Automated Mineralogy of Mine Tailings Using Mineral Liberation Analysis

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Abstract
The Mineral Liberation Analyzer (MLA), an automated mineralogy software suite, uses X-ray mapping in conjunction with scanning electron microscopy for purposes of particle characterization. Although MLA was originally developed for metallurgical testing, environmental applications are growing due to its ability to characterize a variety of materials including fine-grained mine waste such as tailings and contaminated soil. Using the software, mineral grains are differentiated and identified. It allows for particle-by-particle quantification and provides information on each particle's chemical composition, particle size, and shape. Complex particles with multiple mineralogical phases can be broken down into their components and identified. Bulk mineralogy or specific phases of interest can be targeted, and relative percentages of mineral phases present can be determined for quantification purposes. In this research, MLA is used to quantitatively assess the mineralogy of mine tailings from the former New Calumet Pb-Zn Mine. Mineralogy has a significant impact on the bioaccessibility of Pb, which refers to its potential to interact with and be absorbed by an organism. Bioaccessibility testing on weathered PbZn tailings from New Calumet mine show an indirect correlation between % of Pb that is bioaccessible and the total concentrations of Pb, which indicates other factors such as mineralogy and particle size are playing a role that can be assessed using SEM-MLA.

Key Words: automated mineralogy, lead, bioaccessibility

Introduction
Mineralogy plays a significant role in the fate and transport of hazardous elements. The purpose of this study is to explore the possibility of connecting bioaccessibility testing with automated mineralogy to answer questions regarding the mineralogical controls on Pb bioaccessibility from tailings material at the former New Calumet Mine in Quebec, Canada.

Automated mineralogy
The FEI Mineral Liberation Analyzer (MLA) is an automated quantitative mineralogy software program based on scanning electron microscopy. It was originally designed for the metallurgical industry, as mineral processing operations require detailed characterization of the ore and plant feed to optimize metal recovery (Fandrich et al. 2007; Pirrie and Rollinson 2011). A number of measurement systems using scanning electron microscopy have been developed to characterize polished particle sections, but Scanning Electron Microscope (SEM)-based systems allowed for automation and the ability to obtain a statistically significant set of data in a relatively short period of time (Fandrich et al., 2007). The MLA analyzes thousands of particles in multi-hour runs to determine mineralogy as well as particle shape, size, and texture. In the past ten years, modern SEM-based quantitative mineralogy tools have improved significantly, providing decreased measurement times, increased computing power, and sophisticated imaging that allows for analysis of very fine-grained material (Pirrie et al. 2004). Automated SEM analysis reduces operator dependence and allows for the collection of quantitative data that is reproducible (Pirrie et al. 2004). There are two major automated SEM systems, MLA and QEMSCAN (**Q**uantitative **E**valuation of **M**inerals by **SCAN**ning electron microscopy), both owned by FEI Company.

How does it work?

The basis of liberation analysis using MLA is back-scatter electron imagery (BSE) and the generation of high quality sample images. Using SEM imagery, a stable and low-noise back-scatter electron image is collected under a specific set of measurement conditions. Each mineral in the sample should have a defined BSE grey value related to its average atomic number. A particle may host multiple phases including primary forms or secondary minerals produced through weathering, oxidation, precipitation and other transformations. The MLA software can delineate, differentiate, and separate composite particles into different mineral phases based on their homogeneous BSE grey levels and particle shape parameters (Gu 2003).

The MLA software has a number of measurement modes combining BSE analysis and the collection of characteristic X-ray spectra for chemical analysis. The measurement modes vary from a BSE based technique to a mostly X-ray analysis based technique (Gu 2003). In ores that have high BSE contrast, such as lead-zinc ores and copper sulphide ores, BSE image analysis may be the only tool necessary for mineral discrimination. Point X-ray analysis takes one X-ray point for each grey level region identified within a segmented particle or on a single-phase particle (Fandrich et al. 2007). The analysis is collected at the center of a phase. This method is the quickest, as it requires a small number of X-rays to determine the mineral composition of a particle. It can be applied to most samples (Gu 2003). Area X-ray analysis collects analyses over the entire phase area, and is useful in cases where poor BSE contrast can result in two phases not being delineated. X-ray mapping creates a grid over an entire particle and collects X-ray data at each grid point. This analysis method is very time intensive as many more analyses are collected to create a mineral map (Fandrich et al. 2007). Only X-ray analysis can provide elemental information to uniquely identify almost all the minerals in a sample, and it is more useful for fine-grained samples. QEMSCAN, MLA's sister software, operates in a method comparable to MLA's X-ray mapping mode, whereby spectra are measured at defined pixel spacings and each pixel is assigned a mineral name.

