

HEAVY METAL CONTAMINATION OF ROAD DUST IN LANZHOU, CHINA

by

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Presented to the Faculty of the Graduate School of
The University of Texas at Arlington in Partial Fulfillment

of the Requirements

for the Degree of

MASTER OF SCIENCE IN ENVIRONMENTAL & EARTH SCIENCE

THE UNIVERSITY OF TEXAS AT ARLINGTON

May 2012

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ACKNOWLEDGEMENTS

First, I would like to thank my wife Summer. She has always supported me although I have dragged her to some of the most miserable places in the country and when we get settled the Army takes me away for a year or more. She has given me two beautiful daughters, Alexis and Sloane. Between the three of them they take turns driving me crazy and keeping me sane.

Without the assistance of Dr. Andrew Hunt, my advisor and mentor, this thesis would never have been completed. He alternated between gently guiding me and forcefully telling me what I needed to do. If any good information is in this paper it is a direct result of his guidance; any errors are all mine.

Lastly I would like to thank the US Army for giving me this opportunity. The Army is not for everyone, but it has been a very fulfilling career for me. I do not know where I would be without the myriad of opportunities that the Army has given me. The Army has paid for my undergraduate and graduate degrees, and has allowed me to travel the world and feed my kids.

April 30, 2012

ABSTRACT

HEAVY METAL CONTAMINATION OF ROAD DUST IN LANZHOU, CHINA

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Road dusts were collected from the streets of the city of Lanzhou, the capital and largest city of Gansu Province in Northwest China. The potential health hazard posed by contaminated road dusts may be considerable for certain sensitive populations. Specifically young children who, while exploring their environment by mouthing and touching, may inadvertently ingest polluted soils and dusts through hand-to-mouth-activity, and through mouthing contaminated objects. Lanzhou, once ranked as one of the 10 most polluted cities in the world, clearly has, in all likelihood many locales with elevated levels of pollutants in various environmental media (e.g., air, water, soil and dust). In this study, we focus on these environmental media (road dusts), from Lanzhou with the objective of characterizing and quantifying the types of heavy metal contaminants in the medium. To characterize the metal particle constituents of the Lanzhou road dusts we used a combination of Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray spectroscopy (EDS). Road dust samples were collected by brush sampling and bagging from 71 different locations in Lanzhou. Here we present analysis of 9 of these road dust samples. Heavy metals were identified at the individual particle level in the road dusts in various combinations. Many of these metals are recognized as being highly toxic and pose a potential health threat once ingested. The major heavy metals identified were: Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Sn, Pb, and W. The combination of specific elements at the individual particle level, and the morphology of the particles made it possible to attribute the particles to unique contributing sources.

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CHAPTER 1

INTRODUCTION

1.1 City of Lanzhou

Lanzhou is the capital, and largest city, of Gansu Province in Northwest China (Figure 1.1). A census conducted in 2010 estimated that over 3.6 million people live in Lanzhou. Lanzhou is the center of many major industries. Lanzhou's geographical location is one that is conducive to exposure to air pollution. The city is located 1,600 m above sea level in the valley of the Yellow River, and is laid on both sides of the banks of the Yellow River (flowing east to west through the city). It is bounded by the Loess Plateau, Qinghai-Tibetan Plateau, and the Inner Mongolian Plateau. The city occupies over 20 km of urban and suburban land on the south bank of the river. The city is located on the upper course of the Yellow River with mountains (Qilian ranges) located on the south and north sides of the city (Figure 1.2). The region has a temperate, semi-arid continental monsoon climate. However, the city of Lanzhou has very little rain (average rainfall 237 ml), with most of the rainfall occurring between May and October. The city has hot summers and cold and dry winters. Essentially, Lanzhou is located in an arid valley with minimal wind circulation, and it experiences frequent sandstorms.



Figure 1.1. Location of the city of Lanzhou in relation to the rest of China (source: <http://en.wikipedia.org/wiki/Lanzhou>)



Figure 1.2. Topographic map of the environs surrounding the city of Lanzhou

1.2 Lanzhou Industries and Pollution

Lanzhou is a major industrial hub. Gansu Province holds vast natural resources, coal, gold, silver, zinc, and nickel are mined there. Lanzhou has become a center of the country's petrochemical industry and has a large refinery linked by pipeline to the oil fields at Yumen in western Gansu; it also manufactures equipment for the oil industry. In addition, the city produces locomotives and rolling stock for the northwestern railways, as well as machine tools and mining equipment. Aluminum products, industrial chemicals, and fertilizers are produced on a large scale, as are rubber products. Copper is mined in nearby Gaolan. Xigu, the most westerly district (Figure 1.3) is the main industrial region of Lanzhou with major petro-chemical installations, power plants and other heavy industries, including aluminum and textiles. Chengguan, in the eastern part of the city is a large residential area with a coal-fired power station and a wide variety of agricultural, engineering and pharmaceutical industries, research institutes and the main railway station. Within the Qilihe district, to the southeast of Xigu, manufacturing

industries including petro-chemicals, machinery, textiles, electrical appliances, locomotives, plastics and food processing are located. Anning, lying to the north of Xigu and Qilihe on the opposite bank of the Yellow River is largely residential with agriculture and education the main activities.

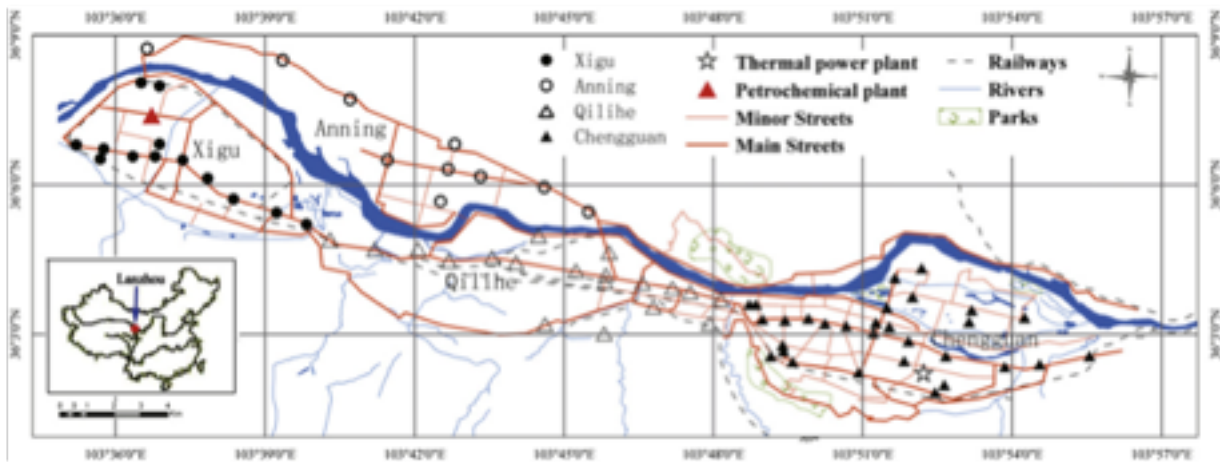


Figure 1.3. Map of districts within the city of Lanzhou and sampling sites.

Lanzhou is particularly susceptible to air pollution episodes. The city is located in a narrow river valley with a major curve in it constraining air movement and there is no free airflow. This means that pollutants produced by local industry are not readily dispersed. Furthermore, the air in Lanzhou suffers from large dust storms originating from the Gobi Desert, these are especially pronounced during the winter and spring seasons. It has been known for some time that the air quality of Lanzhou can be poor, and the conditions are worse in the winter months. A report by the Blacksmith Institute (Staff of the Blacksmith Institute, 2007) on the extent of pollution in developing countries reviewed the most polluted places in the world (places where human health is severely affected). This study identified Lanzhou as being one of the top 30 dirtiest cities in the world with its population all potentially affected by urban pollution. The review identified heavy emissions from industrial processes and the use of coal as the primary fuel source is the major contributors to the pollution in Lanzhou. Also, the study identified the incidence of respiratory ailments as common, which might be expected because of Lanzhou's air quality problems. There have been some improvements; (between 1995 and 1998) atmospheric total suspended particles declined from 1,250 to 778 $\mu\text{g}/\text{m}^3$ (Qian and Tian, 2000). Efforts have been made to reduce

pollution levels in Lanzhou (SEPA, 2011). Nevertheless, in 2009 the World Health Organization, WHO, named Lanzhou the most polluted city in China (WHO, 2009). PM₁₀ levels in Lanzhou were measured to be 150 ug/m³ this level is significantly higher than the WHO Air Quality guideline recommended maximum level of 20 ug/m³. Cancer accounts for 25% of all deaths in Lanzhou and Lanzhou had the highest rate of all respiratory diseases, including pneumonia, in all of China.

1.3 Heavy Metals in Road Dust

Road dusts are useful indicators of the distribution and level of heavy metal contamination in the urban environment. Road dusts are easily resuspended and can contribute to the level of air pollution. One study found that road dusts contributed 28% to PM₁₀ totals and 15.2% of the PM_{2.5} totals (particles less than or equal to 10 um and 2.5 urn, respectively) (Kleeman and Cass,1998). Road dust are also easily washed into storm sewage systems, possibly contaminating surface and groundwater sources. Human health can be threatened by heavy metal contaminated road dust by inhalation of the resuspended particles, and by ingestion of particles, hand to mouth or via drinking contaminated water. Since heavy metals do not degrade they will tend to accumulate in an environment posing an ever increasing threat (Duzgoren-Aydin et al. 2006).

Urbanization with its accompanied increase in roadways and automobiles has resulted in a corresponding increase in environmental pollution. Noise, dust, and heavy metal contamination have all been shown to correlate closely with traffic levels (Pei, Xu, and Liao Chaolin, 2004). The largest mass fraction of resuspended particles, and therefore respirable particles, along roadways are in the 1 - 10 um range (Wang et al. 2005). In a study conducted between July and December 2005, street dust samples were collected from Beijing, Shanghai, and Hong Kong at 25 locations. The study found Aluminum (Al), Calcium (Ca), Carbon(C), Iron (Fe), Magnesium (Mg) , Manganese (Mn), Potassium (K), Silicon (Si), Sodium (Na), Sulfur (S), Titanium (Ti), Vanadium (V), and the heavy metals Cadmium (Cd), Cerium (Ce), Chromium (Cr), Cobalt (Co), Copper (Cu), Lead (Pb), Mercury (Hg), and Zinc (Zn). Abundant Cr, Cu, Ce, and Zn were found in Hong Kong, supposedly due to higher traffic densities. The particles found in Shanghai and Hong Kong contained high proportions of respirable particles with the potential for adverse

health impacts. The aim of this study was to obtain a fingerprint of the dust for each of the three cities by measuring the particle size distributions and elemental composition of urban street dust samples.

The heavy elements are ubiquitous in urban areas as a result of human activities (Fergusson, 1991). Road dusts can be useful indicators of the distribution and amount of contamination in the urban environment. Furthermore road dusts are easily sampled, so they are often utilized to quantify and qualify urban pollution levels (Duzgoren-Aydin et al. 2006).

Road dusts also form a significant non-point source for water contamination. Storm water runoff carries the heavy metals contained in Lanzhou road dust into the surrounding surface water. In Lanzhou this is primarily the Yellow River, which flows through the center of the city. Lanzhou is the first major city along the Yellow River's 3,400 mile length. In 2008 the British national paper, The Guardian, reported that the lower third of the Yellow River is so contaminated that it is "unusable even for agriculture or industrial use." This is due in large part to the contamination from fast-growing cities (Tania 2008).

The source of heavy metal contamination in Lanzhou road dust is probably a combination of automobile emissions, (consisting of exhaust, tire wear, brake lining, and body and paint abrasions), waste incineration, steel plants, smelters, foundries, metal manufacturing, power generation, and deposition of natural sources. Road dust tends to have significantly higher concentrations of heavy metals than what is found in surrounding natural soils (Chang et al. 2009).

1.4 Objectives

The principal objective of this study was to characterize the metal-bearing particles present in a select number of street dust samples from the city of Lanzhou at the individual particle level. Individual particle analysis (IPA) was undertaken by computer controlled scanning electron microscopy (CCSEM). The study goals were:

- Determine the size, shape and chemical composition of the metal-bearing particles in the sample dusts.

- Determine the abundance of the different metal-bearing particle types. Particle types were defined by clustering the metal-bearing particles into homogenous groups based on similarities in chemical composition.

- Assess the likely contributing sources for the metal bearing particles based on composition and sampling location (known industrial zones).

CHAPTER 2

METHODOLOGY

A total of 71 street dust samples were collected by brushing and scooping in January 2006 from pedestrian streets, gardens, roadways with various traffic densities, factories and hospitals in four districts of Lanzhou: Xigu, Anning, Qilihe and Chengguan (Figures 3 and 4). Samples were first put in pocket-sized sealable plastic bags and air-dried in the laboratory, and then a 1-mm sieve was used to remove coarse debris and small stones before and subsequent measurement.

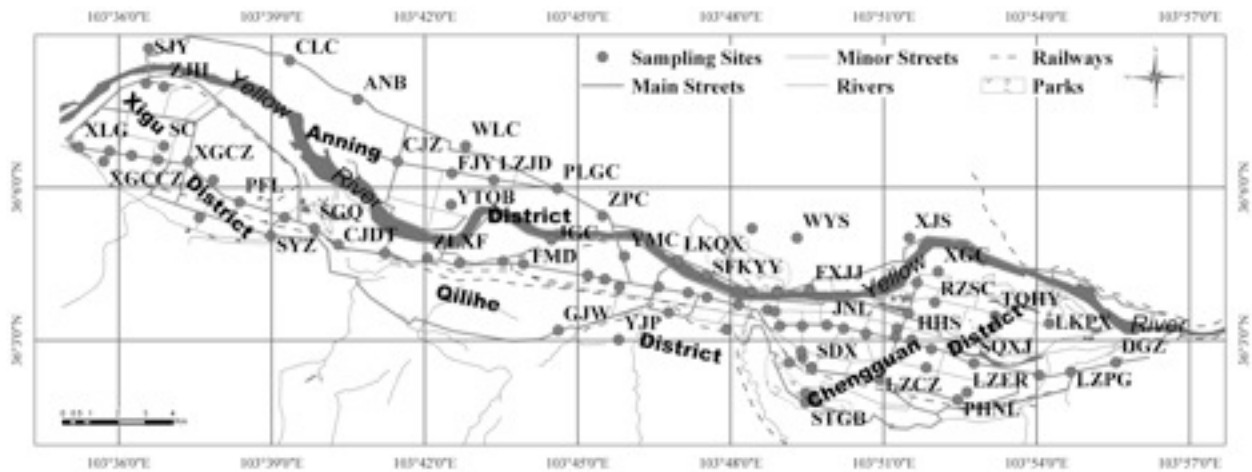


Figure 2.1. Map of city districts in Lanzhou and sampling site codes.

Samples were prepared for computer controlled scanning electron microscopy (CCSEM) analysis by mounting the dust on double sided carbon sticky tape (carbon tape facilitates electron conduction in the SEM). Operator observation of samples of dust showed that many metal bearing particles were present in the dusts, however to analyze all particles present in CCSEM mode would enable only a small number of metal-bearing particles to be characterized (i.e., the metal particle concentration was generally low). To increase the likelihood of a significant number of metal particles being characterized in a dust sample two analysis strategies were employed. First, the decision was made to maximize the number of

dust particles searched in the CCSEM analysis. To accomplish this, dust particles were deposited on a large strip of double-sided tape (adhering to a 4.5 x 2.5 cm glass slide). Dust particles were mounted on the tape by screening through a nylon mesh, with a nominal size of 40 μm , which was held at short distance above the tape, and the $< 40 \mu\text{m}$ particles having passed through the mesh were gravity deposited onto the tape. Once the tape surface was visibly covered in dust, the slide was shaken to remove loose (non-adhering to the slide) dust. This removal process left a monolayer of dust particles adhering to the double-sided carbon tape. The second strategy to maximize the identification was to employ a high threshold backscatter electron imaging selection process (see below).

Computer controlled scanning electron microscopy (CCSEM) was performed on an ASPEX Personal SEM (PSEM). Under computer control, the PSEM primary electron beam and the motorized stage (the area where the sample is located), operate in tandem to perform automated image analysis. The PSEM software package that accomplishes this is called "Automated Feature Analysis" (AFA). The projected two-dimensional image of any object observed in the scanning electron microscope is technically referred to as a feature. Automated Feature Analysis operates by recognizing a feature that is separated from the substrate by some signal produced by the feature when irradiated by the primary electron beam. Typically, the image produced by the collection of Secondary Electrons (SE), or by Backscattered Electrons (BE) is employed for this purpose. The BE image is the most useful as the BE signal strength is related to the average atomic number composition of the feature (for all intents and purposes, the density of the feature). Usually, the substrate that is used, is composed of carbon (in this study double sided sticky carbon tape), as carbon has a low atomic number, therefore the BE yield from a carbon substrate is low. So, any feature with an average atomic number greater than the atomic number of carbon will have a greater BE yield. Thus, the image of the feature can be separated from the substrate with image analysis software based on the BE (yield) image. A BE imaging threshold is set (in the image analysis software) that excludes the background and includes the features. The AFA software is designed so that the primary electron beam steps across a field of view (FOV) as imaged in the PSEM. The step separation for a square FOV is set at typically set at 512x512 point density at an operating magnification of 500x so only features $< 1 \mu\text{m}$ that might fall between the step points would be missed in the search. As

the primary beam steps across the FOV if it steps on a point above the BE image threshold the beam steps across the feature at a higher point density and covers all the above threshold points that describe the feature. From this process the size (maximum, and minimum diameters), the projected surface area, and various shape parameters are recorded. The element composition of the feature is determined from the collection of X-rays produced by the interaction of the primary electron beam with the atoms of the elements present in the feature. Each element atom will produce characteristic X-rays (of specific energy or wavelength) which when collected provides information on the composition of the feature. Here the X-rays were collected EDX spectrometer. The numbers of X-rays collected with depend on the average atomic number composition of the feature (the lower the average atomic number composition the lower the X-ray yield) and the dwell time of the primary electron beam on the feature.

In this study it was decided that to acquire data on significant numbers of metal-bearing particles in the dust that a high BE threshold be set for the AFA. The search operation for the High threshold features was standardized as follows. First, a consistent primary beam current was established of 1 nA. Second, a working distance of approximately 10 mm was set. Third, a BE image threshold was set by imaging a small number of rutile particles (TiO_2) placed on a clean area of the double sided tape. The threshold was set so that these TiO_2 particles would not image above the threshold. This meant that features with an average atomic number just above that of TiO_2 would be observed during the AFA search. In practice, this meant features containing Fe (atomic number 26) and those with an average atomic number greater than 26, would be identified and characterized in the AFA search. During the data collection phase a beam dwell time of 5 seconds was set and the X and Y coordinates of each high threshold feature was recorded. At the start of each analysis the PSEM was also programmed to search a rectangle mapped on the dust sample, under computer control the beam searched consecutive FOVs, with the stage (under computer control) moving the sample to the next FOV so that it was under the primary beam once the previous FOV had been searched. Data on the size, shape, chemical composition was recorded in a data base as the machine operated in an unattended fashion (under computer control) for several hours. This database was subsequently reviewed and those particles with elevated concentrations of the various metals recorded. The PSEM software allowed the stage to be driven back to

the location of any feature analyzed. Here, we returned to each feature a recognized metal-bearing contact for detailed operator characterization.

CHAPTER 3

RESULTS

Analysis of the road dust samples by CCSEM revealed the presence of the following metals: Lead (Pb), Copper (Cu), Zinc (Zn), Nickel (Ni), Chromium (Cr), Cobalt (Co), Tungsten (W), Tin (Sn), Antimony (Sb), and rarely Vanadium (V), Bismuth (Bi), Arsenic (As), and the rare earth elements (Yttrium (Y), Gadolinium (Gd), Holmium (Ho), Europium (Eu), Erbium (Er), Dysprosium (Dy), Cerium (Ce), and Lanthanum (La)).

