Soil Lead Mineralogy by Microprobe: An Interlaboratory Comparison

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Introduction

While the potential hazard of lead (Pb)-bearing soils to children through accidental ingestion is well-known, the estimation of appropriate cleanup levels is based on application of the U.S. Environmental Protection Agency (EPA) Uptake Biokinetic Model (1). The bioavailability factor (e.g., that portion of the ingested Pb burden that is absorbed into the systemic circulation) used in the model is typically assumed to be 30% for Pb-bearing soils (1). However, recent studies of blood-Pb levels in children from mining communities (2, 3) and studies of Pb bioavailability in laboratory animals (4) suggest that Pb in soil from mining communities is less readily absorbed from the gastrointestinal tract than previously thought and that a bioavailability factor of 12% is more appropriate for certain mine wastes (4). One reason for the apparent discrepancy is due to geochemical and biochemical factors such as the proportion of major and minor Pb-bearing phases, the particle size distribution, the mineralogic associations of the Pb-bearing soil particles (i.e., nature and extent of contact with other soil phases), and dissolution kinetics (3, 5, 6) that control Pb solubility in the GI tract. Because of the importance of mineralogy, particle size, and associations in determining soil-Pb bioavailability, electron microprobe analysis (EMPA) is being used with increasing frequency to help assess the health risks associated with Pb-bearing soils at mining sites such as Aspen, CO (7); Leadville, CO (8); and Butte, MT (5, 9).

EMPA techniques enable the precise determination of quantitative chemical composition, grain size, and mineralogic associations of Pb-bearing particles contained within a soil sample. However, unlike most environmental analytical methods, no standardized EMPA methodology exists; therefore, the accuracy of phase identification, size quantification, and phase associations is dependent on the methods and experience of the instrument operator. The qualitative nature of EMPA provides the potential for a high degree of variability between laboratories that routinely conduct these analyses for environmental or health risk assessments. While EMPA methodology has been described in previous papers, the variability in the resulting data has not been addressed in any prior investigation. To quantitatively assess the variability in method application, two mine waste-bearing soils were submitted sequentially to four EMPA laboratories to assess interlaboratory variability and to evaluate the need for additional measures to ensure reproducible EMPA data quality.

Experimental Section

Polished pucks of a calcareous yard soil (pH 7.5, 7000 mg/kg Pb) from Aspen, CO, and a yard soil sample (pH 6.6, 2300 mg/kg Pb) from Butte, MT, were prepared (5) at the Department of Geological Sciences, University of Colorado at Boulder. Pucks were then submitted sequentially to the RJ Lee Group, Inc., Monroeville, PA (Lab A); Geller Microanalytical Laboratory, Peabody, MA (Lab B); Surface Science Western, London, Ontario (Lab C); and the Department of Geological Sciences, University of Colorado in Boulder, CO (Lab D).

The Pb-bearing particles were identified using a combination of energy dispersive spectrometry (EDS), wavelength dispersive spectrometry (WDS), and backscatter electron images (BEI). The relations between Pb-bearing phases were established from BEI images and WDS/EDS analyses as necessary. Each Pb-bearing particle was examined to establish phase association (i.e., cement, inclusion, liberated, or rim), using a novel scheme (Figure 1) in which Pb-bearing particles in soil are classified according to the nature and extent of their contact with other minerals. Representative BEI photomicrographs were produced of selected phases and their associations, with scale bar, magnification, sample identification, and phase identification recorded on each photomicrograph.

Phase associations are defined as follows. Cementation describes an agglomeration of particles in which the individual particles or the cementing material, or both, are made up of Pb-bearing phases (Figure 1). Grains with >50% of the perimeter surrounded by Pb-bearing or non-Pb-bearing primary or secondary phases are classified as included. Grains with <50% of the perimeter protected by other phases are defined as liberated phases. Rim phases are defined as Pb-bearing precipitation or alteration products that completely or partially surround at least 25% of the perimeter of another phase.

Individual Pb-bearing particles were analyzed (representing one point count each) until a minimum of 100 particles had been evaluated or 5 h of machine time had elapsed. Point counts were made by traversing each sample from left to right and from top to bottom in a grid pattern, with each vertical displacement moving only to the adjacent field of view. Magnification settings of 40-100× and 300-600× were used; the latter magnification allowed analysis of the smallest identifiable (1-2-μm) phases. The grain size of each Pb carrier was determined by measuring the dimension of the long axis. Percent composition of each Pb phase was determined by dividing the total length for each phase by the total of all grain lengths recorded and multiplying by 100.

All laboratories utilized comparable instrumentation, although operator experience in analyzing geologic samples varied. Laboratory A used a CAMECA CAMEBAX microprobe. Laboratory B used a JEOL 733 superprobe, a predecessor to the JEOL 8600. Laboratory C used a JEOL 8600 electron microprobe in conjunction with a Noran Instruments image analysis (IA) software package, and Laboratory D used a JEOL 8600. All identifications, measurements, and associations were determined by the instrument operator, with the exception of Lab C, which used IA software for grain counting and area determination. All instruments used in the study operated at 15-20 kV, with 10-20-nA specimen currents and a 1-μm-diameter beam.
Results and Discussion

The calcareous Aspen soil Pb mineralogy consisted of cerussite (PbCO₃), with minor quantities of iron oxide, manganese lead oxide, and lead organic phases (Figure 2), phases reported at < 5 % by all labs are not included. The percent of each phase and the probable error at the 95 % confidence interval were determined using point counting statistics based on the number of grains of each phase as a function of total grains counted (10).