Each X-ray analysis acquired is then compared with a user-generated mineral database library of X-ray spectra known or anticipated to be present in the sample and assigned a mineral name or chemical composition grouping. In addition to modal mineralogy, textures, fabric, shape, and particle size are also analyzed.

Environmental Applications of Automated Mineralogy

The environmental applications of MLA have been limited to date, even though the software has great potential for the characterization of soil, sediments, tailings, and other metal-contaminated materials. QEMSCAN has been used to characterize tailings-contaminated sediments in the Fal Estuary of Cornwall, United Kingdom (Pirrie et al., 2003). The QEMSCAN and SEM analyses were combined with geochemical mapping to demonstrate that Sn, Cu, As and Zn are present as discrete, small (<6 µm) liberated grains of ore minerals from the area such as cassiterite, chalcopyrite, arsenopyrite and sphalerite. These small grains likely represent fine-grained mine tailings that were not captured during mineral processing due to historic poor recoveries. Mineralogical studies show that some sulphide grains have been oxidized and altered, releasing Cu, As and Zn in solution for potential uptake by plants and animals (Pirrie et al. 2003).

QemSCAN has also been utilized for forensic geoscience, providing mineralogical or phase composition of soil and other forensic evidence such as paint flakes, glass, and gunshot residues (Pirrie et al. 2009). The high spatial resolution of modern SEM instruments makes it possible to use this approach for fine-grained materials such as weathered tailings.

Case Study: Weathered tailings from the New Calumet Pb-Zn mine

The New Calumet Mine is located on Ile du Grand Calumet in Quebec, Canada, approximately 90 km northwest of Ottawa, Ontario. The New Calumet deposit has been classified as a metamorphosed massive sulphide deposit (Corriveau et al. 2007). The ore consists mainly of sphalerite and galena with smaller amounts of pyrrhotite, silver, gold, chalcopyrite, and tetrahedrite. Gangue minerals are quartz, feldspar, calcite, amphibole, pyroxene, biotite, orthoclase, plagioclase (anorthite and albite), titanite, goethite, and spinel (Jaggard 2012). The mine operated from 1943 to 1968 during which time 3.8 million tonnes of Pb-Zn ore grading 5.8% Zn, 1.6% Pb, 2.16 oz/tonne Ag, and 0.013 oz/tonne Au were extracted. Approximately 2.5 million tonnes of tailings remain exposed on site in multiple locations. In some areas, the tailings have been revegetated. Acid-base accounting has not been performed but at present drainage from the tailings is pH neutral, likely due to abundant carbonate in the host rock (Donkervoort 2007).

The concentration of Pb in the near surface tailings ranges from 1,740 ppm to 4,730 ppm. Although no guidelines for tailings exist, the industrial soil guideline for lead with regards to contaminated sites in Canada is 600 ppm and the residential soil guideline is 140 ppm (CCME, 2007). The property is privately owned and fenced, and human exposure is minimal. Although there is little risk to human health associated with the New Calumet tailings because of limited access, this case study provides an excellent opportunity to examine the linkages between the mineralogy of weathered Pb-rich tailings and the potential risk to human health should these materials be ingested.

Bioaccessibility is a term that refers to the potential of a substance to interact and be absorbed by an organism. In this study, the element of concern is Pb. Lead is an element that has the potential to cause toxicological harm to the body if excess is inhaled or ingested. Lead bioaccessibility is affected significantly by speciation. The most bioaccessible Pb compounds are Pb carbonates (ex: $PbCO_3$ – cerussite) and Pb oxides (ex: PbO), followed closely by Pb sulphates (ex: $PbSO_4$ – anglesite) and Pb sulphides (ex: PbS – galena) (Plumlee and Ziegler, 2007). Studies of Pb bioaccessibility in swine have shown that it can range from 5% for tailings material comprised primarily of galena (PbS) to 45% for soils where the majority of Pb is found as Fe-Mn-Pb oxides (Casteel et al. 2006). Characterization of mineralogy is an important factor in understanding the geochemical processes that control metal transport and bioaccessibility (Ostergren et al. 1999).

Methods

The goal of the sampling program was to collect representative samples from three tailings areas for geochemical, mineralogical, and bioaccessibility analysis. The focus was characterization of Pb-bearing minerals and bioaccessibility testing. Samples were taken from vegetated and non-vegetated tailings. Non-vegetated samples were taken of the top 5cm of material and vegetated samples were taken down to approximately 20cm to obtain root material including a variety of (immature) soil horizons.

