FINAL REPORT

SARA
GROUP

Sudbury Area Risk Assessment
Volume II

Appendix I:

Speciation of Air, Dust and Soil Samples

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SUDBURY AREA RISK ASSESSMENT
VOLUME II

APPENDIX I: SPECIATION OF AIR, DUST, AND SOIL SAMPLES

The following appendix is composed of thirteen distinct documents, which have been placed in approximate chronological order of occurrence:

- The revised draft of a ***Proposed Approach to Metal Speciation of Environmental Samples for the Sudbury Soils Study*** by the SARA Group. This document provides overview of the summary literature review conducted by the SARA Group to evaluate potential approaches for conducting speciation of media samples for the Sudbury Soils Study (begins on page 5 of this appendix).

- Minutes from a meeting of the ***Metal Speciation Task Force*** on November 3, 2004. The Technical Committee struck a task force composed of expertise available within the member TC organizations to assist the SARA Group in developing a consensus approach to speciation of media samples as part of the Sudbury Soils Study HHRA (begins on page 31 of this appendix).

- ***A Combined Mineralogical and Analytical Study of Speciation of Chemicals of Concern (COC's) in Soils, Dusts and Air Filters*** by SGS Lakefield Research Limited (including appendices of detailed laboratory results). This is the detailed report, dated August 18, 2005, outlining the analytical results from the Tessier leach and SEM analyses conducted by SGS Lakefield (begins on page 38 of this appendix).

- A memo providing ***A Review of Lakefield Research Ni Speciation Results*** from Dr. Fred Ford. This memo, dated September 16, 2005, outlines Dr. Ford's observations of SGS Lakefield's approach for evaluating nickel speciation, and comments on the identification of potential nickel subsulphide within certain air filter and dust samples analyzed by SGS (begins on page 102 of this appendix).

- A report, dated November 23, 2005, from Jeff Warner of Canadian Light Source (CLS) laboratories outlining the results of XANES analyses conducted on a number of air filter samples (begins on page 105 of this appendix).

- A report, dated October 5, 2005, from Dr. Marc Lamoureux of EnviroAnalytix Services titled ***Report on nickel (Ni) speciation in particulate matter collected on filters***. The MOE requested splits of specific air filter samples taken during the year long monitoring survey (though different samples than those analysed by CLS) and contracted Dr. Lamoureux to conduct XANES analyses on these samples (begins on page 123 of this appendix).

- Minutes from a followup meeting of the ***Metal Speciation Task Force*** on January 20, 2006. The purpose of this meeting was to evaluate the speciation data collected to date and provide guidance to the SARA Group on what additional work may be required going forward to address identified data gaps (begins on page 151 of this appendix).

- ***A Mineralogical Study of Speciation of Ni in two Dust- and five Air-Filter Samples: SARA Project*** by SGS Lakefield Research Limited. This report, dated March 17, 2006, provides followup SEM analyses based upon recommendations from the previous Speciation Task Force meeting (begins on page 164 of this appendix).

- A report, dated April 17, 2006, from Jeff Warner of Canadian Light Source (CLS) laboratories outlining the results of XANES analyses conducted on a number of air filter and indoor dust samples recommended during the previous Speciation Task Force meeting (begins on page 182 of this appendix).

- Minutes from a second follow up meeting of the ***Metal Speciation Task Force*** on May 8, 2006. The purpose of this meeting was to again evaluate the speciation data collected to date and provide guidance to the SARA Group on what additional work may be required going forward to address identified data gaps (begins on page 200 of this appendix).

- An email correspondence from Jeff Warner of CLS, dated May 22, 2006, providing information on the theoretical method detection limit for nickel subsulphide in their XANES analyses, as requested in the latest Task Force meeting (begins on page 206 of this appendix).

- A memo from Chris Hamilton of SGS providing further quantification breakdown of of the nickel species fingerprint present in the previously analysed indoor dust and air filter samples, as requested in the latest Task Force meeting (begins on page 207 of this appendix).

- Summary of speciation analyses conducted by the Laboratory for Environmental and Geological Studies (LEGS) on five (5) soil and nine (9) indoor dust samples. The raw data report (which included the results of bioaccessibility analyses) was submitted to the SARA Group on February 12, 2007. The associated raw spreadsheet data for each sample analyses are also included (begins on page 210 of this appendix).

Sudbury Soils Study | Étude des sols sudburois
metals • health • environment
métaux • santé • environnement

Proposed Approach to Metal Speciation of Environmental Samples for the Sudbury Soils Study

Revised Draft

Prepared by:

SARA GROUP

Metal Speciation Rationale
Draft Version 2.1
February 22, 2005

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1.0 EXECUTIVE SUMMARY

Chemists and toxicologists have increasingly realized that determining total concentrations of metals and metalloids cannot always provide the required information about the mobility, bioavailability, and potential toxicity of an element on ecological systems or biological organisms

The geological formations of the Sudbury basin, transformation during the smelting process and weathering in the environment can have implications on the forms in which some of the Chemicals of Concern (COCs; specifically arsenic, cobalt, copper, nickel, lead, and selenium) will be available to biological systems, including people. Specific methodologies are required to determine each particular form of the metal. For example, nickel may be present in the environment in a variety of forms, including soluble nickel, nickel sulphide, and nickel oxides.

The process of determining the actual form of an element present within a given sample matrix is referred to as *speciation*. This is particularly relevant to the assessment of risks related to nickel exposures because the form of nickel in soil (or particulate matter) can have an important impact on its bioavailability and toxicity for both the natural ecosystem and human health.

A preliminary draft of available speciation methodologies was provided to the Technical Committee for discussion from the SARA Group in the fall of 2004. This was followed by a technical meeting on November 3, 2004, to discuss how speciation should be addressed in the current study.

During that meeting, and subsequent discussions, it was agreed that:

- Speciation of nickel is the priority for the Human Health Risk Assessment (HHRA).
- Metal speciation is not necessary for the Ecological Risk Assessment.
- Speciation of nickel in soil and air samples is considered the priority from an exposure pathway perspective.
- Speciation may be carried out on samples of indoor dust if sufficient material is available and it is considered necessary.
- Total metal (metalloid) concentrations will be used to assess human health risks and ecological risks for COCs other than nickel.
- A weight-of-evidence approach to speciation will be employed.
- The recommended primary methodology for sample speciation is the modified Tessier sequential leach extraction.
- The secondary method involving a bulk analysis using a soil trace mineral search technique (also termed QemSCAN) will be performed on approximately 10% of the samples to verify results of the leach extraction procedure.
- Samples will be submitted for QA/QC purposes that may include Certified Reference Material (if available), split samples or round robin testing. Recognizing that speciation analysis is not a common commercially available procedure.

