

New investigations of the mineralogy of silver in the world-class porphyry-lode deposits of Butte, MT

by C.H. Gammons, J. Szarkowski and R. Stevenson

The Butte district of Montana is well-known as one of the biggest historic producers of copper in the world. It is also a classic example of a porphyry copper-molybdenum (Cu-Mo) system that has been overprinted by zoned, polymetallic copper-zinc-lead-silver (Cu-Zn-Pb-Ag) lode mineralization. After copper, silver was the next most important metal mined from Butte, with more than 700 million oz of total silver (Ag) production between 1880 and the present day. Although many papers have been written on the mineralogy of the early porphyry Cu-Mo mineralization and the high-grade Cu-rich lodes in the center of the district, relatively little information exists on the mineralogy of silver in Butte. The purpose of this paper is to summarize past and present silver production trends for the district, and to combine previously published work with new research to examine the mineralogy of silver in the Butte mining district.

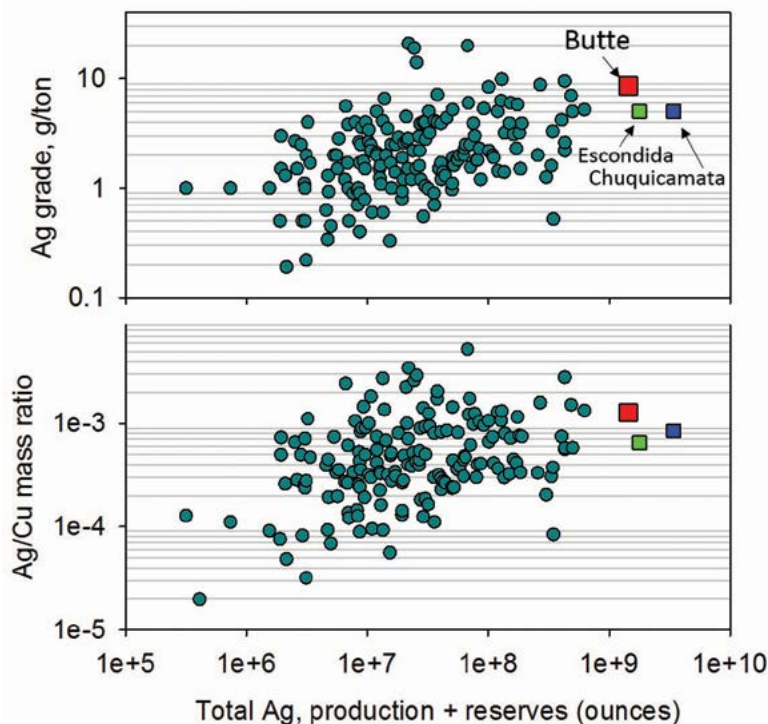
Butte historic silver production

According to a U.S. Geological Survey (USGS) compilation (Singer et al., 2005)

Butte, MT is one of the most silver (Ag) rich porphyry deposits in the world, both in terms of average Ag grade (8.6 g/st) and total production plus reserves (Fig. 1). It is also the second biggest Ag-producing mining district in the United States

(after the Couer d'Alene district, Idaho). Annual silver and copper production data for the Butte district, compiled from various sources (Weed, 1912; U.S. Bureau of Mines, 1963; Czehura, 2006), are summarized in Fig. 2. Peak production of Ag and Cu was in 1917. While Ag production gradually declined in the ensuing decades, Cu production remained strong until the years leading up to the closure of the Berkeley Pit in 1982. In 1984, mining of the nearby Continental Pit resumed under a different operator, and continues to the present day. The Continental Mine produced an average of 35 kt/a Cu and 575,000 oz/year Ag between 1984 and 2004 (Czehura, 2006). These figures do not take into account a period of mine closure in 2001-2003 due to an unexpected hike in utility prices. The

