. Copper, lead, zinc, and possibly silver will be recovered as byproducts.

This preliminary report provides an outline of the geology and mineralogy of the Apex mine as known to date. Possible analogies to other deposits, and a proposed model for its genesis, are also given.

Methods

The mine was visited for four days in late April, 1985. Underground workings, including a decline ramp and four crosscuts down to the 5254 foot (1601 m) level, were examined and sampled. The collapsed shaft and adit of the much smaller Paymaster mine, 275 m SSE of the Apex mine on the same fault zone, were examined at the surface. Other outcrops of the ore zone and host rocks were also observed and sampled, as were the extensive tailings from the old mine workings. Several additional samples were obtained from diamond drill cores at the Apex mine. The samples were analyzed using an automated Rigaku powder X-ray diffractometer at Stanford University, and a Cambridge Stereoscan scanning electron microscope (SEM) with an energy-dispersive X-ray elemental analyzer at the U.S. Geological Survey, Menlo Park, CA.

Several assays of ore samples were made available by Musto Explorations Ltd., the current operators of the mine, through the courtesy of Bernard Dewonck. These assays were performed by Acme Analytical Laboratories of Vancouver, Canada, who used inductively coupled argon plasma analysis (ICP) to measure the concentrations of

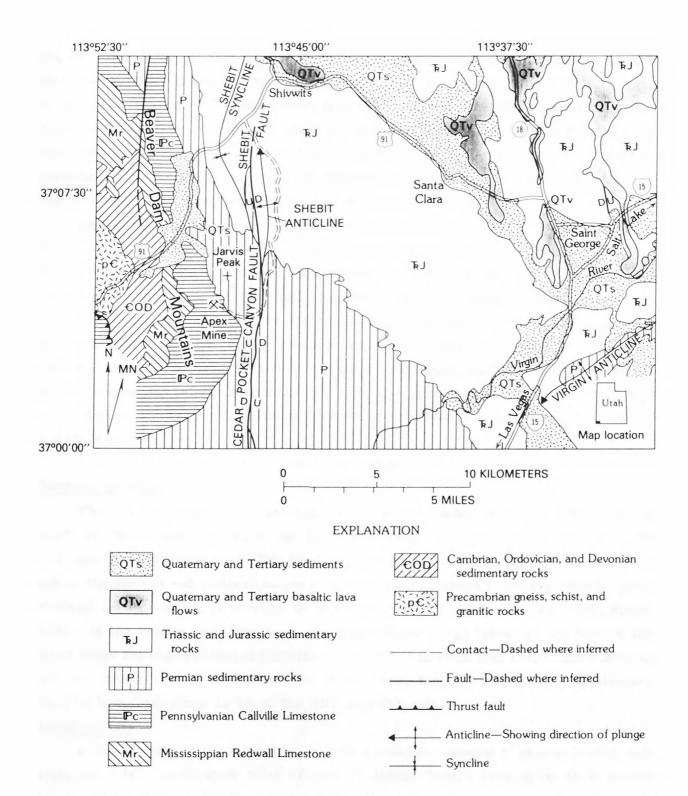


Figure 1. Map showing location of the Apex mine and generalized geology of the surrounding region. Geology adapted from Cook (1960).

Cu, Pb, Zn, Ag, Co, Ni, Mo, Bi, As, Sb, Cd, W, Au, and Si in samples fused with lithium metaborate. Germanium and gallium were measured, with a detection limit of 1 ppm, by graphite furnace atomic absorption spectroscopy on samples dissolved in hot aquaregia and hydrofluoric acid in a pressure bomb. Carbon dioxide was measured by infrared spectroscopy of gas released during heating in a furnace; carbon not present as carbonate was determined by taking the difference in measurements between untreated samples and samples that had been leached in acid to release all the CO₂.

Semiquantitative emission spectrographic analyses were performed on seven additional samples by Richard Lerner of the U.S. Geological Survey, Menlo Park, CA. These analyses were made on hand-picked samples, about 500 mg each, of homogeneous-appearing ore material. Elements Ge and In were analyzed by a 6-step visual semi-quantitative procedure using glass plates, whereas the other elements were analyzed using a direct reading emission spectrophotometer. Due to their high Fe content, the samples were diluted with material containing Si, Al, and K to minimize interferences; this raised detection limits, and also made measurements for Si, Al, and K less accurate (standard deviations of 30-50% of the recorded value, versus 10-20% for the other elements).

