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Geochemistry of Critical Minerals in Mine Waste in Grant, Sierra, and Socorro Counties, New Mexico

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ABSTRACT

Critical minerals are nonfuel minerals, essential to the U.S. economy and national security, whose supply chain may be disrupted. Mine wastes are potential sources of critical minerals. The goal of this project is to estimate and characterize critical minerals endowment in three mining districts in New Mexico: Black Hawk (Grant County), Hillsboro (Sierra County), and Magdalena (Socorro County), and assess their acid-generating potential. The Black Hawk district is an arsenide five-element vein deposit (Ag, Ni, Co, As, U, Bi, and local minerals like Pb, Cu, Zn, W, and Sn). The Copper Flat mine in Hillsboro district is a copper porphyry deposit. The Kelly mine in Magdalena was first mined at 1878 and are carbonate-hosted Pb-Zn deposits. Mine waste rock piles and tailings are sampled using USGS Beta sampling procedure. Geochemistry results show that Black Hawk district mine wastes samples are elevated in Ag (>200 ppm), Co (290 ppm), Ni (2,130 ppm), and Zn (8,463 ppm). Copper Flat mine tailing is elevated in Bi (111 ppm), Cu (7,453 ppm), and Zn (2,360 ppm). Downhole profile plots in Copper Flat show the positive correlation between Cu, S and Te values. Magdalena samples are elevated in Cu (5,700 ppm), Zn (129,500 ppm), and Pb (58,100 ppm). Determination of acid-generating potential in these areas suggests that Black Hawk district mine wastes are non-acid-forming while high S present in some Copper Flat and Magdalena samples can potentially cause acid mine drainage.

INTRODUCTION

Critical minerals are important for many industries including renewable energy, agriculture, and electronics (like smartphones, computer chips, and laptops) (McLemore, 2020). The definition and list of critical minerals vary between countries. Based on Energy Act 2020, critical minerals are nonfuel minerals that are essential to the United States' economy and national security, and whose sources are vulnerable to disruption. Most critical minerals are imported into the U.S. Critical mineral resources in New Mexico must be recognized before government authorities withdraw land from mineral entry, or make other decisions regarding land use. Moreover, future mining of these minerals will directly enhance the overall economic well-being of the United States. Figure 1 illustrates the critical minerals known to occur in New Mexico. Currently, 53 minerals are listed as critical for the United States. The nation currently produces enough copper for domestic use and copper is also imported from countries with which there are secure trade agreements, so the current supply of copper for domestic use is not in jeopardy. Therefore, copper is not considered a critical mineral by the USGS yet, however, the DOE has noted copper as a critical mineral in 2024. Uranium was listed as a critical mineral in 2019 because of its use in Navy nuclear reactors. However, because uranium is used as a fuel, it was removed from the list in 2022. The critical minerals list is reviewed by the government agencies every 2 to 3 years (McLemore and Gysi, 2023).

Mine wastes are important potential resources of critical minerals, particularly because in the original mine production, base and precious metals and not the critical minerals were produced. Consequently, mine wastes would contain any critical minerals in addition to those minerals that are present in the deposit. There are 274 mining district in New Mexico and tens of thousands inactive or abandoned mine features. Many of these mine features have mine wastes that need re-evaluation of the critical minerals potential. There