Tailings samples were air dried and sieved into multiple particle size categories prior to analysis. The fraction sieved to <250 µm was utilized for gastric bioaccessibility testing and thin sections were prepared from splits of this particle size fraction. Sieved samples were mixed with an epoxy resin within a mold; the cast sample was then cut to a thickness of 35 µm, polished, and mounted with no use of water or heat during preparation of the thin sections to prevent chemical alteration of tailings material. Thin sections were carbon coated and analyzed at Queen's University using the FEI Quanta MLA 650 FEG Scanning Electron Microscope.

Total Element Chemistry

Total element geochemistry on the tailings samples was determined at the USGS laboratory in Denver, CO. Samples were analyzed by ICP-MS (Inductively Coupled Plasma Mass Spectrometry) for major, minor and trace elements. The apparatus used at the USGS is the ICP-MS, Perkin Elmer Elan 6000. The reagents used throughout the multi-acid digestion include:

- Deionized (DI) water
- Hydrochloric acid (HCL), conc. reagent grade (37%)
- Nitric acid (HNO_3), conc. reagent grade (70%)

- Perchloric acid ($HClO_4$), conc. reagent grade (70%)
- Hydrofluoric acid (HF), conc. reagent grade (48%)
- 1% HNO_3: dilute 10 mL conc. HNO_3 to 1000 mL with DI water
- Hydrogen peroxide (H_2O_2), solution (30%)

Bioaccessibility Testing

In vitro bioaccessibility tests (IVBA) are physiologically-based extraction tests designed to estimate the bioaccessibility of elements along ingestion exposure pathways (Morman et al. 2009). Simulated gastric fluids were exposed to tailings samples sieved to <250µm. The <250µm samples were selected for gastro-intestinal extractions since this is the fraction most likely to adhere to the hands of children and be ingested. The gastric fluid used during this study is a standard method by Drexler and Brattin (2007) and is approved by the US Environmental Protection Agency to measure bioaccessibility and estimate relative bioavailability of Pb. The gastric fluid is produced using concentrated HCl, glycine solution and deionized water. The solution is warmed in a water bath until it reaches 37°C. The pH of the solution is adjusted to a value of 1.50 ± 0.05. After placing the sample material (solid-to liquid ratio of 1:100 – 1 g in 100 mL of solution) into a new acid-washed bottle, the simulated gastric fluid was added and the bottles were placed in a MaxQ incubator shaker unit to provide a constant temperature of 37^{o}C and constant agitation. After one hour, 10 mL of solution was removed and filtered into a new acid-washed bottle. The filtered solutions were stabilized with HNO_3 until analysis could be completed (Drexler and Brattin 2007). The extracted solutions were analyzed by inductively coupled plasma-mass spectrometry (ICP-MS) for trace elements. To obtain the % bioaccessibility, the amount of material leached is divided by the total concentration and multiplied by 100.

Results

Bioaccessible Pb concentrations in the <250µm fraction of tailings sampled from Calumet Mine range from 23 to 69% Pb (Jaggard 2012). The results show that there is not a direct correlation between total Pb concentration in ppm and total % bioaccessibility.

The primary mineral hosting Pb in the Calumet mine tailings is galena. Investigation of galena grains on the SEM resulted in observation of alteration rims and dissolution textures surrounding a number of galena grains. Typically, the altered rims were more prevalent if the galena grain was on the edge of a host grain and less altered (or not altered at all) if found within a host grain. Using more advanced techniques such as synchrotron-based µXRD (Jamieson et al. 2011), identification of these rims confirmed the presence of cerussite with lesser occurrences of hydrocerussite (see Figure 1, below). It is likely that the amount of galena and cerussite differs in each sample analyzed. Cerussite is much more bioaccessible then galena in gastric fluids (Ostergren et al. 1999), suggesting that the samples with higher % bioaccessible Pb perhaps have more cerussite than galena.