Geologic Setting

Regional geology

The Apex mine is on the east slope of the Beaver Dam Mountains, a NW trending uplift at the boundary between the Basin and Range province to the west and the Colorado Plateau to the east. The ore-hosting Pennsylvanian Callville Limestone crops out on the eastern and southern slopes of the mountains, where it rests on Mississippian Redwall Limestone and is overlain by Permian Pakoon Limestone (Cook, 1960; Steed, 1980). In the Beaver Dam Mountains and Virgin River Gorge (about 11 km SSW of the Apex mine) the shallow-marine Callville is 200-210 m thick (Steed, 1980). Igneous rocks are not known in the vicinity of the Apex mine, though fresh-looking Quaternary basaltic lava flows occur 13 km to the NNE near Shivwits.

Local geology

In the vicinity of the mine, the Callville Limestone consists of gently-dipping beds typically a few centimeters thick (Figure 2), though locally ranging up to 6 meters thick. The bedding generally dips 5-10°E to N, with local warps producing dips up to 50W, and is commonly irregular and discontinuous. Irregular chert nodules up to at least 50 cm across, locally forming short discontinuous layers, are abundant; quartz in these nodules is commonly recrystallized to grains up to several millimeters across. Rounded quartz grains up to a few millimeters across are locally common in the limestone, and discontinuous sandstone beds up to several meters thick occur in places.

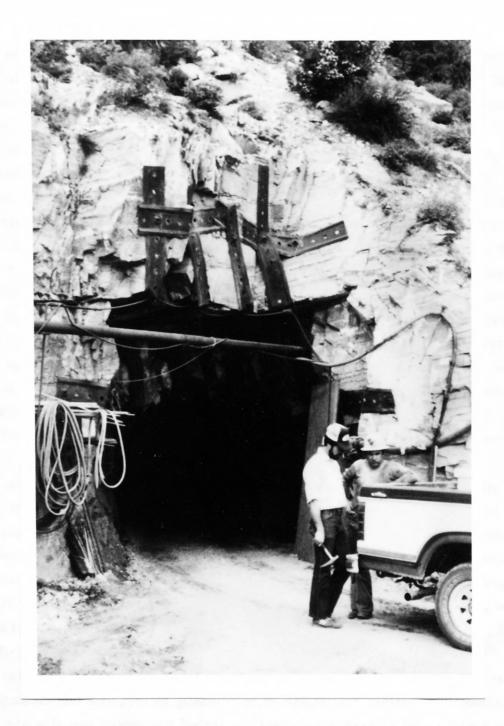


Figure 2. Main adit of the Apex mine, showing gently dipping beds of the Callville Limestone.

Scattered shaly beds up to a few centimeters thick are also present, as are some dolomitic zones. Poorly preserved fossil horn corals are locally common. Solution cavities ranging from a few centimeters across to caves several meters across are found in the mine; these generally contain small stalactites or calcite crystals.

The most prominent structural feature near the mine is the Apex fault, which strikes NNW and dips 640-710W (Figure 3). The fault is readily observed at the shafts of the Apex and Paymaster mines where the sheared and brecciated zone is 5-7 meters wide, but elsewhere it is covered by slopewash and is apparently narrower. The fault can be traced approximately at the surface by the sporadic presence of iron oxides, azurite, and malachite in the slope wash. At the Apex and Paymaster shafts, the fault zone consists of limonite- and goethite-impregnated gouge containing small amounts of malachite and azurite, with dolomite breccia in the footwall and apparently unaffected limestone in the hanging wall. The dolomite breccia observed at the surface has angular to subrounded dolomite clasts in a fine-grained dolomite matrix, whereas that in the mine commonly has a limonite-goethite matrix. Evidence on the direction of displacement for the fault was not observed. Kinkel (1951), mapping a distinctive sandstone bed, proposed the fault to be reverse with about 75 m vertical displacement.

Ore Geology

The ore at the Apex mine is defined as a goethite-limonite-hematite zone containing local concentrations of plumbian jarosite, azurite, malachite, and other supergene copper, iron, lead, and zinc minerals. It forms a highly irregular, branching, chimney-like body (or bodies) within fault breccia, gouge, and fissures associated with numerous subparallel faults in the footwall of the Apex fault. Mining and drilling data are currently insufficient to define the irregular shape of the ore zone or zones, but ore thicknesses of 1 to about 20 m can be observed, with a NW-SE strike length of at least 107 m confirmed by drilling (Lalonde, 1983).