Despite the general agreement between all laboratories regarding the relative abundances of both the major and minor Pb phases, no agreement was reached regarding the absolute percent composition of the major phase, cerussite. Lab C was the only laboratory to report lead silicates at 5 %, a chemically complex phase described as iron oxide by the other three labs. Lab D was the only laboratory to observe the presence of lead organics, which can be easily overlooked due to their low Pb concentration, resulting in a low BEI response. The large probable error and relatively low cerussite counts exhibited by Lab D is a function of the small number of total particles counted, which was necessitated due to pock surface contamination by silver paint, which occurred during a previous analysis.

Cerussite was generally interpreted to occur as liberated particles and less commonly as inclusions, cement, or rims by all labs providing association data. Lab C found more cerussite particles with a smaller average grain size, possibly due in part to the IA software that was used for the phase determinations. Depending on instrumental
parameters, IA may quantify one large, petrographically complex cemented grain as numerous smaller Pb-bearing particles, possibly resulting in an overestimation of included particles and an underestimation of the number of cemented particles and of average grain length.

The Butte yard soil contained a complex mixture of Pb-bearing phases, consisting predominantly of iron lead oxides, iron lead sulfates, manganese lead oxides, and lead phosphate phases, with minor quantities of anglesite, cerussite, lead silicate, slag, and lead oxide. All four labs identified the four major phases, but reported varying percent compositions for the iron lead oxides and the manganese lead oxides. These variations are due in part to phase nomenclature differences, especially for the Fe-Mn-Pb solid solution series, which exhibits complex and variable chemistry, containing elements such as O, Si, S, Al, Zn, and other metals in addition to Fe, Mn, and Pb. The three laboratories that provided association data for the Butte soil showed qualitative agreement with lead phosphate associations (Figure 3), with the majority occurring as inclusions, a lower frequency as liberated and rim particles, and a minor amount as cement.

The primary differences noted between labs were the presence and relative concentrations of the minor phases, such as anglesite, cerussite, lead silicate, and slag. This variability was probably due to several factors, such as the location of the analysis on the sample puck, size of puck shield used, counting statistics, and operator experience. Association determination and quantification can be complicated when chemically similar particles are referred to by different names (e.g., iron lead and manganese lead oxides), and as a result of complex petrologic textures that result in ambiguous mineralogic associations. Also, for less abundant phases and associations, point counts will decrease, resulting in a larger probable error.

Conclusions

Data from EMPA analyses for major phases were comparable between laboratories, as were mineralogic association data for phases with accepted nomenclatures and chemical formulas (i.e., galena-PbS, and cerussite-PbCO3). Samples containing only a few phases of simple composition result in less interlaboratory variability than samples containing multiple primary phases with more complex chemical compositions. Analytical variability results from the total number of particles counted, type of image analysis used (i.e., operator or electronic), operator technique, and instrumental variables.

Because of the increasing use of EMPA in estimating human health risk at mining sites, employing different analytical methods and interpretations, it is apparent that a more rigorous quality assurance program is necessary to ensure consistency and comparability in data reporting. For example, although the data were comparable among labs for the Aspen yard soil, the reported relative occurrence of cerussite ranged from 60 to 97%, a difference that could affect estimates of soil-Pb bioavailability. To improve analytical consistency, we suggest that a multiphase standard reference material (SRM) be prepared, for which a catalog of spectra and photomicrographs would be provided to allow consistent interpretation of phase identifications and mineralogic associations.

Acceptance of a standard association nomenclature (e.g., Figure 1) would also aid in reducing association discrepancies between operators. With the delineation of additional association types (e.g., "envelopment" to identify a phase completely included within a primary host mineral), modifiers (e.g., "Pb-bearing" and "Pb-free"), and quantifiers to indicate the degree of liberation or inclusion (e.g., "partial" to indicate a rim of <50%, "predominant" to indicate a rim of >50%, and "completely"), as indicated in the proposed scheme presented in Figure 1, the standardization of soil mineralogy nomenclature and estimates of bioavailability from EMPA will improve.

In addition to these measures, including a compilation of representative image and EDS files in EMPA data packages would aid in resolving interlaboratory inconsistencies in phase and association identifications caused by variable solid solution composition and complex mineralogic texture by permitting independent data review. Several EMPA software packages already exist that are capable of storing image and spectral data for postanalysis data review.

Finally, although the use of IA software enables a large number of point counts to be determined over a short period of time, data interpretation is dependent on instrument parameters and cannot match the capabilities of human observation in differentiating and categorizing complex Pb phases. IA software used in conjunction with EMPA should therefore be limited to studies in which the...
data produced will meet study goals within the recognized limitations of the method.

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Literature Cited


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