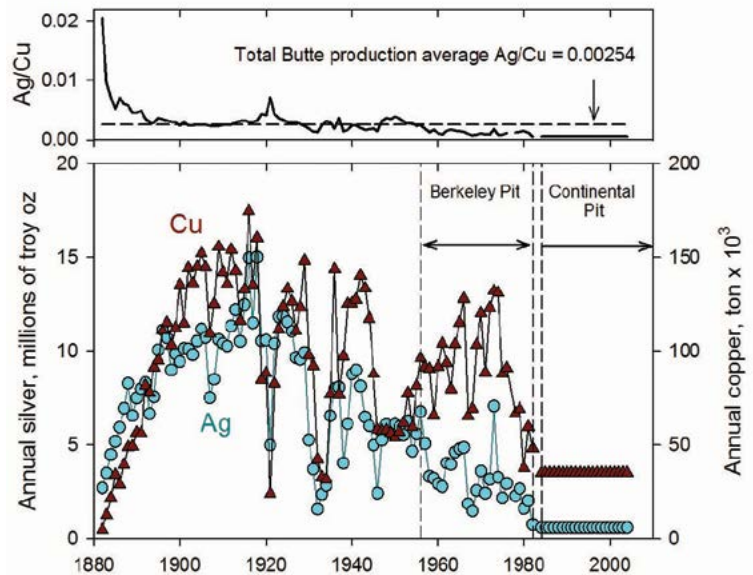
Figure 1
Average silver grade, Ag/Cu mass ratio, and total Ag production + reserves for the global database of porphyry copper deposits (Singer et al., 2005).



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Figure 2

Annual production of Ag and Cu from Butte, and changes in the Cu/Ag ratio of the ore over time. Data for the Continental Pit represent the average for the period 1984 to 2004 (Czehura, 2006).



long-term decline in Ag/Cu ratio of ore mined in Butte (Fig. 2) is due to several factors, including: 1) changes in metal prices; 2) a downward decrease in Ag/Cu ratio of most of the lodes with depth below surface and 3) a shift in mining methods from selective underground mining of high-grade veins to openpit mining of the bulk rock.

Mineralogy of silver in Butte: Previous studies

The most comprehensive study on the mineralogy of the porphyry-lode deposits in Butte is that of Guilbert and Zeihen in 1964. Separate mineral lists were provided for the pre-Main Stage porphyry-style mineralization and the overprinting Main Stage veins and lodes. The latter were subdivided according to district-wide metal zonation trends into the Cu-rich central zone, the Cu-Zn-rich intermediate zone and the Pb-Zn-Mn-rich peripheral zone. Figure 3, modified from Duaimé et al. (2004) shows the approximate boundaries between these zones, and also serves as a location map for many of the mines mentioned in this paper. Although it is often assumed that most silver production in Butte was from underground mines in the peripheral zone, the Main Stage lodes of the intermediate and central zones also produced enormous quantities of silver.

A list of Ag-bearing minerals identified by Guilbert and Ziehn, 1964 is given in Table 1, and is divided into “hypogene” and “supergene” categories. Although the list of supergene minerals is short, supergene enrichment most likely played a large role in increasing the Ag tenor of many of the mines, especially the Main Stage lodes which were generally of higher overall Ag grade than the openpit mines.

In addition to its presence as discrete Ag-bearing minerals, silver can also be present as a solid solution in other sulfide minerals. This is particularly true for the

copper sulfide minerals, given the similarity in charge and ion size of Cu^+ and Ag^+ (Brimhall et al., 1974) used a mass balance approach to estimate the Ag content of a number of important Cu-bearing sulfide minerals in

Figure 3

Map of some of the major underground and surface mine workings in Butte. The Marget Ann mine is roughly 1 km to the NNW of the Alice mine (top-center). The active Continental Pit is off to the east side of the map.