In terms of relative abundance (as the dominant element in a particle), the most common elements observed (in descending order of average number of particles per sample (n)) were: Pb (\pm other elements) $n = 69 >$ CrFe (\pm other) $n = 57 >$ Zn (\pm other) $n = 31 >$ Cu (\pm other) $n = 28 >$ W(\pm other) $n = 15 >$ Ni (\pm other) $n = 3 >$ Other(Sn and Sb) (\pm other) $n = 2$. The identified metal-bearing particles were clustered into chemically homogenous groups or particle types (sometimes referred to as particle classes). The abundance of particle types or classes for the street dusts are listed in Table 1. In terms of abundance by particle types, among the Pb particles, Pb in the absence of other metals (i.e., Pb only in the particle) constituted 75% of the Pb-rich particles present. The ZnS particles comprised 48% of the Zn-rich particles; the CuS class constitutes 50% of the Cu-rich particles, and the CrFe particles made-up 100% of the Cr-rich particles. Among the W-rich particles, 47% were composed of W-only, while 53% were composed of WCo (approximately 25% of which also contained Ni). Finally, the Ni-only particles made-up 33% of the Ni-rich particles, while the other Ni-bearing particles constituted 67% of the particles

Table 1.1: Numbers of Heavy Metal Particles found in Four Lanzhou Road Dust Samples

Particle Type/Class	Sample Code			
	LZPG	#14	WYS	DGZa
Pb	74	7	119	9
Pb and Cr	7	1		
Pb and Ti (\pm Zn)			9 (4+(5))	
Pb and Zn and/or Cu (\pm V)	5 (4+(1))	3 (3+(0))	8 (8+(0))	2 (2+(0))
Pb and Sn	1		1	
W(\pm Other)*	26			2 (0+(2))
W and Co (\pm Ni)	28 (21+(7))	1 (1+(0))		
Cu(\pm Fe)	10 (10+(0))		4 (3+(1))	18 (0+(18))
Cu and S (\pm Fe)	33 (30+(3))	4 (2+(2))	3 (1+(2))	13 (2+(11))
Cu and Zn (\pm S)	19 (9+(10))	1 (1+(0))	3 (3+(0))	
Ni (\pm S)	5 (5+(0))	1 (0+(1))		
Ni and Cu and Zn	6	1		
Cr and Fe (\pm Ni)	194 (193+(1))	9 (8+(1))	8 (7+(1))	17 (15+(2))
Zn (\pm S)	36 (1+(35))	3 (1+(2))	9 (3+(6))	11 (2+(9))
Zn and Ba and S	7	6		5
Zn and Fe (\pm S)		3 (2+(1))	11 (7+(4))	30 (25+(5))
Sn (\pm Cu)	3 (2+(1))			
Sb	5			
Total # of Heavy Metal Particles	459	40	175	107
Total # of Particles in Sample	4,937	2,930	2,544	6,013

Table 1.1 Continued

Particle Type/Class	Sample Code			
	DGZb	#1	#9	#3
Pb	30	30	28	11
Pb and Cr				
Pb and Ti (\pm Zn)				
Pb and Zn and/or Cu (\pm V)	5 (3+(0))	5 (0+(5))	1(1+(0))	7(6+(1))
Pb and Sn	2			
Pb and As	2			
W(\pm Other)*	26		4	
Pb and Cu	3			
Pb and Cl	11			
W and Co (\pm Ni)	2 (0+(0))			
Cu(\pm Fe)		2	3	1(1+(0))
Cu and S (\pm Fe)	8 (17+(91))	1(0+(1))		1(1+(0))
Cu and Zn (\pm S)		3 (3+(0))		1(1+(0))
Ni and Fe (\pm S)	0 (2+(0))			1(1+(0))
Ni and Cu and Zn				
Cr and Fe (\pm Ni)		7 (7+(0))	1(1+(0))	
Zn and Fe (\pm S)	0 (5+(120))	25 (0+(25))	11(9+(2))	14(8+(6))
Zn and Ba and S		2	3	1
Sn (\pm Cu)				
Sb				
Total # of Heavy Metal Particles	325	78	58	37
Total # of Particles in Sample	4,962	10,000	10,000	10,000

The road dust samples revealed morphological differences within individual classes and between different classes.

The Pb-rich particles exhibit four distinct particle morphologies (Figures 3.1 - 3.4). The four morphological classes can be characterized as:

1. Large blocky particles, often approaching a cube like form. (Fig. 3.1a)
2. Large aggregates of what appear to be small individual particles. (Fig. 3.1b)
3. Small particles dispersed in the matrix of a larger particle. (Fig. 3.1c)

4. Small isolated individual particles sometimes morphologically unremarkable (Fig. 3.1d) and sometimes crystalline (Fig. 3.2a and 3.2b)

5. Large spherules or small spherules the latter in chain aggregates suggestive of a Pb fume.
(Appendix A)

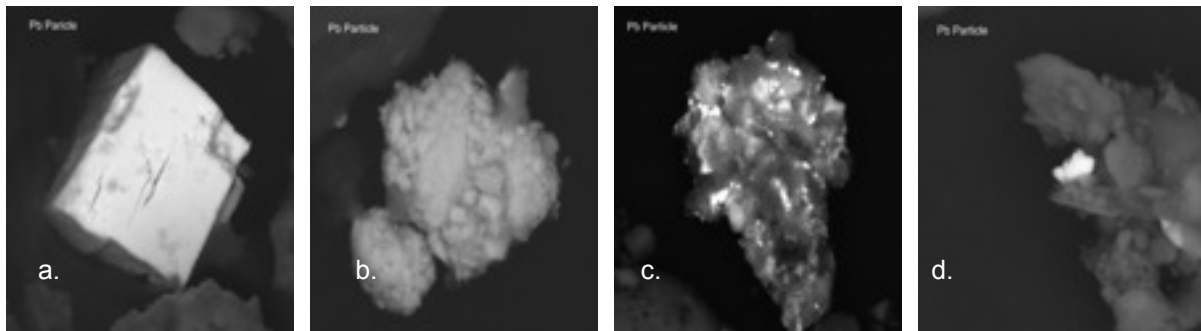


Figure 3.1 Pb bearing particles of various forms: large blocky (a), large aggregate (b), small dispersed in grain matrix (c) isolated small morphologically unremarkable (d).

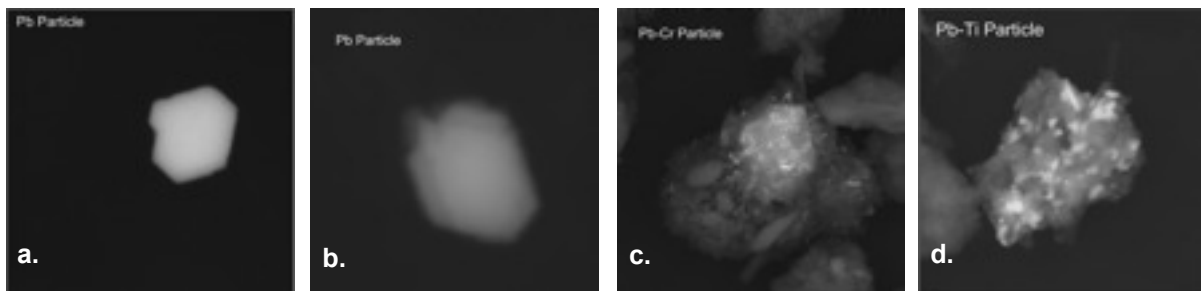


Figure 3.2 Pb-bearing particles of various forms: crystal habit (a and b), small dispersed in Cr-bearing matrix (c) small dispersed in Ti-bearing matrix (d).



Figure 3.3 Pb-bearing particles of various forms: small dispersed in Zn-bearing matrix (a) small composed of Pb-Cu-Zn (b), spherical composed of Pb-Sn (c)

The presence of Pb-rich particles with a hexagonal form (morphological class 4) (Fig. 3-2a and 3-2b) are consistent in form with Pb particles that form the aggregates (Fig. 3-1b). These particles are suggestive to Pb-paint pigments used in older Pb-based paints. The morphologies associated with the other Pb-rich particles (Pb-Cr, Pb-Ti (\pm Zn), Pb-Zn (\pm V), Pb-Cu, and Pb-Sn) are quite varied; however, the majority of the particles show small Pb particles dispersed in a matrix composed of other heavy metals (Fig. 3-3). Other examples of the morphology exhibited by the Pb-rich particles in the street dust samples are presented in Appendix A.

The W-rich particle class produced mostly morphologically unremarkable particles, whereas the W-Co and W-Co-Ni particle classes produced more interesting morphologies (Fig. 3.4). Typically they appeared to be aggregates of smaller particles.

The Cu-rich particle class produced morphologically distinct classes (Figs. 3.5) which we defined as:

1. Large Cu-S spherule-like/pseudo botryoidal clusters (Fig. 3.5a).
2. Large blocky Cu-Fe-S particles (Fig. 3.5b).
3. Large metal scrapings/shards of Cu-Zn (Fig. 3.5c).

The morphologies associated with the Ni-rich particles \pm other heavy metals (Ni- only, Ni-Fe, and Ni-Cr) were somewhat varied (Fig. 3.6); however, most of them were morphologically unremarkable.

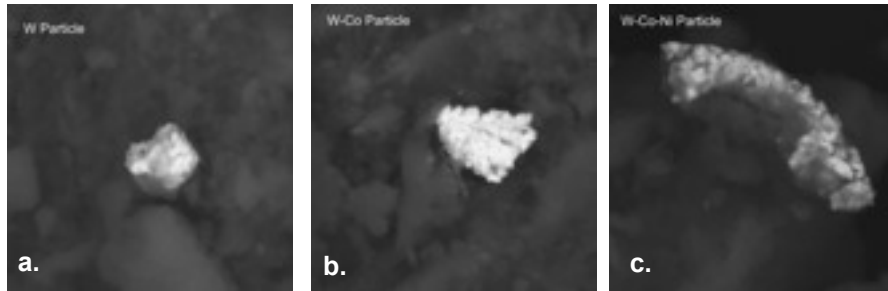


Figure 3.4 W-bearing particles of various forms: small containing only W (a) aggregates of W-Co (b), aggregates of W-Co-Ni (c)

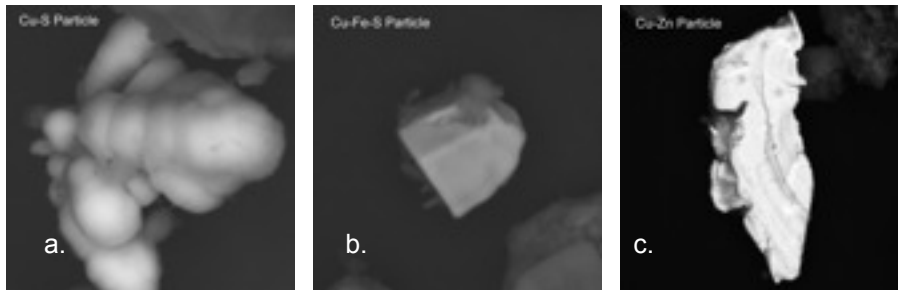


Figure 3.5 Cu-bearing particles of various forms: large spheroidal (a) large blocky (b), large shard-like (c).

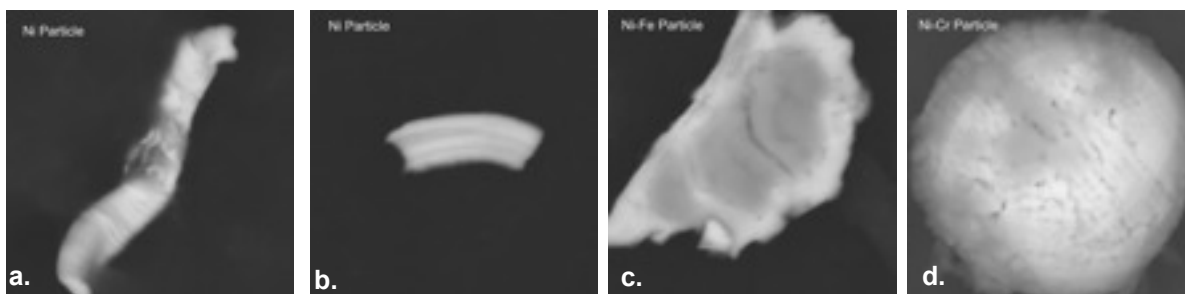


Figure 3.6 Ni-bearing particles of various forms: shard like Ni-only (a and b), irregular Ni- Fe (c) spherical Ni-Cr (d).

CHAPTER 4

DISCUSSION

4.1 Tracing the Sources of Metal Particles in Lanzhou Street Dusts

The wide variety of metal-bearing particles identified in the Lanzhou dusts is not untypical, many metals have been found in road dusts by several studies. Lead has widely identified in road dusts. For example, Barrett et al. (2010) identified in dusts collected in Manchester, UK, PbCrO_4 , Pb-sorbed on goethite, with lesser quantities of PbO , PbCl_2 , Pb-carbonates. The same group (Barrett et al., 2011) found Zn occurring with Cu, Pb and Sn in metal rich grains. Other metals are also routinely identified road dusts. Han et al. (2008) found elevated levels of Cr, Cu, Hg, Pb, Sb, and Zn, compared to background soils, in road dusts from Xi'an (capital of Shaanxi province), China. In road dusts from Baoji (second largest city in Shaanxi province), China, elevated levels of Pb, Zn and Cu were widely present (Lu et al., 2009).

Many different metal particle types were identified in the street dusts collected from Lanzhou, China. Considering the chemical composition and morphological forms of the metal-bearing particles in the dusts, we can infer some specific source for a portion of these particles.

Micrometer sized Pb particles bound in aggregates, or dispersed in the matrix of a larger particle, or as isolated individual particles exhibiting a hexagonal form are consistent with Pb carbonate-like pigment particles that were used historically in Pb-based paint. Lead exhibiting cubic morphology was consistent in habit with the mineral galena (PbS). This Pb-sulfide mineral is not a typical constituent of street dusts. It must be concluded that this Pb mineral was raw material for some industrial processing operation requiring Pb in some form in the end product. As this cubic habit of PbS is in an unaltered state clearly this is a fugitive emission from some form of smelting operation.

Tungsten (W) and specifically W particles containing Co and/or Ni are typical of a compound called "hard metal." Hard metal is composed of cemented tungsten carbide. It is an extremely hard compound that has a number of uses (e.g., used to coat the teeth of cutting saws). The presence of hard metal particles in the street dust is suggestive of either a hard metal grinding operation nearby, or recent cutting activities (perhaps road surface cutting). Nevertheless, cemented tungsten carbide is extremely rare, and has specialized applications. To find particles of this material in street dust suggests a tool grinding operation with uncontrolled emissions (Abraham and Hunt, 1995).

The Cu-rich particles exhibit several forms, the apparent aggregates of spherical particles argue for a high temperature combustion process source (melting of the copper sulfur material, with subsequent cooling would, because of surface tension effects, lead to spherical forms). The shard-like Cu particles are suggestive of mechanical abrasion, and are likely derived from some type of wear process. The Cu particles with blocky forms appear to have a fracture origin, but a specific source for such particles can only be speculated on. However such blocky particles with a CuFeS composition are indicative of the mineral chalcopyrite. Chalcopyrite is a common copper ore mineral. It seems likely that these blocky CuFeS particles are from a supply of raw material for copper smelting. Potential sources for these Cu-particles are metallurgical processes, waste incineration, and industrial applications.

The Cr particles were dominated by two morphological types. The shard-like Cr particles are consistent with mechanical abrasion, and are probably derived from some type of wear process. The CrFe particles with blocky forms are indicative of the mineral chromite. Chromite is one of the two main sources of the metal Cr. Ferrochrome, also has a CrFe composition, and is produced by electric arc melting of chromite. The largest use of ferrochrome is the production of steel, the production of stainless steel with a Cr content of 10 to 20% is an especially important consumer of ferrochrome. The blocky FeCr particles were either derived from a supply of Chromite to be used as a source of Cr, or were from a source of ferrochrome that had been produced for steel.

The Zn particles mostly fell into two morphological types. The ZnS particles had a distinctive blocky form, while the Zn-only particles appeared to have a degraded/corroded pockmarked surface appearance. The only ZnS mineral of importance is goslarite (hydrous zinc sulfate: $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$). However, goslarite is a secondary mineral and is of no commercial significance. This suggests the ZnS particles found in abundance are from a ZnS production process (produced by treating Zn with H_2SO_4), or from a commercial operation using ZnS as a raw material. The most significant commercial use of ZnS is as a coagulant in rayon manufacture. It is also used in the production of the white pigment lithopone. Zinc sulfate is also Zn source in animal feeds, fertilizers, and agricultural sprays.

It is clear, from these analyses, that the assemblages of metal particles in each of the separate street dusts were quite different. This suggests that the sources of the metals in the dusts were fairly localized. It also suggests that a variety of metal pollution generating operations were working in Lanzhou when the samples were collected. Obviously, the potential for metal pollution downstream of street run-off is of concern. Further analysis of other Lanzhou road dust samples will provide a clearer picture as to whether the metal contaminants in these samples were an isolated case, or whether road dust contamination by metal particles in Lanzhou is systemic.

To date, little work has been done on apportioning the sources of metals in road dusts. It has been argued Cu and Sb may be used as reliable tracers of brake wear particles in the urban environment (Thorpe and Harrison, 2008). However we would contend that, at least in Lanzhou, Cu is present in many different particles forms and only a fraction of Cu in the dust can be attributed to tire wear. Similarly it is doubtful that Zn released from tire wear, which it can be in substantial quantities (Councell et al., 2004), would be a suitable tracer in urban dust tire wear. Certainly in the Lanzhou dust Zn is present mostly as Zn or ZnS, and do correspond to matrix (tire wear) bound Zn. In a study of road dust from the Gold Coast, Southeast Queensland, Australia (Gunawardana et al., 2012), it was suggested that Zn Cu, Pb, Ni, Cr, and Cd are traffic related including tire abrasion fly-ash from asphalt, and combustion by-products. Likewise, a study of road dusts from Buenos Aires, Argentina (Fujiwara et al., 2011) concluded the metals Cu, Fe, Ni, and Sn in the dust were natural or anthropogenic origin, while the metals Cd, Mn, Pb, Sb, and

Zn in the dust were traffic related. Clearly Sb in road dust is likely a traffic related element (Fujiwara et al., 2011). However, from the analysis of Lanzhou dusts we would agree with conclusions drawn by Wei and Yang (2010), who reviewed metal contamination urban road dusts from China, that the main sources for metals in road dusts are of traffic and industrial in origin. Further avenues of study might include determining the location of samples containing a large proportion of heavy metals in relation to local industries.

4.2 Health Threat Posed by Metals in Lanzhou Street Dust

Heavy metals may cause both human health issues and adverse environmental effects. The principal pathways for human exposure are by inhalation and via inadvertent ingestion through hand-to-mouth activity. The inhalation threat is posed by particulate road dust that is suspended by air currents and by the action of vehicular traffic that mechanically re-suspends the dust. The inhalation threat is the most immediate for road dust metal particles that are readily biosoluble. Until the removal of Pb as an additive in gasoline, elevated levels of Pb in blood were a constant across the United States population. This was a result of the inhalation of airborne Pb emitted in vehicular exhaust. The various metals in Lanzhou street dust have the potential to cause various inhalation resulting health problems. Lead was identified in all of the Lanzhou dusts, and the effects of inhaling Pb are well documented. The impact on sensitive populations (young children, pregnant women, etc.), is the most significant. Intake of Pb by infants and toddlers, even at low levels, can lead to IQ and other neurophysiological deficits (e.g., Lanphear et al., 2000; Chiodo et al., 2004; Kordas et al., 2006; Hu et al., 2006; Sarkin et al., 2007). The inhalation of Cu particles can cause respiratory distress in susceptible individuals (e.g., Donoso et al., 2007). Also, prolonged inhalation of cemented tungsten carbide particles can lead to focal peribronchiolar inflammation, diffuse interstitial fibrosis and honeycombing of the lung (Navi et al., 2008).

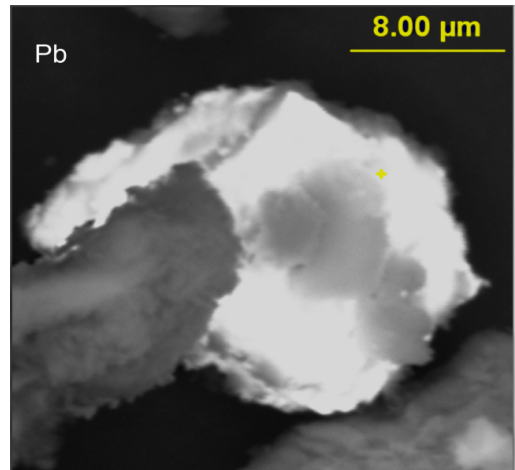
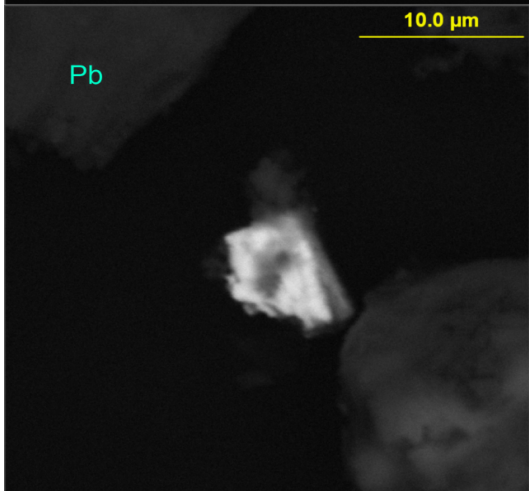
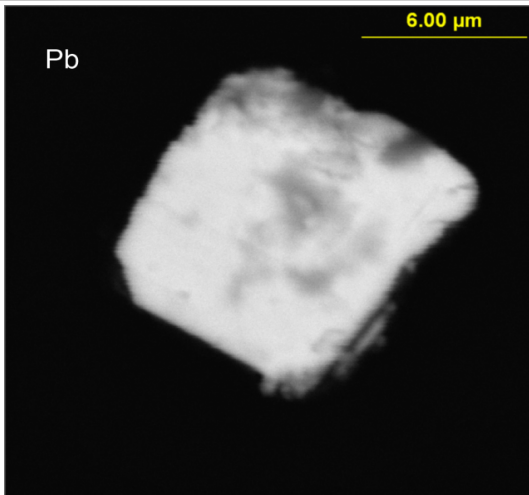
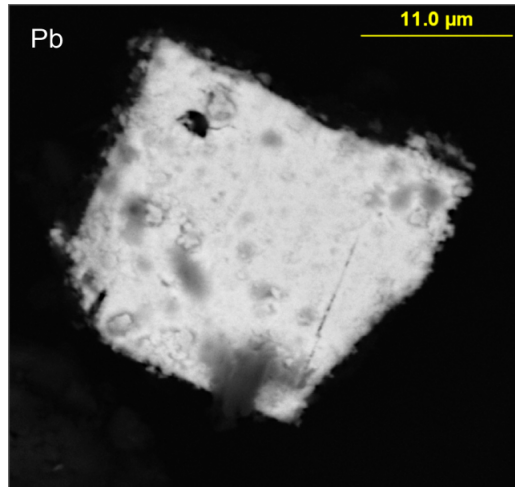
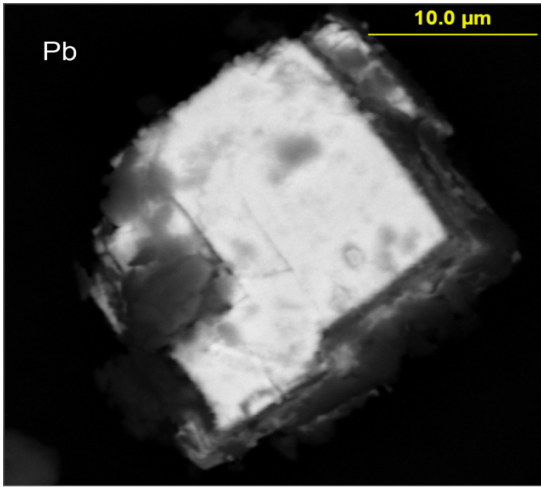
Metals in street dusts can pose an ingestion threat to certain populations. Infants and toddlers whose exploratory mouthing behavior makes them especially susceptible to inadvertent ingestion of dust material with which they come in contact. Infants and young children tend to mouth their hands and

objects by habit and by sucking reflex (Groot et al., 1998). So, exposure can be by direct mouthing of objects, unintended ingestion through hand-to-mouth activity, or the consumption of food contaminated by hands (Stanek et al., 1998). Large amounts of surface dust can be collected on the hand. A study found that up to approximately 15 mg/cm² of moist soil could be picked up by placing a hand palm down on a container of soil followed by gentle agitation for 30 s (Kissel et al., 1996a). Under worst case conditions, loading values in excess of 1 mg/cm² have been recorded for children playing in mud (Kissel et al., 1996b). The transfer of surface contaminants to hands can also increase with the number of hand-to-surface contacts due to increased palm surface exposure. Inadvertent ingestion of substantial quantities of Pb that is mobilized in the stomach can lead to excessive absorption and as noted previously can result in neurological deficits. Even the excessive ingestion of particulate Zn can pose health problems. While Zn is an essential nutrient, stomach acid that contains HCl which can easily dissolve particulate zinc readily produces corrosive ZnCl that can cause damage to the stomach.