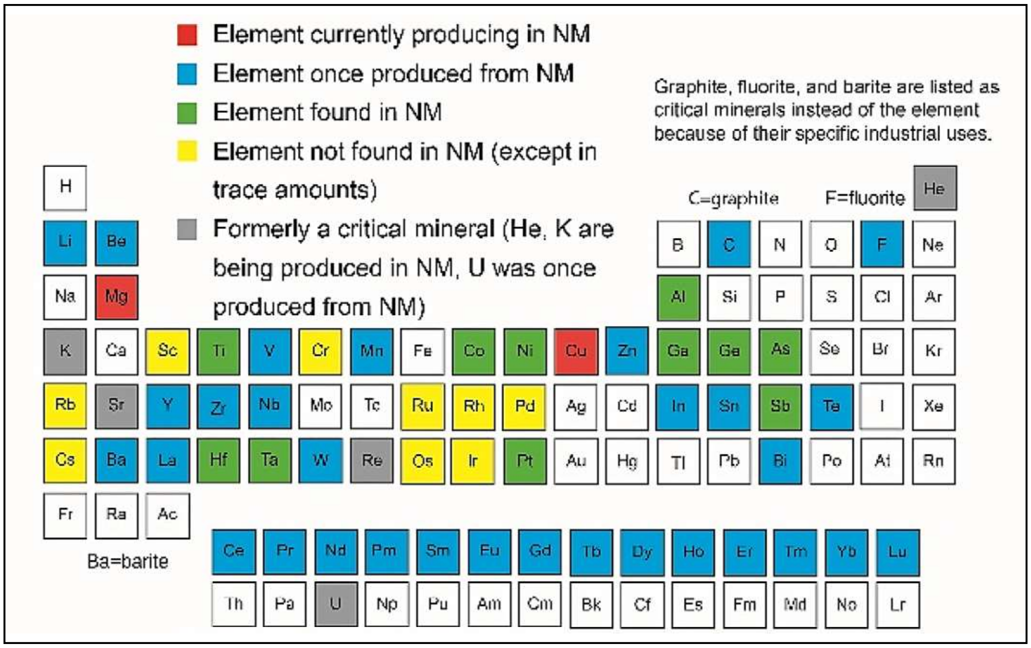

Figure 1. Periodic table shows critical minerals in New Mexico (revised from McLemore and Gysi, 2023)

is a need to classify these wastes to understand their chemical composition, mineralogy, and to evaluate their potential critical minerals potential.

Acid rock drainage (ARD) occurs in mine waste rock, tailings, and structures like pits and underground workings. pH levels in mine waste can predict the mobility and availability of acid drainage. Some critical minerals could dissolve or leach more readily in acidic or alkaline conditions (EPA, 1993). For instance, certain rare earth elements (REE) and metals like aluminum and iron are more soluble in acidic environments. Therefore, understanding the pH levels in mine waste is important for assessing the potential release, and migration of critical and other minerals (Plante et al., 2012; Shu et al., 2001). Paste pH is a straightforward static test that determines whether stored acidity is present in mine waste samples (Lapakko 2002, European Commission 2009), which is used in this study.

STUDY AREAS

Three different deposit types in New Mexico are selected for this paper to represent three different types of mine wastes (Figure 2).

Black Hawk District, Grant County

The Black Hawk district is located in Burro Mountains in southwestern New Mexico (Figure 3) and is one of the few localities of arsenide five-element veins in the U.S. Arsenide

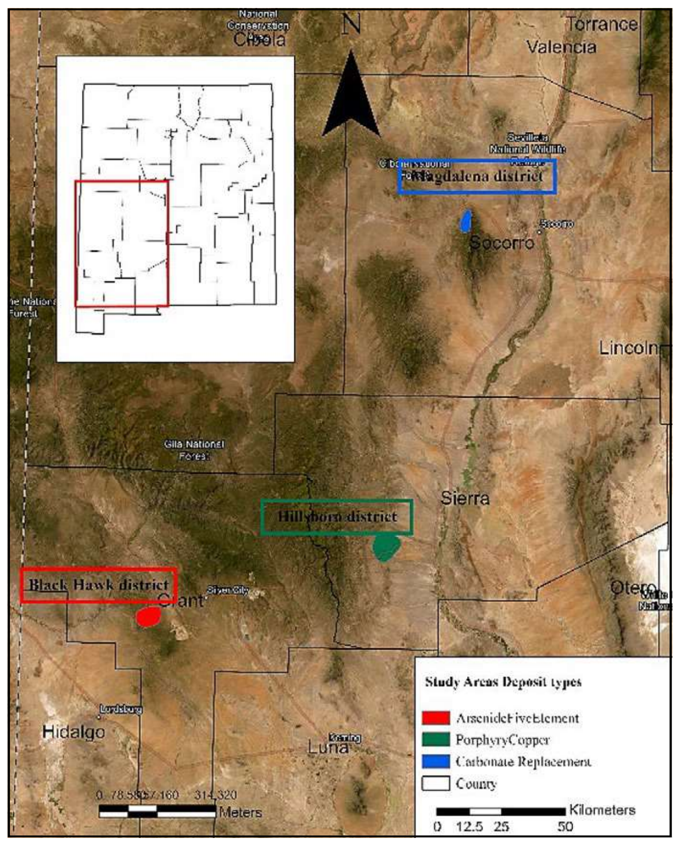

Figure 2. Location of Black Hawk district (Grant County), Hillsboro district (Sierra County), Magdalena district (Socorro County)

