

Comparative Mineralogy of the 5-Element Arsenide Vein Systems of the Black Hawk District, Grant County, New Mexico

Jakob Newcomer

New Mexico Tech, Socorro, NM

Virginia T. McLemore

New Mexico Bureau of Geology and Mineral Resources Socorro, NM

Evan J. Owen

New Mexico Bureau of Geology and Mineral Resources, Socorro, NM

Zohreh Kazemi Motlagh

New Mexico Tech, Socorro, NM

ABSTRACT

Five-element style deposits are unusual hydrothermal systems that are typically characterized by a nickel-cobalt-arsenic-silver-bismuth metal assemblage. This mineralization is often represented by abundant native silver, arsenic, or bismuth, and followed by nickel, cobalt, and iron arsenides (skutterudite, safflorite, nickeline, rammelsbergite, and lollingite). The Black Hawk district in Grant County, New Mexico is one of the few examples of this mineralization style in the United States. Despite the differences in formation temperature, depth of emplacement, and host rocks between five-element style deposits worldwide, there are commonalities in mineralogy, ore texture, and composition. A detailed exploration of the native metal and arsenide phases will be performed to compare ore forming fluids between systems and the effects on styles of mineralization and paragenesis, as well as to aid in broader classification of the deposit style. Mineralogy and mineral relationships of the Black Hawk District and other five-element deposits worldwide will be characterized by reflected light petrography, scanning electron microscopy, X-ray diffraction, and electron microprobe analysis. Mineralogical phase diagrams will be generated to better understand the driving processes and evolution of the systems through native metal and arsenide precipitation.

PURPOSE OF STUDY

The purpose of this study is to analyze the five-element vein deposits of New Mexico's Black Hawk District in Grant County by performing detailed mineralogical and chemical analyses. This unusual type of deposit, being enriched

in nickel, cobalt, silver, and uranium, makes it a target to explore for critical minerals. A more detailed understanding of the mineralogy and compositions of the deposit, as compared to other five-element deposits around the world, will better inform sourcing and production of critical minerals. Critical minerals of interest from this deposit style include cobalt, nickel, arsenic, and bismuth.

Five-element deposit types are uncommon around the world and are unusual in the elements present as well as the minerals that form (Markl et al., 2016). Typical five-element deposits contain a silver-nickel-cobalt-arsenic-bismuth assemblage, sometimes alongside copper, uranium, lead, zinc, mercury, and antimony. These often occur as native silver, bismuth, and arsenic, with minor sulfides, as well as arsenides of cobalt and nickel. The arsenides are of particular interest, because previous studies described several different mineral species, some of which have since been discredited, namely smaltite and chloanthite, which were erroneously determined to be arsenic deficient members of the skutterudite group (OEN et al., 1984). These arsenides have been reported from other deposits to show chemical zoning of nickel, cobalt, and iron, giving greater insight into ore fluid evolution.

PREVIOUS STUDIES

Despite the historical and modern importance of this deposit style, the processes of formation have been poorly understood. The study by Markl et. al. (2016) attempts to explain the main formation mechanism of five-element style deposits. By examining many classical European five-element deposits, and compiling information on other



Figure 1. Districts of southwestern New Mexico with Laramide porphyry copper deposits, polymetallic veins, skarns, and plutons. (Gillerman & Whitebread, 1953)

worldwide deposits, the study describes features typical of the deposit type. These deposits typically have a general paragenesis of low grade, ordinary sulfides, followed by native metal and arsenides/antimonides, then by arsenides/antimonides alone, then sulfosalts and sulfides, and lastly by carbonate gangue minerals. The native metals, and sometimes the arsenides, typically form large dendritic or skeletal aggregates. The succession of arsenides shows mono-arsenides forming first, with nickel following native silver, and cobalt following native bismuth. These are succeeded by di- and tri-arsenides, often grading from nickel to cobalt to iron away from native silver aggregates. The native phases show re-absorption textures after arsenide precipitation, leaving hollow crusts of arsenides that are later filled by carbonate gangue. They describe the importance of the redox state of the system, as sulfides are present before and after the native metal and arsenide precipitation, and the unusual textures indicate rapid precipitation far from equilibrium. Their model to adequately describe their observations involves a rapid influx of methane or other sulfur poor hydrocarbons released by “natural fracking” and fracturing of the host rock to release these highly reducing compounds into a highly saline metal rich fluid. This leads to precipitation of observed native metal aggregates in zones where the oxidized ore fluid contacts the reduced organic rich fluid.