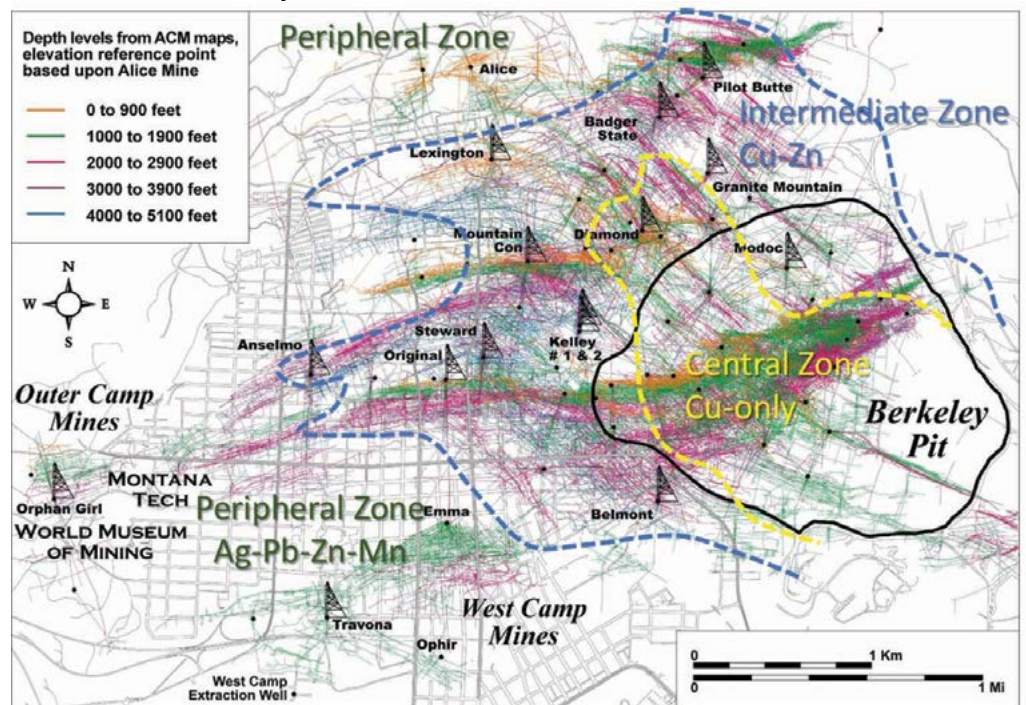


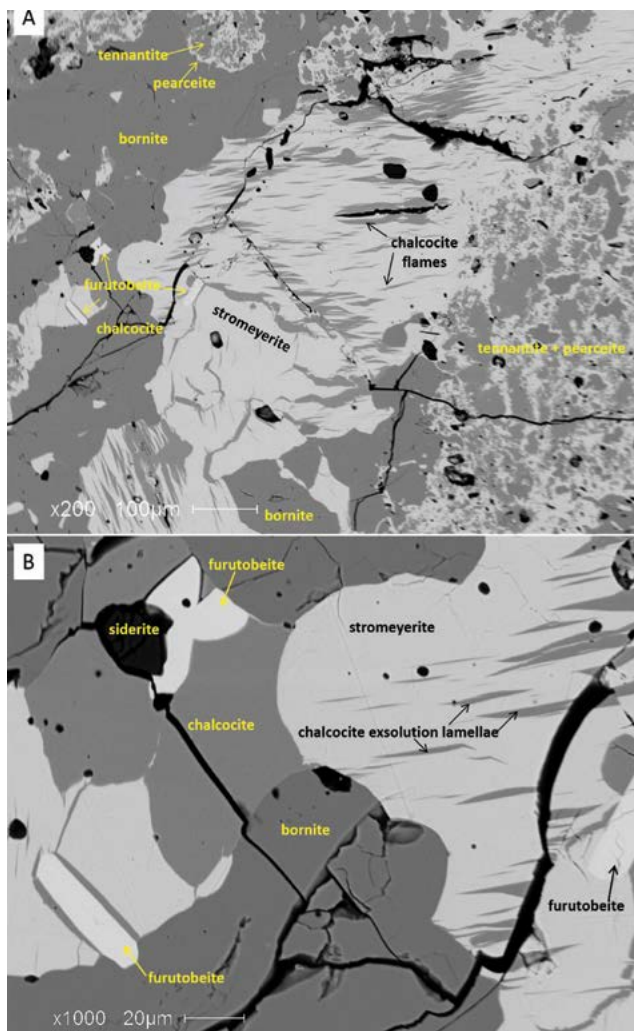
Table 1

Butte silver minerals.

Mineral (Group)	Formula	Guilbert & Ziehen, 1964	This study
Hypogene			
Argentite	Ag ₂ S	X	X
Jalpaite	Ag ₃ CuS ₂		X
Pearceite-polybasite	(Ag,Cu) ₁₆ (As,Sb) ₂ S ₁₁	X	X
Proustite-pyrrargyrite	Ag ₃ (As,Sb)S ₃	X	X
Stephanite	Ag ₅ SbS ₄	X	
Andorite	PbAgSb ₃ S ₈	X	
Stromeyerite	AgCuS	X	X
Ag-tetrahedrite	(Ag,Cu) ₁₂ Sb ₄ S ₁₃	X	X
Larosite	Cu _{18.5} Ag ₄ Fe _{0.2} PbBiS ₁₅		X
Furutobeite	(Cu,Ag) ₆ PbS ₄		X
Electrum	AgAu		X
Argentite	Ag ₂ S	X	X
Supergene			
Acanthite	Ag ₂ S	X	X
Silver	Ag	X	X
Cerargyrite	AgCl	X	

Figure 4

Ag-rich minerals in a vein from the Mt. Con Mine (AMC # 591). The bottom image (B) is a closeup view of the left-center part of the top image. Both images were taken using SEM-BSE.