2.0 INTRODUCTION

Within the last two decades toxicologists, environmental chemists and scientists have increasingly realized that determining total concentrations of an element cannot provide the required information about the element's mobility, bioavailability, and potential toxicity on ecological systems or biological organisms (Michalke, 2003; Peijnenburg and Jager, 2003). Therefore, methods have been developed for identifying and measuring the different forms of metals (or metalloids) in environmental matrices (*i.e.*, soil, air, water, biological tissues). The process of determining the actual form of a metal present within a given sample matrix is referred to as *speciation*.

The metal species or form of a given metal or metalloid will influence its bioavailability and bioaccessibility in the environment as well as biological systems. The "bioavailable fraction" is the fraction of the total amount of a chemical present in a specific environmental compartment that, within a given time span, is taken up by (micro)organisms, plants or animals (including humans), either through direct absorption from the microenvironment surrounding an organism, or by the ingestion of food. On the other hand, the "bioaccessible fraction" refers to the amount of a chemical available for uptake.

The relative risk of trace metals and elements in the environment will depend upon the state of solubility or "bioaccessability". Different forms of the same metal can range from essential to innocuous to toxic (Caruso and Montes-Bayon, 2003). Metals in particular interact as parts of macromolecules (proteins, enzymes, hormones, *etc*.) according to their oxidation state. Health risk research that focuses on speciation may eventually lead to regulatory criteria based on maximal element species concentrations rather than total element concentrations (Michalke, 2003). For the purpose of health protection and risk assessment, it is inadequate to consider only the total quantity of a trace metal or metalloid that might be evaluated for the purpose of exposure assessment.

Speciation analyses are required to perform adequate risk assessments for potential exposure to metals within a community. For example, inorganic arsenic species are clearly toxic, while the innocuous organic form of arsenic, arsenobetaine (commonly found in seafood), poses little risk and does not influence the outcome of a community-based health risk assessment. Chromium, like arsenic, can be either essential (*i.e.*, Cr(III)) or harmful (*i.e.*, Cr(IV)), depending on its oxidation state.

Speciation information relating to specific hazardous species in soils and Particulate Matter (PM) can be used to augment epidemiological and toxicological studies that would otherwise be based solely on elemental composition data alone. Reliable data for *both* the concentration and bioavailability of specific hazardous species contributes to the assessment of initiators of adverse health effects associated with the inhalation of airborne soils or PM (Huggins *et al.*, 2004).

It is, therefore, important to develop quantitative methods of speciating elements in the sample media to correlate the presence of specific chemical species with the potential for adverse effects on the human body, and to improve our understanding of their formation and reaction mechanisms. Direct determination of such species would both improve the quality of predictions of human health risks, and aid epidemiological studies by providing unambiguous data on specific, potentially toxic, inorganic substances. For example, the correlation between total nickel and health effects in a sample population is *unlikely* to be the same as the correlation with health effects of a minor, toxic species such as nickel sulphide (Huggins *et al.*, 2004).

"Elemental speciation" has been defined "as the analyses that lead to determining the distribution of an element's (or metal's) particular chemical species in a sample" (Caruso and Montes-Bayon, 2003; Caruso *et al.*, 2003). A chemical species is defined as a specific form of a chemical element, such as molecular or complex structure or the oxidation state of a metal. Consequently, a speciation analysis is defined as the analytical activity of identifying and measuring species as necessary (Caruso *et al.*, 2003).

It is the purpose of this document to provide information on available methodologies that could be applied to the analysis of media samples for the purpose of establishing the relative abundance of metals in specified oxidation states in different sample matricies (*e.g.*, soil, TSP, PM_{10} and $PM_{2.5}$). More importantly, methods are recommended for proceeding with the Sudbury Soils Study.

For the purpose of the Sudbury Soils Study, only speciation of COCs in soil samples and atmospheric particulate matter (gathered as part of the air monitoring survey) is proposed. With respect to food materials (*e.g.*, those gathered as part of the vegetable garden survey), the available literature suggests that the COCs would already be in an organically bioavailable form within the media, therefore, speciation of food materials is not recommended for the current study. As well, speciation of water samples is not felt to be necessary given any present COCs will be in a soluble form, and would be evaluated as such within the risk assessment. Speciation of indoor dust samples will be considered if deemed necessary.

3.0 GENERAL ASPECTS OF METAL SPECIATION

Complete speciation schemes consist of sampling, sample preparation, species analysis, and evaluation. Without proper sampling and sample preparation procedures, there is little chance that any speciation analysis will provide reliable data upon which human health or environmental decisions can be based (Caruso *et al.*, 2003; Caruso and Montes-Bayon, 2003). Quality control approaches and statistical data handling are a must for providing reliable results. A review on sample collection, pretreatment, and storage of a wide range of sample types has been published by Szpunar (2000).

3.1 Chemical Separation Methodologies

Conventional inductively coupled plasma-mass spectrometry (ICP-MS) is used as part of speciation analysis in a series of carefully planned sequential steps (Vincent *et al.*, 2001; Profumo *et al.*, 2003; Fernádez Espinosa *et al.*, 2004). Recent developments in this branch of analytical chemistry have been reviewed by Beauchemin (2002). Unexpected changes to the metal of interest might occur during either sample collection or preparation (*e.g.* changed oxidation state). Such changes alter the original species identity and its amount and therefore will defeat the purpose of the analyses (to inform and characterize the risk to health).

Two general approaches are available (Caruso and Montes-Bayon, 2003). These include: (1) the segregation of bioaccessible from relatively biologically inert forms of a metal by sequential application of separation techniques, and 2) the speciatation of metals through the application of non-destructive techniques that retain the sample integrity (*e.g.*, X-ray or high energy methods). These methods are discussed below in Sections 3.1.1 and 3.1.2, respectively.

There is no standard method accepted by any regulatory agency that explicitly describes an “agency certified” methodology for chemical speciation in environmental samples. Extraction and fractionation of chemical species based on relative solubility of a substance is a technique that is available for metals speciation. Physical-chemical separation methods that retain the unaltered form of a metallic species in a mixture begin with the mildest extraction conditions possible to segregate the metal ionic forms from one another and from the sample matrix (Michalke, 2003). Chemical separation techniques have been used to characterize eleven metals by valence in fine air particulate from urban sites (Fernádez Espinosa *et al.*, 2002). Sometimes sample preparation can be expedited by such techniques as microwave-assisted extraction (MAE). This methodology can be carried out at atmospheric pressure, at variable temperature, and using variable solvents or extraction time to achieve the mildest extraction conditions (Caruso and Montes-Bayon, 2003).