The texture of the ore zone varies considerably. Most of the ore consists of broken fragments and stringers of goethite or hematite in a matrix of limonite (here used to denote soft iron oxides and hydroxides that give a weak to non-existent powder X-ray diffraction pattern). In places only limonite is present, whereas in other places (generally at the footwall of the ore zone) hard, vuggy goethite is present. Vugs in this goethite range from a few millimeters to several centimeters across, commonly containing botryoidal crusts or crystals of azurite, malachite, conichalcite, rosasite, or brochantite. In appearance, such ore resembles the gossans of many sulfide deposits, particularly those that contain arsenates such as that at Mapimi, Mexico (Hoffmann, 1968). Limonite-matrix dolomite breccia occurs in places, with the dolomite clasts commonly having a selvage of malachite or azurite. Plumbian jarosite occurs as

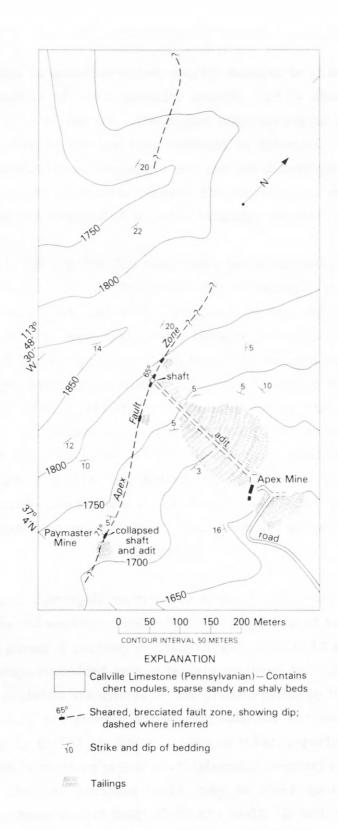


Figure 3. Geologic map showing locations of the Apex and Paymaster mines and the Apex fault zone. Compiled from Kinkel (1951) and field work by L.R. Bernstein, 1985.

discrete mustard-yellow to brownish-yellow, sparkly zones up to at least 1.5 m thick. It also occurs in the matrix of some dolomite breccia, and is disseminated in small amounts throughout much of the ore. The copper minerals appear to be concentrated towards the hanging wall of the ore zone adjacent to dolomite. They also replace dolomite fragments within limonite-goethite ore, and are disseminated through much of the ore in small quantities. Contacts between the ore and wall rocks are commonly gradational, with fracture coatings of limonite extending several meters into the wall rocks.

Limestone within the ore zone has been converted to dolomite or microcrystalline quartz, with dolomitization or silicification locally extending 1 to 2 meters into the wall rocks. Dolomitization was pervasive throughout the ore and fault zones, whereas silicification appears to have been most intense towards the hanging wall and at depth.

As the extent of the ore zone has not yet been fully defined, particularly at depth, grade and tonnage estimates are preliminary. The ore defined to October, 1983 is estimated by Lalonde (1983) at 242,768 tons containing 0.064% Ge, 0.032% Ga, 1.63% Cu, 0.77% Pb, 1.58% Zn, 0.50% As, 16.73% Fe, and 1.21 oz/ton (38 ppm) Ag. In addition, the surface dump from the old mine is estimated (Lalonde, 1983) to contain about 50,000 tons having 0.037% Ge, 0.019% Ga, and 1.55% Cu. Some chemical analyses of representative ore samples are presented in Table 1. Chemical analyses of some homogeneous-appearing, nearly monomineralic samples are presented in Table 2.

Mineralogy

Primary ore

The ore has been thoroughly oxidized to at least 425 m below the surface (the maximum depth of the old workings), and only a few fragments of sulfide minerals have been found. Several pieces of coarsely crystallized galena up to 10 cm across have been found on the old dump, embedded in and largely replaced by anglesite. Within the galena and adjacent anglesite are masses of fine-grained pyrite up to 1 cm across, sooty black covellite replacing pre-existing Cu-bearing sulfides, and very scarce grains of residual chalcopyrite up to 100 m across. Lalonde (1983) reported very fine-grained galena disseminated in "a mustard yellow mud" (plumbian jarosite) in drill hole 83-16 at He also reported "dark gray to black quartz-pyrite-sphalerite 160 feet (48.8 m). stringers" in limonitic zones in drill holes 83-20 and 83-25. In drill hole 85-1 at 93 feet (28.3 m) a layer of fine-grained pyrite 4 cm thick was found in the center of a mass of dense goethite. Small amounts of barite and quartz are intergrown with the pyrite. In the SEM, scarce scattered grains of galena 1-10 μ m across were observed, as were a grains of an unidentified Pb- As- Cu- S-rich mineral 1-5 Mm Approximately 75 ppm Ni and 15 ppm Co were detected in this pyrite (Table 2).