Butte. Brimhall et al. reported maximum Ag concentrations of 10,000 ppm in covellite, 1,075 ppm in bornite, 1,700 ppm in enargite, 926 ppm in chalcocite, 211 ppm in chalcopyrite, and 9 ppm in pyrite. Electron microprobe and LA-ICP-MS work by Brian Rusk has confirmed high Ag concentrations in Cu-sulfide minerals, as well as galena, from Butte (B. Rusk, pers. commun., 2015).

Methods

Approximately 40 samples of mineralized veins and lodes from the Butte district were collected for preparation of polished mounts. Most of these samples came from the Anaconda Minerals Co. collection (AMC collection), which is an archived collection of several thousand hand samples and thin sections from the Butte mines stored on the campus of Montana Tech. Each sample has notes on the date sampled, the mine and mine level, and the sample mineralogy. These notes have been digitized into an Access database, making it possible to search the index for samples that have specific mention of the presence of Ag-minerals or a high Ag assay. The hand samples were then retrieved from the AMC collection and a small piece of the sample was sawn for preparation of a polished slab (the rest of the sample being returned to the collection). Additional samples for this study were collected in the underground workings of the Orphan Boy and Orphan Girl mines (presently accessible as part of Montana Tech's Underground Mine Education Center), and from small Main Stage veins exposed on benches in the active Continental pit. In all cases, a high Ag content was confirmed by a portable X-ray Fluorescence spectrometer (pXRF).

All polished specimens were examined by reflected light microscopy. Selected samples were further examined by scanning electron microscopy-energy dispersive spectroscopy (SEM-EDS) using a Leo 1430VP SEM (25kV, 18 mm working distance) at the Center for Advanced Mineral Processing (CAMP) at Montana Tech. SEM photographs were taken in backscatter electron (BSE) mode in which minerals with high average atomic mass appear bright whereas minerals with low atomic mass are dark.

Results: This study

Ag-bearing minerals identified in this study are listed in the last column of Table 1. The authors found most of the minerals reported by Guilbert and Ziehen (1964), with the

Figure 5

Another complex mineral assemblage from the Mt. Con Mine (AMC #5933). Top view is SEM-BSE. Bottom view is reflected light. Str = stromeyerite; cc = chalcocite.

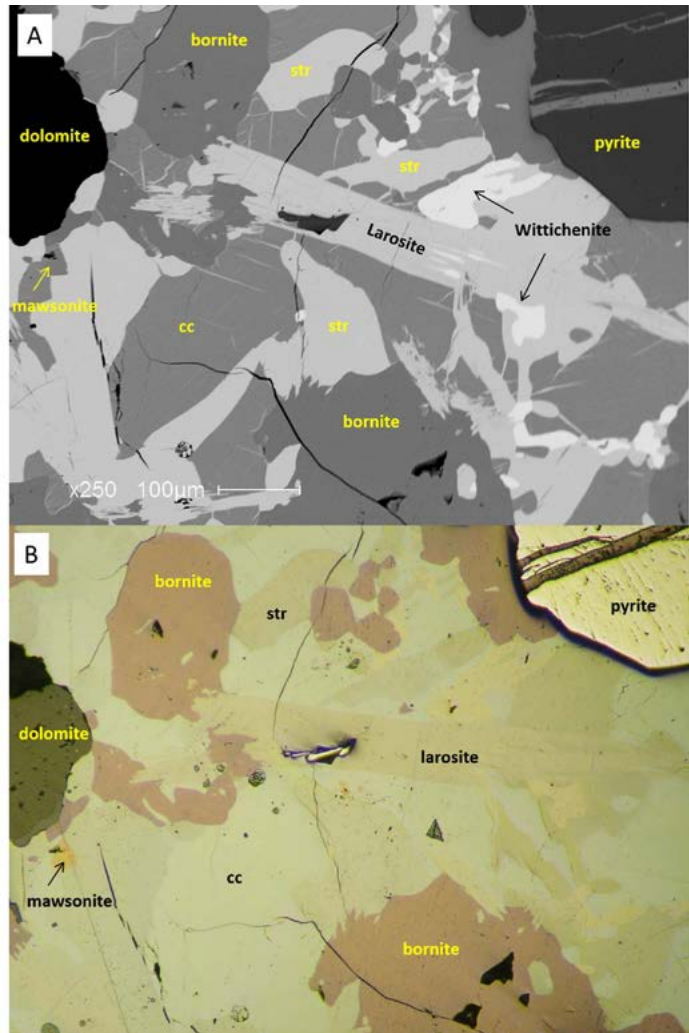
exception of andorite and stephanite. Several minerals not previously reported from Butte, including furutobeite, larosite and jalpaite were also found. Pearceite and argentite/acanthite were particularly abundant in Ag-rich samples from the Orphan Boy/Girl, Marget Ann and Lexington mines. Stromeyerite was abundant in Ag-rich samples from the Anselmo and Mt. Con mines.