It should be noted that wet extraction procedures have presented serious challenges for analyses of samples in matrices other than aquatic sediments or soils. Thermodynamic equilibrium is rarely achieved in natural systems and consequently the predictive power of generalized speciation techniques applied to “soil” or “sediments” remains poor (Gaillard *et al.*, 2001). Sequential extraction protocols are also prone to artifacts (Tipping *et al.*, 1985) and require careful evaluation and calibration before being used on a specific sample (Tessier and Campbell, 1988; Profumo *et al.*, 2003).

3.1.1 Sequential Leaching Methodologies for Speciation of Metals in Solid Samples

Sequential leaches are a long-standing, documented analytical technique used to predict metal association in soils. The chemical models that provide the rationale for these methods have been based on equilibrium reactions, or on empirical determinations from wet chemical methods that rely on the sequential extraction of various phases (Tessier *et al.*, 1979; Tessier and Campbell, 1988; Gaillard *et al.*, 2001; Fernádez Espinosa et al, 2002). Recently, Profumo *et al.* (2003) and Vincent *et al.* (2001) have described the determination of species of inorganic nickel in particulate matter through the application of a sequential dissolution method. Species of nickel have been identified in several standard reference materials including coal fly ash (SRM 1633b), urban particulate (SRM 1648) and urban dust (SRM 1649). Nickel was also identified in particulate matter collected on filter media operating under low flow (0.1 to 1.0 L min^{-1}) or in a hi-vol PM_{10} sampler or cascade impactor (Fernádez Espinosa *et al.*, 2002; Huggins et al, 2000b; Profumo *et al.*, 2003). High recoveries (approximately 100%) were reported for nickel concentrations of 7 to 10 μg/gram particulate matter recovered (Profumo *et al.*, 2003).

Although there have been some identified errors with this approach overall it appears to be as useful technique, especially when wet-chemical leaches can be combined with mineralogical examination of the soil samples. As discussed above, the principle of elution and separation of metal species based on relative solubility under differing conditions of pH is a well investigated approach to metal speciation. *Conceptually,* the solid material can be partitioned into specific fractions which can be extracted selectively by using appropriate reagents; considering the similarities between sediments and soils, extraction procedures can be borrowed or adapted from the methods of sediment chemical analysis.

For the current study, the sequential leach protocol referred to as a modified Tessier method is recommended (Tessier, Campbell, and Bisson, 1979). This technique partitions the metals of interest into six fractions (water soluble, exchangeable, bound to carbonates, bound to Fe-Mg oxides, bound to organics, residual).

Tessier Sequential Leach Method

Tessier *et al.* (1979) developed experimental procedures to assist in the determination of chemical species in particulate trace metals. These procedures have been grouped into: (i) methods designed to effect the separation between residual and non-residual metals only (2-5); and, (ii) more elaborate methods making use of sequential extractions.

In defining the desired partitioning of trace metals, Tessier *et al.* (1979) took care to choose fractions likely to be affected by various environmental conditions. The following five fractions were selected:

Fraction 1: Exchangeable
In studies on sediments or on their major constituents (*e.g.*, clays, hydrated oxides of iron and manganese, humic acids), the adsorption of trace metals may be the result of simple ionic attraction; a change in water ionic composition is likely to affect sorption-desorption processes.

> (i) *Exchangeable.* The sediment was extracted at room temperature for 1 h with 8 mL of either magnesium chloride solution (1 M MgCl, pH 7.0) or sodium acetate solution (1 M NaOAc, pH 8.2) with continuous agitation.

Fraction 2: Bound to Carbonates
Significant trace metal concentrations can be associated with sediment carbonates; this fraction would be susceptible to changes of pH.

> (ii) *Bound to Carbonates.* The residue from (i) was leached at room temperature with 8 mL of 1 M NaOAc adjusted to pH 5.0 with acetic acid (HOAc). Continuous agitation was maintained and the time necessary for complete extraction was evaluated.

Fraction 3: Bound to Iron and Manganese Oxides
Iron and manganese oxides exist as nodules, concretions, cement between particles, or simply as a coating on particles; these oxides are excellent scavengers for trace metals and are thermodynamically unstable under anoxic conditions (*i.e.*, low Eh).

> (iii) *Bound to Fe-Mn Oxides.* The residue from (ii) was extracted with 20 mL of either 0.3 M $Na_2S_20_4$ + 0.175 M Na-citrate + 0.025 M H-citrate, or 0.04 M NH_20H- HCl in 25% (v/v) HOAc. The latter experiments were performed. at 96 ± 3 ^oC with occasional agitation.

Fraction 4: Bound to Organic Matter
Trace metals may be bound to various forms of organic matter: living organisms, detritus, coatings on mineral particles, *etc*. The complexation and peptization properties of natural organic matter (notably humic and fulvic acids) are well recognized, as is the phenomenon of bioaccumulation in certain living organisms. Under oxidizing conditions in natural waters, organic matter can be degraded, leading to a release of soluble trace metals.

(iv) *Bound to Organic Matter*. To the residue from (iii) were added 3 mL of 0.02 M $HN0_3$ and 5 mL of 30% H_2O_2 adjusted to pH 2 with HNO_3, and the mixture was heated to 85 ± 2 ^oC for 2h with occasional agitation. A second 3-mL aliquot of 30% H_20_2 (pH 2 with HNO_3) was then added and the sample was heated again to 85 ± 2 ^oC for 3h with intermittent agitation. After cooling, 5 mL of 3.2 M NH_40Ac in 20% (v/v) HNO_3 was added and the sample was diluted to 20 mL and agitated continuously for 30 min. The addition of NH_4OAc is designed prevented adsorption of extracted metals onto the oxidized sediment.

Fraction 5: Residual

After removal of the first four fractions, the residual solid should contain mainly primary and secondary minerals, which may hold trace metals within their crystal structure. These metals are not expected to be released in solution over a reasonable time span under the conditions normally encountered in nature.

(v) *Residual.* The residue from (iv) was digested with a 5:1 mixture of hydrofluoric and perchloric acids ($HF-HClO_4$). Sediment was first digested in a platinum crucible with a solution of concentrated $HClO_4$ (2 mL) and HF (10 mL) to near dryness; subsequently a second addition of $HClO_4$ (1mL) and HF (10 mL) was added and evaporated to near dryness. Finally, $HClO_4$ (1 mL) alone was added and again the mixture was evaporated until the appearance of white fumes. The residue was dissolved in 12 N HCl and diluted to 25 mL. This solution was analyzed by flame atomic absorption spectrometry for trace metals using standard techniques.