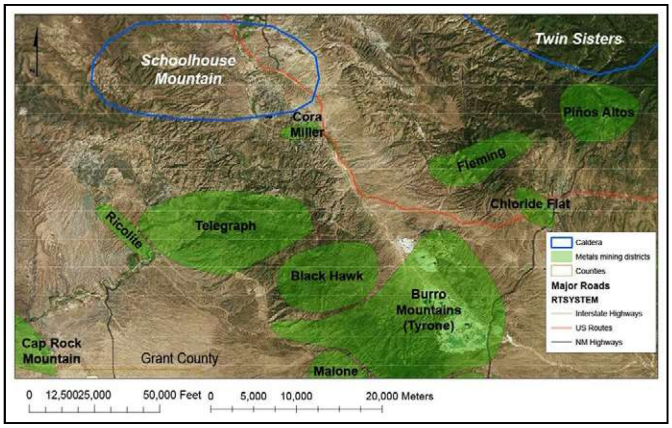

Figure 3. Southwestern New Mexico mining districts

five-element veins are hydrothermal veins that contain silver (Ag), cobalt (Co), nickel (Ni), bismuth (Bi), and arsenic (As) along with other elements like base metals (Pb, Cu, and Zn), U, Sn, and others. They contain high-grade silver (1000s g/t Ag), but are low tonnage (<1 Mt) and low in Au and Cu. Ag, Bi, and As are commonly found as native elements, whereas Co and Ni are found as arsenides and/or sulfides. This deposit type is complex and these minerals usually are not found together in the same environment. There are many subtypes or variations of this deposit type, since some elements do not occur at all localities.

In 1881, development began in the district with the discovery of the unusual Ag-Co-Ni deposits at the Alhambra mine (Gillerman and Whitebread, 1953). Although production records are lost, it is estimated that over $1,000,000 was produced from the district from1883 to 1893, when silver prices dropped due to the silver panic of 1893 (McLemore, 2024). In 1920, pitchblende (uraninite) was recognized in mine dumps in the area, and in 1949 the area became of interest as a possible source of U, Ni, and Co. Types of additional deposits found in the Black Hawk mining district include: Laramide veins, W placer deposits, REE-bearing episyenites and pegmatites.

Total metal production from 1883–1960 is estimated at 1,286,000 oz Ag, 3,000 lbs Cu, and 4,000 lbs Pb (McLemore et al., 1996; McLemore, 2024). The production primarily came from narrow carbonate-dominated veins mined at five occurrences, with the Alhambra and Black Hawk mines being the most significant. In addition, 10,542 short tons of (2.7–71% WO_3) tungsten ore (Richter and Lawrence, 1983; Dale and McKinney, 1959) and 615 short tons of fluorspar ore have been produced from the district (Williams, 1966; McAnulty, 1978). Critical minerals in Black Hawk district include Co, Ni, As, Cu, Ba, and Zn, but only copper was produced. Mine dumps were sampled for this project.

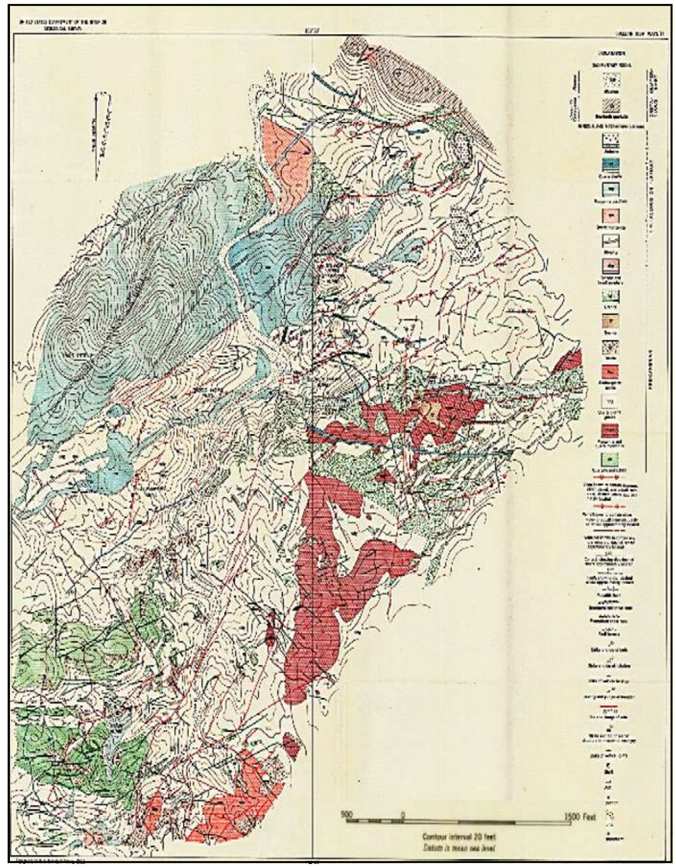

Figure 4. Geologic map of the Black Hawk mining district, Grant County, New Mexico. From (Gillerman and Whitebread, 1953)

Proterozoic quartz-diorite gneiss and granite are the predominant rock types in the area, approximately 1.4 billion years old (Hedlund, 1981), and are intruded by pegmatite, diabase, and aplite dikes, as well as the Late Cretaceous Twin Peaks monzonite porphyry, which is around 75.0–75.7 million years ago (Amato et al., 2017). The veins in this region are generally hosted within Proterozoic quartz diorite gneiss (Figure 4).