Some of the most interesting samples examined in this study were from the Mt. Con Mine, the biggest Cu producer of any of the underground mines in Butte. Figure 4 shows a complex mineral assemblage including stromeyerite, chalcocite, bornite, pearceite, tennantite and the rare mineral furutobeite (Sugaki et al., 1981). Stromeyerite and chalcocite show flame-like intergrowths suggesting exsolution of a higher temperature $\text{Ag}_2\text{S-Cu}_2\text{S}$ solid solution. Furutobeite occurs as individual, rod-shaped crystals up to 50 μm long. Based on EDS analysis, the formula is approximately $\text{Cu}_{6.4}\text{Ag}_{1.2}\text{Pb}_{1.2}\text{S}_4$, which is in fair agreement with the ideal formula of $(\text{Cu},\text{Ag})_6\text{PbS}_4$ for this mineral.

Figure 5 shows another sample from the Mt. Con Mine containing pyrite, dolomite, stromeyerite, chalcocite, bornite, wittichenite (Cu_3BiS_4), mawsonite ($\text{Cu}_6\text{Fe}_2\text{SnS}_8$), and the rare Ag-bearing mineral larosite^{9,10}. Larosite occurs as individual, lath-like crystals several hundred μm long. The formula based on EDS for the crystal shown in Fig. 6 is $\text{Cu}_{18.5}\text{Ag}_{4.0}\text{Fe}_{0.19}\text{Pb}_{1.05}\text{Bi}_{1.00}\text{S}_{15}$. This is very close to the stoichiometry of larosite reported by Cook et al. (2010) of $\text{Cu}_{20.47}\text{Ag}_{3.68}\text{Fe}_{0.22}\text{Pb}_{1.01}\text{Bi}_{1.06}\text{S}_{15.0}$.

Although the textures and final mineral compositions in Figs. 4 and 5 have undoubtedly been modified by cooling to room temperature, the mineral assemblages in both cases are considered to be hypogene. Although not shown in the photographs, several grains of colusite ($\text{Cu}_{12}\text{VAs}_3\text{S}_{16}$) were also found in the Mt. Con samples. Colusite, also known as “bronze tetrahedrite,” was first described from the East Colusa Mine of Butte (Landon and Mogilnor, 1933), and was an important Cu ore mineral in many of the Main Stage lodes of the central and intermediate zones.

Although not known as being a major gold producer, the hard rock mines of the Butte district have produced nearly 3 million ounces of gold, mostly as a smelting byproduct. In this study, the only samples found with high gold content were from the Marget Ann Mine. This mine is located to the north of the main Butte mine complex and is one of the highest elevation mines in the district.



Figures 6 and 7 show high-grade Au-Ag ore from the Marget Ann. The assemblage in Fig. 6A includes pearceite, quartz, sphalerite and electrum, whereas Fig. 6B shows a fine-grained intergrowth of argentite, jalpaite, quartz, adularia, rhodochrosite and rhodonite. Adularia, a common mineral in “low sulfidation” epithermal gold deposits, has not previously been described from Butte, to the best of the author’s knowledge.

Figure 7A provides a closer look at jalpaite from Marget Ann. The mineral is intergrown with electrum ($\text{XAu} = 0.56$ to 0.59) and galena, and is surrounded by a gangue of quartz, rhodochrosite, and rhodonite. Based on EDS analysis, the central grain has a stoichiometry of $\text{Ag}_{3.01}\text{Cu}_{1.05}\text{S}_2$, which is close to the ideal formula for jalpaite, Ag_3CuS_2 . Figure 7B, again from Marget Ann, shows a coarse grain of galena that is rimmed by rhodochrosite and quartz and cut by a veinlet of calcite +

Figure 6

High-grade precious metal mineral assemblages from the Marget Ann Mine (Top is AMC #4316; Bottom is AMC #5060).