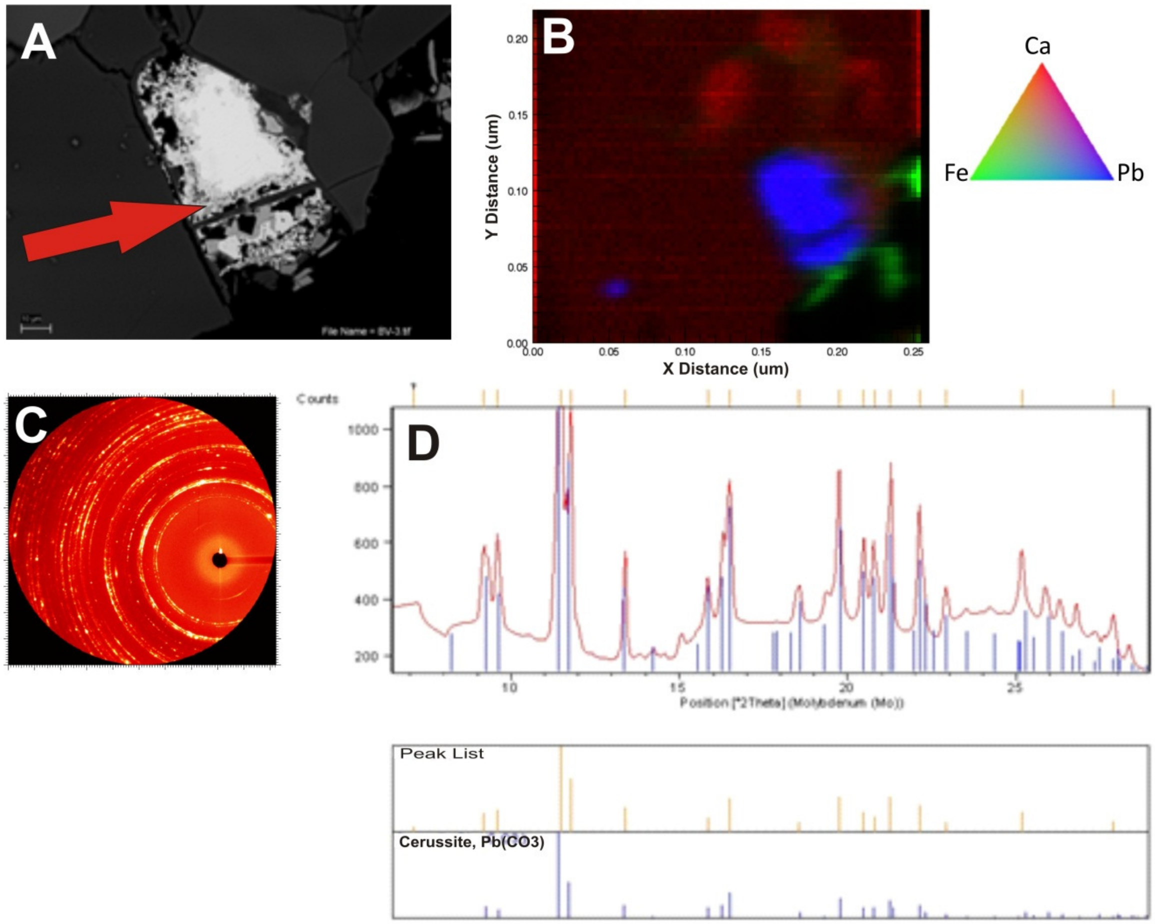

Fig. 1. Weathered galena grain from near-surface tailings at the New Calumet mine. A. BSE image showing galena core with rim of secondary alteration products. Arrow points to spot analysed by synchrotron-based microXRD. B. Element map of the same galena grain combining Fe (green), Ca (red) and Pb (blue). Galena is bright blue and the alteration rim is less intense blue. C. Two-dimensional microXRD pattern corresponding to spot on alteration rim indicated by arrow in A. Smooth arcs indicate that the alteration product is nanocrystalline. D. One-dimensional microXRD pattern generated by integrated the information in C. Peaks correspond well to the reference pattern for cerussite.

Mineralogical Controls on Bioaccessibility using Automated Mineralogy

Automated mineralogical analysis on the bioaccessibility tailings samples is ongoing as part of the lead author's master's research. MLA provides detailed information not just on mineralogy, but also factors that control bioaccessibility such as particle size, texture, and degree of liberation (Ruby et al. 1999). There are some challenges presented with the analysis of the New Calumet samples, including quantifying Pb and S due to peak overlap, and quantification of carbon due to the carbon coating on samples. In addition, cerussite is typically present as small rims on some, but not all, galena grains. Synchrotron-based analysis methods have been utilized with these samples to characterize galena and cerussite, but this analysis method does not provide the quantitative mineralogy that answers the mineralogical questions brought up by the bioaccessibility results. The challenges of characterizing metal-bearing phases from mine waste have been successfully dealt with in the past (Miler and Gosar 2010) through careful comparison of atomic ratios between heavy metals (such as Pb) and oxygen. The challenges of distinguishing galena and cerussite, both Pb-bearing minerals, have been largely resolved with careful development of a standard reference library within the MLA software and use of X-ray mapping of Pb-bearing grains.