Copper Flat Mine, Hillsboro District, Sierra County

The copper Flat mine is a porphyry copper deposit located in Hillsboro mining district in central Sierra County, 20 miles from Truth or Consequences. The district was discovered in 1877 and produced 1.5 million short tons ore containing Cu, Au, and Ag in from March to June 1982 (McLemore, 2000, 2017) before production ceased in 1982. The known critical minerals found in the Copper Flat tailings include Cu, Te, and Zn.

The porphyry copper at the Copper Flat mine has low-grade copper disseminated and in veinlets among a matrix consisting of quartz, feldspars, and various copper minerals.

The primary minerals found are pyrite, chalcopyrite, chalcocite, azurite, malachite, and cuprite. Additionally, smaller quantities of molybdenite, galena, bornite, tetrahedrite, sphalerite, and fluorite are present (McLemore, 2016). Mine dumps and tailings were sampled for this project.

The Kelly Mine, Magdalena District, Socorro County

The Kelly Mine is located in the Magdalena mining district in Socorro County, central New Mexico. The district has had significant lead, zinc, and silver production. The Magdalena district consists predominantly of tilted and faulted carboniferous sedimentary rocks, overlying Precambrian basement rocks and volcanic formations mainly (Titley, 1959). In 1903, zinc carbonate ore became a dominant resource, particularly after the introduction of milling processes for sulfide ores. The main production from the district includes lead, zinc, and smaller quantities of copper, gold, and silver (Loughlin and Koschmann, 1949). During the period of 1866 to 1970, the Magdalena district produced more than $46,000,000 of Zn, Pb, Cu, Ag, Mn, Au, and perlite (McLemore, 2017).

The Kelly limestone layer is the primary host for ore deposits due to replacement processes along faults and fractures. Structural faulting in the district, including major longitudinal and transverse faults, significantly influenced the localization and distribution of ores. Replacement deposits of zinc and lead minerals, often forming along networks of minor faults and bedding planes within the Kelly limestone, were the main sources of ore (Loughlin and Koschmann, 1949). Mine dumps were sampled for this project.

PURPOSE

The purpose of this research is to provide comprehensive data on mine wastes from the Black Hawk district (Grant County), Magdalena district (Socorro County), and Hillsboro districts (Sierra County) in New Mexico. This includes a detailed characterization and estimation of the critical minerals potential. Additionally, it focuses on determining the acid-generating potential of the mine waste rock piles, which is essential for assessing environmental impacts. Another goal of this study is also to offer valuable information to support the planning and development of future mining operations.

MATERIALS AND METHODS

Sampling and Sample Preparation

Following the USGS sampling procedures, large features with varying characteristics, such as color or radioactivity, are divided into separate sampling units (McLemore and Owen, 2024). For example, Black Hawk mine wastes rock piles have been subdivided by different radioactivity levels. Once units are identified, each is subdivided into around 30 cells for composite sampling using markers. Samples are sieved, air-dried if necessary, and homogenized for analysis. Oversized material from waste rock piles may require additional processing to collect representative chips. Soil samples were collected and separated as fine (<2mm) and coarse (>2mm). Figure 5 shows the Black Hawk mine waste sample locations.

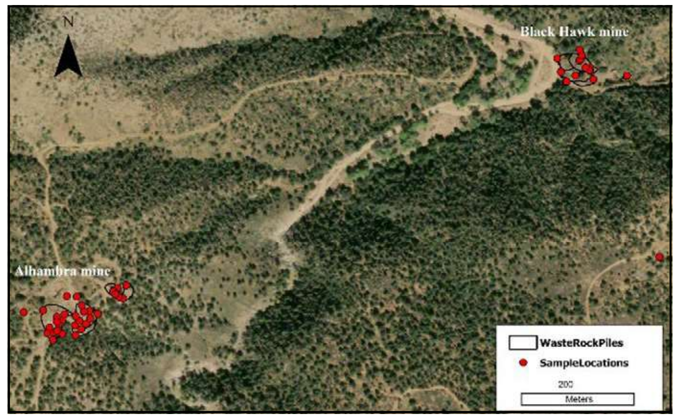

Figure 5. Black Hawk district mine waste composite sample locations

At Copper Flat mine tailings, a 3-foot pit was dug to sample along a vertical profile. The surface of the profile was cleaned with a small trowel. Observations like variations in lithology such as color, thickness, texture, and grain size are recorded in a field notebook. Samples are carefully collected by scraping directly into labeled bags or clean containers to prevent cross-contamination between lithologies (Figure 6).