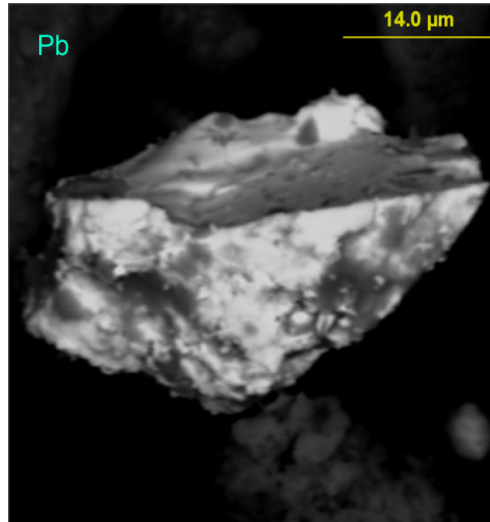
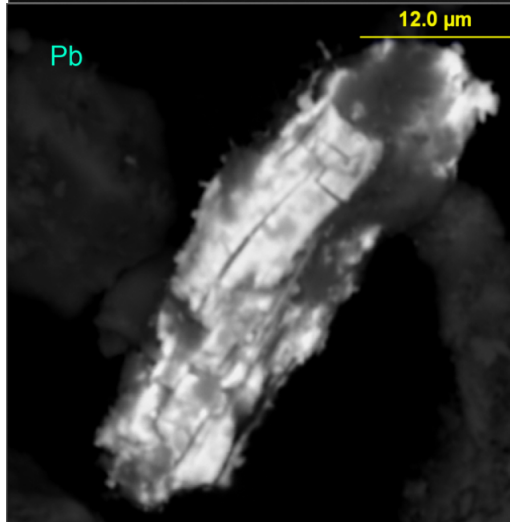
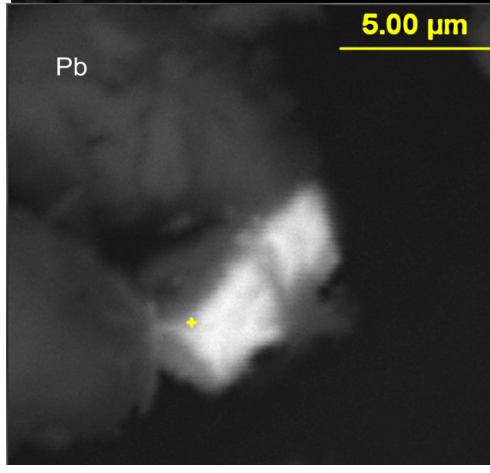
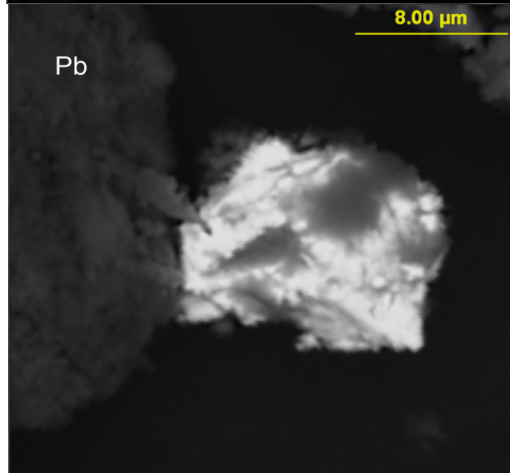
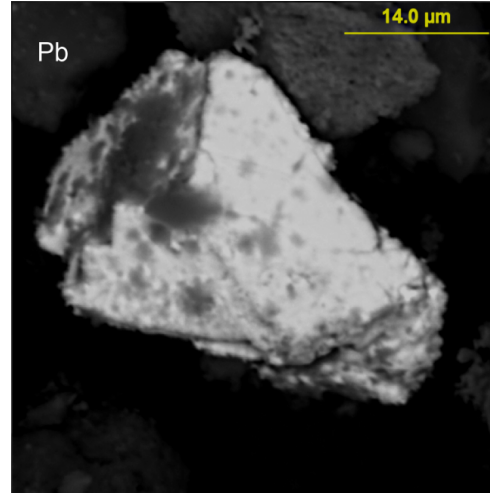
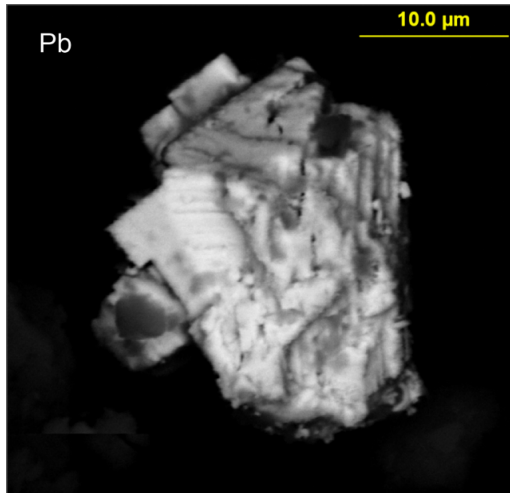
Further study might include determining if the sample locations with large quantities of heavy metals are near susceptible populations. Since all were samples were collected at the same time, additional sampling at different points in the year may show seasonal variability.

Excessive exposure to highly contaminated Lanzhou dusts by susceptible populations has the potential to cause severe adverse health effects. Overall the use of the SEM allowed for a highly detailed look at the collected road dust samples. This made it possible to determine the level of contamination and provided an accurate picture of the composition of the road dust constituents. With this information it is possible to identify the sources of contamination and hopefully help form mitigation strategies.

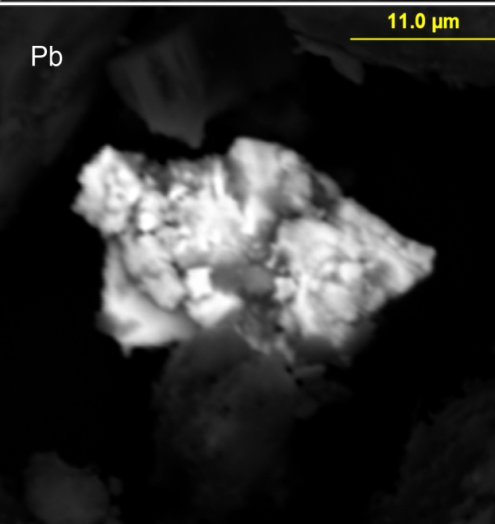
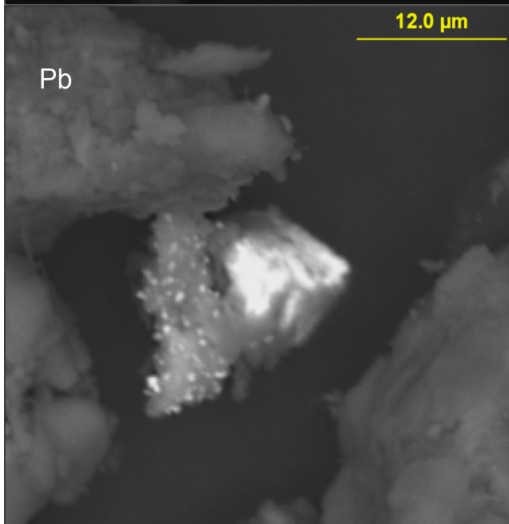
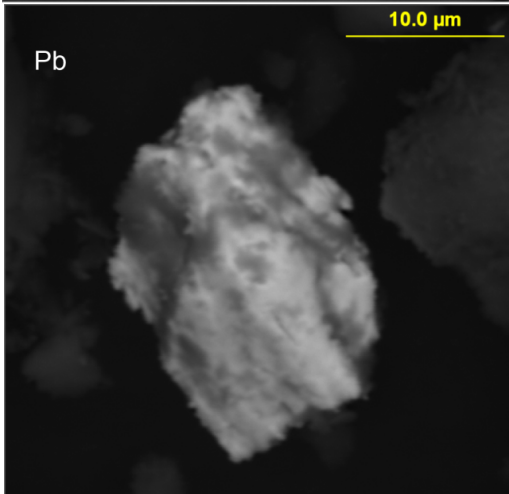
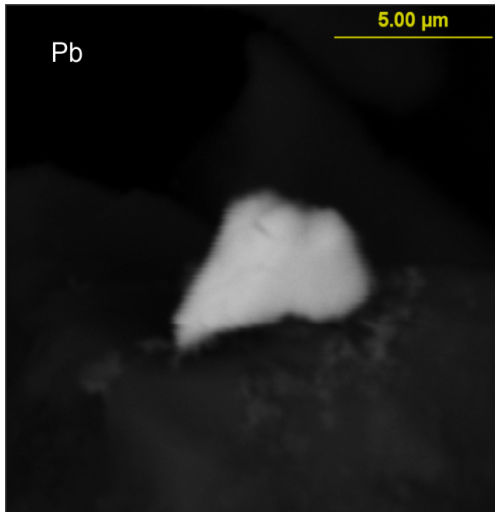
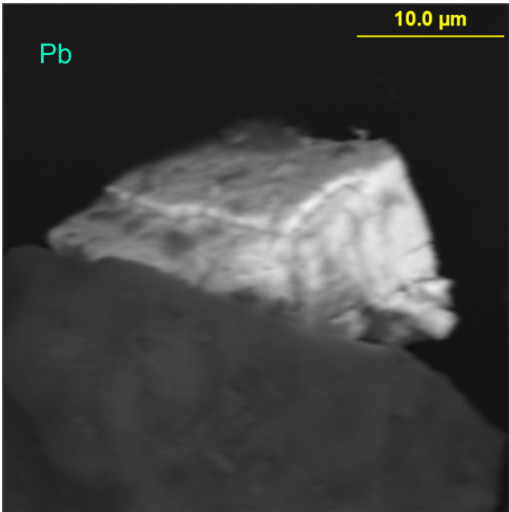
APPENDIX A
ELECTRON MICROGRAPHS OF VARIOUS LEAD-BEARING PARTICLES PRESENT IN
LANZHOU STREET DUSTS



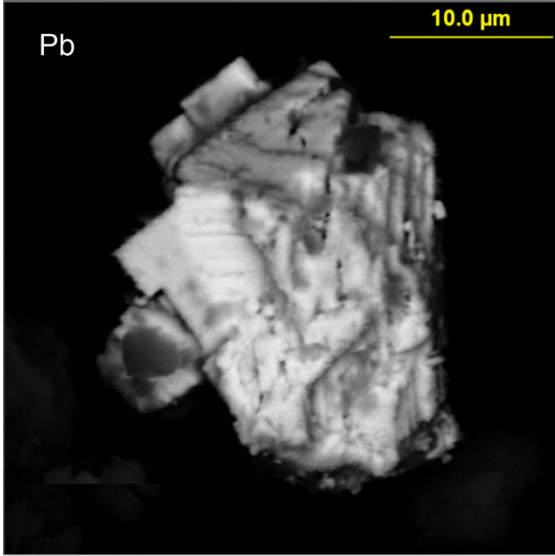
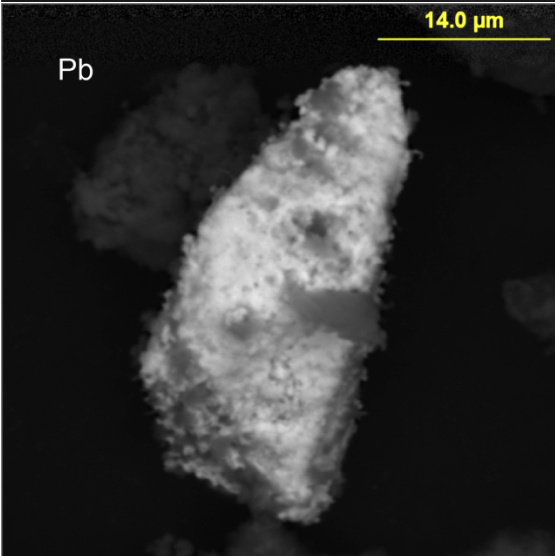
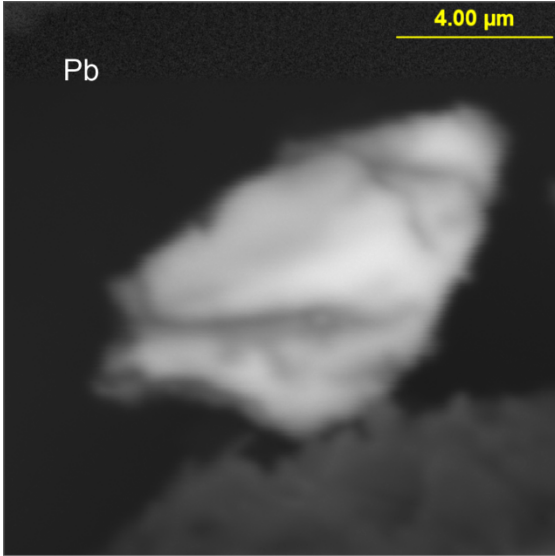
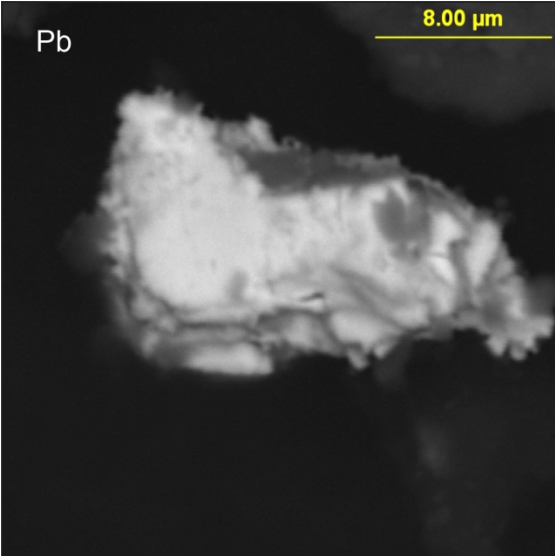
CUBE-LIKE



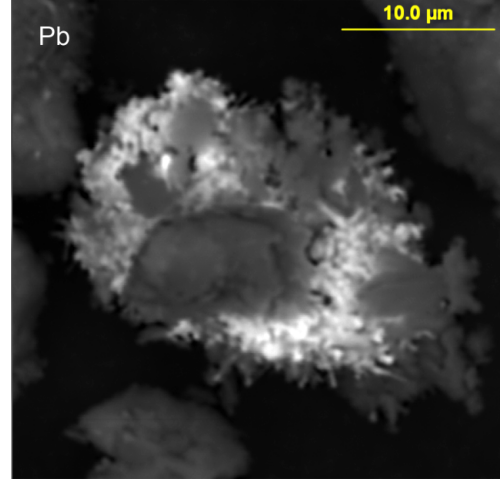
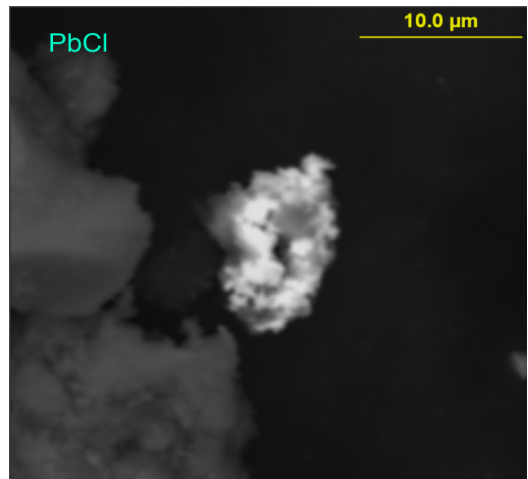
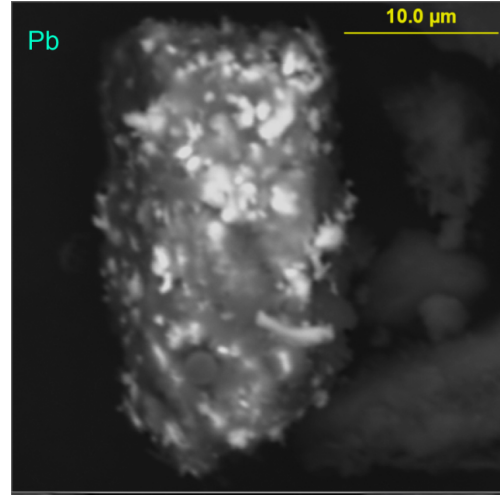
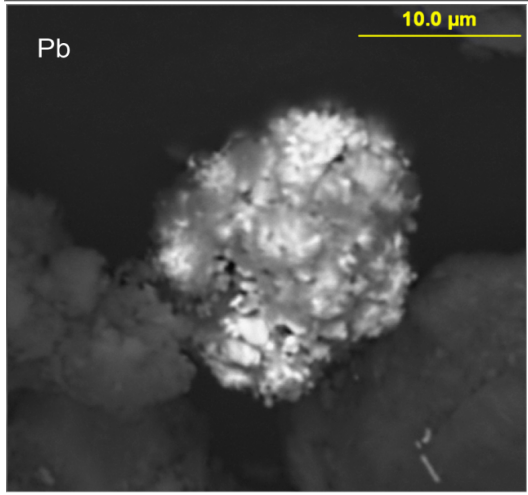
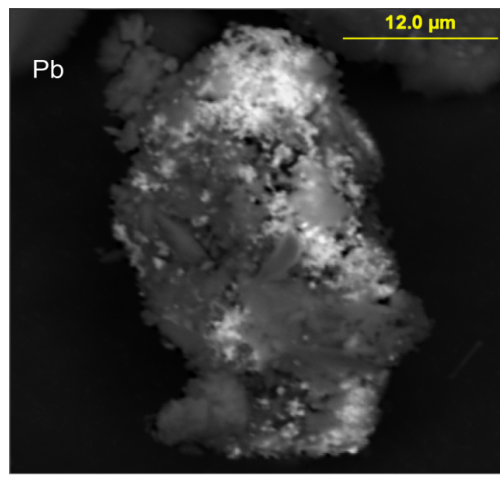
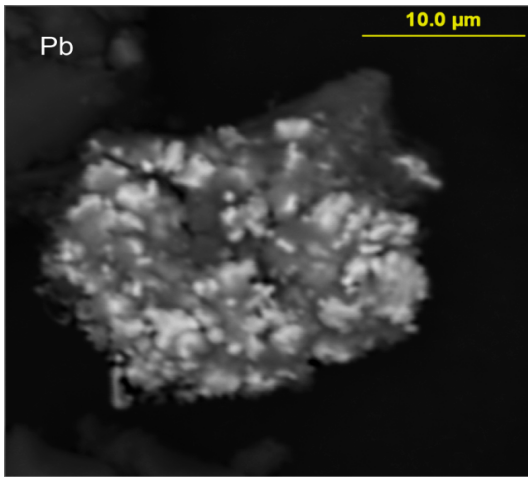
BLOCKY