Table 1. Chemical analyses of some representative ore samples from the Apex mine.

		Samples								
	1	2	3	4	5	6	7	8		
Weight percent:										
Ge		0.198	0.460	0.382	0.108	0.224	0.065	0.09		
Ga	0.032	0.033	0.086	0.148	0.119	0.086	0.040	0.08		
Cı	3.08	0.65	0.16	12.00	0.10	0.31	0.17	1.42		
Pb	0.09	0.51	0.10	0.42	0.74	5.48	4.10	0.87		
Zr	1.59	1.06	0.33	0.62	0.13	0.26	0.12	0.53		
As	0.09	1.10	2.10	4.38	0.70	2.74	1.03	2.71		
Ві	0.001	0.01	0.01	0.001	0.01	0.001	0.004	0.053		
Cd	0.00	0.01	0.01	0.01	0.00	0.001	0.001	0.00		
Co	0.01	0.01	0.01	0.04	0.00	0.001	0.001	0.01		
Mo	0.004	0.032	0.027	0.038	0.039	0.013	0.043	0.057		
Ní	0.03	0.02	0.02	0.06	0.01	0.01	0.01	0.01		
Sb	0.001	0.012	0.089	0.077	0.055	0.037	0.143	0.257		
Fe	26.18	40.70	31.92	19.20	12.12	25.43	22.36	14.05		
Ca	1.73	0.16	0.42	1.31	0.11	0.35	0.14	0.58		
Mg	1.23	0.06	0.09	0.07	0.06	0.04	0.02	0.05		
S10 ₂		25.24	37.04	41.23	69.48	30.12	28.95	65.74		
CO ₂	5.54	0.49	0.33	4.36	0.37	0.24	0.14	0.61		
Parts per milli	on:									
Ag		8	77	161	97	197	235	674		

Compositions determined by inductively coupled argon plasma analysis for Cu, Pb, Zn, As, Bi, Cd, Co, Mo, Ni, Sb, Fe, Ag, Ca, Mg, and Si; atomic absorption for Ge and Ga; and infrared spectroscopy for CO₂. Analyses performed by Acme Analytical Laboratories, Vancouver, Canada; provided through the courtesy of Musto Explorations, Ltd.

Sample descriptions (some quartz is present in all the samples):

^{1.} Dense, vuggy goethite with some limonite. 5347 level, N. rib.

^{2.} Mainly dense, vuggy goethite. DDH85-9, near 96'. 3. Mixed, fractured goethite, hematite, limonite. DDH85-9, 148.5'-155'.

^{4.} Friable goethite with azurite, conichalcite, and some plumbian jarosite. 5330 level, S. rib. 5. Mixed friable goethite, limonite, and a little plumbian jarosite. DDH85-9, 143.5'-148.5'. 6. Laminated, earthy, red-brown limonite and yellow plumbian jarosite. 5253 level, N. rib. 7. Mostly plumbian jarosite. 5253 level, N. rib. 8. Mostly slightly-plumbian jarosite. 5330 level, S. rib.

Table 2. Chemical analyses of some nearly monomineralic samples from the Apex mine.