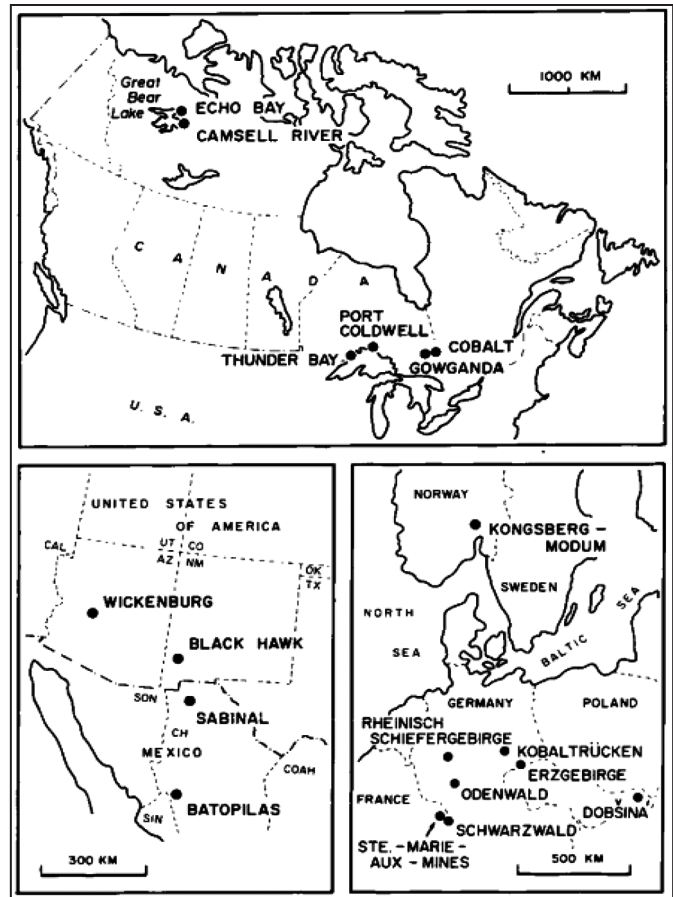


Figure 2. Location map of five-element style and similar deposits worldwide. (Kissin, 1992)

Crystallization is kinetically limited to seed crystals, leading to monomineralic clumps of large skeletal and dendritic crystal aggregates.

Gillerman and Whitebread (1953) investigated the Black Hawk district as part of a study on the geology of uranium. They reported small quantities of pitchblende from the Black Hawk and Alhambra mines of the district, and the study generated detailed surface maps of both mines, as well as an overview of the general geology and mineralogy of the deposit. Minerals were collected from the dumps, as the mines were inaccessible, and were analyzed using powder X-ray diffraction and reflected light microscopy. They identified many ore and gangue minerals, including pitchblende, native silver, niccolite (nickeline), pyrite, and carbonates, as well as tentatively identified arsenides like skutterudite, nickelskutterudite, smaltite, chloanthite, and rammelsbergite. Previous studies also reported argentite, cerargyrite (chlorargyrite), ruby silvers (proustite, pyrargyrite), millerite, sphalerite, galena, stannite, and bismuthinite, among others.

Von Bargen (1979) examined the silver- antimony-mercury system using laboratory experiments, as well as the mineralogy of the Black Hawk district. Much more detailed mineralogy was conducted, with descriptions of four primary and two secondary mineral bodies. These include descriptions of native elements, arsenides, sulfosalts, sulfides, and many secondary phases. The same phases as described in Gillerman and Whitebread (1953) are present, including the aforementioned smaltite and chloanthite, another discredited phase bravoite, and gersdorffite, pearceite, mckinstryite, siegenite, and more.