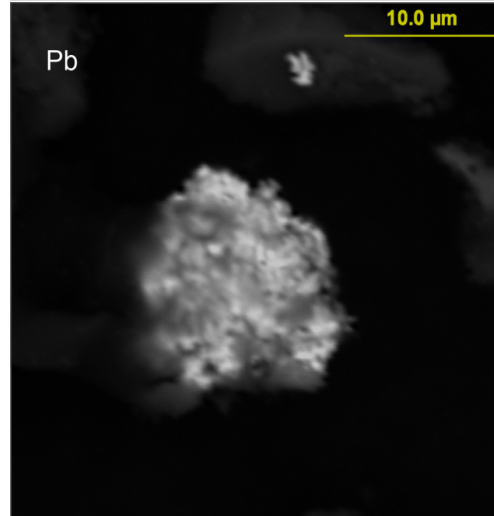
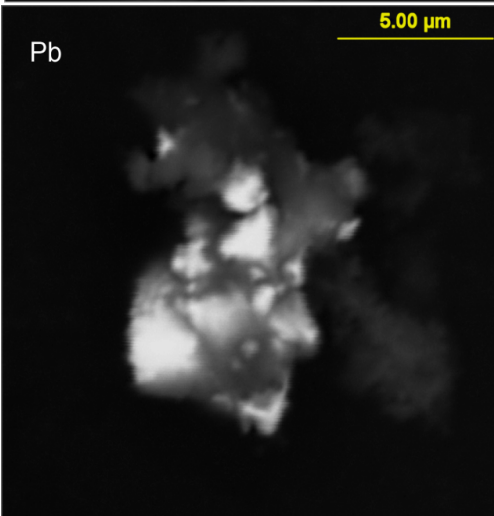
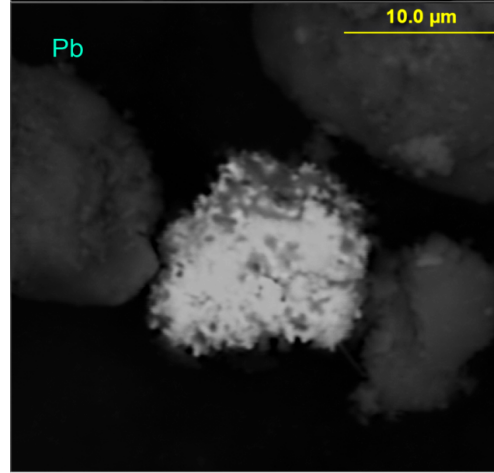
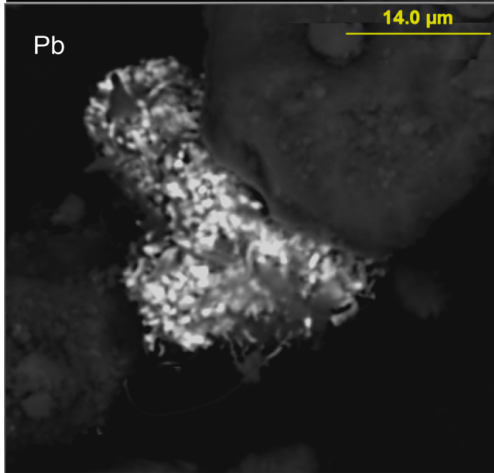
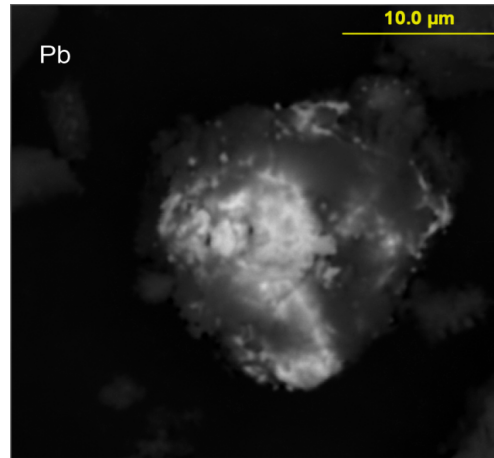
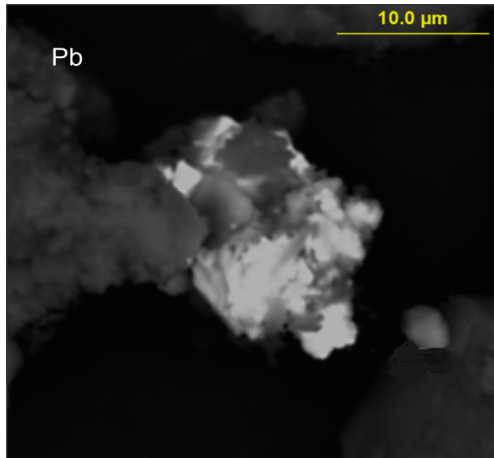
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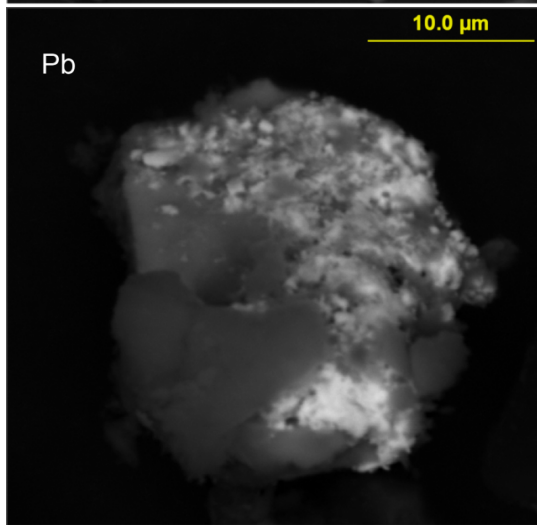
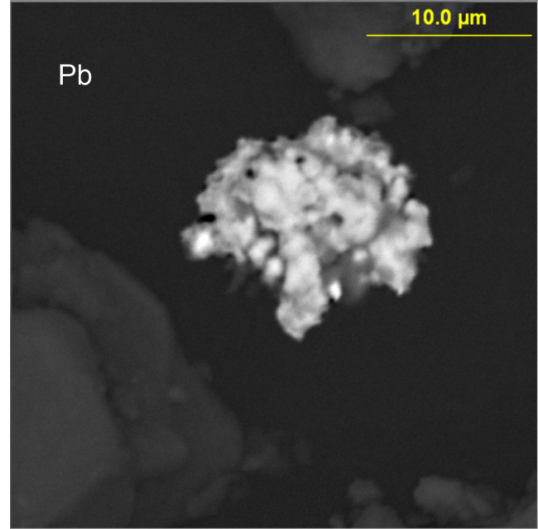
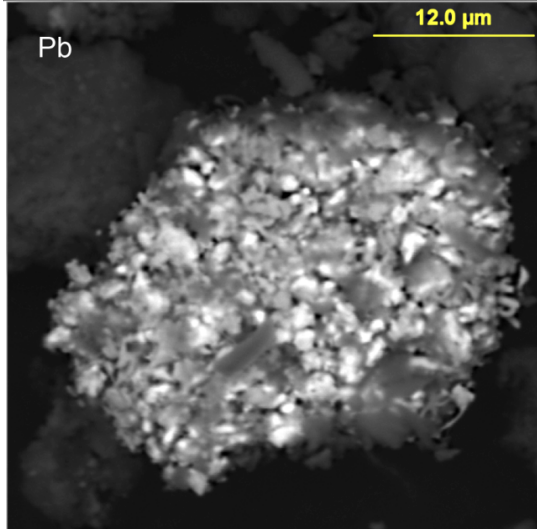
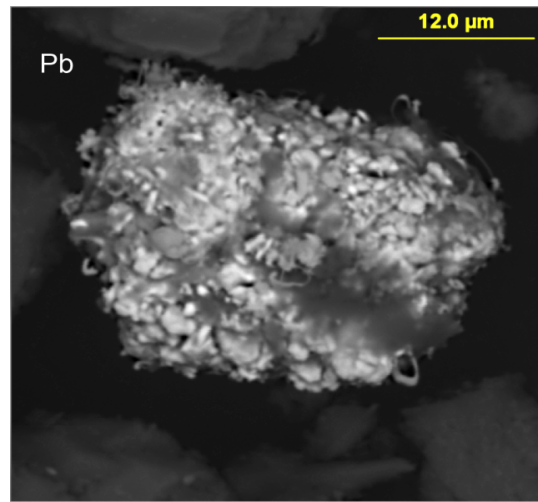
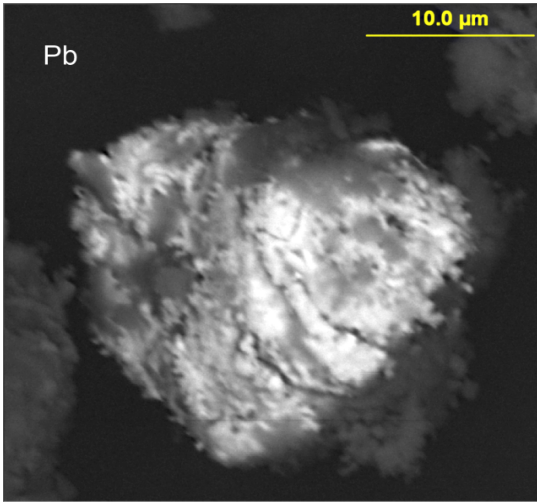
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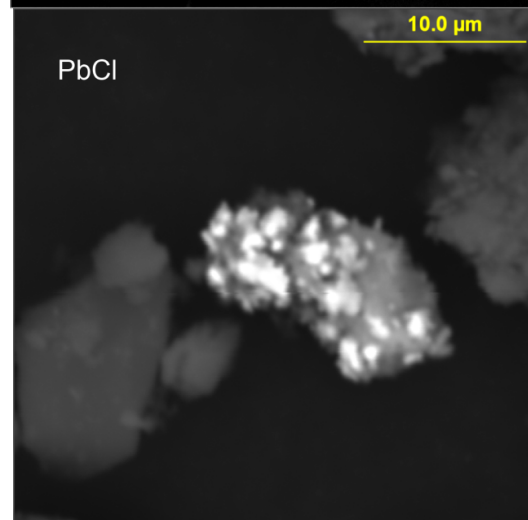
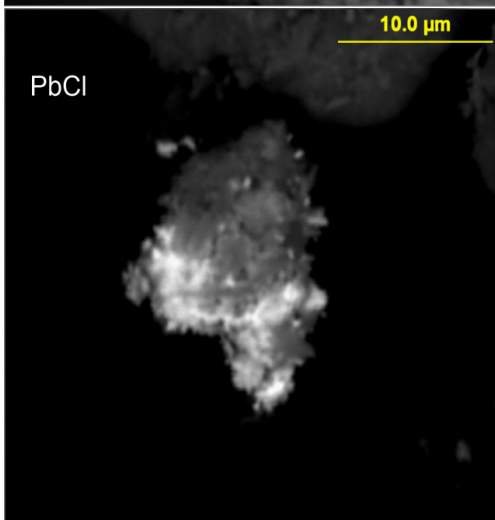
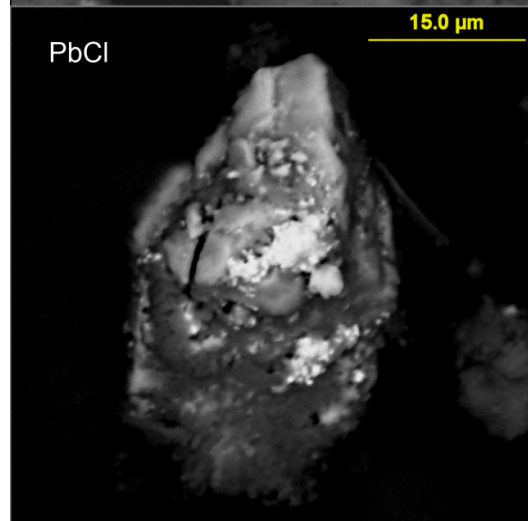
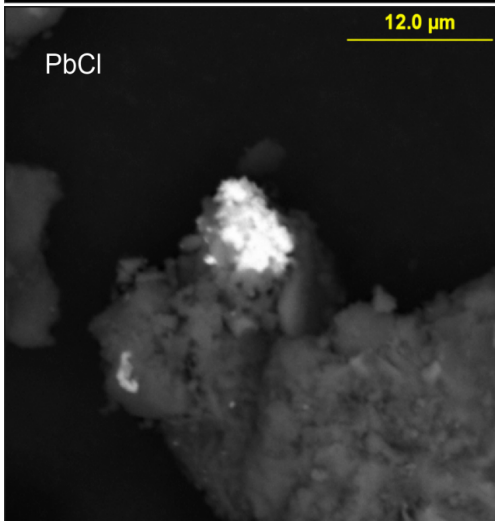
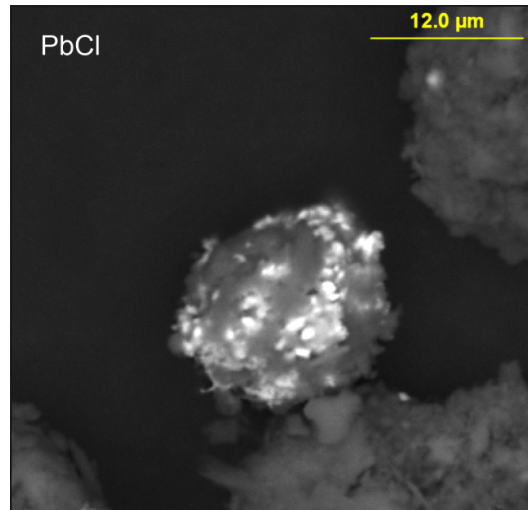
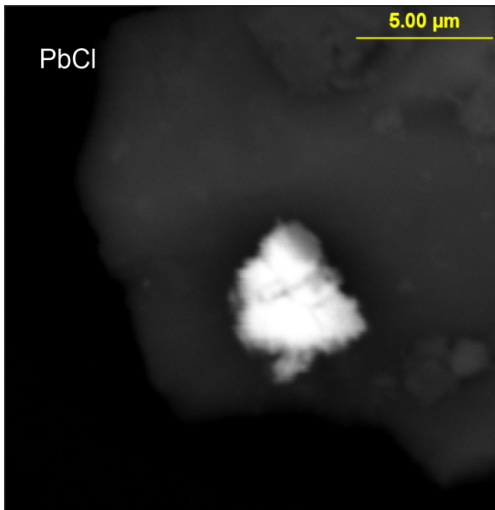
AGGREGATE



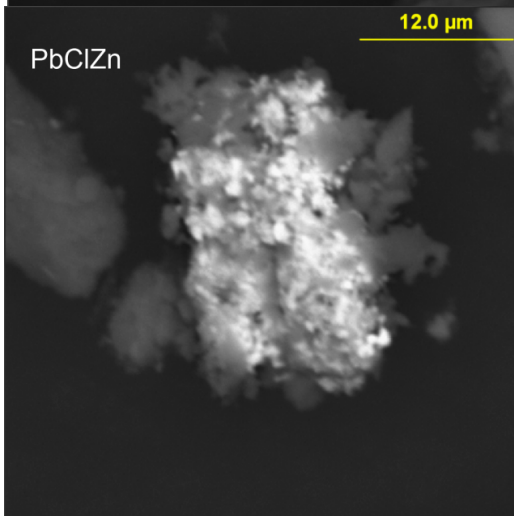
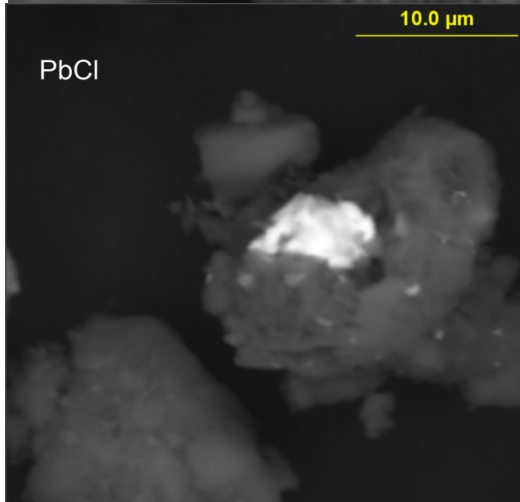
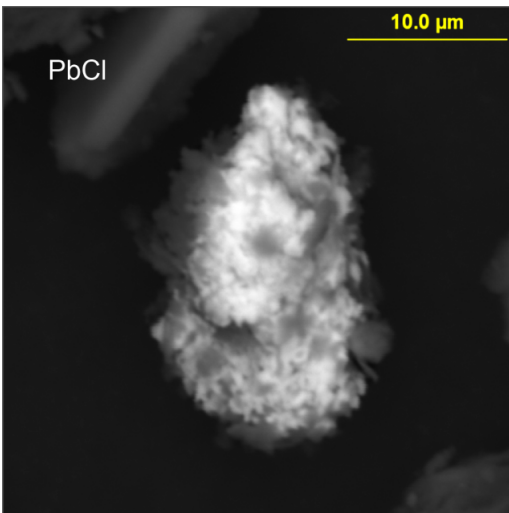
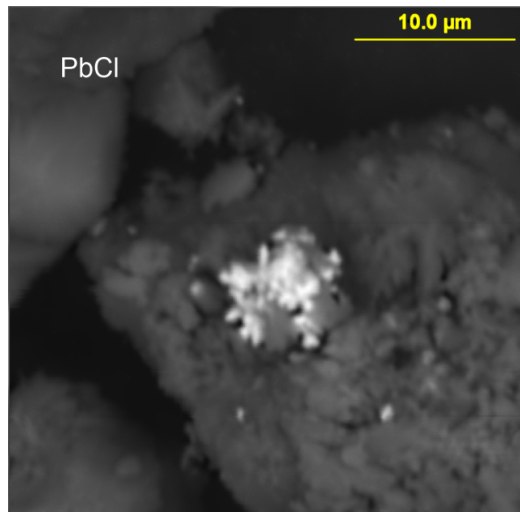
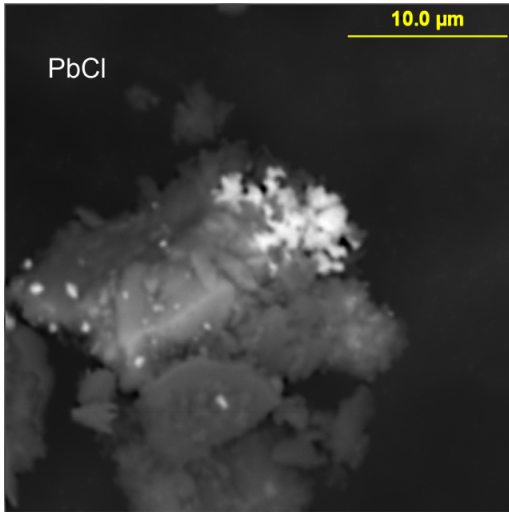
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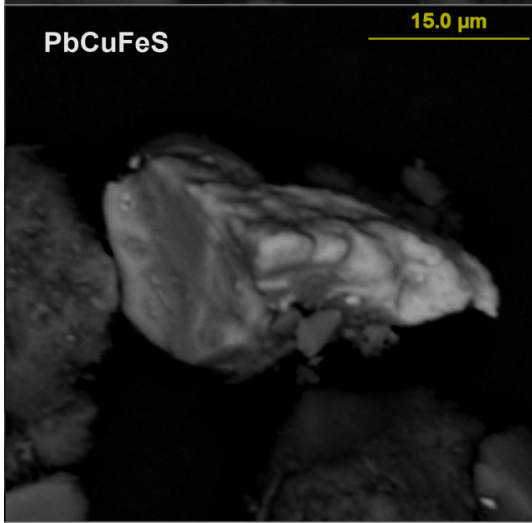
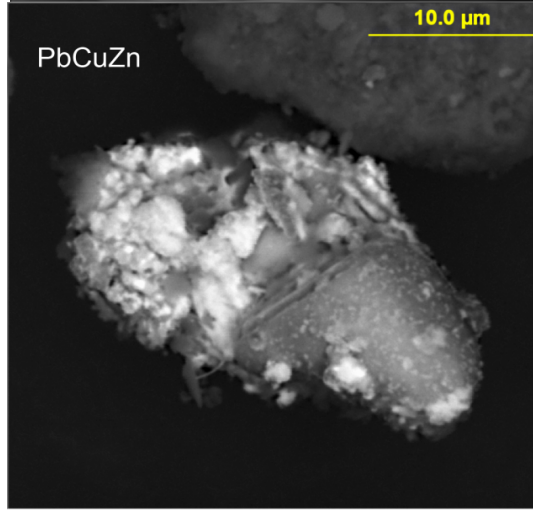
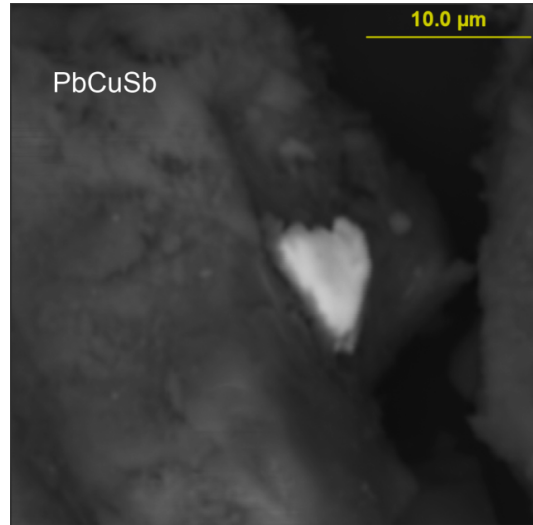
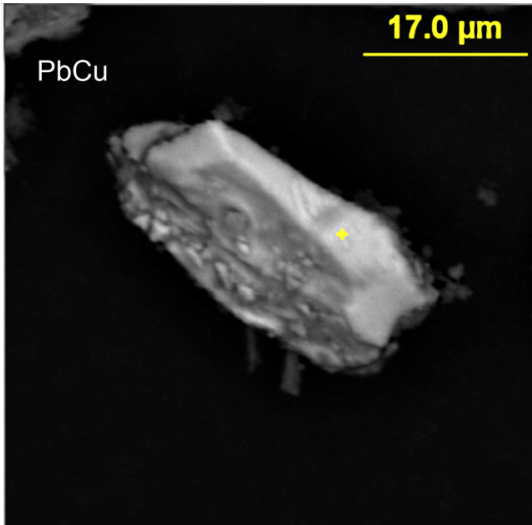
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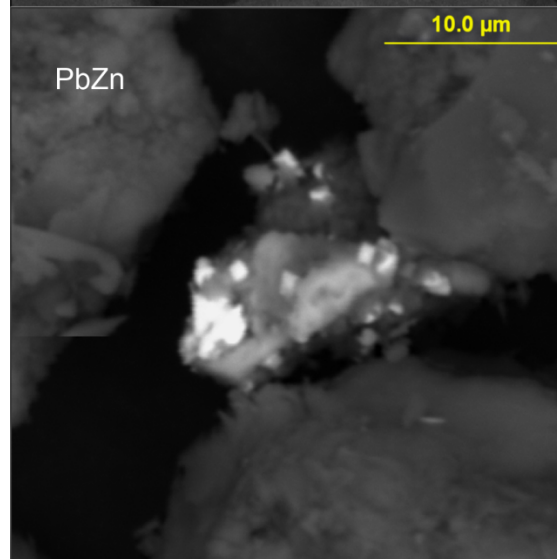
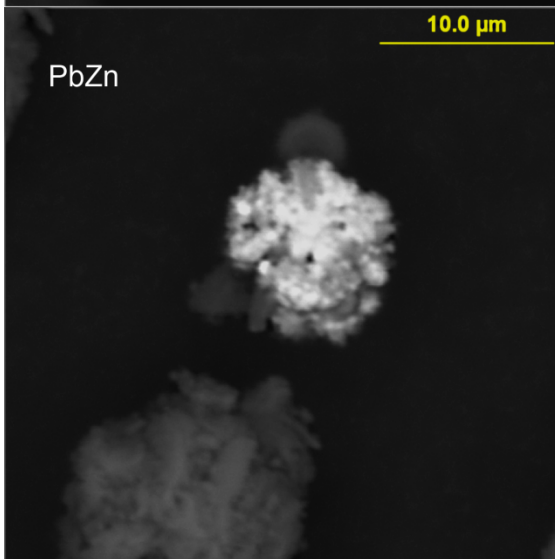
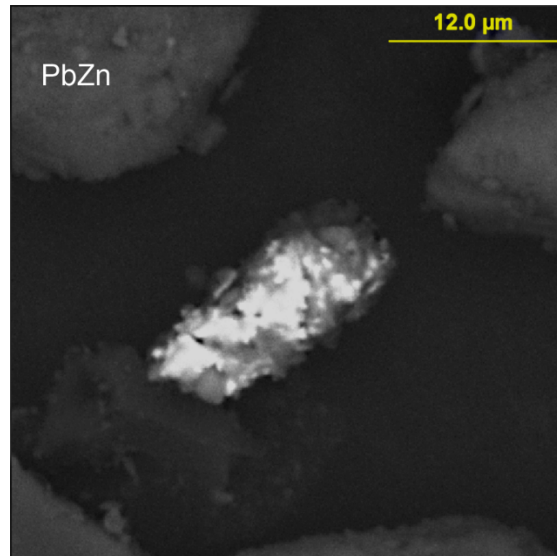
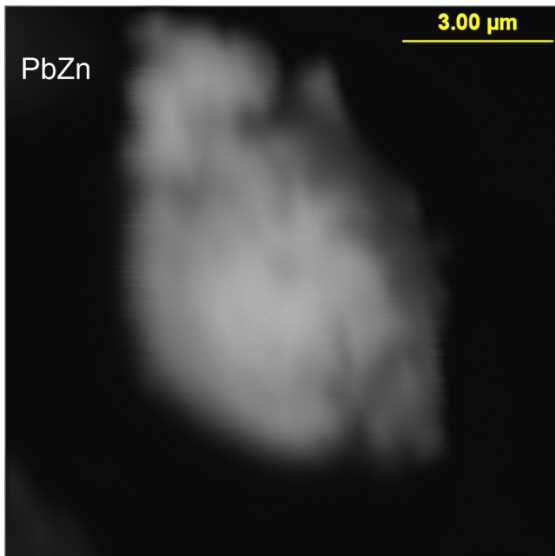
LEAD AND CHLORINE