Preliminary results of the samples with the highest and lowest bioaccessibility show a complex interaction of particle size, liberation of Pb-bearing minerals, and cerussite/galena ratios. The sample with the highest bioaccessibility, GD-VEG1 (bioaccessibility = 69% Pb) is finer grained than sample MS-nonVEG (lowest, bioaccessibility = 23% Pb). Texturally the two samples are very different. MS-BULK is made up of much larger, more discrete particles, as seen in a side-by-side comparison of MLA results in Figure 2. GD-VEG1 contains many thousands more particles, and Pb-bearing minerals are usually found in loosely cemented combination particles, not locked within grains as in sample MS-nonVEG (Figure 2). The Pb-bearing particles are much smaller in sample GD-VEG1. Smaller particles have a larger surface area and are more leachable and bioaccessible (Ruby et al. 1999), which may explain why GD-VEG1 is more bioaccessible while having a lower total Pb content than MS-nonVEG.

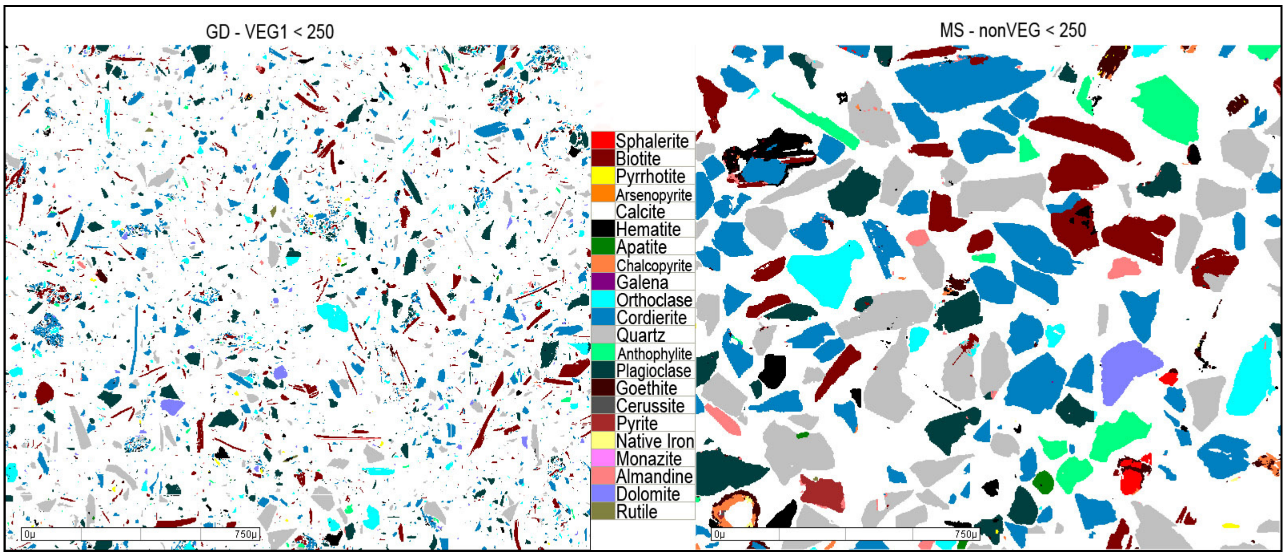

Fig. 2. Comparison of GD-VEG1 <250 µm (left, highest bioaccessibility) and MS-nonVEG <250 µm (right, lowest bioaccessibility) at the same scale.

Conclusions and Future Research

Preliminary results show that MLA has the potential to answer a number of questions regarding the mineralogical controls on Pb bioaccessibility in the New Calumet Mine Tailings. Data from the MLA software can provide very detailed information on liberation, particle size, and particle shape of each sample. The goal of future research is to determine what factors contribute to the differing total % Pb bioaccessibility between all six bioaccessibility samples.

Automated mineralogy can be applied to a number of mineralogically-based issues in mine waste management, including assessment of the relative proportion of potentially acid-generating sulfide minerals and neutralizing phases, and the variation of these from sample to sample. This requires, however, accurate identification of the minerals present or anticipated to be present in order to develop an appropriate mineral library. Thus a combination of careful microscopy and microanalytical techniques combined with automated mineralogy is optimal. The most powerful contribution of automated mineralogy is its ability to ensure that results are representative of a large quantity of mine waste material. Since many individual particles in multiple samples can be characterized relatively quickly, this approach is particularly useful for prediction.

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