The SARA Group proposes the application of a sequential leach procedure based on Tessier (Tessier, Campbell, and Bisson, 1979) and further refined by NIST (Shultz, Inn, and Burnett, 2002).

Information on alternative sequential leach methods is provided in Appendix A for interest and reference.

3.1.2 Other Speciation Techniques

Less aggressive methods than are necessary for soil analyses have been developed to characterize metal species in air particulate samples.

The main inorganic nickel compounds that are expected to be present in the atmospheric particulate emissions of industrial production include metallic nickel, Ni (0), soluble Ni (II) nickel salts, insoluble or slightly soluble nickel compounds such as NiO (1.1 mg/L), Ni_3S_2 (517 mg/L) and $NiCO_3$ (93 mg/L), and finally silicides and non-stoichiometric nickel compounds (Profumo *et al.*, 2003). Soluble nickel compounds (~20^oC) for which biological data are available include $NiCl_2$ (642 g/L); $Ni(SO_4)_2$ (293 g/L); $Ni(NO_3)_2$ (2385 g/L) (ATSDR, 2003).

Mineralogical Analyses

Mineralogical analysis of the soils is typically conducted in 2 phases: 1) trace mineral analysis and 2) bulk mineral analysis. These vastly different objectives require different methodologies. The trace mineral analysis involves detailed, systematic, high magnification scanning of polished grain mounts prepared from soil size fractions, with the COC-bearing phases characterized by elemental composition, particle size and association (Stanley and Laflamme, 1998). Bulk mineral analysis involves X-ray diffraction and QEMSCAN microscopy to characterize mineral weight%, particle size, calculated chemistry and elemental/mineral associations (Jambor and Blowes, 1998).

Soil Trace Mineral Search Technique

Each soil sample would be air dried (as per MOE methodology for environmental samples). A subsample is then subjected to water leaching to determine the presence of water soluble nickel. If the results of the water leach are negative (*i.e.*, very low soluble nickel), the sample will be wet screened into three size fractions: 1) +48 mesh (295 µm), 2) -48 mesh/+400 mesh (44 µm) and –400 mesh. These fractions represent the coarse sand, fine sand/silt and silt/clay (respirable) size fractions, respectively, and combine MOE soil and respirable dust protocols. One polished grain mount will be prepared from a representative portion of each size fraction.

Each grain mount will be analyzed in detail (systematic high magnfication scans) using the LEO 440 Scanning Electron Microscope in backscatter electron mode. The instrument is equipped with 4 light element X-ray detectors capable of detecting the presence of low atomic number elements such as oxygen and carbon (*e.g.,* distinguishing between metal, metal alloy, metal oxide, metal carbonate, metal sulphide, metal sulphate, *etc*.) and the Isis X-ray microanalyzer that provides semi-quantitative elemental determination. A population of COC-bearing particulates can be identified and characterized with respect to: 1) bulk composition, 2) particle size, 3) mineral association/locking. Representative photomicrographs can be prepared to illustrate key morphological and textural information (*e.g.*, Figure 2 and 3 illustrate Ni-oxide/hydroxide and Ni-metal spheres identified in a contaminated soil sample, Figure 4 illustrates soil particles cemented by secondary Fe-Pb-Cu oxide, and Figure 5 illustrates a coke particle with pores filled by Pb-sulphate) (Source: SGS-LRL).

<u>Method Considerations:</u>

- EDS (energy dispersive spectrometry) measures elemental data with a detection limit of approximately 0.5 wt.% metal. Sample components (*e.g.*, Organics or Fe-oxyhydroxides) with COC contents below 0.5 wt.% should be measured by another technique (eg. using electron microprobe (EMP) or ion probe (SIMS) analysis).
- Analysis by size fraction is recommended to homogenize sample components, eliminate nugget-effects and provide more representative data.
- The electron beam diameter is nominally 1 µm (both in area and depth of penetration). Particles down to approximately 1 µm may be detectable, but will exhibit spectral overlap with adjacent phases. Detection limits are dependent upon magnifications used.
- Scanning Electron Microscopy (SEM) methodology does not provide structural data (such as is provided by XRD-X-ray Diffraction analysis or XAS-X-ray Atomic Spectroscopy analysis).
- SEM methodology does not recognize H, and therefore cannot differentiate between oxide and hydroxide minerals.

Soil Bulk Mineralogical Analysis

A variety of methodologies are available to conduct bulk mineralogical analyses on soil or particulate samples.

<u>X-ray Diffraction Analysis</u>

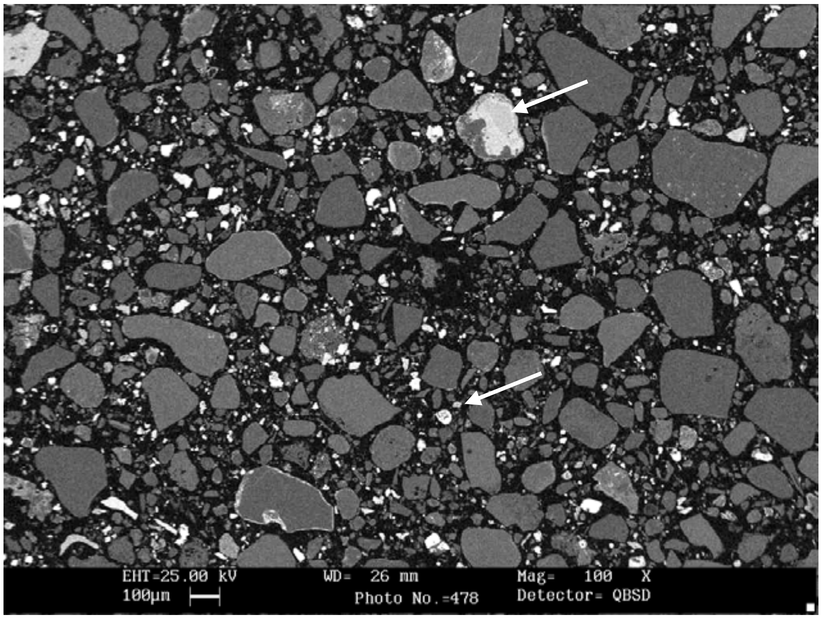
In this analysis, a portion of each head/size fraction would be pulverized and subjected to X-ray diffraction analysis using a Siemens D5000 diffractometer equipped with a Co radiation source and graphite monochrometer. The XRD patterns will be interpreted using both automated search/match software and manual analysis. The semi-quantitative crystalline components of each head/size fraction will be reported as major, moderate, minor or trace/tentative based on peak intensity.