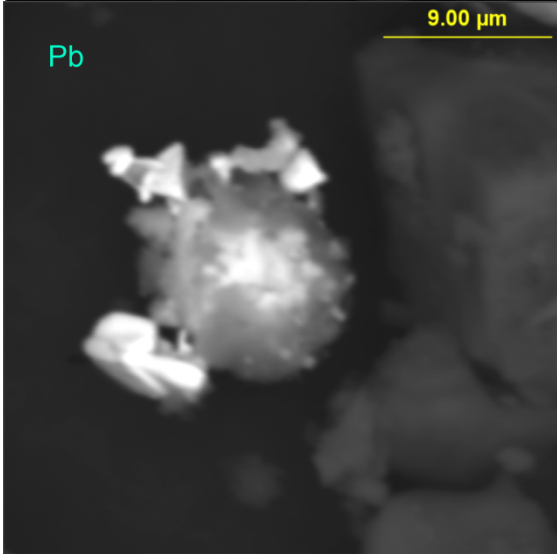
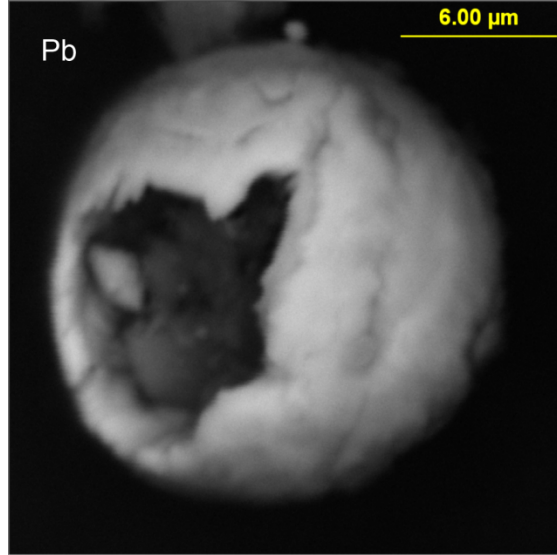
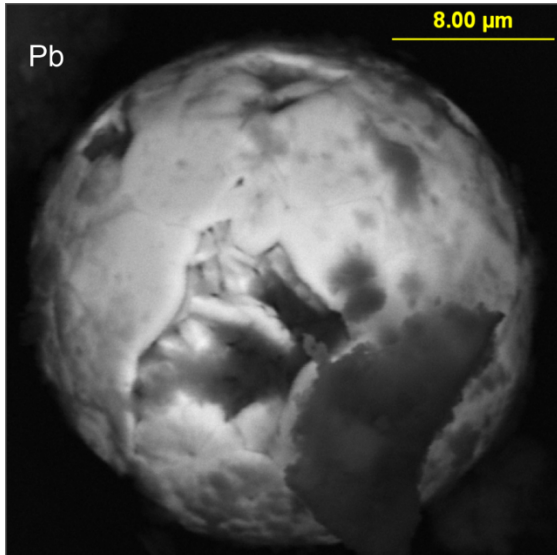
LEAD AND CHLORINE



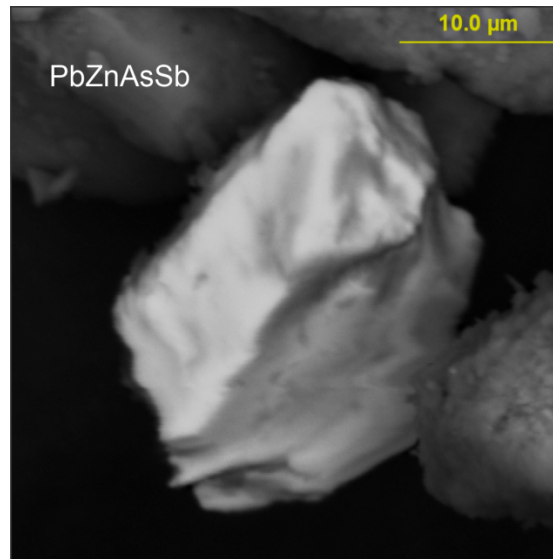
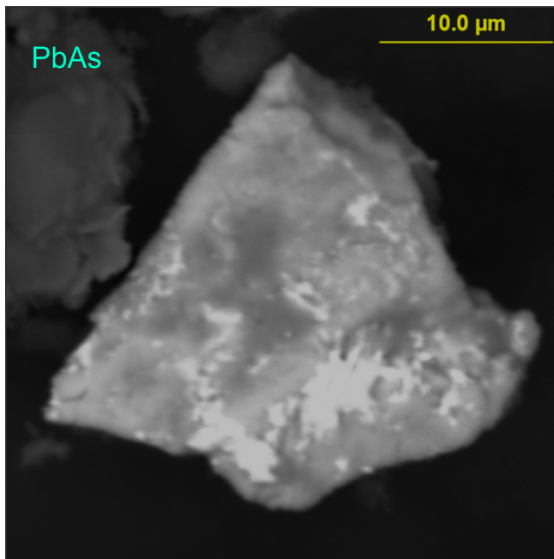
LEAD AND COPPER



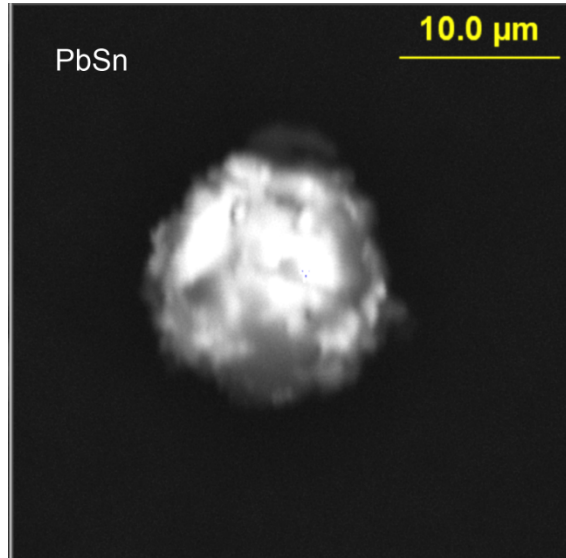
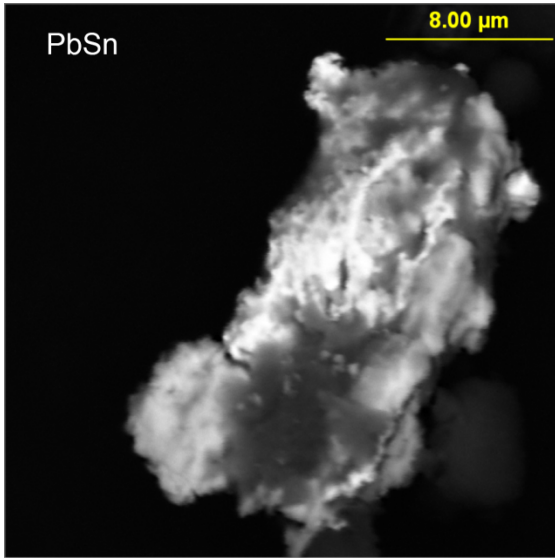
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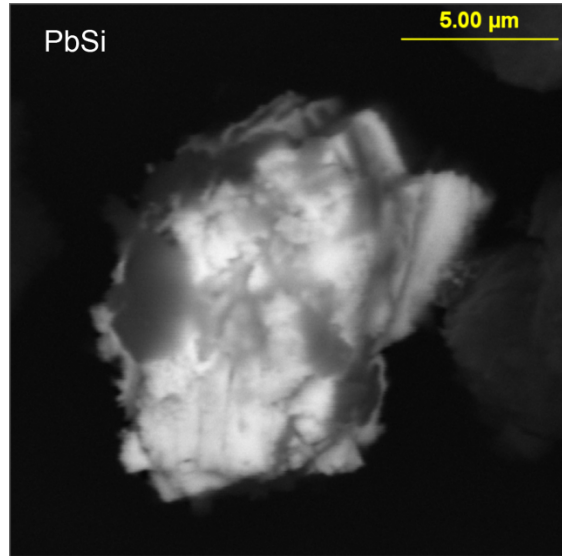
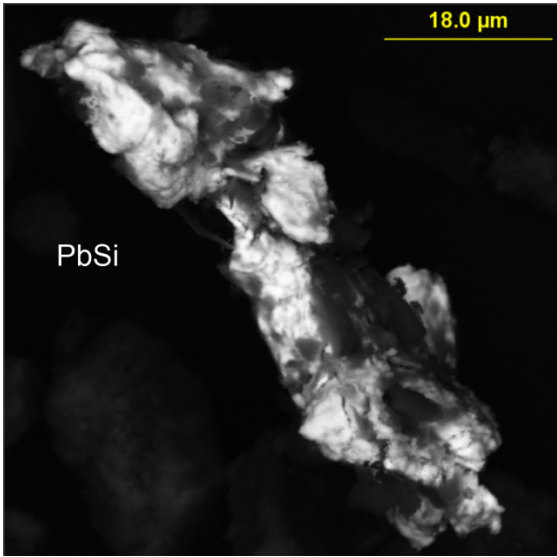
LEAD-BEARING SPHERULES



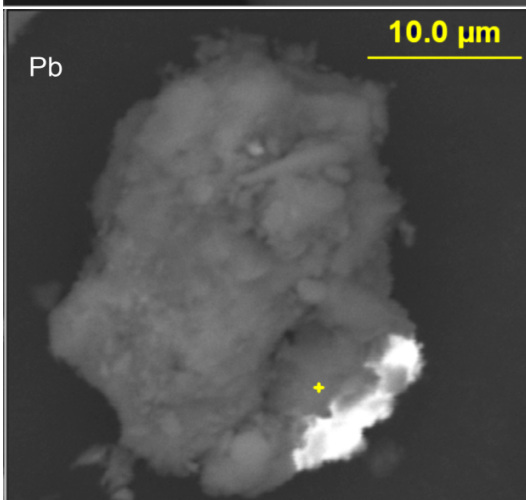
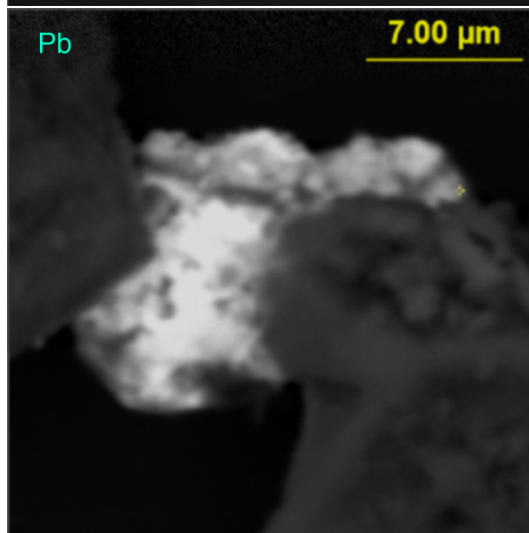
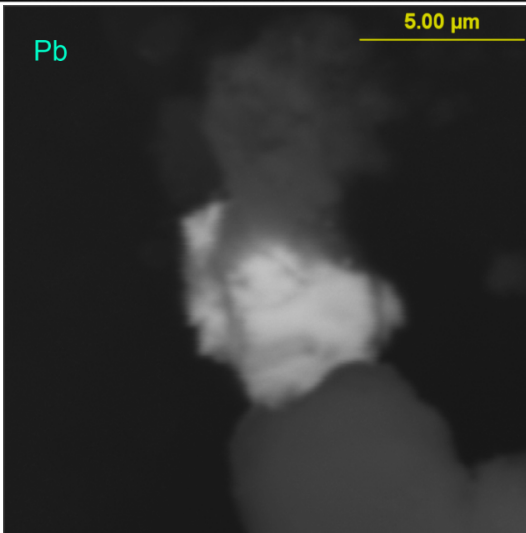
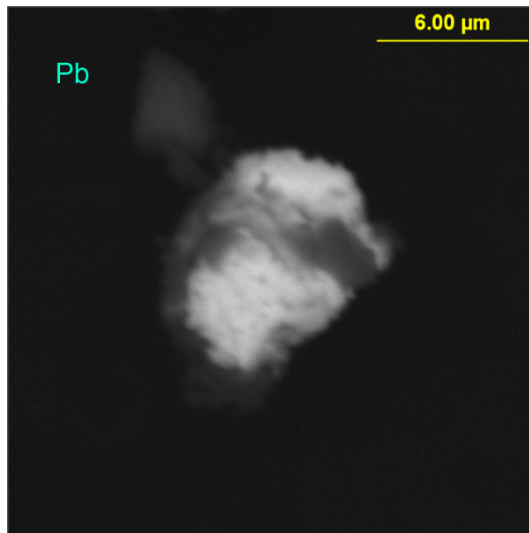
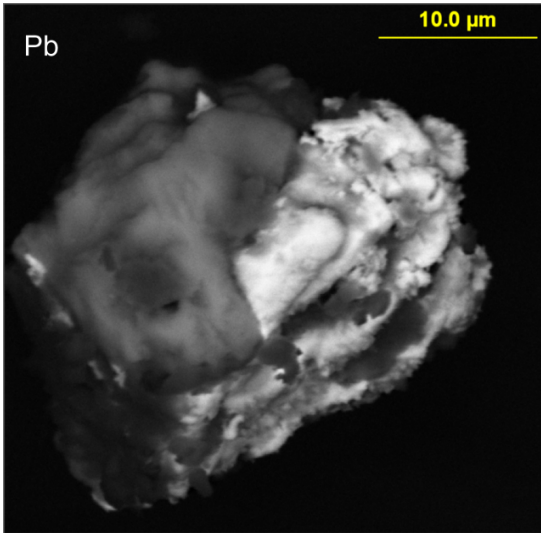
LEAD AND ARSENIC