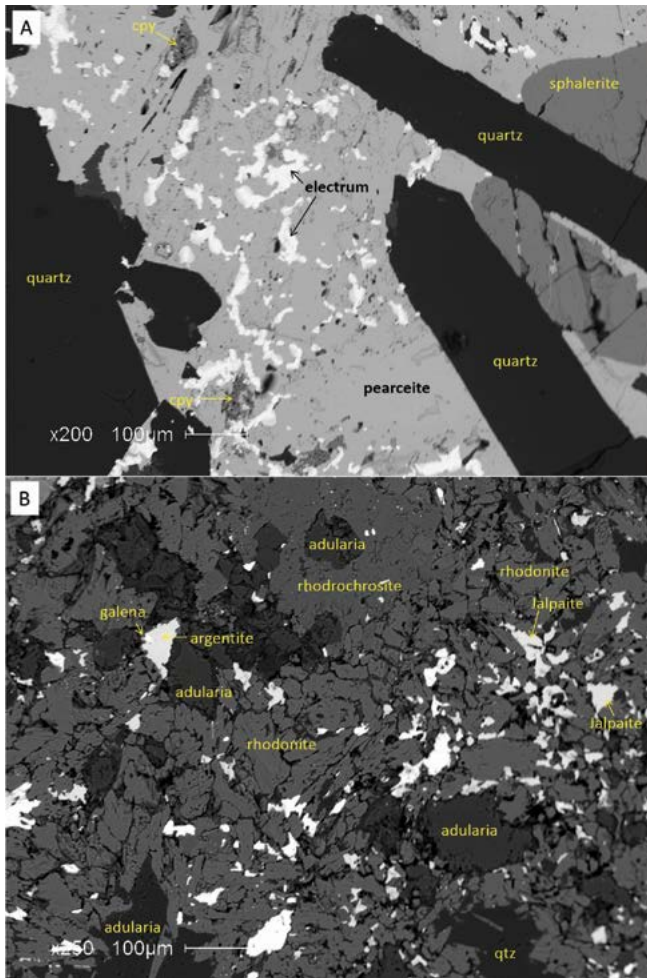
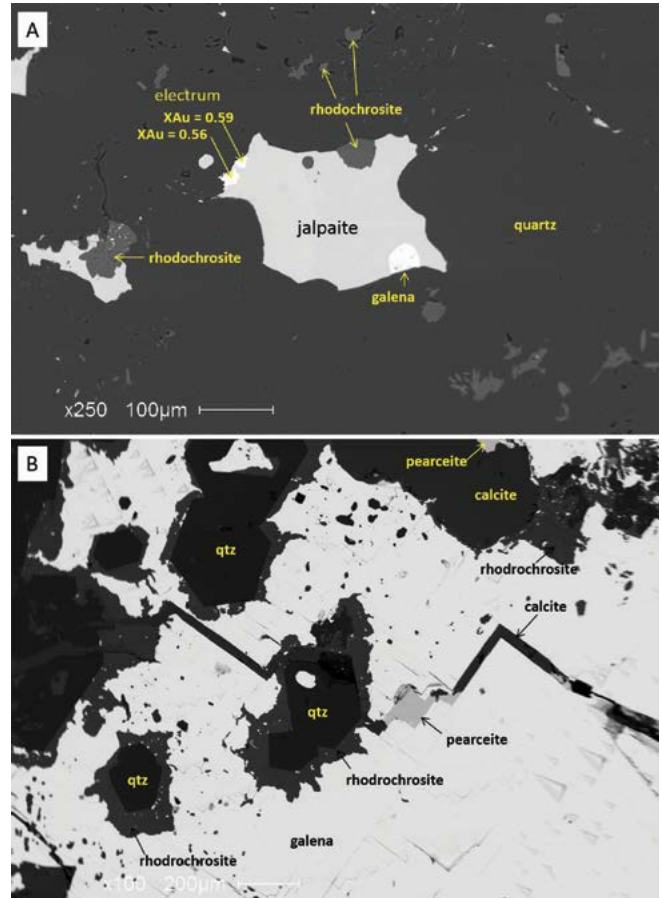


Figure 7

Additional SEM-BSE images of Ag-rich mineral assemblages from the Marget Ann Mine. Top photo: AMC # 5060. Bottom photo: AMC # 4316.

