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Introduction

The Silver Queen Mine is in a sequence of late Mesozoic to early Tertiary intermediate volcaniclastics, sills, and dikes. Some younger volcanics also crop out in the area. Sulfide mineralization occurs in a series of subparallel fractures and shear zones that are surrounded by argillic to advanced argillic alteration envelopes with abundant disseminated pyrite. The ores are polymetallic, with average grades of (very roughly) 9.5% Zn, 1.7% Pb, 1.6% Cu, 19 oz/ton Ag, 0.07 oz/ton Au, 43 ppm Ge, and 15 ppm In. Ore materials from different veins and different portions of veins, however, vary substantially in their metal content. The purpose of this study is to determine the mineralogy of several ore types, and attempt to locate the sites of the various metals, particularly Ge, In, and Ag.

Materials and Methods

Several samples were received by mail from Houston Metals Corporation. One sample came from the M3 vein (SQ1) and others came from the Number 3 extension vein (SQ2 - SQ6). I then visited the property and collected several more representative samples (SQ7 - SQ13) from the various veins. Portions of all the samples were made into polished thin sections, and a total of 20 such sections were produced. The sections were observed in both transmitted and reflected light in a petrographic microscope. Powder x-ray diffraction was employed to help identify several minerals; an automated diffractometer with monochromatized CuK_{α} radiation was used. In addition, most of the sections were observed with a scanning electron microscope (SEM) equipped with energy dispersive x-ray elemental analysis equipment (EDX). This equipment can be used to make semi-quantitative chemical analyses of individual grains, with a detection limit of about 0.1 wt. percent for most elements. In the descriptions below, the symbol (x) following a mineral name indicates that the mineral was confirmed by powder x-ray diffraction, and an (s) indicates that the mineral was confirmed by SEM-EDX analysis.

Descriptions

Detailed sample descriptions are presented below. A summary of the mineralogy is given in Table 1, which follows these descriptions.

M3 vein (SQ1, 11)

SQ1

Macroscopic: Mostly massive yellow-brown sphalerite and wurtzite with some very fine-grained pyrite. A strong sulfurous odor is present.

Microscopic: This sample consists mostly of bladed colorless, yellow, to orange-red wurtzite (x,s), commonly in radiating aggregates. Anhedral to subhedral sphalerite (x,s) of similar colors is common together with wurtzite. The sphalerite generally appears earlier than wurtzite. As much as several percent Fe occurs in the sphalerite and wurtzite, though most grains of these minerals contain only a trace of Fe. Pyrite (x,s) is abundant as fine-grained material, some of which is colloform or framboidal. Late networking veinlets of carbonate and chalcedony commonly contain fine-grained pyrite and some iron oxides. A few galena (s) grains are present, commonly with euhedral quartz. Scarce grains of tennantite (s) are also present. The matrix consists largely of fine-grained rhodochrosite (x,s) containing a few percent of Ca and Fe. Late manganoan calcite (s), commonly filling late fractures, is also common. Quartz (s) is also present, as are relict crystals of orthoclase (s) and a little illite (s). A few grains of svanbergite (s), $SrAl_3(PO_4)(SO_4)(OH)_6$, were also observed, as were a few grains of black, sulfur-bearing carbonaceous material (s).

Discussion: The textures observed in this sample indicate early deposition of sphalerite and pyrite, followed by deposition of wurtzite and pyrite with minor galena and tennantite together with rhodochrosite. Late Mn-calcite, chalcedony, and fine-grained pyrite were also deposited. The presence of wurtzite and svanbergite strongly suggests acidic conditions during ore deposition.

SQ 11

Macroscopic: Crudely layered, fine-grained rock containing zones of massive gray sphalerite and some pyrite, massive red-brown sphalerite with barite and pyrite, and massive yellow-brown sphalerite with soft, massive, gray, very fine-grained pyrite (x).