LEAD AND TIN



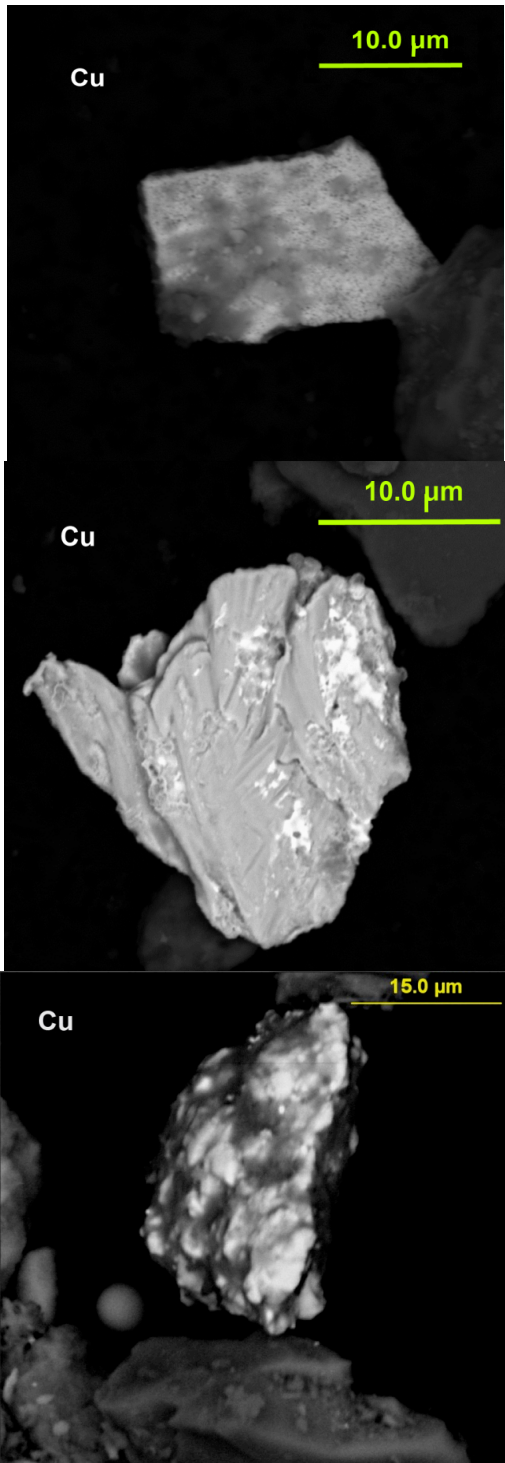
LEAD AND SILICON



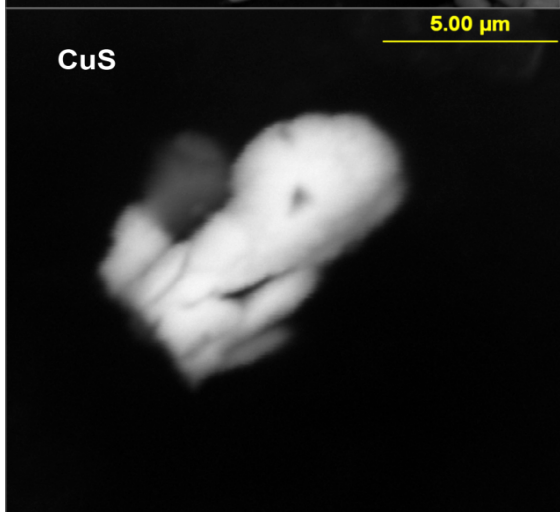
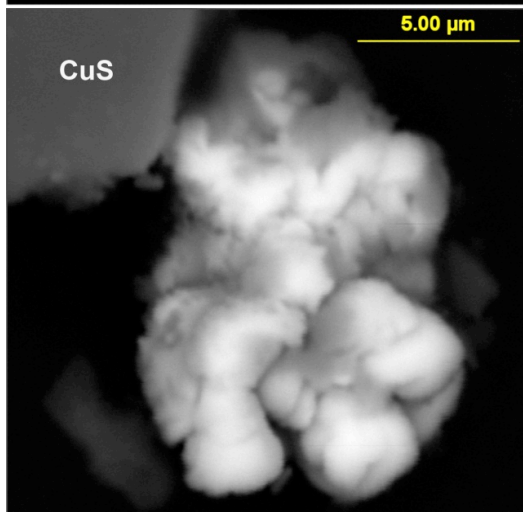
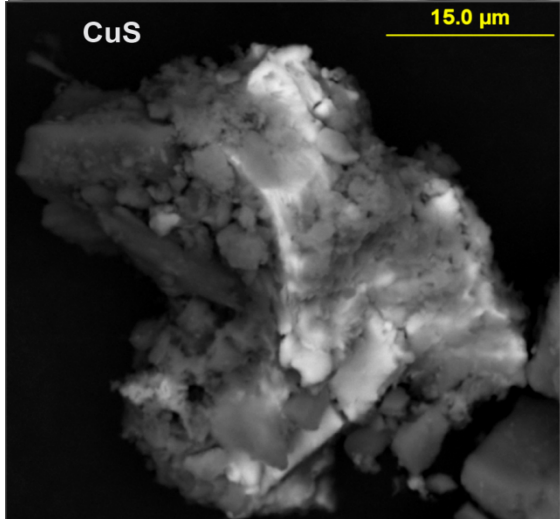
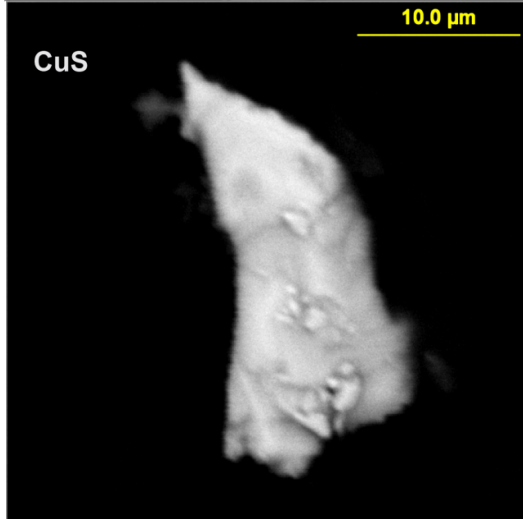
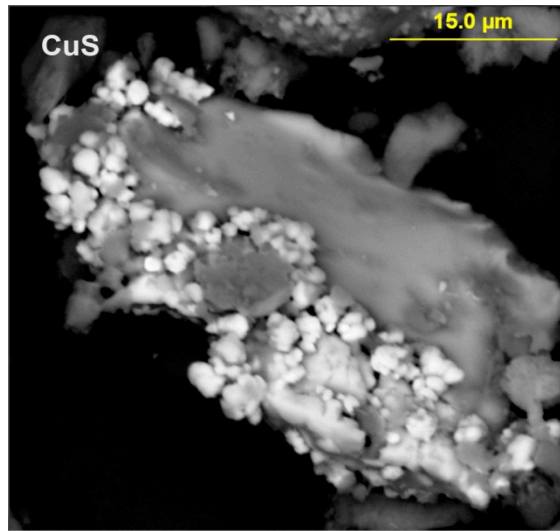
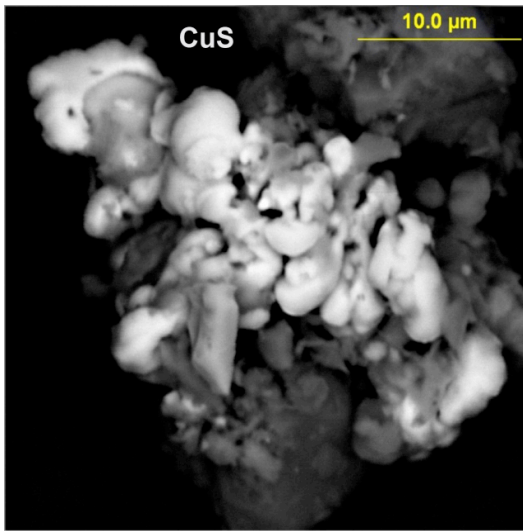
LEAD IRREGULAR SHAPE

APPENDIX B

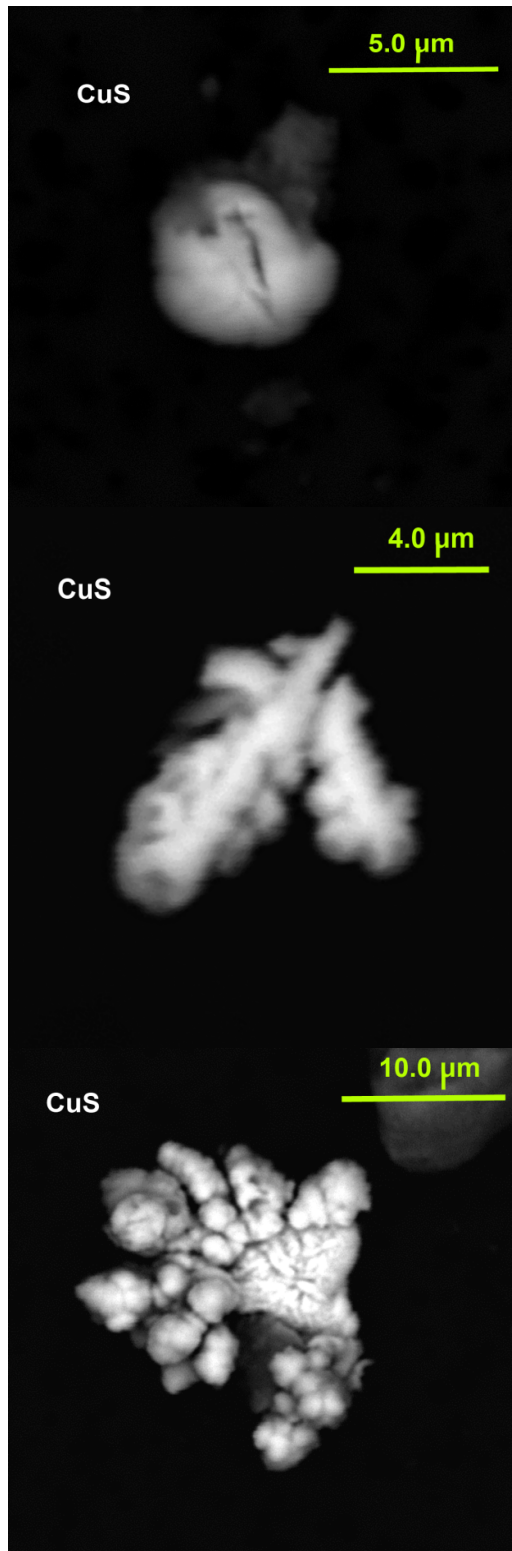
ELECTRON MICROGRAPHS OF VARIOUS COPPER-BEARING PARTICLES PRESENT IN
LANZHOU STREET DUSTS



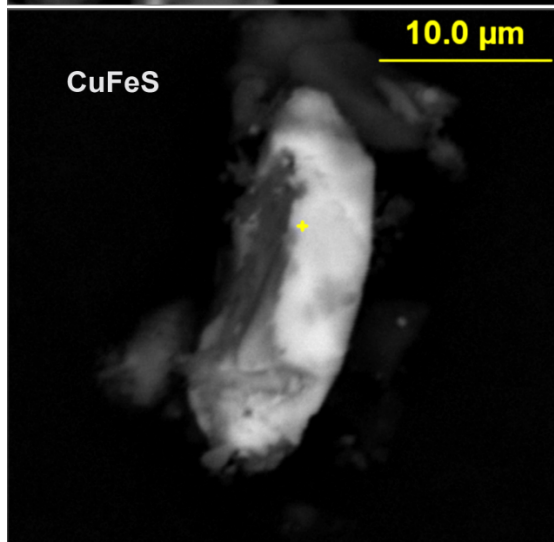
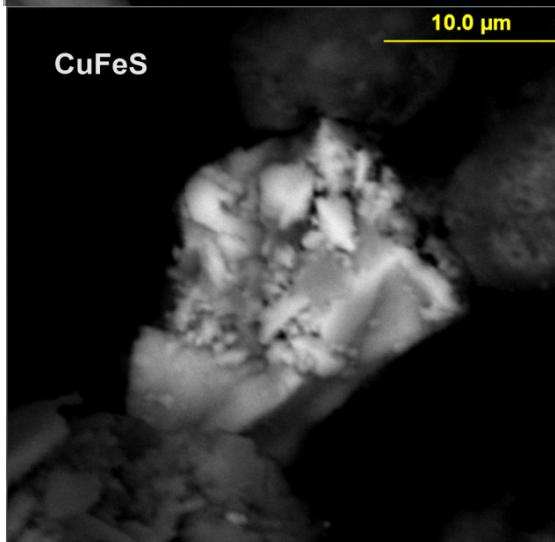
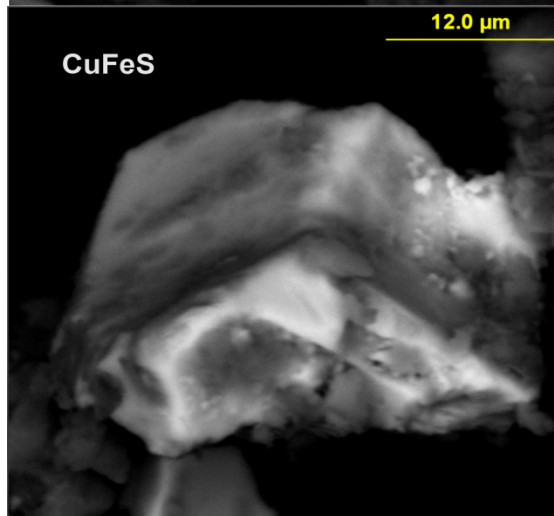
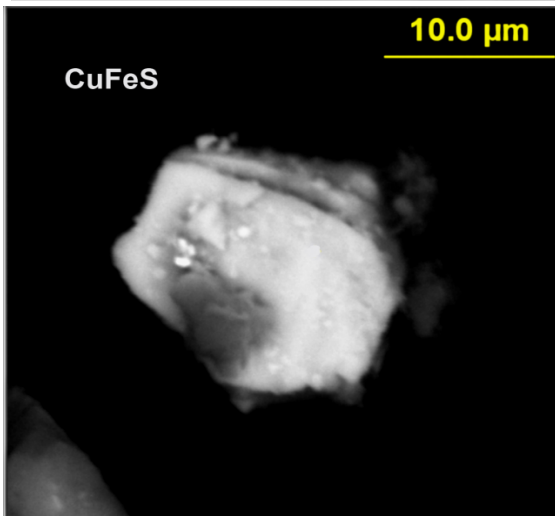
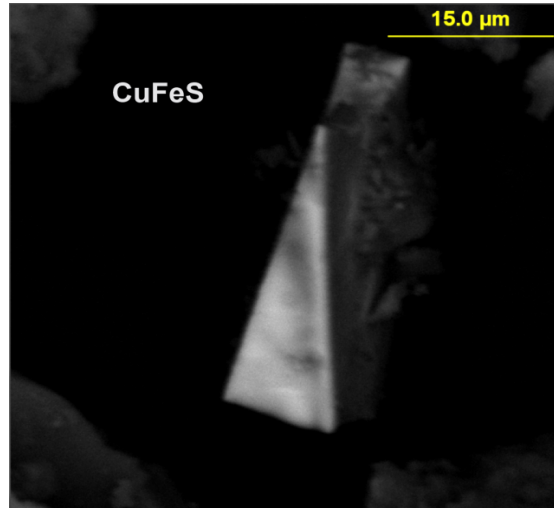
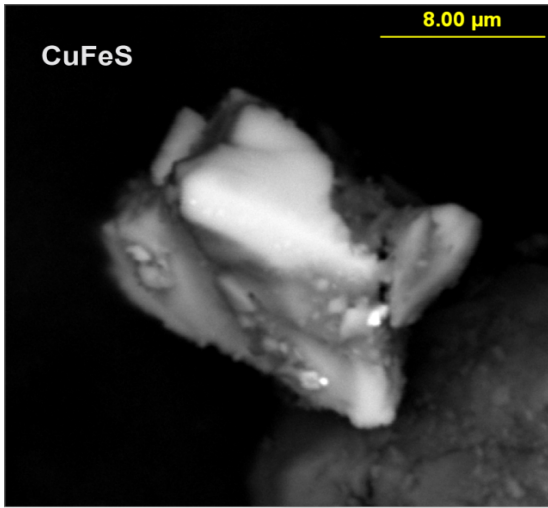
COPPER METAL



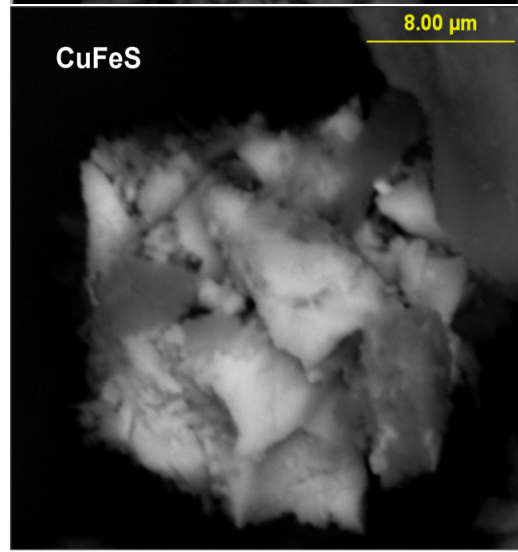
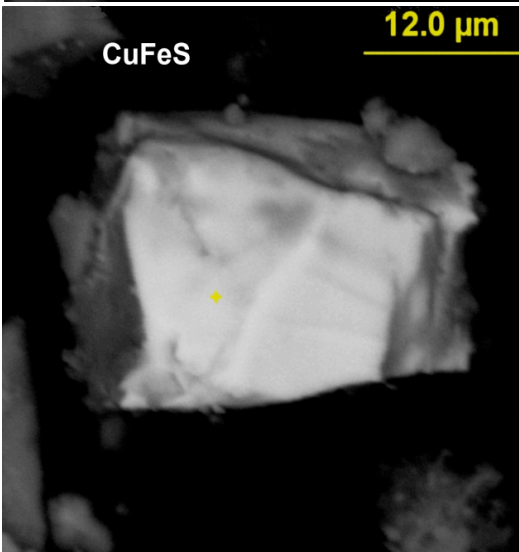
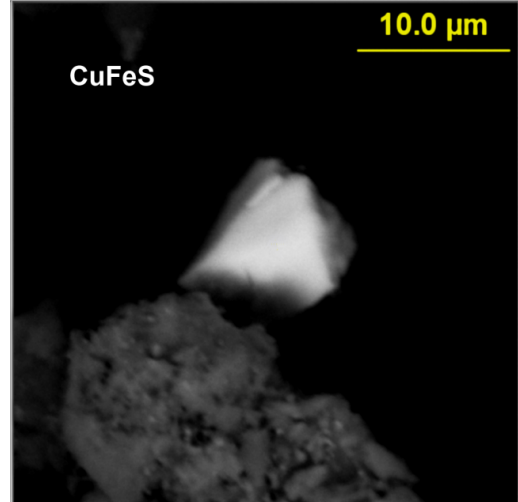
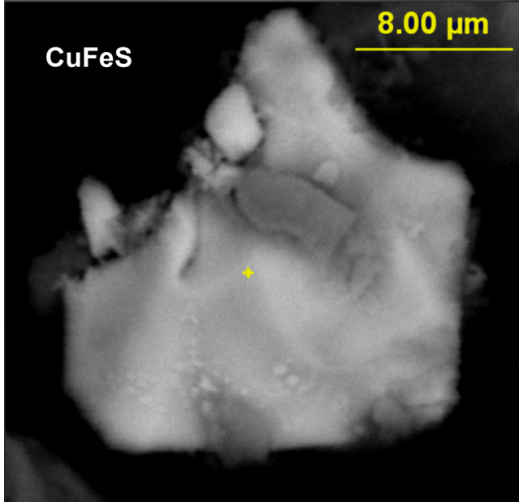
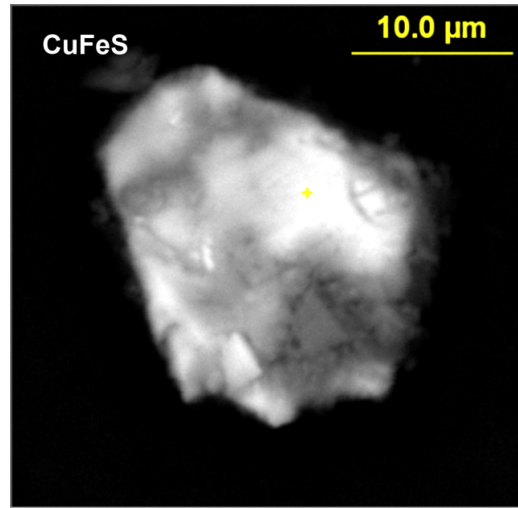
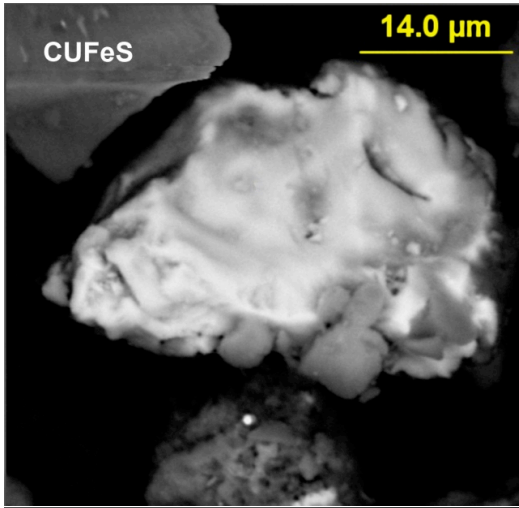
COPPER SULFATE