		Samples							
	1		2	3	4	5	6	7	
Parts per mill:	ion:								
-		<7	150	7000	3000	2000	2000	3000	
(Ga <:	20	<50	150		100	200	150	
(Cu 190		250	620		>5000	1800	1300	
	Pb >500		290	110		1600	330	5000	
	Zn <10		1100	1500		>5000	2600	1000	
	As <40		<1000	>5000		>5000	>5000	>5000	
A	Ag (56	<5	45	100	<5	48	1200	
F		20	<50	50	<50	<50	50	<50	
F	3a <4	40	640	150	410	<100	150	420	
F	3i <2	20	<50	<50	<50	<50	<50	80	
(Cd <	(8)	<20	50	50	50	100	<20	
(Co <	(2	15	37	70	100	100	70	
M	fo <2	20	<50	50	<50	<50	50	950	
N	Ni I	18	75	130	80	250	200	43	
S	sb <20	00	<500	1200	<500	<500	<500	4200	
5	Sr 61	.0	650	2900	750	920	4300	>5000	
T	1 <2	20	<50	<50	<50	<50	<50	170	
V	<2	20	<50	<50	<50	55	<50	<50	
Weight percent:									
F	e 0.3	16	50.	34.	45.	46.	29.	20.	
T	0.0)4 <	(0.10	0.15	<0.10	<0.10	0.15	<0.10	
A	1 <0.2	.5	0.40	2.0	0.46	0.83	2.3	0.85	
C	a <0.1	.0 <	(0.25	0.40	1.2	0.25	0.80	<0.25	
M	g <0.2	.0	0.70	0.65	0.70	0.70	0.60	<0.50	
K		8	0.15	1.5	0.30	0.20	0.10	2.0	
N	a <0.3	0 <	(0.75	<0.75	<0.75	<0.75	<0.75	1.0	
S	102 <16.		6.	31.	<16.	22.	36.	25.	

Compositions determined by semiquantitative emission spectroscopy performed by R. Lerner of the U.S. Geological Survey. Standard deviations are about 10-20% of the indicated value, except for Si, K, and Al, for which they are 30-50%.

Samples: 1. Galena with a few percent anglesite. Tailings of old workings. 2. Pyrite with a few percent of quartz plus traces of barite and galena. DDH85-1, 93'. 3. Granular hematite with intimately intergrown microcrystalline quartz plus small amounts of jarosite and possibly other minerals. DDH85-9, 148.5-155'.

4. Reddish-brown limonite with a few percent of jarosite. 5253 level, N. rib. 5. Dense, vuggy goethite with microcrystalline quartz plus small amounts of jarosite and possibly other minerals. DDH85-9, 96'. 6. Goethite with microcrystalline quartz plus small amounts of jarosite and possibly other minerals. DDH85-9, 148.5-155'. 7. Slightly-plumbian jarosite with microcrystalline quartz. 5330 level, S. rib.

Elements not detected at the indicated detection limits (ppm) for samples 2-7 (detection limits for sample 1 are 40% of these, due to less sample dilution): Au(50),Be(5),Ce(500),Cr(50),Hg(2500), In(7),La(100),Li(250),Mn(1000),Nb(125),P(1000),Re(250),Sc(50), Se(1000),Sn(50),Te(250),W(500),Y(50),Zr(100).

Supergene ore

Goethite - Goethite is the most abundant mineral in the ore zone, occurring in several habits. It is most common as fragments and stringers mixed with fine-grained quartz and coated with limonite or plumbian jarosite, forming yellow-brown locally friable masses. It also occurs as zones of hard, dense, brown, vuggy material, particularly towards the footwall. In the SEM, this material is found to be intimately admixed with microcrystalline quartz, accounting for its great hardness. A few masses of dense lustrous goethite a few cm across having a conchoidal fracture were found.

Goethite is the primary host for Ge, containing up to at least 5300 ppm (Dutrizac et al., in press). In the SEM, no discrete Ge minerals were observed, and the Ge appears to be distributed fairly uniformly in the goethite itself (either within the crystal lattice or in grain boundaries). Typical, "clean"-looking areas of goethite were always found to contain up to several percent of Si, Al, Ca, K, As, and Zn, with traces of Pb and Ge. The hard conchoidal material contains the smallest amounts of all these elements. Discrete hexagonal plates of plumbian jarosite 5-10 µm across are commonly observed dispersed in all the goethite.

Limonite - This term is used to denote the abundant yellow-brown to red-brown, friable, commonly earthy mixture of iron-rich oxides, hydroxides, and oxysalts that produce only small, broad peaks (if any) in powder X-ray diffraction patterns. Quartz and goethite are almost always present, but most of this material is either amorphous or is so fine-grained that it will not produce sharp diffraction peaks. It occurs (1) interstitially to goethite and hematite, (2) as the matrix of some dolomite breccia, (3) impregnating fault gauge, and (4) as vug and fracture fillings throughout the ore. An area of laminated red-brown, earthy limonite was observed in the north rib of the 5253 foot (1601 m) crosscut that contains numerous parallel layers about 1-2 mm thick of yellow plumbian jarosite, suggestive of a banded texture in the primary sulfide ore (see analysis 6, Table 1). In the SEM, limonite samples are found to contain up to several percent Si, Ca, Al, K, As, Pb, Cu, and Zn. Gallium is not usually detected in the SEM (<500 ppm), but zones of limonite a few tens of micrometers across containing up to about 2 weight percent Ga were observed in the laminated sample (Table 1, analysis 6). These small zones also contain 1-2 weight percent Ca, Pb, As, K, and Al. Germanium is detected using the SEM in many limonite samples (>500 ppm, up to about 2000 ppm), but not in others.