Considerations: Non-crystalline phases such as glass are not detected by this technique. Detection limit ranges from 0.5 to 2 wt.% mineral and is highly dependent upon mineral crystallinity.

<u>QemSCAN Bulk Modal Analysis</u>

For this analysis, one polished grain mount is prepared from representative portion of each head/size fraction. Bulk modal analysis (vol.% / wt.%) of the mineral, slag and/or organic components of the soil is determined using the LEO 440 QemSCAN (Quantitative Evaluation of Materials using Scanning Electron Microscopy). More than 100,000 data points per head/size fraction are typically analysed. Output from a typical bulk modal analysis provides mineral content, particle size information and assay reconcilliation by size fraction. Figure 1 illustrates the typical mineral particle size, grain morphology and presence of metal-oxides in a soil sample containing elevated metal concentrations.

Figure 1 Low magnification image of a contaminated soil dominated by potassium feldspar and quartz. Minerals made up of high atomic number elements, such as Fe, Pb and As, show up as bright regions (arrows) (Polished grain mount with Backscatter Electron Image)



It should be noted that the LEO 440 QemSCAN is a high quality scanning electron microscope fitted with 4 light element X-ray detectors, Isis X-ray microanalyzer, secondary, backscatter and X-ray detectors, digital image processing, automated multi-sample stage and sample management/analysis software designed by CSIRO. It is a state-of-the art instrument for mineralogical analysis and is currently being utilized by significant mining companies for ore characterization and metallurgical plant audits.

Considerations: LOD for EDS analysis is approximately 0.2 wt.% metal. Mineral identifications and chemical reconciliations are based on species identification program (SIP) data which are based on published mineral chemistry or site specific electron microprobe analyses).

Electron Microprobe Analysis (EMP)

Selected soil components may require detailed mineral-chemical analysis using a JEOL 733 Super probe fitted with four wavelength dispersive spectrometers (WDS). The EMP analyses provide both major and trace mineral chemistry with a detection limit of approximately 0.02 wt.% element. These analyses may be critical to detect low level C-of-C's within the structure of other soil components (such as Fe-oxide/hydroxides). These analyses are also important in the development site-specific QemSCAN SIPs.

A more detailed overview of other potential speciation techniques are provided in Appendices A and B of this document.

4.0 RELEVANT EXPERIENCE FROM THE PORT COLBORNE PROJECT

In its soil investigation for the Rodney Street Community in Port Colborne, the Ontario Ministry of the Environment examined different methods for speciation of nickel present in a limited number of soil samples. Nickel speciation was conducted by several groups for the purpose of comparing results across different methodologies and analytical techniques. One laboratory (Northern Development and Mines Geoscience Laboratory in Sudbury) reported only nickel oxide as present. Similarly, a report prepared for INCO, and a Jacques Whitford Environmental Ltd. report also concluded that elemental nickel and nickel oxide (NiO) were the only forms of the metal present in samples analysed. Neither Nickel sulphate or nickel subsulphide were observed.

In addition to routine analysis, the MOE requested that two additional methods be exploited to prepare a quantitative speciation of nickel forms in contaminated soils. Twenty samples were sent to Lakefield research where a non-standard wet chemical approach sequential elution approach to metals speciation was utilized. A second set of six samples were submitted to X-ray absorption fine structure spectroscopy (XAFS) at the Stanford Synchrotron facility in California.

The XAFS samples revealed only NiO present (MOE, 2001; Lamoureux, 2001). Additional scanning electron microscope methods applied by Enpar (2001) or by Inco Analytical Services (2001) also reported only NiO in the samples examined.

On the other hand, the Lakefield sample methodology of sequential elution produced ~0.4% soluble Ni, 7.7% Ni sulphide and 11.3% nickel metal. The remainder of the nickel observed by Lakefield was NiO. The MOE soils study at Port Colborne was unable to draw definitive conclusions on the basis of the conflicting results available.

Additional scanning electron microscope methods applied by Enpar (2001) or by Inco Analytical Services (2001) also reported only NiO in the samples examined (*i.e.*, they were specifically looking for NiO or nickel subsulfide or metallic nickel in specific soil samples).

A major concern with the results of metal speciation analyses is whether or not species interconversion takes place during any of the steps undertaken during a particular speciation analysis. Compensation may be available when quantifiable conversions of metal species can be identified as a component of sample preparation. Clearly, the need for exacting protocols in the sampling and sample preparation process is critical (Caruso and Montes-Bayon, 2003).

5.0 CONCLUSION AND RECOMMENDATIONS

Speciation of metals present as a mixture can be accomplished by the careful application of sequentially stronger solvents capable of releasing different species of metal under highly specified conditions. The proposed methodology would involve the use of the modified Tessier sequential leach analyses, to provide baseline speciation of each of the COCs. This is a common approach taken when evaluating sediment samples, and these methodologies have also been successful applied to the speciation of small air particulate samples (Fernádez Espinosa *et al.*, 2002, 2004; and Profumo *et al.*, 2003). The analyses will be able to identify: (1) soluble and exchangeable metals; (2) carbonates, oxides and reducible metals; (3) metals bound to organic matter, oxidizable and sulphidic metals; and (4) residual metals.

However, as each different type of analyses provides a different clue as to the speciation of a given sample, it is advisable to take a “weight of evidence” approach, and use a number of analyses in combination to provide an accurate speciation picture. As such, to verify the findings of the sequential leach procedure it is recommended that approximately 10% of the soil samples be submitted for physical analysis by soil trace mineral search techniques, such as QemSCAN.

For the purpose of the current study, only speciation of the COCs in soil samples and atmospheric particulate matter (gathered as part of the air monitoring survey) is proposed. With respect to food materials (*e.g.*, those gathered as part of the vegetable garden survey), the available literature suggests that the COCs would already be in an organically bioavailable form within the media; therefore, speciation of food materials is not recommended for the current study. As well, speciation of water samples is not felt to be necessary given any present COCs will be in a soluble form, and would be evaluated as such within the risk assessment. Speciation of indoor dust samples will be considered when the dust survey results are reviewed and the importance of this exposure pathway is fully evaluated.

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APPENDIX A

ALTERNATIVE SPECIATION METHODOLOGIES

Zatka and Modified Zatka Sequential Leach Methods

An alternate methodology is available for the speciation on nickel in soils, bulk dust samples and air-quality monitoring samples. The methodology has risen out of INCO's continued work on speciation of nickel, and is a modification of a method originally developed by Zatka (1990) to evaluate compounds found to be present during smelting and refining of nickel sulphide ores. As such, it is important to note that Zatka's method (as well as modifications to it) have not be verified for soils, sediments or ambient air, with verification only having been conducted within occupational settings.