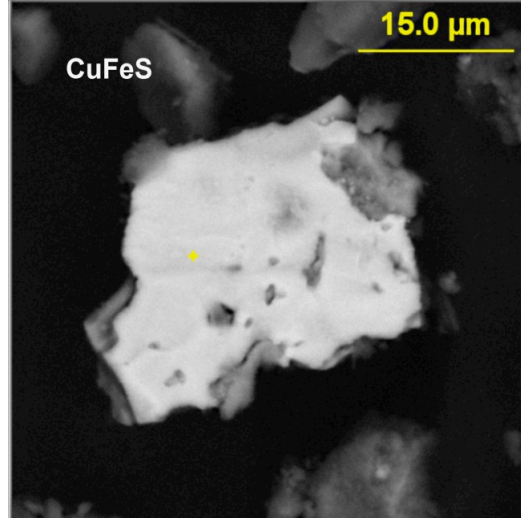
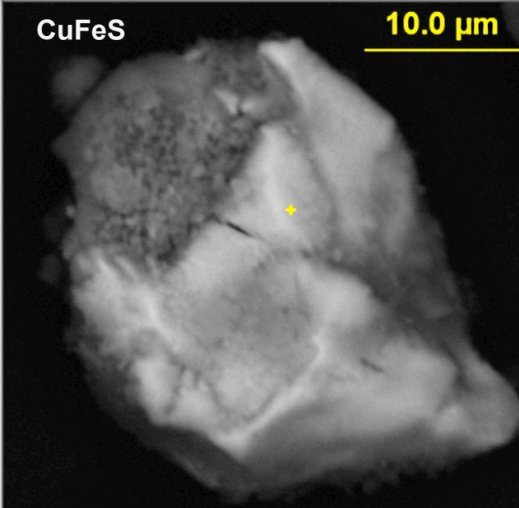
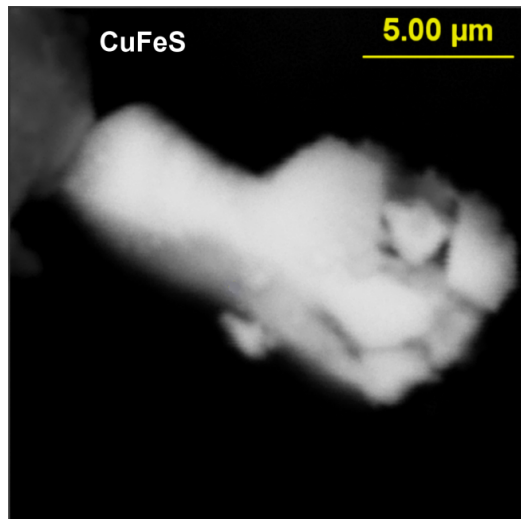
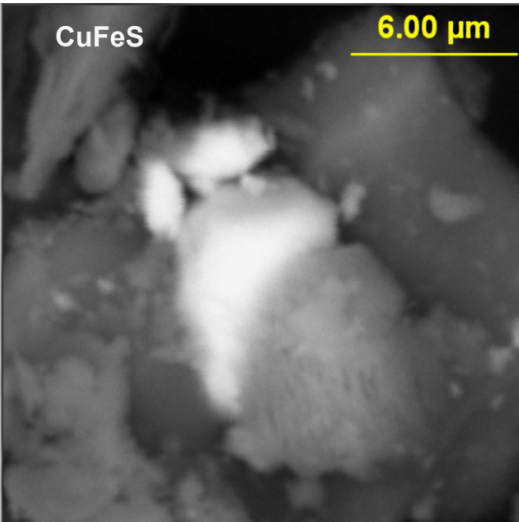
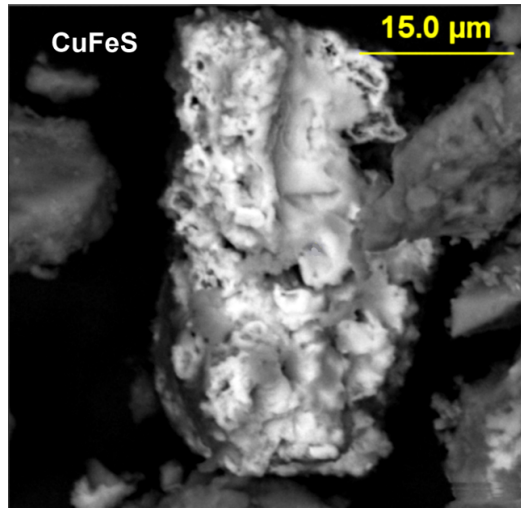
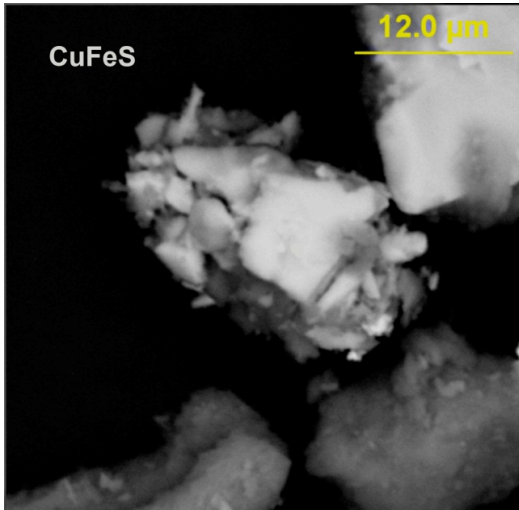
COPPER SULFATE



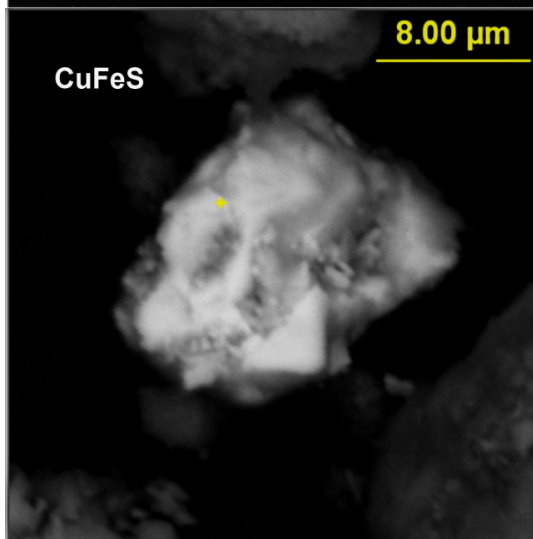
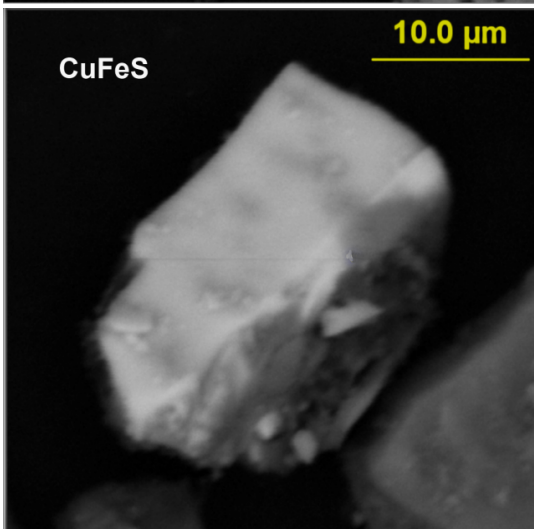
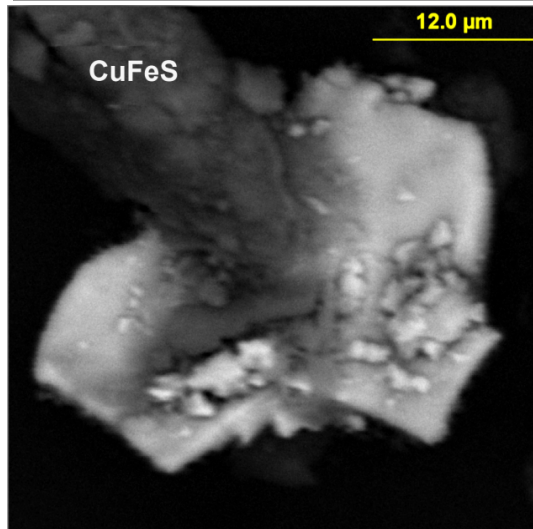
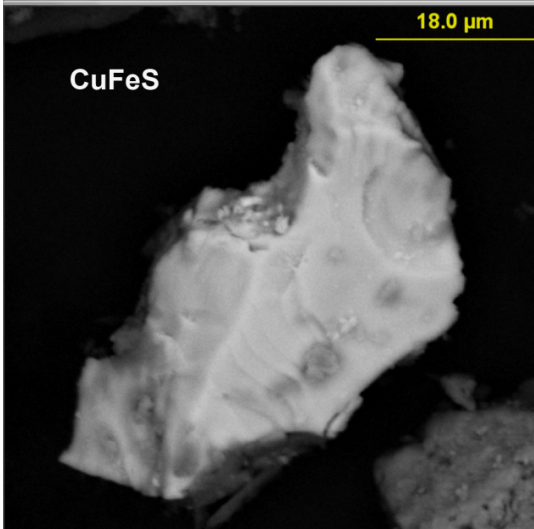
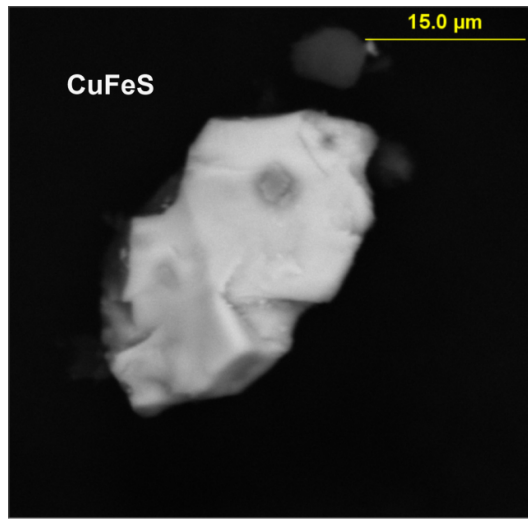
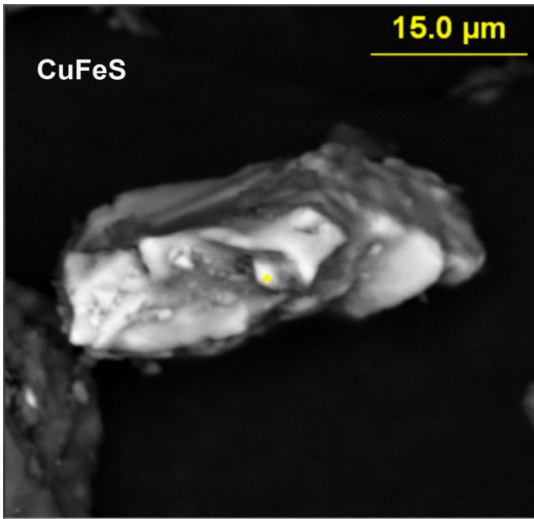
CHALCOPYRITE



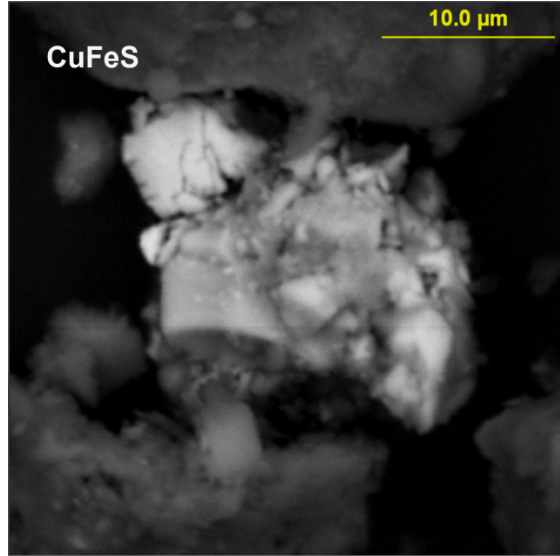
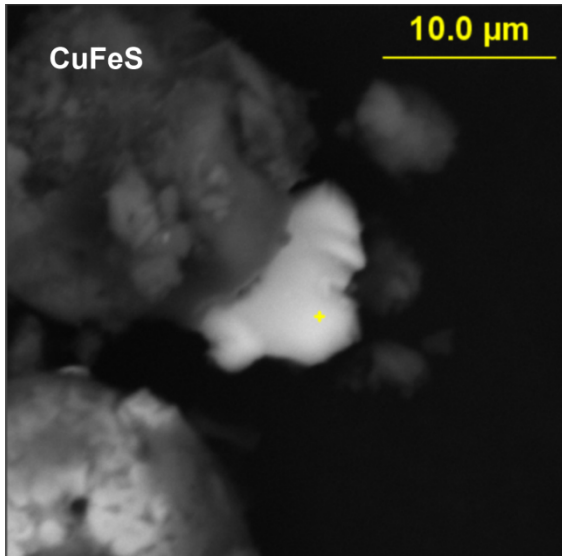
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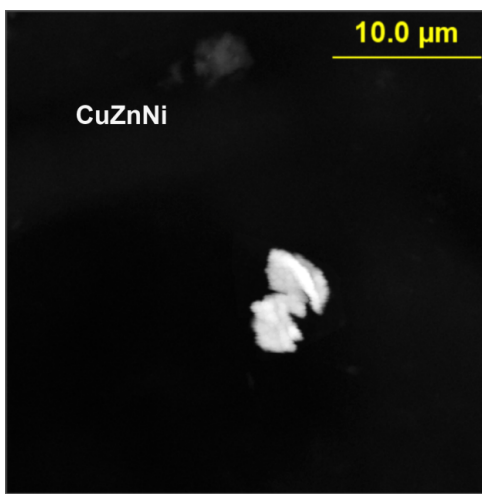
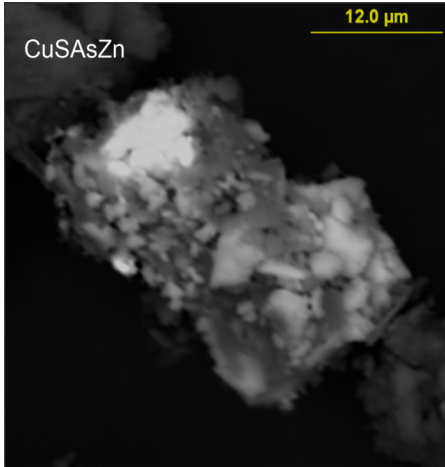
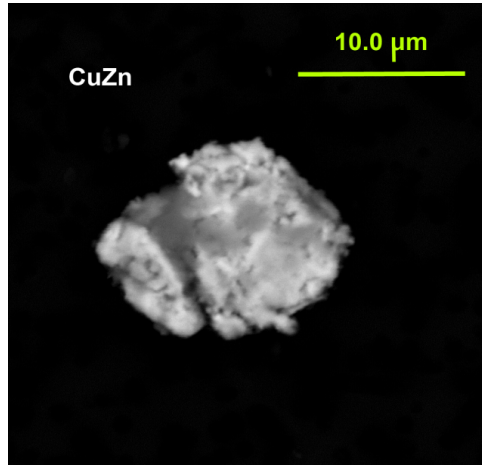
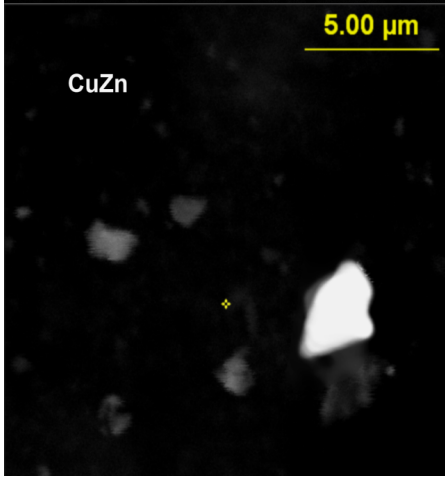
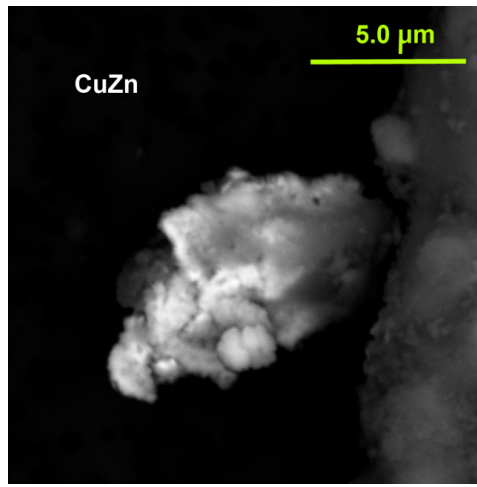
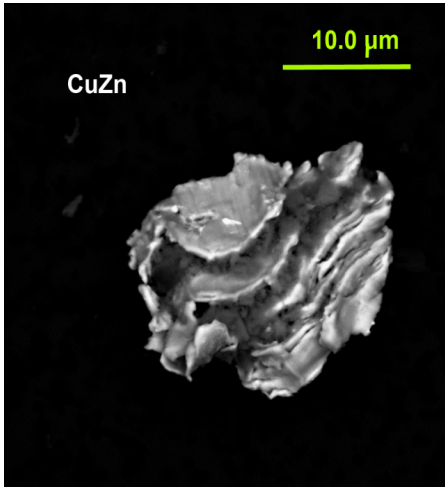
CHALCOPYRITE



CHALCOPYRITE

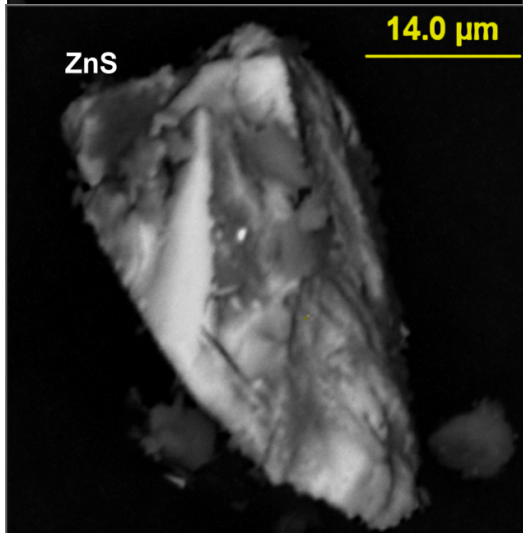
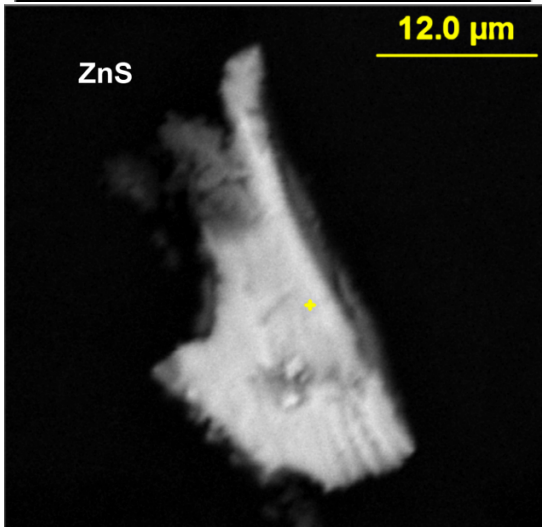
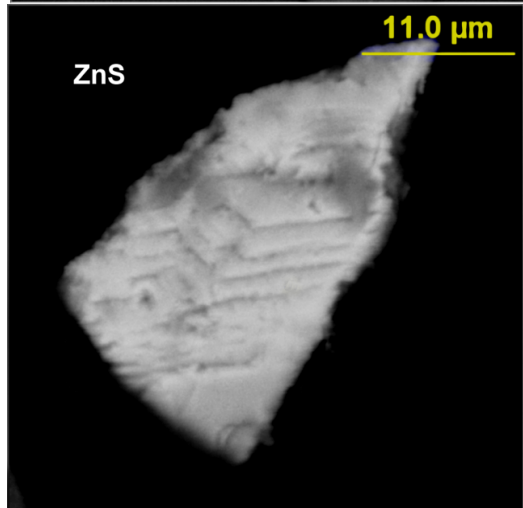
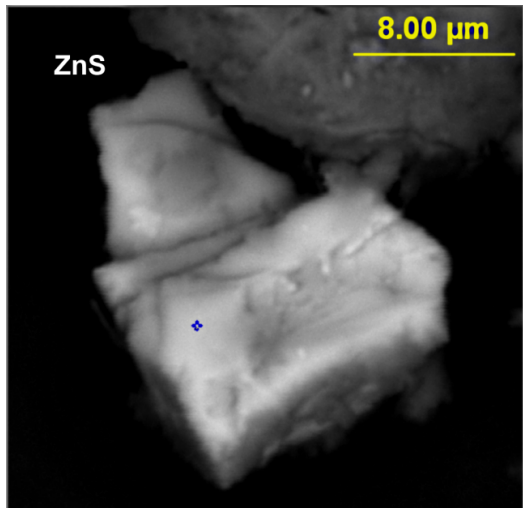
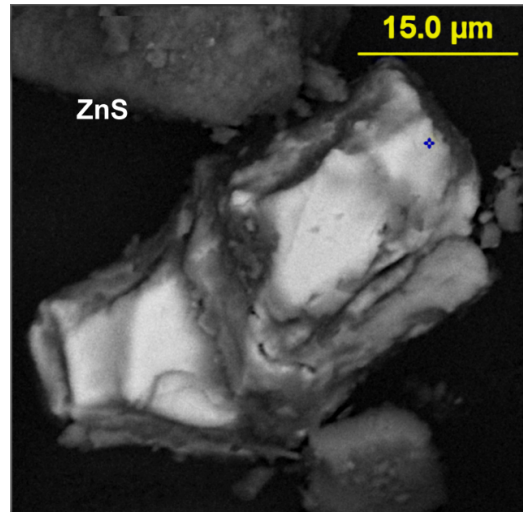
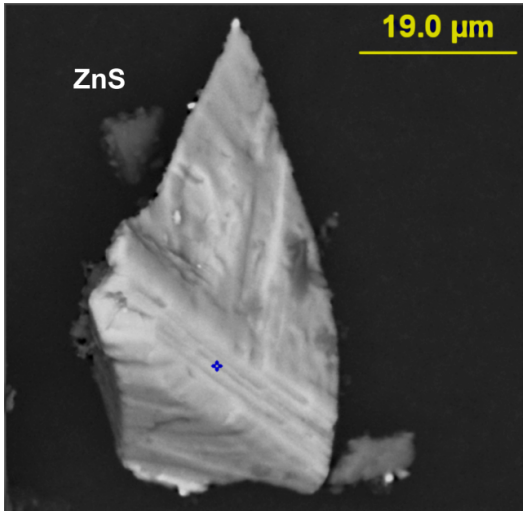