<u>Hematite</u> - Hematite is much less abundant than goethite or limonite, occurring as red-brown, hard nodules and fragments encrusted with limonite and plumbian jarosite. It is admixed with abundant fine-grained ($< 1 \mu m$) quartz. The hematite is found to contain up to several percent Si, Ca, K, and As, and somewhat more Ge than

was observed in goethite. Emission spectroscopy detected roughly 7000 ppm Ge in one specimen (Table 2). The extreme fine-grained ($\angle 1 \mu m$) nature of this material makes the host(s) for these elements uncertain. Powder X-ray diffraction detected only hematite and quartz. Adsorption of some of the minor elements in grain boundaries is a possibility.

Plumbian jarosite - This material is bright yellow to brownish yellow, slippery feeling, and has a fine-grained sparkly appearance. It forms zones up to at least 1.5 m thick, as well as occurring in breccia matrix and dispersed in smaller quantities throughout much of the ore. Under the SEM it is seen to consist of platy hexagonal crystals 5-10 m across that are always mixed with quartz, which is fibrous in some specimens (Figure 4). It contains variable amounts of Pb and K, being intermediate between jarosite and plumbojarosite. Dutrizac et al. (in press) and the current study found the cell parameters as determined by powder X-ray diffraction techniques to lie between those of the two endmembers, without the doubling of the c-axis found for plumbojarosite. Plumbian jarosite is a major host for Ga in the ore, with up to 0.70 weight percent Ga substituting for Fe according to Dutrizac et al. (in press). They reported an average composition based on 11 electron microprobe analyses to be:

 $(K_{0.682}Na_{0.166}Pb_{0.183}Ag_{0.034})_{1.02}(Fe_{2.953}Zn_{0.016}Ga_{0.027})_{3.00}(SO_4)_{2.00}(OH)_{5.96}$. Plumbian jarosite is a major host for Ag, which substitutes for K and Pb (see Tables 1 and 2). The cores of many plumbian jarosite crystals are occupied by rhombohedral crystals of goyazite-svanbergite 1-10 μ m across.

Goyazite-svanbergite - Dutrizac et al. (in press) report the presence of rhombohedral crystals about $10\,\mu m$ on edge of sulfate-bearing goyazite $(SrAl_3(PO_4)(OH)_5H_2O)$, forming a solid solution with svanbergite $(SrAl_3(PO_4)(SO_4)(OH)_6)$, in two samples of plumbian jarosite. Measureable quantities of Ge and Ga were not detected (<300 ppm). Similar crystals were observed in this study together with jarosite from the 5330 level. Most of these goyazite-svanbergite crystals form the cores of jarosite crystals. Small amounts of As (1000-7000 ppm) were detected in this mineral under the SEM.

Azurite - Based on observations of the underground workings and of the old dump, azurite, $\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$, appears to be the most abundant copper mineral in the ore. As nearly all the high-grade copper ore was previously mined out, however, its content in the original ore may have been different. It is most concentrated filling cavities up to at least several cm wide in partly silicified dolomite in the hanging wall. Here it forms botryoidal crusts up to 2 cm thick covered by drusy crystals up to a few mm across. It also occurs as euhedral crystals up to a few millimeters across lining vugs in



Figure 4. Scanning electron micrograph showing tabular, hexagonal plumbian jarosite crystals with some acicular quartz crystals. Apex mine, 5253 level.

goethite, and as partial replacements of isolated dolomite fragments in the limonite-goethite ore. In some places azurite is replaced by malachite, and in other places it is replaced by X-ray amorphous light-blue chrysocolla-like material.

Malachite - Malachite, Cu₂CO₃(OH)₂, is less abundant than azurite, though both minerals occur in the same environments. It forms botryoidal crusts of radial-fibrous crystals up to about 1 cm thick, and it also replaces azurite locally. In places, spheres of radiating fibrous crystals several mm across are observed on goethite.