This methodology is similar to the Tessier leach analyses, but partitions the nickel into the following fractions:

Fraction 1: Soluble Ni
Fraction 2: Ni sulfide and Ni sub sulfide
Fraction 3: Ni Metallic
Fraction 4: Ni Oxides.

One caveat on this methodology is the non-specificity of the nickel sulfide leach and the possibility that nickel bound up in the organic phase of a soil may also leach, resulting in high sulfidic nickel results. Combinations of this procedure with the Tessier sequential leach outlined above, and confirmation by mineralogical analysis and soil TOC analysis will provide a more complete understanding of the phases of nickel found within the soil samples.

Profumo Procedure

A simplified fractionation scheme for the segregation of different inorganic nickel compounds from complex matrices is presented by Profumo *et al.*, 2003. Weighed amounts of the sample (synthetic mixtures or standard reference materials) were treated with a few millilitres of water, and sonicated for 5 min. The solution was filtered on 0.22 μm membrane. The solution containing the soluble salts of Ni(II) was diluted with water volumetrically (25 ml) [**S1**] and analysed.

The residue **[R1]**, which contained Ni(0), nickel sulphide and nickel oxide and other nickel insoluble compounds, was treated with 10 ml of 0.01 M $FeCl_3$ in 0.1 M HCl, sonicated for 5 min, and gently heated with reflux for 10 min. In this step, Ni(0) is oxidized by Fe(III) to Ni(II). Higher concentrations of Fe(III) must be avoided, because of the nickel impurities present also in the purest iron salts. The acidity prevents $FeCl_3$ hydrolysis and the subsequent problems in the filtration. Fe(III) compounds that can be present in the particulate matter did not interfere because the first step of the procedure was performed in water at room temperature, and the redox reaction is favoured in hot acidic. After cooling and filtration, a solution containing nickel from the metal and a residue **[R2]** were obtained. The solution was then diluted to volume (25 ml) **[S2]** with water for the analysis.

The residue **[R2]**, containing all the insoluble species, was refluxed for 20 minutes in a mixture of a few milliliters HNO_3 (70%) and HCl (37%), (ratio 1:3), reduced near to dryness and diluted to volume with water, filtered, if necessary to obtain the solution **[S3]**. This solution was analysed to determine nickel from insoluble compounds, such as nickel sulphide and nickel oxide. Finally, the residue **[R3]**, that can contained highly insoluble nickel compounds such as silicates, silicides and non-stoichiometric sulphides, was digested with a few drops of hot HF (48%) till dryness, diluted to volume with distilled water, filtered and analysed **[S4]**.

Analysis and Speciation of Standard Reference Materials

Standard Reference Materials (SRMs) from NIST (National Institute of Standards and Technology) are supplied with certified values for trace metal content. These reference concentrations found in soils and particulate matter provide a standard by which the efficiency of extraction and recovery of trace metals using analytical chemical methods may be judged. The use of such standards in complex matricies is essential for the purpose of determination of quantities of specific trace metals in environmental samples.

Profumo *et al.* (2003) applied a scheme to replicate samples of 80 to 100 mg of standard reference materials. The results are shown in Table A-1.

Table A-1 Trace metals in various SRMs in μg/g (SD not shown), unless otherwise noted

SRM	Description	As	Fe	Co	Cu	Ni	Pb	Se
1648	Urban Particulate	115	3.91*	(18)	609	82	0.655*	27
2709	San Joaquin Soil	17.7	3.50*	13.4	34.6	88	18.9	1.57
2711	Montana Soil	105	2.89*	(10)	114	20.6	1162	1.52
2782	Industrial Sludge	166	26.9*	(66.3)	2594	154.1	574	0.44
1633b	Coal Fly Ash	136.2	7.78*	(50)	112.8	120.6	68.2	10.26
3136	Nickel standard soln.					9738		

( ) indicates non-certified value, or reference concentration; * indicates mass fraction, percent

Application of Sequential Extraction to Speciation of Metals in Samples of Urban Fine PM

Detection of metals found in air particulate samples has generally relied upon some form of inductively coupled plasma atomic emission spectrometry (ICP-AES). The chemical speciation of metals in fine particles (< 0.61 μm average aerodynamic diameter) at concentrations in the ng/m^3 has been reported (Fernádez Espinosa *et al.*, 2002; Fernádez Espinosa *et al.*, 2004). Secondary reactions occur both on air particulate matter during collection and as a result of separation techniques, no matter how rigorously the chemical speciation scheme is optimized (Fernádez Espinosa *et al.*, 2004). For the analysis of urban air fine PM, each analyses (sixth stage of a cascade impactor) utilized one-fourth of a quartz filter (thus retaining sample for cross comparison *via* other methods). Comparisons were made to similar back-up filters that had not received exposure to urban air.

In contrast to the speciation scheme proposed by Profumo *et al.* (2003) that was optimized for nickel speciation, the scheme developed by Fernádez *et al.* (2000), and Fernádez Espinosa *et al.* (2002, 2004) is one focused on the characterization of multiple metals and their species as they occur in urbanized rether than highly industrialized environments. This approach to speciation of multiple metals, and the exploitation of readily available separation and identification technology of atomic absorption/mass spectrometry, suggests the potential of relatively high sample throughput.

Urban air quality is influenced mainly by vehicular traffic, also by the resuspended soil particles and some industrial releases. Because the study of the chemical distribution of the toxic metals is of great interest for the health of the population of large cities, 11 metals were studied by chemical speciation. The objective of earlier studies to evaluate bioavailable toxicity was to use mild extraction processes for the trace metals to mimic the release of chemical forms that could be biologically available to the respiratory tract of the human body. Therefore, the experimental conditions of earlier extraction schemes were determined based upon conditions of deposition and solubilization most likely to be found in the lung.

These resulting conditions were different from the Tessier's or the scheme derived by Profumo *et al.* (2003). The metal speciation scheme applied to air particulate fractions by Fernádez Espinosa *et al.* (2002, 2004) were considerably more aggressive than conditions likely to be encountered in biological tissues, but not as strong as those first developed by Tessier *et al.* (1979). In brief, the main differences of the scheme can be summarized as follows:

- Water was used instead of high ionic strength sodium acetate or magnesium chloride. The soluble metallic species (chlorides, sulphates, nitrates, acetates, *etc*.) were found to be quantifiably extracted in addition to the exchangeable metallic species by inherent ionic strength produced initially from dissolution of metallic species in the particles.