Microscopic: Mostly coarse, massive, anhedral pyrite (s) and colorless to brown sphalerite (s) with quartz (s) and some calcite (s) containing a few percent of

Fe and Mn. Much of the sphalerite contains several percent Fe, about 1% Cu, and a trace of Cd. Galena (s) is fairly common, in places as late veinlets, and contains a trace of silver. A few tiny (<50μm) grains of tennantite (s) are present in pyrite, which contain a few percent Sb and no Ag. Calcian svanbergite (s) is fairly common, often with closely related strontian hinsdalite, $(Pb,Sr)Al_3(PO_4)(SO_4)(OH)_6$.

#3 Vein Extension (SQ2 - 6, 12)

SQ2

Macroscopic: Medium-grained rock containing gray quartz and white clay minerals with abundant disseminated pyrite, sphalerite, and galena. Pyrite-rich lenses and veins, commonly vuggy, containing galena and brown sphalerite occur in this rock. Bladed white barite crystals, some over 1 cm long, are locally abundant in these lenses and veins.

Microscopic: The matrix consists of intergrown quartz (s) with clay minerals, mostly illite (s) and kaolinite (s), and disseminated coarse (to 1 cm) pyrite (s). Scarce calcite (s) crystals containing a few percent of Mn and Fe are also present. Segregations of fine-grained brown-red sphalerite (s) with coarse (to 1 cm) anhedral to subhedral pyrite and fine-grained galena (s) are common. The coarse pyrite throughout the rock appears older than the other sulfides.

Discussion: The matrix of this sample was affected by argillic alteration.

SQ3

Macroscopic: Similar to SQ2, but with less sphalerite. Pyrite-rich veins, lenses, and nodules occur in silicified gray rock. Veins of concentrated fine-grained tennantite are common.

Microscopic: Fine (<20μm) to coarse (1 cm) anhedral, fractured pyrite (x,s) crystals are abundant. Fine-grained tennantite (x,s) is also abundant, and is younger than most of the pyrite, filling interstices. It contains as much as a few percent Fe and Zn plus several tenths of a percent Ag, with traces of Sb and Pb. Some late calcite (s) crystals occur with the tennantite. Red-brown sphalerite (x,s) is locally common, containing a trace of Cu and Fe. The matrix contains quartz (x,s), illite/kaolinite (s), manganoan calcite (s), lesser barite (s), and some calcian and potassian svanbergite (s).

Discussion: Ore deposition was accompanied by argillic to advanced argillic alteration, as indicated by the presence of illite/kaolinite and svanbergite.

Carbonate deposition appears to be late.

SQ4

Macroscopic: Similar to SQ2, but with a higher proportion of sulfides. Brown sphalerite-rich zones and vuggy pyrite/tennantite-rich zones are present.

Microscopic: The matrix consists of anhedral, intergrown quartz (s) with lesser chalcedony. Small amounts of manganoan calcite (s) and barite (s) are also present. Red-brown sphalerite (s) is locally abundant, containing about 0.5% Cu and a trace of Fe. Coarse, massive pyrite (s) is common. Other sulfides appear younger. These include tennantite (s) (containing some Zn, Fe, Pb, and a trace of Ag), galena (s), and small amounts of a Cu-Pb-As-sulfosalt (s) containing a little Zn, Fe, and a trace of Ag (possibly seligmannite, $PbCuAsS_3$).

Discussion: The paragenetic sequence appears to be: py; sp-py; tn-gn-sp-sulfosalt-qtz; qtz-calcite.

SQ5

Macroscopic: Very similar to SQ4, but with more barite.

Microscopic: The matrix is mostly quartz (s) with abundant tabular barite (s) crystals to 5 mm long. Small amounts of illite/kaolinite (s) and svanbergite (s) are also present. Fine to coarse grained anhedral to subhedral pyrite (s) is abundant. Later veinlets contain mostly pale orange sphalerite (s) with some galena (s), pyrite (s), barite (s), and quartz (s). The sphalerite and barite are commonly corroded against the quartz. Chalcocite (s) is locally common with pyrite, appearing younger than pyrite.