Petrography and Mineralogy

Mineralogy of selected samples was determined by examining under a microscope and using X-ray diffraction (XRD) analysis. XRD analysis was performed on either whole rock or mineral separates on a PANalytical X- Pert PRO® diffractometer at the NMBGMR XRD Diffraction Laboratory. Analyses were conducted using 45 kV X-ray beam tension and 40 mA X-ray beam current. XRD scans were identified using X'Pert HighScore Plus® software, which identifies intensity peaks and matches patterns to a Powder Diffraction File database. XRD data will be available in the final report.

Figure 6. Copper Flat mine tailing profile sampling

GEOCHEMICAL ANALYSES

Geochemical data are a critical part of evaluation of critical minerals resources. Geochemical analyses of samples collected for this study were determined by ALS Laboratories and the USGS laboratory. Samples were submitted to the laboratory. Duplicate samples and standards were analyzed and uncertainty of analyses is generally <5%. Chemical plots were created using ioGAS-64 (ioGAS™ - REFLEX (reflexnow.com). Chemical analyses will be released in future reports.

Particle Size Analyses

As part of characterizing the mine waste, some samples were sieved into different particle size fractions in order to compare concentrations of critical minerals in different size fractions. Two samples from the Black Kawk district (Alhambra mine wastes) were selected. The test was performed according to ASTM D422-63 standard test method for particle size analyses of soils using stainless-steel sieves, specifically No. 4 (4.75mm), No. 14 (1.40mm), No. 40 (0.417mm), No. 60 (0.246mm), No. 80 (0.177mm), and No 200 (0.074mm).

Paste pH and Fizz Test

When sulfidic minerals (mostly pyrite (FeS_2)) are exposed to air, water, and bacteria, these sulfidic minerals can oxidize and break down to form acid drainage. The acidic conditions enable various heavy metals within the minerals to dissolve into the ground and surface water. A sample is typically considered acid generating if the pH is less than 4 (Borden, 2001). In order to determine the pH of the pore water produced by the dissolution of secondary mineral phases on the surfaces of oxidized rock particles, paste tests are used to assess the geochemical behavior of mine waste materials subject to weathering in the field (Figure 7A).

Also, fizz test was performed to determine how much hydrochloric acid (HCl) needs to be added to a 2 g sample in order to digest carbonate (and other neutralizing minerals) and then determine the amount of NP (Figure 7B).

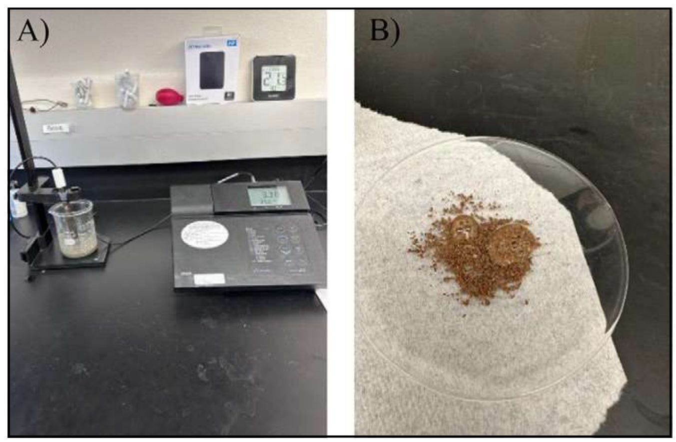

Figure 7. A) Paste pH test on sieved samples, B) Fizz test on mine waste sample

RESULTS AND DISCUSSION

Petrography and Mineralogy

The petrographic analyses of mine wastes samples showed that predominant minerals are quartz, potassium feldspar and clay. Overall, 33 samples from Black Hawk district mine waste rock piles and 36 samples form Copper Flat mine tailings were analyzed using XRD analyses to better understand the mineralogy.