- Hydroxylamine chloride was used rather than acidification by acetic acid. The temperature of the extraction was maintained at close to environmentally relevant levels. High temperatures are unlikely to extract the bioavailable chemical forms of trace metals.

- pH (Tessier *et al.* use nitric acid and hydrogen peroxide) as well as the concentration of ammonium acetate are different. Nitric acid is not used. These experimental conditions are less aggressive, thus leaving this fraction extract only bound to organic matter, oxidisable and sulphidic chemical forms and not part of the residual metals.

- The more important differences are in the first two fractions; therefore, the expected important changes in their percentages will affect the percentages of the last two fractions. Since these are generally considered to have negligible bioavailability/bioaccessibility in human tissues, the important metal speciation should focus on those metals likely to be available to express a toxic effect.

The sample extractions of quartz filters were analysed in four chemical fractions for 11 elements (Mg, Ca, Ti, V, Mn, Fe, Co, Ni, Cu, Cd and Pb) by inductively coupled plasma atomic emission spectrometry (ICP-AES) or optical emission spectrometer (ICP-OES) (Fernádez Espinosa *et al.*, 2002, 2004).

After collection, air particulate sample filters stored desiccated prior to weighing. The suspended particulate matter concentration was determined by dividing the net mass of the particulate matter on the filter volume air drawn through the filter. Chemical speciation of the metals was determined by applying the sequential extraction scheme.

The sequential procedure used is presented in Table A-2.

Table A-2 Chemical Speciation Scheme[a]

Metallic Fraction	Reagent	Experimental conditions
1: Soluble and exchangeable metals	15 mL H_2O (pH = 7.4)	Shaker, 3 H at RT[b]
2: Carbonates, oxides & reducible metals	10 mL $NH_2OH•HCl$ [0.25M] at pH = 2.0	Shaker, 5 H at RT
3: Bound organic matter, oxidizable and sulphidic metals.	a) 7.5 mL H_2O_2, 30% b) + 7.5 mL H_2O_2 30% c) + 15 mL NH_4AcO [2.5M] at pH = 3.0	Shaker at ΔT (95 °C)[c] Shaker at ΔT (95 °C) Shaker, 90 min at RT
4: Residual metals	10 mL (HNO_3 : HCl : $HClO_4$) [ratio = 6:2:5]	5 H + Shaker at ΔT (95 °C)

[a] Adapted from Fernádez Espinosa *et al.*, 2004.
[b] RT = room temperaqture; [c]ΔT = applied heat

Fraction 1 in Table A-2 contains soluble metal easily interchangeable with water by sorption-desorption processes.

Fraction 2 in the table contains metal carbonates (or other forms susceptable to release by changes in pH), and bound hydrated oxides (susceptible to release under reducing conditions).

Fraction 3 contains metal bound to organic matter of biogenic origin. This fraction includes metals generally found adsorbed to living organisms, detritis, coatings on proteins, fats, mineral particles, etc. easily released under oxidizing conditions. The conditions described in Table A-2 for this fraction less agressive than earlier procedures (Fernandez *et al.*, 2000) that relied upon sequential treatment with combinations of hydrogen peroxide and nitric acid, followed by nitric acid with ammonium acetate.

Fraction 4 primarily contains residual metal found in elementary form, and in the crystalline structure of primary and secondary minerals, silicates, cements, passivated oxides, *etc*. These can only be extracted under tough, strong acid conditions.

Experimental conditions of the soluble and exchangeable fraction were applied to one quarter of a quartz filter (Cascade impactor, PM size < 0.61 μm average aerodynamic diameter). Then in sequence, extraction of carbonates, oxides and reducible fraction was applied to the residue of the backup filter treated with the previous fraction of extraction reagents, and so on until the fourth fraction. Chemical speciation was carried out in polypropylene centrifugal tubes. Fifteen millilitres of each reagent was consistently added to the tubes. Extractions were carried out in a rotator at ambient temperature. Centrifugation was performed at 5000 rpm for 10 min.

Once the extraction process was complete, the volume in the tube was reconstituted, and metals concentrations measured by ICP-AES. The matrix effect due to the particle and filter matrix was studied through the standard addition technique in the four speciation fractions. There was no evidence of a matrix effect. Calibration curves were prepared from same matrix as each one of the four fractions. A set of unexposed backup filters was analysed using the same procedure used for actual samples. The mean unexposed filter value was subtracted from each sample to obtain the best estimate of each element in the particulate matter.

Table A-3 Metal speciation of fine urban particulate matter[a]

Fraction	**Ni (percent)**	**Co**	**Pb**	**Cu**	**Fe**
Fraction1	39.9 % [Ni^{II}]	35.1	3.8	26.5	3.7
Fraction 2	19.1 % [Ni^0]	27.9	33.2	9.7	15.9
Fraction 3	28.1 % [from insoluble Ni^{II}]	12.1	35.3	42.7	25.8
Fraction 4	12.9 % highly insoluble, dissolved and analysed as Ni^{II}	24.9	27.7	21.1	54.6

[a] Adapted from Fernádez Espinosa *et al.*, 2002.

X-Ray Absorption Fluorescence Spectroscopy

The first paper to mention the use of this spectroscopic tool to probe the speciation of metals in environmental samples was published over 20 years ago (Jaklevic *et al.*, 1980). The approach was to use linear combinations of XAS spectra to quantify the different fractions of metal compounds present in air particles. Despite the fact that this technique has been applied as a research tool for some time, its use can not be considered routine of commonplace in the field environmental analysis. Within the last decade, an increased number of high energy X-ray research facilities have been constructed that permit the examination of fundamental chemical states. The construction of various synchrotron radiation rings has provided the scientific community with intense X-ray photon sources that can be used to probe the local coordination environment of most of the metals of environmental importance (Gaillard *et al.*, 2001). The application of **X**-Ray **A**bsorption **F**luorescence **S**pectroscopy (XAFS) to environmental samples has flourished since the establishment of the theoretical foundation for the interpretation of its spectra (Sayers *et al.*, 1971; Teo, 1986).

The analysis of XAFS spectra is well described in the literature (Huggins *et al.*, 2000a). Basically, the spectrum is divided into separate **X**-ray **a**bsorption **n**ear-**e**dge **s**tructure (XANES) and extended XAFS (EXAFS) regions. An *absorption edge* is that region of the emission spectrum of an element where the energy dependence of the photoelectric cross section of an element can be measured. These may be at the K shell absorption spectrum for a particular atom (also referred to as the K-shell binding energy or *K edges*) (Jaklovic *et al.*, 1980). Each region is analysed separately. This method is attractive since it is element specific, it can be applied to crystalline or amorphous samples, and it is thought to be non-destructive.