<u>Conichalcite</u> - Conichalcite, CaCu(AsO₄)(OH), is nearly as common as malachite. It forms thin emerald-green crusts on goethite, generally associated with azurite.

<u>Aurichalcite</u> - This mineral, $(Zn,Cu)_5(CO_3)_2(OH)_6$, is sparsely found in goethite as turquoise-blue radiating fibrous crystals up to nearly 1 cm long. It is generally not associated with the other copper minerals.

Rosasite - A few blue-green spheres of radiating fibrous crystals several millimeters across of rosasite, $(\text{Cu,Zn})_2(\text{CO}_3)(\text{OH})_2$, were found in vuggy goethite with malachite, azurite, and conichalcite.

Brochantite - Brochantite, $\text{Cu}_4\text{SO}_4(\text{OH})_6$, was found in a sample of hard vuggy goethite on the dump, where it forms transparent, green, euhedral crystals a few millimeters across on a crust of malachite.

<u>Cuprite</u> - A lens of cuprite (Cu₂O) about 30x23x8 mm was observed in drill hole 85-12 at 74.5 feet (22.7 m). The cuprite has an average grain size of about 0.5 mm. The lens is surrounded by a selvage of malachite, which is in turn surrounded by a selvage of azurite, which is enclosed in earthy decomposed dolomite containing clay minerals and limonite. Malachite has replaced cuprite within the lens along fractures.

Anglesite - White, gray, and yellow massive anglesite (PbSO₄) surrounds and partly replaces galena in a sample from the dump. No elements other than Pb and S were detected in the SEM.

<u>Covellite</u> - Sooty bluish-black covellite (CuS) masses up to about 1 cm across occur with pyrite, anglesite, and traces of chalcopyrite in a sample of coarse-grained galena found on the dump. Small amounts of covellite occur in fractures within the galena crystals.

Black manganese oxides - Thin coatings of black manganese oxides locally occur in fractures and vugs in goethite. A high concentration was noted in goethite in the 5330 foot (1625 m) level together with azurite and conichalcite.

<u>Chrysocolla</u> - X-ray amorphous, light-blue, chalky to hard conchoidal material is a common late alteration product of azurite in cavities.

Other reported minerals - Bullock (1967) reports the presence of native copper, cerussite, hydrozincite, adamite, and smithsonite from the Apex mine, though these were not observed in the present study.

Discussion and Conclusions

Primary ore deposition

Deposition of ore at the Apex mine was structurally controlled, confined to brecciated, fissured, and sheared zones associated with the Apex fault. Kinkel (1951) noted that although the ore-hosting limestone has abundant solution cavities, only those directly connected with the fault zone were mineralized. Dolomitization and silicification are associated with the fault zone, extending up to several meters beyond the ore into the wallrocks. As only one geologic formation is present (Callville Limestone), structural data on the geologic ages of faulting and of ore deposition are not available.

No large samples of primary ore have been found at the Apex mine, but aspects of its composition can be inferred. The ore was certainly rich in iron and copper. It also contained considerable amounts of lead, lesser zinc and arsenic, and small amounts of germanium and gallium. It is very unlikely that Ge and Ga were introduced during supergene alteration, as these elements are always highly depleted in carbonate rocks (by roughly two orders of magnitude) relative to their average crustal abundance (Bernstein, 1985; Burton et al., 1959). The available fragments of primary ore show the presence of fine-grained pyrite, which was probably abundant, coarse- and fine-grained galena, sphalerite, chalcopyrite, and a little barite. The great abundance of copper now observed indicates the former presence of abundant copper-bearing sulfides such as bornite, chalcopyrite, and chalcocite. The abundance of arsenic strongly suggests the presence of sulfosalts such as tennantite or lead-arsenic sulfosalts. Significantly, the relatively high concentrations of germanium and gallium indicate that sulfides containing these elements were present. Such sulfides possibly included renierite $(Cu_{11-x}Zn_xGe_{2-x}As_xFe_4S_{16})$, germanite $(Cu_{11}Ge(Cu,Ge,Fe,Zn,W,Mo,As,V)_{4-6}S_{16})$, and gallite (CuGaS2). The relatively small amounts of Zn in the ore preclude the possibility that sphalerite was the major host for Ge and Ga.