Based on Black Hawk district mine wastes XRD results:

- Quartz (SiO_2) is the most predominant mineral.
- Samples contain clay minerals such as illite ($K_{0.65}Al_2[Al_{0.65}Si_{3.35}O_{10}](OH)_2$) and kaolinite ($Al_2Si_2O_5(OH)_4$).
- Also, a few samples contain sphalerite (ZnS) and dolomite ($CaMg(CO_3)_2$), albite ($NaAlSi_3O_8$).

Based on Copper Flat mine tailing samples XRD results:

- Samples consist of rock forming minerals, quartz (SiO_2), albite ($NaAlSi_3O_8$), and variable micas/muscovite ($KAl_2(AlSi_3O_{10})(OH)_2$).
- Samples also include clay mineral groups like quintinite ($Mg_4Al_2(OH)_{12}(CO_3)\cdot 3H_2O$), hydrotalcite ($Mg_6Al_2(CO_3)(OH)_{16}\cdot 4H_2O$), illite ($(K_{0.65}Al_2[Al_{0.65}Si_{3.35}O_{10}](OH)_2)$), and montmorillonite ($(Na,Ca)_{0.33}(Al,Mg)_2(Si_4O_{10})(OH)_2 \cdot nH_2O$).

Geochemical Analyses

Overall, 127 samples (54 samples from Black Hawk district mine wastes rock piles, 53 samples form Copper Flat mine tailings and 20 samples from Magdalena district) were submitted for whole rock geochemical analyses. Figure 8 shows a spider plot of chondrite normalized REE plot of Black Hawk district, Copper Flat mines and Magdalena district. The results show samples are slightly enriched in light REE of up to 400–500 times chondritic values. Black Hawk district mine waste samples also have higher light REE enrichment as compared to the other districts.

Figure 9 shows concentrations of Black Hawk district mine waste rock samples, Hillsboro district tailing samples, and Magdalena district mine waste rock samples normalized to average crustal abundance (Figure 9). These three different deposits compared with the average crustal abundance represent either highly enriched or depleted zones for particular elements. For example, carbonate-hosted deposits (Magdalena district), represented in blue, show a strong peak for zinc, indicating significant enrichment compared with arsenide five-element veins (Black Hawk district in red line.

Nickel (Ni) and cobalt (Co) are critical minerals and Figure 10 shows correlation of 0.80 between Ni and Co for mine wastes in the Black Hawk district, correlation of 0.79 between Ni and Co for Magdalena district and correlation of 0.02 between Ni and Co for Hillsboro district (Figure 10).

Lead (Pb) and bismuth (Bi) show correlation of 0.07 for Black Hawk district samples, correlation of 0.92 for Magdalena district samples and correlation of 0.33 for Hillsboro district samples (Figure 11).

Tellurium (Te) and copper (Cu) show correlation of 0.36 for Black Hawk district samples, correlation of 0.76 for Magdalena district samples and correlation of 0.20 for Hillsboro district samples (Figure 12).

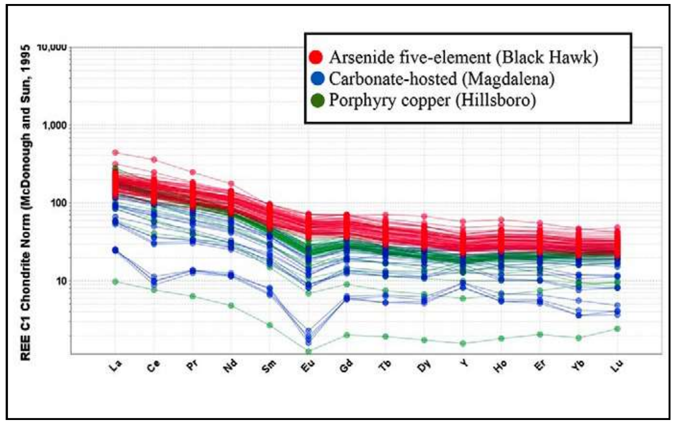

Figure 8. Chondrite-normalized REE plot of Black Hawk district mine waste rock samples, Hillsboro district tailing samples, and Magdalena district mine waste rock samples