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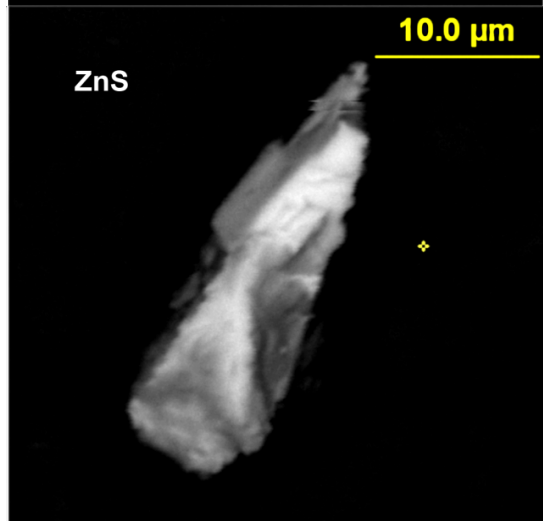
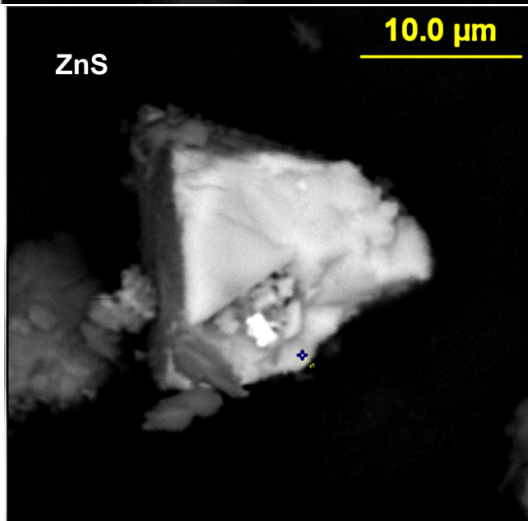
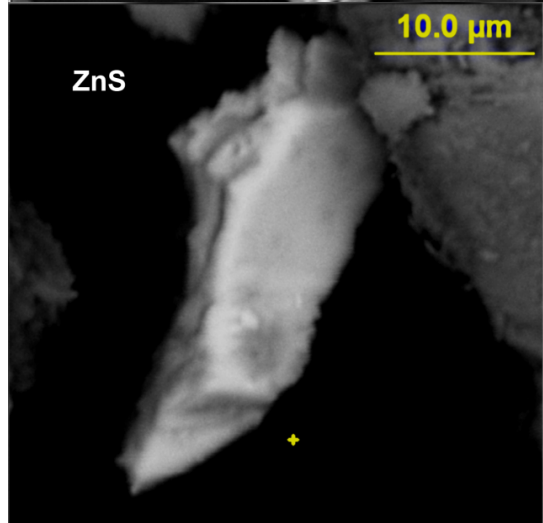
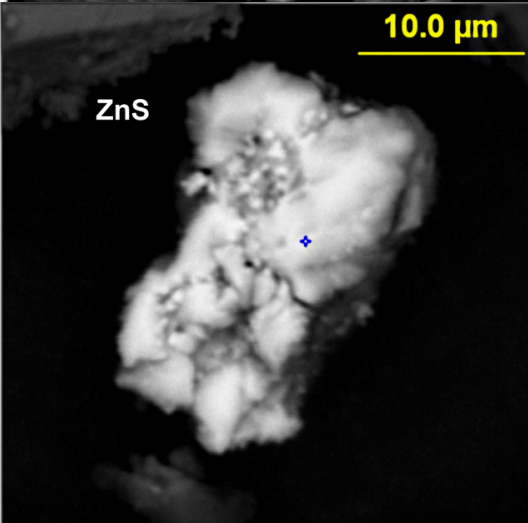
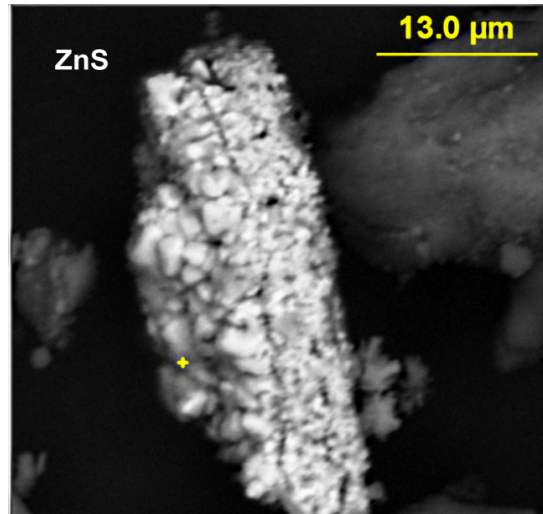
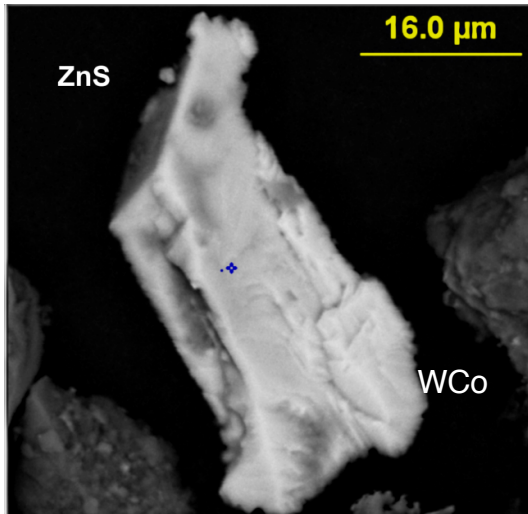


COPPER AND ZINC

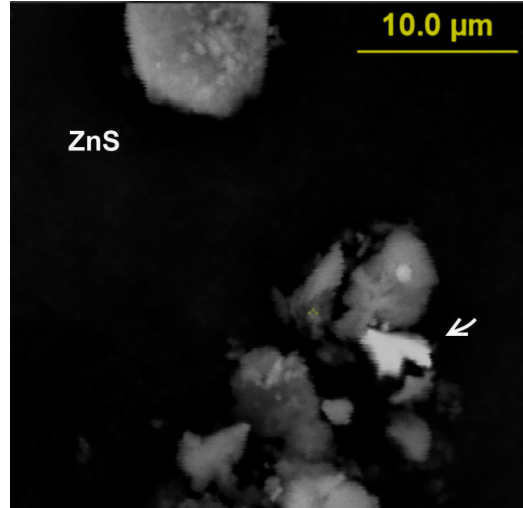
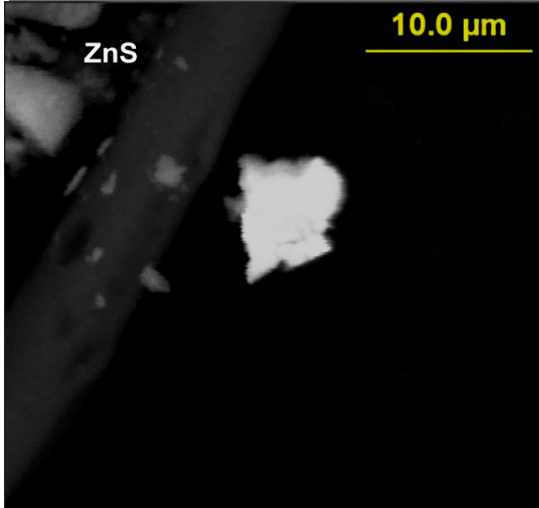
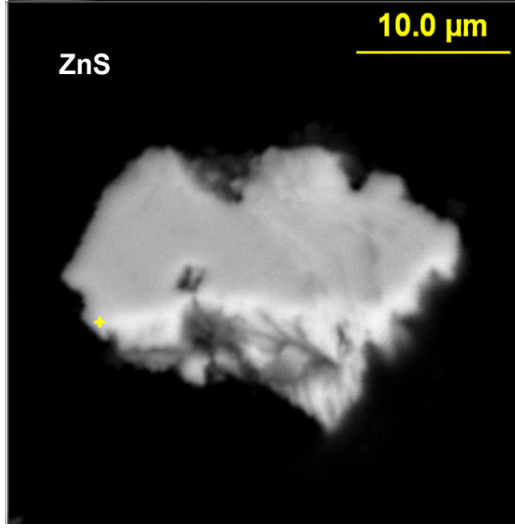
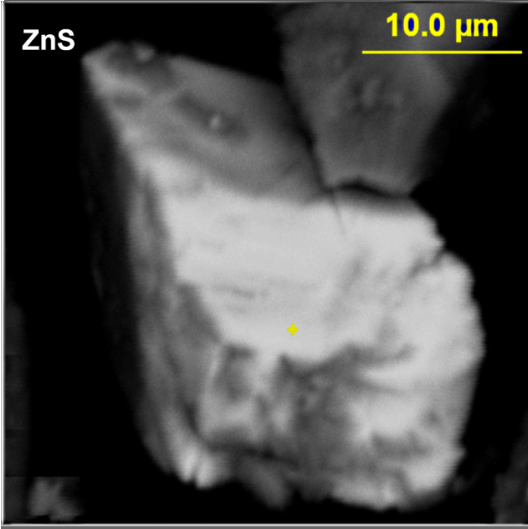
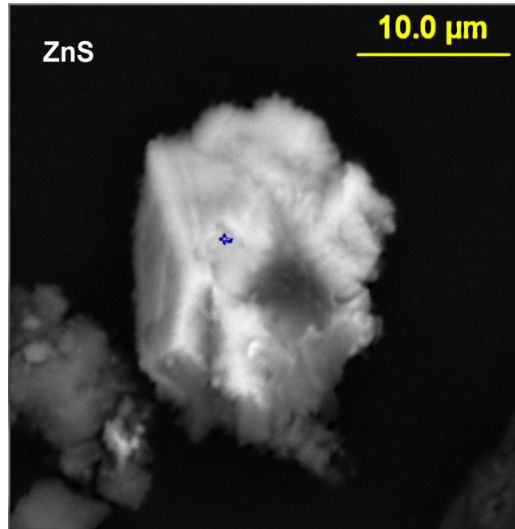
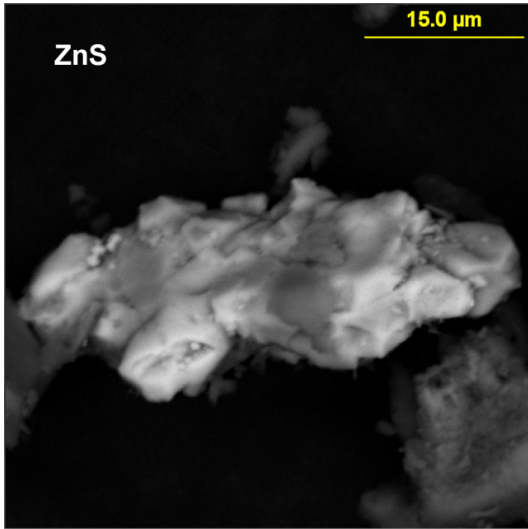
APPENDIX C
ELECTRON MICROGRAPHS OF VARIOUS ZINC-BEARING PARTICLES PRESENT IN
LANZHOU STREET DUSTS



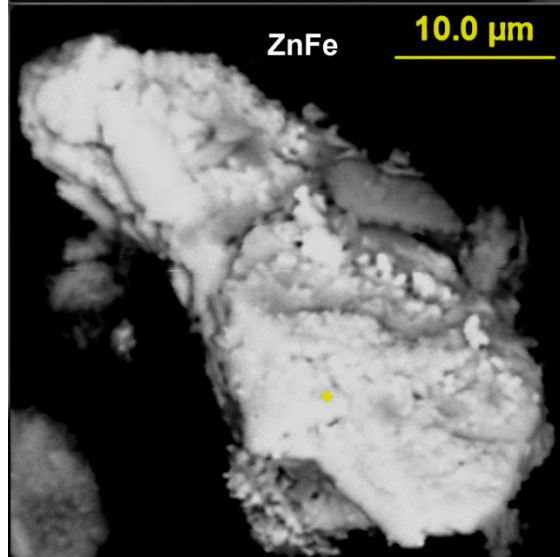
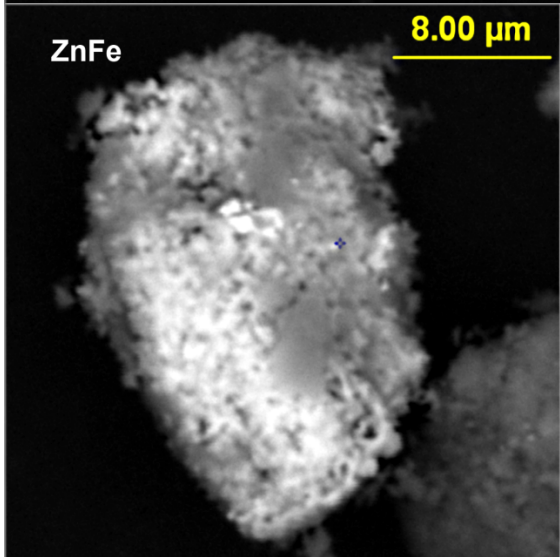
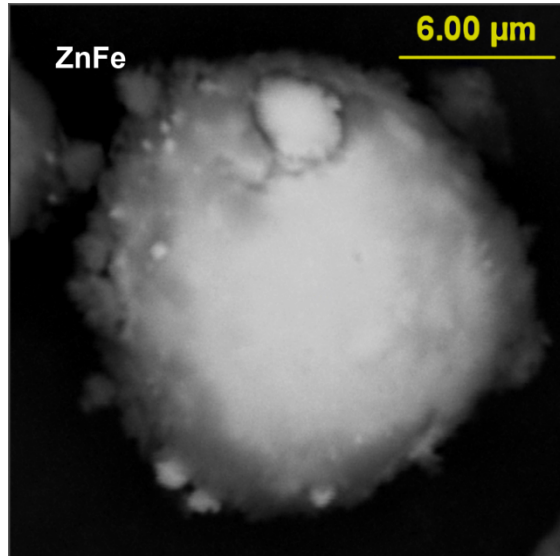
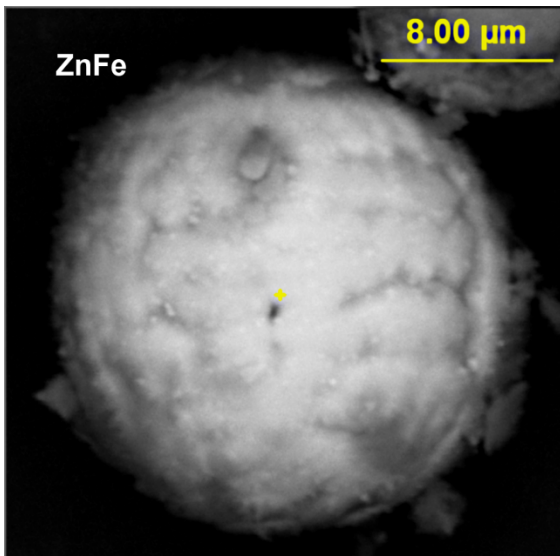
ZINC AND SULFUR (SPHALERITE)



ZINC AND SULFUR (SPHALERITE)



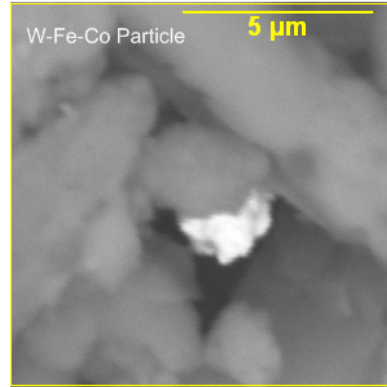
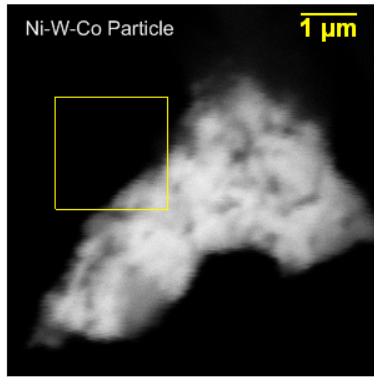
ZINC AND SULFUR (SPHALERITE)



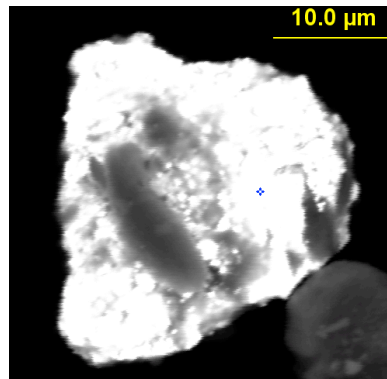
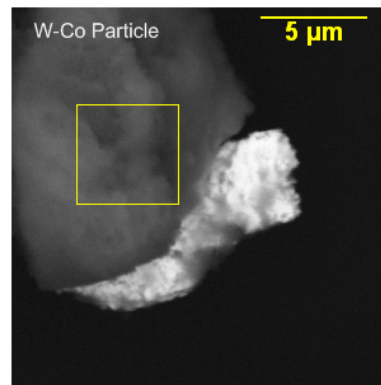
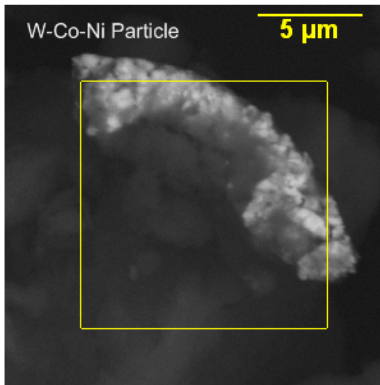
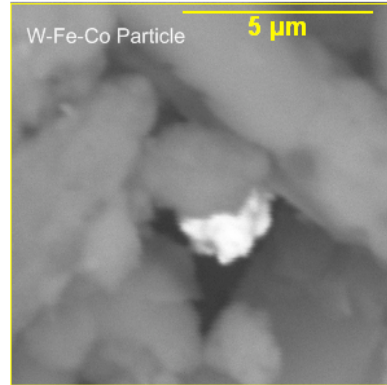
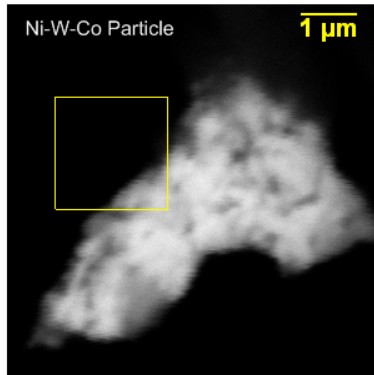
ZINC AND IRON

APPENDIX D

ELECTRON MICROGRAPHS OF VARIOUS TUNGSTEN-BEARING PARTICLES PRESENT IN
LANZHOU STREET DUSTS

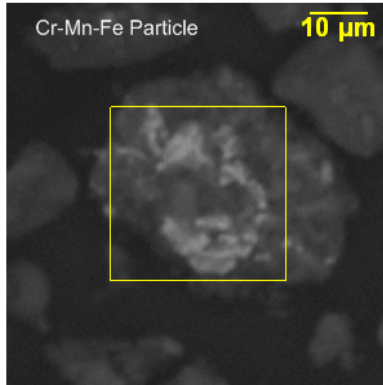
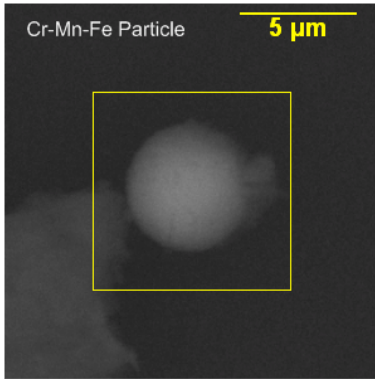
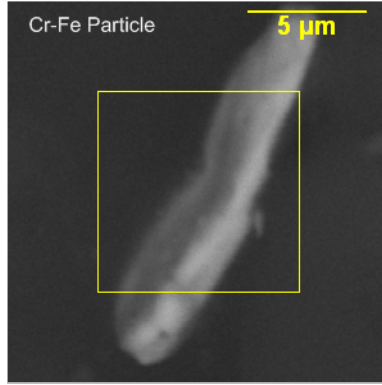
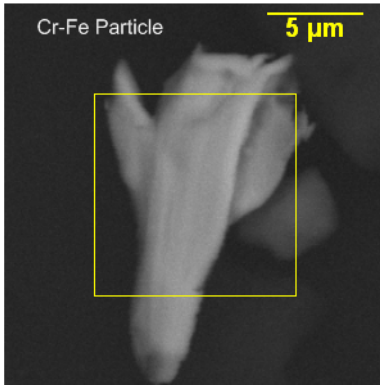
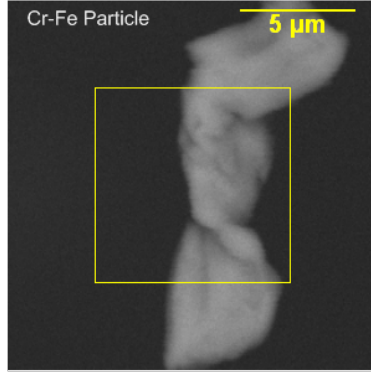
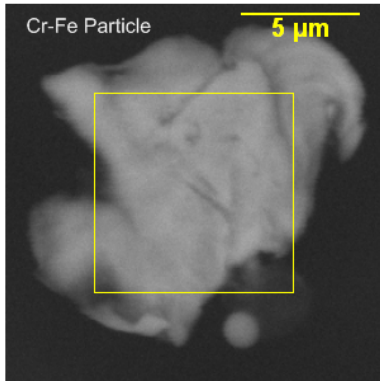


TUNGSTEN PARTICLES



CEMENTED TUNGSTEN CARBIDE

APPENDIX E
ELECTRON MICROGRAPHS OF VARIOUS CHROMIUM-BEARING PARTICLES PRESENT IN
LANZHOU STREET DUSTS



IRON CHROMATE

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Major Hiett was awarded a Bachelor of Science degree in Exercise and Sport Science from the University of Utah in 1996. He then obtained a Bachelor of Arts degree in Mathematics from Cameron University in 2002.