SQ6

Macroscopic: Fine-grained, gray, pyritic rock containing abundant vugs as much as 1 cm across. Pyrite is disseminated through the rock, as well as being concentrated in irregular veins, lenses, and nodules. Clear, tabular, euhedral barite crystals project into the vugs. Small amounts of galena and red-brown sphalerite occur, occasionally within the vugs. Drusy pyrite and calcite locally occur in the vugs.

Microscopic: The matrix consists mostly of tabular to massive barite (s) and quartz (s), with small amounts of illite/kaolinite (s) and calcian svanbergite (s). Disseminated subhedral pyrite (s) is abundant, some of which coalesces to massive material. Brown-orange anhedral sphalerite (s) is locally common, often together with galena (s). A few grains of tennantite (s) are also present.

Discussion: Most of the pyrite is older than the other sulfides, though a little late drusy pyrite occurs in some vugs.

SQ12

Macroscopic: Very similar to SQ4.

Microscopic: Crudely layered silicified rock (fine-grained quartz (s)) with some relict orthoclase (s) crystals partly altered to clays. Calcite (s) containing a few percent of Fe and Mn is locally common. Massive anhedral pyrite (s) is abundant, as is colorless to yellow-brown sphalerite (s) that contains a trace of Cu and Fe. Galena (s) is fairly common, containing a trace of Ag. Calcian svanbergite (s) is also fairly common in masses as much as 1 mm across, commonly with strontian hinsdalite (s). Tennantite (s) is scarce, and contains as much as several percent Sb, but no detectable Ag.

<u>#3 Vein (SQ 8, 9)</u>

SQ8 (near the #2 vein)

Macroscopic: Wide veins containing fine-grained pink rhodochrosite, coarse dark-brown sphalerite crystals, lesser coarse chalcopyrite, and smaller amounts of fine to medium grained tennantite and galena. Layering is very crude to absent.

Microscopic: The matrix consists of fine-grained, massive rhodochrosite (s) (with a few percent of Ca and Fe) and later manganoan calcite (s), with subhedral barite (s) crystals up to 1 mm. Fine-grained pyrite (s), chalcopyrite (s), galena (s), and sphalerite (s) are disseminated in this matrix. Coarse yellow to brown-red sphalerite (s) (containing about 1% Cu and Fe) and chalcopyrite (s) are intergrown. Remnants of earlier fine-grained framboidal pyrite, which sometimes forms atoll structures, also occur. Later euhedral cubes of pyrite are also present. Galena (s) is fairly common, and contains as much as 0.5% Ag. Tennantite is also fairly common, containing some Zn and Fe with traces of Ag and Sb. Lesser amounts of tetrahedrite (s) also occur, locally in contact with tennantite, which contains as much as 1% Ag. Chalcocite (s) is locally present. Small amounts of a Cu-Pb-As-sulfosalt (possibly seligmannite) are also present.

Discussion: These veins are apparently fissure fillings, though syndepositional movements disrupted banded textures.

SQ9 (near the Bulkley crosscut)

Macroscopic: Massive specular hematite cut by veins of siderite and of barite. Pyrite is locally concentrated as grains or lenses in the hematite.

Microscopic: Subradial, sheaf-like aggregates of specular hematite (s) form the bulk of the sample. A few subhedral pyrite (s) crystals are present. A couple of zones in the hematite have been replaced by pyrite, which preserves the original texture. In a similar way siderite (s) has replaced hematite along veins, again preserving the original texture.

Discussion: Specular hematite was apparently an early-formed mineral, with pyrite and siderite forming later. As germanium can be concentrated in hematite, a portion of this sample has been submitted for analysis to determine its germanium content.

#2 Vein (SQ7)

SQ7

Macroscopic: Banded veins with abundant pink rhodochrosite, some with colloform or botryoidal textures, dark gray-brown coarse sphalerite, and some galena crystals in sphalerite.