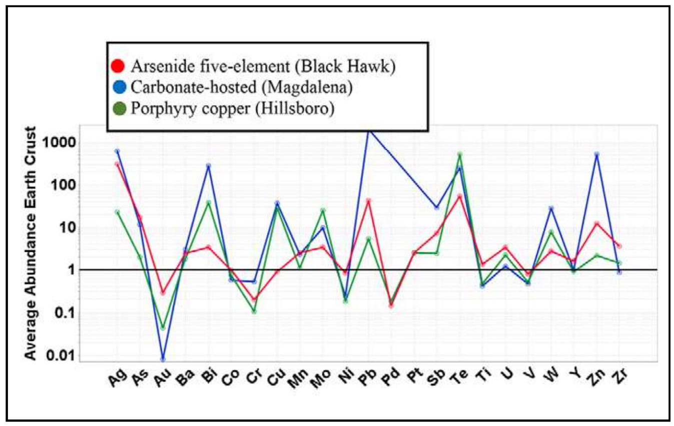

Figure 9. Geochemistry of Black Hawk district mine waste rock samples, Copper Flat mine tailing samples at Hillsboro district, and Magdalena district mine waste rock samples normalized to average crustal abundance

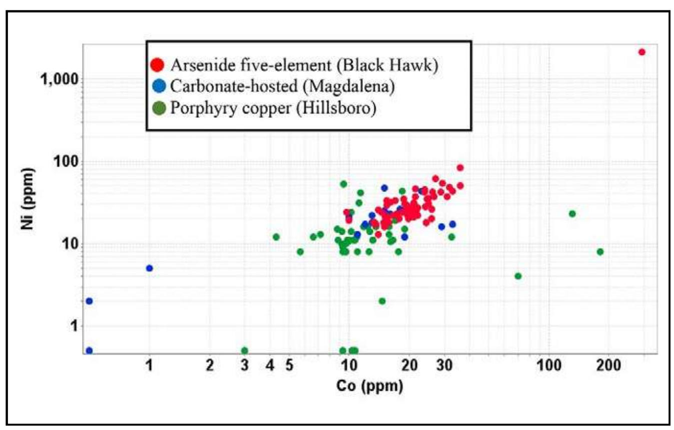

Figure 10. Ni-Co scatter plot of Black Hawk district mine waste rock samples, Copper Flat mine tailing samples at Hillsboro district, and Magdalena district mine waste rock samples

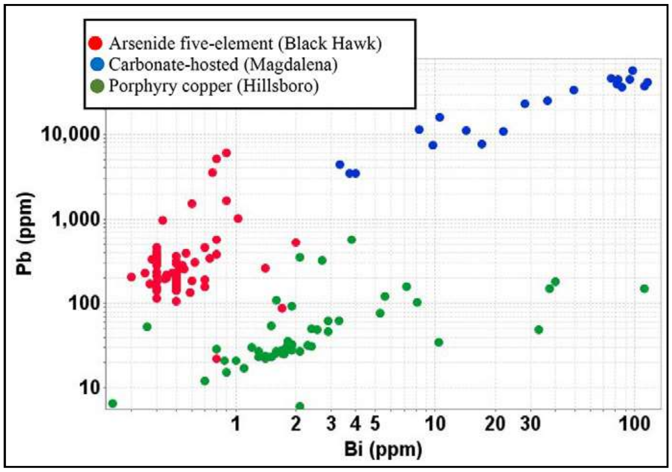

Figure 11. Pb-Bi scatter plot of Black Hawk district mine waste rock samples, Hillsboro district tailing samples, and Magdalena district mine waste rock samples

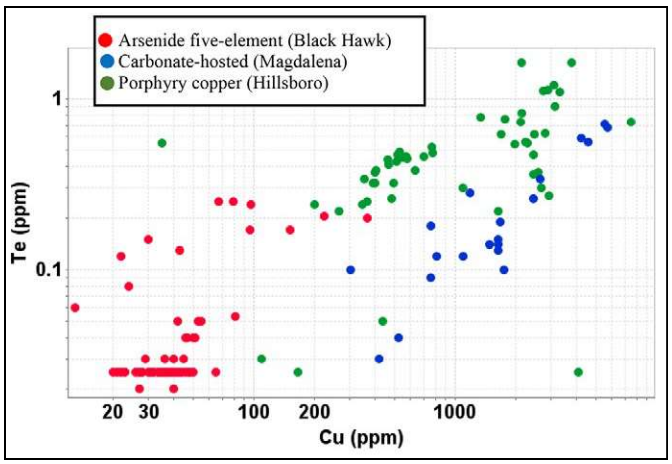

Figure 12. Te-Cu scatter plot of Black Hawk district mine waste rock samples, Copper Flat mine tailing samples at Hillsboro district, and Magdalena district mine waste rock samples

Based on the box plots the average of Cu concentrations of Copper Flat mine tailings samples (porphyry copper) at Hillsboro district is higher than the average of Cu concentration of Magdalena district (carbonate-hosted) samples and Black Hawk district (arsenide five-element vein) mine waste samples (Figure 13).