Gerwe (1986) examined the overall geology of the deposit and used mineralogy and fluid inclusion data to estimate depth of emplacement. Whole rock geochemistry was analyzed, showing anomalously high values for cobalt and nickel in the host rock. K/Ar dating was used to date the argillic alteration assemblage to about 65 ma.. Coupling the geology, fluid inclusions, and geochemistry, Gerwe (1986) proposed that the deposit was associated with a Laramide epithermal system that was deeper and hotter than typical epithermal systems. Gerwe (1986) describes similarities to other five-element systems as similar carbonate vein occurrences in Precambrian plutonic rocks, as well as early sulfide phases and similar silver mineralization temperatures. Differences included variable ages of mineralization, depth of emplacement, and composition of host rock.

SIGNIFICANCE

This study is significant due to the growing interest in critical minerals worldwide, and the unusual nature of this deposit type. The Black Hawk district is one of a handful of five-element deposits, and of nickel and cobalt mineralization, in the United States. The nature of these deposits being pods of mineralization in carbonate veins makes discovering continuing trends of mineralization difficult. However, ore fluid evolution and precipitation conditions will lead to a better understanding of where and why these deposits occur and add constraints to the extent of their mineralization.

Nickel, cobalt, bismuth, zinc, and arsenic are all listed as critical minerals according to the 2022 USGS listing, Burton (2022), and are known to occur in the Black Hawk district. Uranium is also present, though it is no longer listed as a critical mineral. Many elements reported to occur in these deposit styles are rarely concentrated to this magnitude in other deposits styles. A greater understanding of the geochemical relationships between the unusual mineralogy and the fluids that precipitated them will help facilitate a

better understanding of this deposit style, as well as benefit the search for critical minerals in New Mexico and around the world.

METHODS

Mineralogical samples will be collected from dumps, core, and any other available sources. We also have obtained a suite of mineralized samples from Santa Fe Gold from the Black Hawk mine. Available drill core will be examined and sampled. Samples from my personal collection are available from Black Hawk and other worldwide localities. These samples will be examined petrographically in polished section as well as by X-ray powder diffraction, scanning electron microscope, and electron microprobe for mineral identification and mineral chemistry. Mineral chemistry will be correlated with mineral paragenesis to identify relationships to deposit formation. Mineralogy will be correlated between deposits to improve understanding of ore forming fluids.

PRELIMINARY RESULTS

The mineralogy of the native metal-arsenide systems of the Black Hawk District of New Mexico and the Cobalt-Gowganda Region of Ontario, Canada, are explored below using reflected light petrography and electron microprobe analysis. Both deposits show similar overall mineralogies and primary mineral textures. This is characterized by early precipitation of native metals as dendritic, skeletal, and massive aggregates, followed by Ni-Co-Fe arsenides as coprecipitates and rims in and around the native metals.

Overall, both deposits share a remarkably similar mineral assemblage, while some major elements are abundant in the Cobalt district, they are not observed at Black Hawk. Early observations show the predominance of native silver and Ni-Co-Fe arsenides in both deposits. These arsenides include nickeline, skutterudite, and several that need further characterization to accurately identify. As its name suggests, the Cobalt deposit is dominated by cobalt, though there is still a significant nickel presence. Also observed is native bismuth, and several antimony rich phases, dyscrasite and breithauptite. This enrichment of bismuth and antimony is not observed at Black Hawk, however. Black Hawk shows a greater abundance of nickel than cobalt, as seen in the arsenides.

Below are select reflected light and back-scattered electron (BSE) images of samples from Black Hawk and Cobalt, Ontario.

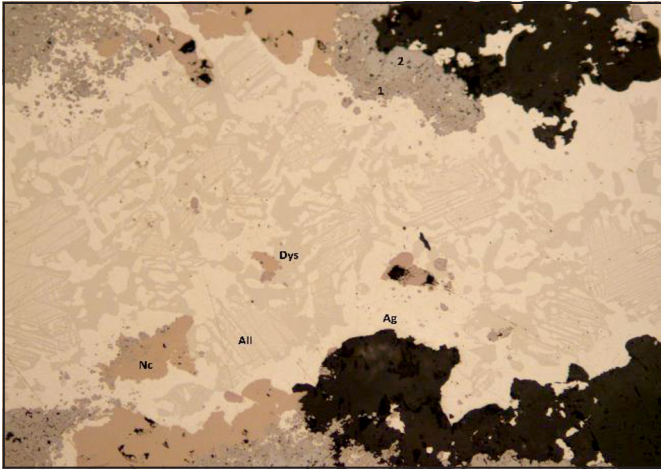


Figure 3. Reflected photomicrograph from Cobalt-Gowganda region. FOV 3 mm. Large vein of white native silver (Ag) heavily included by grey blobs of dyscrasite (Dys) and exsolution lamella of allargentum (All). Associated are orange-peach grains of nickeline (Nc), violet-pink breithauptite (Bhp), and unidentified blue-grey cobalt arsenides (1,2) in dark quartz matrix