Microscopic: Coarse, internally zoned, subhedral yellow-brown sphalerite cut by fine-grained rhodochrosite and quartz. The rhodochrosite appears later than the sphalerite and quartz, and partly replaces quartz. Pyrite and galena are commonly intergrown with the sphalerite, though some pyrite appears contemporaneous with the rhodochrosite. Some galena and pyrite are intergrown with euhedral quartz crystals.

Discussion: The textures indicate that these veins filled open fissures. A crude paragenetic sequence appears to be: sp-gn-py; qtz-gn-py; rhodochrosite-py; late quartz veinlets.

Footwall Vein (SQ10)

SQ10

Macroscopic: Mostly massive, coarse, brown sphalerite and fine disseminated pyrite, with a fine-grained gray quartz and pyrite matrix. A few vugs contain carbonate crystals or drusy quaratz.

Microscopic: The matrix consists mostly of fine-grained intergrown quartz (s), with some areas of coarser quartz (up to 1 mm). Svanbergite (s) is locally common, and a little barite (s) is also present. A crude layering is apparent.

Sphalerite (s) is abundant as anhedral to subhedral yellow to brown and dark red-brown crystals; some coarse dark yellow-brown crystals occur with the coarser quartz (it contains as much as 1% Cu and Fe). Pyrite (s) is also abundant as fine anhedral to coarse (1 mm) subhedral crystals. Galena (s) is fairly common as anhedral grains as much as 1.5 mm across; it generally contains a few tenths of a percent silver. The galena appears younger than the pyrite. Scattered chalcopyrite (s) grains are also present. Tennantite (s) is locally common, and does not contain detectable Ag, and has as much as a few percent Sb. Small amounts of tetrahedrite (s) are present that contain as much as 2% Ag, with some Cd and possibly In.

Discussion: Silver in this sample is concentrated in tetrahedrite and galena, though not in tennantite.

#5 Vein (SQ13)

SQ13

Macroscopic: Wide veins containing coarse red-brown to gray-brown sphalerite, coarse chalcopyrite, lesser coarse galena, lesser massive tennantite, with quartz, barite, and rhodochrosite. Some quartz, barite, and rhodocrosite appear contemporaneous with sphalerite, whereas some late veins of quartz and rhodochrosite also occur. Vugs in the ore usually contain rhodochrosite and sphalerite crystals; a few vugs contain quartz and sphalerite crystals. Clots as much as 1 cm across of vitreous black carbonaceous material are locally present. The sample is somewhat similar to SQ8.

Microscopic: Chalcopyrite (s) and sphalerite (s) (with small amounts of Cu and Fe) are abundant in a matrix of fine-grained to coarse quartz (s) and locally rhodochrosite (s) that contains a few percent Fe. A little manganoan siderite (s) is also present. Fine to coarse galena (s) is fairly common; no Ag was detected. Early, fine-grained, framboidal pyrite (s) is present, some with atoll structures. Some later, coarser pyrite is also present, commonly intergrown with chalcopyrite. Argentian tetrahedrite (s) (1-2% Ag) is fairly common; it also contains several percent As and Zn, a little Cd, and a trace of Fe and possibly In. Some tennantite (s) is also present, which contains a few tenths of a percent of Ag. A few grains (100 μm) of aikinite (s), $PbCuBiS_3$, containing about 1% Ag were also observed.

Discussion: These veins in part filled open fractures and fissures, allowing for coarse crystallization. Silver is concentrated in tetrahedrite, tennantite, and aikinite, and not in galena.

Table 1. Summary of minerals observed in samples from the Silver Queen Mine.