The inferred primary ore is similar to bornite-chalcopyrite-tennantite[±]galena[±]sphalerite ore found at Tsumeb, Namibia (Söhnge, 1964), Kipushi, Zaire (Intiomale and Oosterbosch, 1974), and Ruby Creek, Alaska (Bernstein and Cox, in press). Ore at these deposits is highly copper-rich in certain zones, occurs in dolomitized carbonate host rocks that are commonly brecciated, and contains germanium-bearing copper sulfides. The ore zone at the Apex deposit, though much smaller, appears to be most like that at Kipushi, in the Zaire-Zambia copper belt. The

orebody at Kipushi forms a highly irregular subvertical pipe at the faulted boundary of dolomitic shale and marine dolomite, commonly within breccia zones (Intiomale and Oosterbosch, 1974; DeVos et al., 1974). Some sulfide replacement extends along bedding planes and fracture zones. The bulk of the ore consists of the assemblages chalcopyrite-pyrite, chalcopyrite-bornite-tennantite, bornite-chalcocite, and sphalerite-pyrite-galena. Renierite, with lesser germanite and briartite $(Cu_2(Fe,Zn)GeS_4)$, are locally common in copper-rich ore, often near zinc-rich ore. Gallite is present in small quantities as inclusions in renierite, germanite, and sphalerite.

Supergene alteration

At the Apex mine, supergene alteration of the ore has occurred at least down to an elevation of 1230 m, the maximum depth of the old workings. The water table had not yet been reached at that level. The thorough oxidation of the ore is certainly due to the high permeability of the limestone, and particularly of the fault zones, which allowed the ore access to air, meteoritic water, and Thiobacillus bacteria that can break down sulfides (Duncan, 1967).

It is not clear if the general separation of iron-rich and copper-rich ore now observed reflects the original distribution of sulfides, or is a product of supergene alteration. The occurrence of the richest copper ore in and adjacent to carbonate rock, and the complete lack of residual primary copper minerals, suggests that copper was fairly mobile during supergene alteration, precipitating mainly by reaction with carbonate wallrocks and breccia fragments. The similar distribution of zinc-bearing minerals to copper-bearing minerals suggests that zinc behaved in much the same way. Lead, however, precipitated mainly as sulfates (plumbian jarosite and anglesite). Gallium was concentrated mainly in plumbian jarosite, substituting for Fe, and in limonite, either substituting for Fe or being adsorbed onto surfaces. Most of the iron in the ore was left in a spongy to dense mixture of limonite, goethite, and hematite.

Germanium became concentrated mainly in goethite, hematite, and limonite, though it is uncertain whether it is primarily adsorbed onto these minerals or is incorporated into their lattices. Some solid solution between magnetite and the related spinel brunogeierite ($GeFe_2O_4$) has been reported (Otteman and Nuber, 1972), probably through the coupled substitution $2Fe(III) \leftrightarrow Ge(IV) + Fe(II)$. The same or similar coupled substitutions may account for the presence of Ge in goethite and hematite. Burton et al. (1959), for example, reported up to 83 ppm Ge in hematite from Cumberland, England. Experiments have shown that Ge has a high affinity for iron hydroxide: Burton et al. (1959) found 95% of dissolved Ge to be precipitated from seawater by $Fe(OH)_3$, and Pazenkova (1963) found 93% of dissolved Ge to be precipitated by

 $\operatorname{Fe}(\operatorname{OH})_3$ in waters having a pH greater than about 6; less Ge was incorporated from more acidic waters.

Implications

Future mining operations at the Apex mine may eventually reach primary sulfide ore, permitting better comparisons with other deposits and allowing a more thorough understanding of the supergene alteration that has occurred. Primary ore may occur below the current water table, where it would not have been exposed to severe oxidizing conditions. The position of the water table in the vicinity of the mine is, however, not known. A flowing spring (Cave Spring) is located 4.9 km east of the mine at an elevation of 1160 m (70 m below the deepest workings), while the perennial Virgin River is about 11 km to the southeast at an elevation of about 750 m (480 m below the deepest workings), which would be a minimum level for the water table.

The similarity was previously noted between the supergene ore at the Apex mine and the gossans at many sulfide ore deposits, particularly at those containing considerable arsenic. This observation, combined with observations that germanium is commonly concentrated in carbonate-hosted copper-rich deposits, sometimes associated with organic material (Bernstein, 1985), may be useful in the exploration for additional germanium deposits. The occurrence of gallium in jarosite-group minerals and limonite at the Apex mine similarly provides new directions in the exploration for this metal.

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