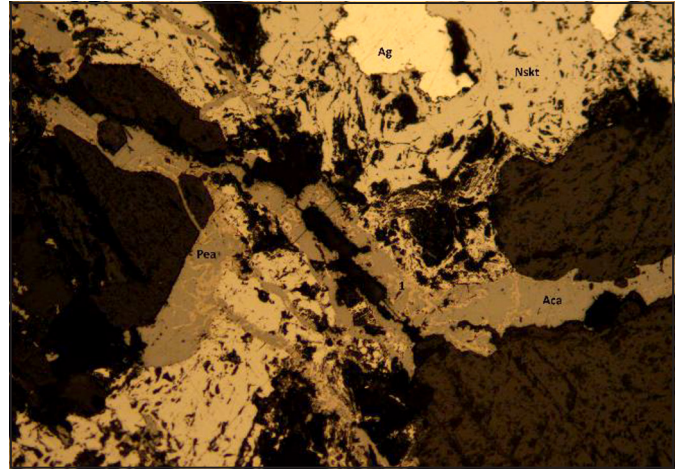


Figure 5. Reflected photomicrograph from Black Hawk District. FOV 3 mm. Massive white native silver (Ag) aggregates rimmed by massive grey iron-rich nickelskutterudite (Nskt). Crosscut by dark grey vein of acanthite (Aca) and pearceite (Pea), with fine orange-pink lamellae of unidentified nickel-cobalt sulfide (1). All in dolomitic carbonate breccia

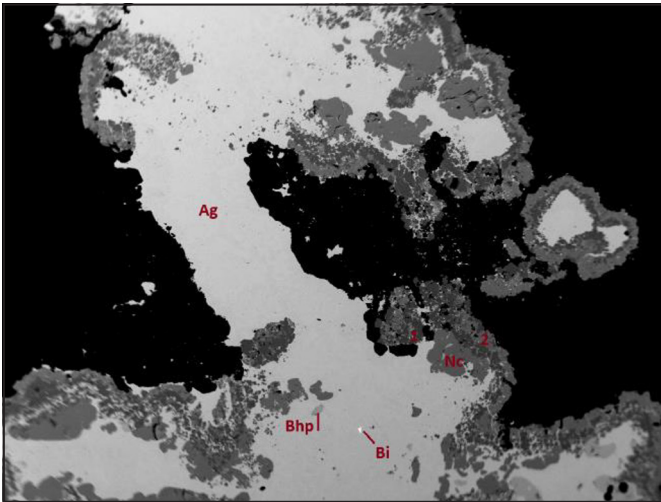


Figure 4. BSE image from Cobalt-Gowganda region. FOV 2.5 mm. Large grey vein of native silver (Ag). Tiny, bright white grain of native bismuth (Bi). Included in the silver, light grey breithauptite (Bhp) and medium grey nickeline (Nc), scattered throughout. The vein is rimmed by unidentified cobalt arsenides, first a dark grey (1), sulfur rich phase, and later a lighter grey sulfur poor phase (2)