Vein:	M3		#3 Extension						#3		Foot-wall	#2	#5
Sample No.:	1	11	2	3	4	5	6	12	8	9	7	10	13
Chalcocite Cu_2S						X			X				
Chalcopyrite $CuFeS_2$									X			X	
Galena PbS		X	X		X	X	X	X	X		X	X	X
Pyrite FeS_2	X	X	X	X	X	X	X	X	X	X	X	X	X
Sphalerite ZnS	X	X	X	X	X	X	X	X	X	X	X	X	X
Wurtzite ZnS	X												
Aikinite $PbCuBiS_3$													X
Seligmannite $PbCuAsS_3$					X				X				
Tennantite $(Cu,Zn,Fe,Ag)_{12}(As,Sb)_4S_{13}$	X	X		X	X		X	X	X			X	X
Tetrahedrite $(Cu,Zn,Fe,Ag)_{12}(Sb,As)_4S_{13}$									X			X	X
Hematite Fe_2O_3										X			
Calcite $CaCO_3$	X	X	X	X	X			X	X				
Rhodochrosite $MnCO_3$	X								X		X		X
Siderite $FeCO_3$										X			X
Barite $BaSO_4$		X	X	X	X	X	X		X	X		X	X
Hinsdalite $(Pb,Sr)Al_3(PO_4)(SO_4)(OH)_6$		X						X					
Svanbergite $(Sr,Ca)Al_3(PO_4)(SO_4)(OH)_6$	X	X		X		X	X	X				X	X
Illite $K(Al,Mg,Fe)_2(Si,Al)_4O_{10}[(OH)_2,H_2O]$	X		X	X	X	X	X	X					
Kaolinite $Al_2Si_2O_5(OH)_4$			X	X	X	X	X	X					
Quartz SiO_2	X	X	X	X	X	X	X	X	X	X	X	X	X
Carbonaceous matter	X												X

Discussion

The ore mineralization at the Silver Queen Mine can be characterized as volcaniclastic-hosted epithermal Zn-Pb-Cu-As-Ag sulfide-rich veins. Silicification and argillic alteration envelopes are associated with these veins. Pyrite is ubiquitous in the veins, and is commonly the predominant sulfide. It is generally the earliest formed sulfide, though some later, generally coarser pyrite also occurs. Disseminated pyrite is characteristic of the alteration envelopes.

Sphalerite is also ubiquitous in the veins, varying in color from nearly colorless to shades of yellow, brown, and dark red to red-brown. Most of the sphalerite contains little iron (less than 2%), which suggests fairly low depositional temperatures and/or high activities of sulfur (in this case, the latter is probably true). Much of the sphalerite, particularly that with a red or red-brown color, contains as much as 1% Cu. In my experience, such sphalerite generally contains the highest values of Ge, Ga, and In. Such sphalerite is particularly common in the M3, Footwall, and #5 veins.

Galena is fairly common in all the veins, and commonly contains a few tenths of a percent of silver. Tennantite is also fairly common, also commonly containing traces of silver. Tetrahedrite is less common, and was observed in samples SQ8, 10, and 13. It always contains considerable silver, commonly over 1 percent. Other silver-bearing sulfosalts are sparsely distributed in the veins: seligmannite (?) was found in SQ4 and 8, and aikinite was found in SQ13.

The common occurrence of the aluminum phosphate sulfate minerals svanbergite and hinsdalite throughout the veins is significant. These minerals appear to have formed at the same time as the sulfides or shortly after, and do not appear to be supergene. Recent studies (Stoffregen and Alpers, Canadian Mineralogist, v.25, p.201-211, 1987) show that these minerals are characteristic of acidic, sulfate-rich environments, such as found during advanced argillic alteration. The presence of wurtzite in SQ1 (M3 vein) also suggests an acidic environment, as do the silificiation and illite-kaolinite-pyrite alteration observed around the veins. Such an environment indicates that the veins were deposited by acidic sulfur-rich solutions, probably associated with volcanic or near-surface igneous activity, and possibly associated with a deeper lying porphyritic intrusion. The ore-forming fluids were rich in many volatile elements, particularly As and Sb, with lesser Ge, In, Ga, Bi, and Hg. It is possible that the less volatile elements, including Au and Ag, will be somewhat more concentrated close to the igneous source.