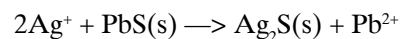


pearceite. The veinlet has split the galena grain along its cleavage planes, and consequently has an interesting right-angle geometry.

Figure 8 shows two different occurrences of elemental silver. The top photo, from the Lexington Mine, shows a well-crystallized aggregate of galena, argentite/acanthite, elemental silver and pearceite surrounded by a gangue of quartz and rhodochrosite. Given the mutually intergrown textures, it is probable that this assemblage is hypogene. In contrast, the elemental silver in the bottom photo of Figure 8 exists as a narrow rim on a large grain of pearceite that is intergrown with galena, chalcopyrite, pyrite and sphalerite. This sample was collected from a weathered vein outcrop at the 100 ft level of the Orphan Girl Mine, which is very close to the pre-mining water table. Therefore, it is assumed that the elemental silver in Fig. 8B is supergene.

Another example of supergene enrichment of silver is shown in Fig. 9. Here, acanthite forms a narrow rim on - and appears to be

replacing - galena. This is a classic example of supergene enrichment in which silver, which forms the less soluble sulfide mineral, scavenges reduced S from galena:



In the supergene environment, lead released from this reaction is often deposited as anglesite (PbSO_4) or cerrusite (PbCO_3) close to the original galena grain. Chalcocite and/or covellite can also form rims on weathered galena, but in the presence of silver it will be acanthite that forms. Acanthite can also replace other hypogene sulfide minerals, such as pyrite, sphalerite and tetrahedrite.

As a follow-up to the work of Brimhall et al.(1984), we examined several Ag-rich specimens from the Mt. Con Mine by electron probe microanalysis (EPMA) at Washington State University. Besides confirming the identification of the rare minerals encountered in this study (Iarosite, furutobeite) the

Figure 8

Two examples of elemental silver. The top image (reflected light) shows silver of probable hypogene origin intergrown with argentite, galena and pearceite from the Lexington Mine (AMC #4638). The bottom image (SEM-BSE) shows a rim of silver, probably supergene, coating pearceite from the 100 ft level of the Orphan Girl Mine.

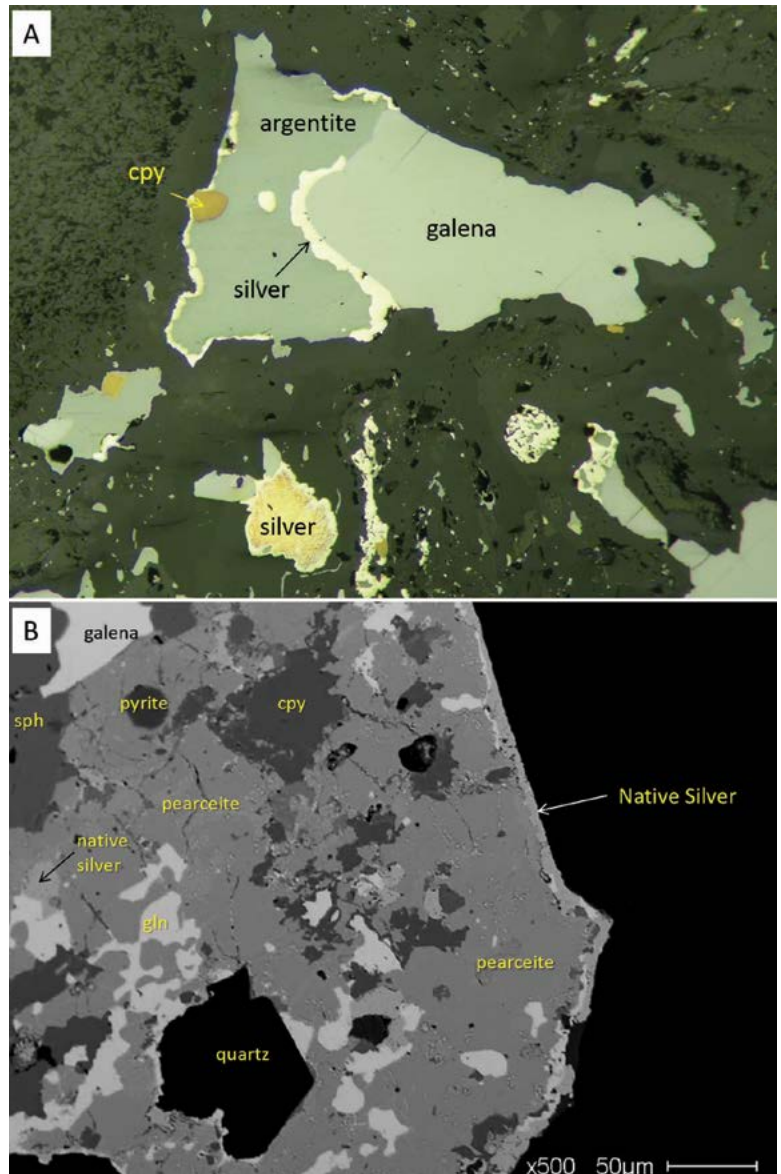
instrument provided high-quality information on the Ag-content of the more common Cu-sulfide minerals in the same specimens. The average Ag concentrations in chalcocite and bornite were 0.59 weight percent ($n = 9$) and 0.44 percent ($n = 10$), respectively. Because these samples contain discrete Ag minerals (stromeyerite, larosite, etc.) the Ag contents of the coexisting chalcocite and bornite are probably close to the maximum allowable Ag concentrations under the conditions of formation of the polymetallic veins. By the same reasoning, many mineral deposits that contain lower overall Ag concentrations than Butte may have few if any discrete silver minerals. In most cases, silver will be present as solid solutions in the more common Cu-(Fe)-sulfide minerals, as has been shown to be the case for the Bingham Canyon deposit of Utah (Ballantyne et al., 1997).