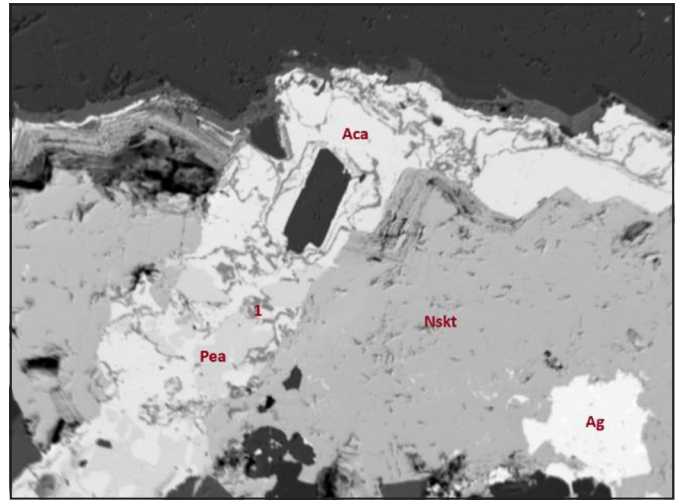


Figure 6. BSE image from Black Hawk District. FOV 2 mm. White vein of acanthite (Aca), with included light grey pearceite (Pea) and veinlets of unidentified nickel-cobalt sulfide (1). Massive white native silver (Ag), bottom right. Medium grey iron rich nickelskutterudite (Nskt), pervasive. Dark grey carbonate gangue

PRELIMINARY CONCLUSIONS

The Ni-Co-As-Ag ore mineral assemblage at Black Hawk is remarkably similar in to the typical five-element style of the Cobalt district in Ontario, Canada. There are notable differences, however, in mineral assemblage, texture, and composition. As compared to the Cobalt region, Black Hawk is

seemingly deficient in cobalt during arsenide mineralization and is overall lacking appreciable antimony. This is shown by the lack of the primary antimony phases breithauptite and dyscrasite within the main silver aggregates, with only nickeline observed. The succeeding nickelskutterudite contains appreciable iron and negligible cobalt, showing that cobalt was not abundant during its precipitation, given the

Table 7. List of minerals and respective chemical formulae.
***Discredited species by International Mineralogical Association (IMA)**

Acanthite	Ag ₂ S
Allargentum	(Ag _{1-x} Sb _x) (x ≈ 0.09-0.16)
Bravoite*	(Fe,Ni)S ₂
Breithauptite	NiSb
Chloanthite*	(Ni,Co,Fe)As _{2-2.5}
Dyscrasite	Ag ₃ Sb
Ferroskutterudite	(Fe,Co)As ₃
Nickeline	NiAs
Nickelskutterudite	(Ni,Co,Fe)As ₃
Pearceite	[Ag ₆ As ₂ S ₇][Ag ₉ CuS ₄]
Rammelsbergite	NiAs ₂
Safflorite	(Co,Ni,Fe)As ₂
Skutterudite	CoAs ₃
Smaltite*	CoAs _{3-x}

typical Ni-Co-Fe trend for skutterudite group minerals. The later stage sulfide minerals, however, contain roughly equal concentrations of nickel and cobalt as sulfide seemingly exsolving from the acanthite. At Cobalt, the late stage arsenides are cobalt dominant, and have much more variable compositions, with up to several percent components of sulfur, antimony, and bismuth. Their metal to arsenic ratio has presented challenges for their accurate identification, and further analysis is required. Lastly, the later arsenides at Cobalt precipitate in two distinct phases, both cobalt dominant, but with quite different metal to arsenic ratios. At Black Hawk, nickelskutterudite is prevalent, and the composition only varies within the constraints of the species, and forms alternating bands of nickelskutterudite and carbonate gangue in places along the arsenide-gangue

boundaries. This texture is not observed at Cobalt. Both deposits display the hallmarks for a five-element style hydrothermal vein system, and as more details are explored this assessment will be further refined.

REFERENCES

- [1] Gillerman, E., & Whitebread, D. H. (1953). The uranium-bearing nickel-cobalt-native silver deposits in the Black Hawk district, Grant County, New Mexico. In *Trace Elements Investigations* (261). U.S. Geological Survey. doi.org/10.3133/tei261
- [2] Kissin, S. A. (1992). *Five-element (Ni-Co-As-Ag-Bi) Veins*.
- [3] Markl, G., Burisch, M., & Neumann, U. (2016). Natural fracking and the genesis of five-element veins. *Mineralium Deposita*, 51(6), 703–712. doi.org/10.1007/s00126-016-0662-z
- [4] Oen, S., Dunn, P. J., & Kieft, C. (1984). The nickel-arsenide assemblage from Franklin, New Jersey: Description and interpretation. *The Nickel-Arsenide Assemblage from Franklin, New Jersey: Description and Interpretation*, 150(3), 259–272.
- [5] Von Bargen, D. J. (1979). *The Silver-Antimony-Mercury System and the Mineralogy of the Black Hawk District, New Mexico - ProQuest*.
- [6] www.proquest.com/openview/4f438ad5acf86cd53facac6d0b4a73ef/1.pdf?pq-origsite=gscholar&cbl=18750&diss=y
- [7] Gerwe, J. E. (1986). Ag-Ni-Co-As-U
- [8] Mineralization in the Black Hawk Mining District, Grant County, New Mexico (Doctoral dissertation, New Mexico Institute of Mining and Technology).
- [9] Burton, J. (2022). U.S. Geological Survey Releases 2022 List of Critical Minerals. www.usgs.gov/news/national-news-release/us-geological-survey-releases-2022-list-critical-minerals