As can be seen in the above sample descriptions, discussion, and Table 1, the mineralogy of the veins does not differ qualitatively from one to another; only the proportions of the minerals vary, and these commonly vary as much within a vein as among veins. Very generally, there appears to be an increase in sphalerite and rhodochrosite to the northwest and of pyrite and silicification to the southeast (suggesting a fluid and heat source to the southeast). Silver and gold values vary erratically, and are somewhat correlated to tetrahedrite, tennantite, and other sulfosalt concentrations.

As mentioned, silver was found in tetrahedrite, tennantite, seligmannite, aikinite, and some galena. Small amounts (<50 ppm) probably occur in some of the Cu-rich reddish sphalerite as well. No gold was detected in this study, though it can be assumed that it probably occurs with the silver in the sulfosalts, as well as with some pyrite.

Germanium did not occur in sufficient quantities to be detected in this study, but its distribution can be theorized with some confidence based on my experience. As much as 500 ppm probably occurs in sphalerite, particularly the red and red-brown Cu-rich varieties. As much as 500 ppm also probably occurs in the As-rich sulfosalts, such as tennantite. Smaller amounts (<100 ppm) probably occur in the chalcopyrite. It is also possible that as much as 0.1% occurs in the sparse specular hematite. In general, black carbonaceous matter is an excellent indicator for Ge, and parts of the deposit containing large amounts of this material should have relatively high concentrations of Ge (and possibly In and Ga).

Indium was also not directly detected, except for possible traces in some tetrahedrite. In general, indium should be concentrated in the Cu-rich sphalerite and to a lesser extent in sulfosalts and possibly galena.

Conclusions

1. The Silver Queen deposit is a low to moderate temperature epithermal volcaniclastic-hosted complex of Zn-Pb-Cu-As-Ag fracture and fissure filling veins that trend NW. The presence of the aluminum-phosphate-sulfates svanbergite and hinsdalite, plus wurtzite, illite/kaolinite, and silicification all indicate acidic, sulfur-rich ore-forming solutions. These solutions probably originated from a nearby volcanic or shallow intrusive source. An increase in sphalerite and rhodochrosite to the northwest and of pyrite and silicification to the southeast suggest a heat and fluid source to the southeast.

2. The veins contain varying proportions of the sulfides pyrite, sphalerite, galena, and tennantite, with small amounts of wurtzite, tetrahedrite, chalcocite, seligmannite (?), and aikinite. The gangue consists of varying proportions of quartz, rhodochrosite, calcite, siderite, barite, kaolinite/illite, svanbergite, and hinsdalite. The proportions of the minerals vary widely within veins and among veins. Except for the trend mentioned above in Conclusion 1, patterns of mineral distribution are not evident.

3. Silver is concentrated in galena ($\leq$0.5%) and in the sulfosalts tetrahedrite ($\leq$2%), tennantite ($\leq$0.5%), seligmannite ($\leq$1%), and aikinite ($\leq$1%). Concentrations in these minerals vary from place to place; tetrahedrite consistently has the highest values. Smaller amounts ($<$50 ppm) also probably occur in Cu-rich, red to red-brown sphalerite. Gold was not directly detected, but probably occurs with silver in sulfosalts, and also probably occurs with pyrite.

4. The concentration of germanium was too low for direct detection in this study; no Ge minerals were found. Based on experience with other deposits, Ge probably occurs in sphalerite, particularly the Cu-rich red to red-brown variety ($<$500 ppm). It also probably occurs in As-rich sulfosalts such as tennantite ($<$ 500 ppm), possibly in hematite ($<$1000 ppm), and in smaller amounts ($<$100 ppm) in chalcopyrite. Black carbonaceous material is often an excellent indicator for high Ge concentrations (and possibly for In and Ga).

5. Indium was not directly detected, except for possible traces in some tetrahedrite. It is probably concentrated in the Cu-rich sphalerite, and to a lesser extent in sulfosalts and possibly galena.