Paste pH tests and Net Acid Generation graph

Static tests are geochemical analyses to predict the potential of a waste sample to produce acid. The generation of acid in sulfidic wastes can be determined by Acid Base Accounting (ABA) and Net Acid Generation (NAG) tests. To enable waste sorting, the NAGpH value is typically plotted against the Neutralization Potential Ratio (NPR) value (Figure 14).

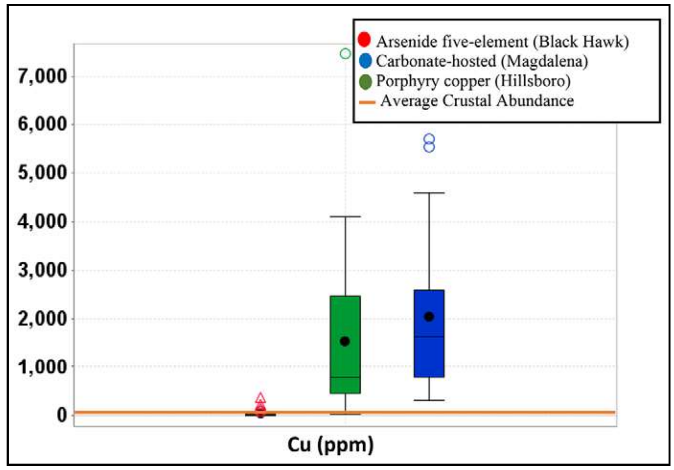

Figure 13. Box plots compare the copper (Cu) concentrations of Black Hawk district mine waste rock samples, Copper Flat mine tailing samples at Hillsboro district, and Magdalena district mine waste rock samples

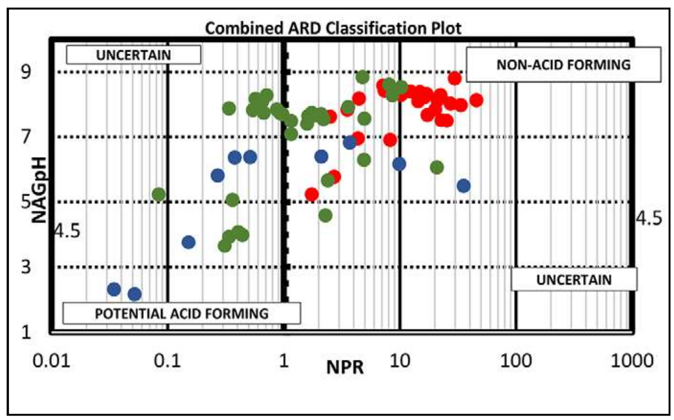

Figure 14. Combined ARD classification of Black Hawk district mine waste rock samples, Copper Flat mine tailing samples, and Magdalena district mine waste rock samples

The Acid Potential (AP) is measured by analyzing the sample for its sulfur content. The Neutralization Potential (NP) is determined by analyzing the acidity consumption of a sample in acid (HCl or H_2SO_4). Net Neutralization Potential (NNP) gives the waste's capacity to neutralize any acid generated and is the difference between the Acid Potential and the Neutralization Potential. The ratio NP/AP, known as the Neutralization Potential Ratio (NPR) (Lottermoser, 2010).

$$AP\ (kg\ CaCO_3/tonnes) = wt.\%\ S \times 31.25$$
$$NP\ (total\ C) = wt.\%\ C \times 83.3$$
$$NNP = NP - AP,$$
$$NPR = NP/AP$$

PRELIMINARY CONCLUSIONS

The main objective of this study was to evaluate the critical minerals in mine wastes of three districts. The presence of these critical minerals in the waste material could be of economic interest. The recognition of critical minerals could be important for enhancing the overall economic well-being of the United States. Copper Flat mines tailings (Hillsboro district) are elevated in Bi, Co, Cu, Ga, Te, Zn, and Zr. Black Hawk district mine waste samples are elevated in Ag, Co, Ba, Cu, Ni, Zn, and TREE, and Kelly mine, Magdalena district mine waste samples are elevated in Cu, Zn, and Pb. Mining companies need to determine if these concentrations could be economic. Determination of acid generating potential in the area suggests that Black Hawk mine wastes are non-acid forming. Determination of acid-generating potential in the area suggests that Black Hawk District mine wastes are classified as non-acid-forming. High S in some samples from Hillsboro and Magdalena districts results in a classification of acid forming and can potentially cause acid mine drainage.

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