Concerns with the Environmental Susceptibility of Mine Utility Vehicle and Rubber-tired Mantrip LITHIUM-ion Batteries

D.S. Yantek

CDC NIOSH, Pittsburgh, PA

C.B. Brown

CDC NIOSH, Pittsburgh, PA

ABSTRACT

The mining industry is beginning to implement lithium-ion batteries (LIBs) to power mine utility vehicles (MUVs) and rubber-tired mantrips (RTMs). However, the ability of LIBs to withstand the harsh conditions for these applications has not been rigorously evaluated. Concerns with the use of LIBs in the mining environment will be discussed including the effects of mechanical shock and vibration, temperature extremes, and moisture exposure. This paper will discuss adverse effects of the mining environment on LIBs and provide an overview of scientific gaps associated with the environmental susceptibility of LIBs used on MUVs and RTMs.

INTRODUCTION

Several mining vehicle manufacturers currently sell or plan to sell battery-electric vehicles (BEVs) powered by lithium-ion batteries (LIBs). Manufacturers of large BEVs that use LIBs and their battery suppliers have engineered LIB systems for such vehicles. After acquiring Artisan Vehicle Systems, Sandvik offers a truck and a few loaders powered by LIBs [1]. The model TH550B truck has a battery capacity of 354 kWh and the TH514BE and TH518B loaders have capacities of 74 kWh and 353 kWh, respectively. Each Sandvik vehicle uses lithium-iron-phosphate (LFP) LIBs [2]. Epiroc has partnered with Northvolt [3] to deliver several load-haul-dump vehicles. The ST7 model uses a 165-kWh Artisan LIB made with LFP cells [4]. The ST14SG and ST18SG models use Northvolt's proprietary Lingonberry NMC cells with capacities of 300 kWh and 450 kWh, respectively [5]. Komatsu sells several

underground scoops including the 02ESV36 with a 158-kWh LIB, the 02ESV56 with a 214.8-kWh LIB, and the 02ESV60 with a 286-kWh LIB [6]. Caterpillar uses batteries from Lithos Energy, Inc. [7, 8]. Lithos Energy, Inc. does not explicitly state the battery chemistry it uses, but due to claims of higher energy density of 170 Wh/kg and lower cycle life of 500–1,500 cycles, it is likely that the company uses NMC chemistry [9]. Recently, Siemens has patented a mobile mining truck that utilizes LTO cells [10].

Recently, a group of NIOSH researchers have had multiple discussions with various mining industry personnel regarding LIB-powered mine utility vehicles (MUVs) and rubber-tired mantrips (RTMs). While large LIB-powered BEVs have been engineered specifically for the application, the lead-acid batteries on smaller vehicles such as MUVs and RTMs could be swapped out for commercially available LIBs that are not designed to withstand the harsh mining environment. Some underground coal mines have been switching their outby MUVs from traditional batteries to LIBs. Some of these vehicles use 6V or 12V automotive-type batteries. Other mines have reportedly begun working with RTM manufacturers on LIB-powered vehicles. One of the concerns with using LIBs in these applications is that there are currently no guidelines for installing LIBs in these vehicles. Even though these are outby vehicles, a LIB thermal runaway (TR) in the outby area of an underground coal mine would be problematic because the surrounding coal could catch on fire. Mines from other sectors also use these types of vehicles. Because off-the-shelf automotive-type LIBs can be easily retrofitted into such vehicles, MUV and RTM manufacturers and mines could easily swap out