Conclusions

The Butte mining district of Montana has produced more than 700 million oz of silver and is one of the most Ag-rich porphyry Cu deposits in the world. The mineralogical form of silver at Butte falls into three categories: 1) as a trace to minor impurity (solid solution) in hypogene sulfide minerals, such as chalcocite, covellite, and bornite; 2) as discrete Ag-bearing minerals in hypogene veins and lodes; and 3) as supergene coatings and replacements of elemental silver and acanthite. Most of the silver in the Cu-rich Central Zone of the district, which includes the Berkeley Pit, probably originated as impurities in Cu-sulfides. In contrast, veins in the outer, Peripheral Zone of Butte were poor in Cu and rich in Ag-minerals. Our ongoing study has found three Ag-bearing minerals that were not previously described from Butte: furutobeite, larosite, and jalpaite. Thanks to the existence of the Anaconda Minerals Co. collection, it is possible that many more new mineral occurrences will be discovered using modern instrumentation. In general, more work is needed to document the Ag-contents of hypogene and supergene minerals of porphyry Cu deposits.

Acknowledgments

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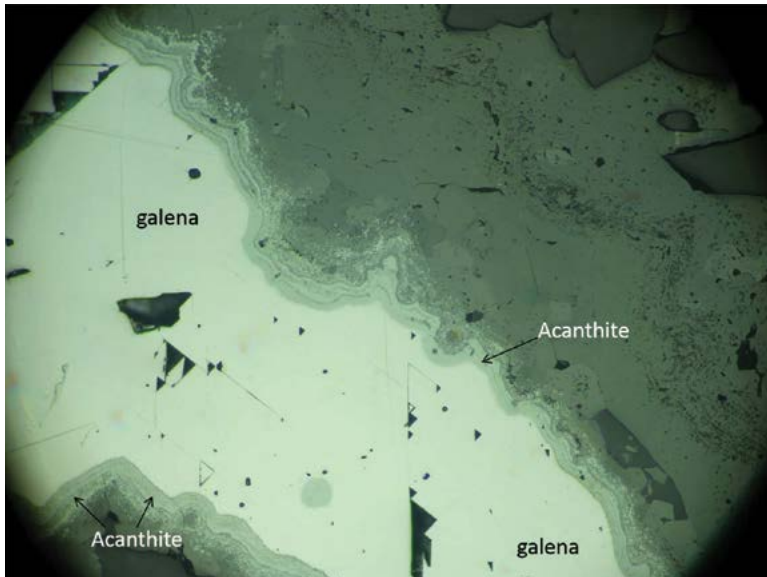
State University) for help with the EPMA analyses. Montana Tech students Brian Kuhn and Kyle Eastman also helped out on this project. We are particularly grateful to the late Lester Zeihen, who had the determination to see that the AMC hand sample and thin section collection was safely archived after the tumultuous collapse of the Anaconda Co.

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Figure 9

Galena rimmed and replaced by supergene acanthite. Reflected light. Alice Mine (AMC #5191).



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