XAFS spectroscopy records the energy dependence and measures the variation (fine structure) of the X-ray absorption coefficient associated with one of the characteristic *absorption edges* of the absorbing element (*e.g.,* Ni, Cr, As or other metal). The technique is performed at a synchrotron source in order to take advantage of the high intensity and other properties of synchrotron radiation (Jaklevic *et al.*, 1980; Huggins *et al.*, 2000a). The energy scale of the XAFS spectra for each element is calibrated with respect to the position of the corresponding absorption edge in a standard material. Standard materials may include pure metal foils or metal salts in various oxidation states (Giauque *et al.*, 1986).

In the non-destructive analysis of metallic species, the XANES region is used without significant further manipulation as a *fingerprint* for the occurrence of the element in the experimental material under investigation. Data from the EXAFS region, on the other hand, requires additional mathematical manipulation.

XAFS spectroscopy has been used to speciate both nickel and chromium in samples of residual-oil ash. An analysis Ni and Cr XANES spectra suggested that both elements were most likely present in the ash as the sulfates, $NiSO_4 \bullet xH_2O$ and $Cr_2 (SO_4)_3 \bullet xH_2O$ respectively (Huggins *et al.*, 2000a). A comparison of the Ni XANES spectra for various standard nickel compounds shows that the spectra of nickel sulfides is very different from that of Ni compounds observed in residual oil ash. The best agreement for the spectrum of the ash was that exhibited by crystalline nickel sulfate (Huggins *et al.*, 2000b). Quantification and description of the differences observed at the absorption edges contribute to the characterization of chemical species in the environmental sample.

XANES and Particulate Matter Samples

A significant proportion of urban respirable PM_{10} and $PM_{2.5}$ may derive from combustion of fossil fuels (electrical power generation, vehicular exhausts). Such particulate contains variable quantities of metals. XAFS spectroscopy was performed at the S, Cl, V, Cr, Mn, Cu, Zn, As, Br and Cd *K edges* for both the Urban and Diesel Standard Reference Material (SRM) samples available from NIST (Huggins *et al.*, 2000b). A PM_{10} filter sample of urban air collected in Lexington, Kentucky was only examined at the S, Cl, Cr and As *K edges* (Huggins *et al.*, 2000a). Both the *coarse* ($PM_{2.5+}$) and *fine* ($PM_{2.5}$) particulate matter fractions generated from combustion of three residual oils, *viz*., low sulfur No. 6 (LS6), high sulfur No. 6 (HS6), and baseline No. 5 (BL5) have been analysed using XAFS spectroscopy to characterize metal species. Similar PM fractions generated by coal combustion of Pittsburgh bituminous coal from the eastern U.S. and Montana sub-bituminous coal from the western U.S., were also submitted for analysis. Bioavailable metal species were determined from PM-leachate after gentle treatment with deionized water. Additional, less soluble metal species, termed “not readily bioavailable” were determined from leachate of PM fractions after treatment with 1N HCl. Typically, the extraction protocol required samples ranging from 250 to 400 mg of the PM fractions were exposed to 50 mL solutions for times up to 1 hour with intermittent agitation (Huggins *et al.*, 2004).

XAFS spectroscopy was performed on the solid residues of the leaching experiments as well as on the original unleached $PM_{2.5}$ or $PM_{2.5+}$ samples at the Stanford Synchrotron Radiation Laboratory (SSRL) at Stanford University, California, or at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory, New York. Typically, three to six separate scans were made and averaged to provide a single spectrum with an improved signal/noise ratio.

Table 4 Distribution of Ni among sulphide, sulphate and oxide (Ferrite) forms for ROFA PM samples and aquatic leaching residues by fitting XANES spectra[a]

Oil combustion as PM source	Nickel in µg/g	Percent Ni as: Sulphate (Ni^{II})	Sulphide Ni^{II} (insoluble)	Ferrite Ni as Ni-Zn-
Low Sulphur #6				
$PM_{2.5}$	480	66	—	35
$PM_{2.5}$ leach (H_2O)	—	16	21	72
High Sulphur # 6				
$PM_{2.5}$	8020	92	—	8
$PM_{2.5}$ leach (H_2O)	—-	29	49	25
Baseline #5				
$PM_{2.5}$	8800	56	10	30
$PM_{2.5}$ leach (H_2O)	4870	18	22	60

[a] Adapted from Huggins *et al.*, 2004.

Table 5 Distribution of As among as As^{III}, and As^{V} in coal PM samples and aquatic or acidic leaching residues by fitting XANES spectra[a]

Coal combustion as PM source	Arsenic in µg/g	Percent Arsenic as: As^{III}	As^{V}
Pittsburgh Coal PM			
$PM_{2.5}$	310	3	97
$PM_{2.5}$ leach (H_2O)	—	7	93
$PM_{2.5}$ Acid leach in HCl	—	39	61

[a] Adapted from Huggins *et al.*, 2004.

XANES Spectroscopy and Environmental Monitoring Samples of PM2.5

The application of XANES spectroscopy to residues from simple leaching tests on PM fractions derived from the combustion of fossil fuels provides quantitative speciation of elemental species that are of significant concern for human health. The combined XANES and leaching protocol determines the potential "bioavailability" of such hazardous metal species. Arsenic (As^{V}) species were more readily dissolved than the more toxic As^{III} species in PM collected from combustion of coal. For heavy oils that contain Ni and Vanadium, the combustion products include residual oil fly ash (ROFA). $PM_{2.5}$ as well as larger PM fractions showed evidence of readily bioavailable Ni in the form of nickel sulfate. A nickel-containing sulfide that was observed as a minor Ni component in the coarse $PM_{2.5+}$ fraction was concluded to be less readily bioavailable based on the criterion of solubility in aqueous or acidic leachate. This Ni-containing sulfide in ROFA PM was not readily identifiable on the basis of the XAFS data presented (Huggins *et al.*, 2004).

It may be questionable whether sufficient sample size would be available for XANES analysis from routine monitoring samples in the Sudbury area. It may be more realistic to pool samples based on similar meteorological or other characteristics. This might be a means to provide a general characterization of the metal species in air samples over a given period. Unlike the urban particulate analyses performed by Fernádez Espinosa *et al.* (2002) on fine PM (<0.61 μm), the methods for speciating metals in the environment by XANES remains in the experimental and developmental stages.

Electrothermal or Acetylene Flame Atomic Absorption Spectrometry

Profumo *et al.* (2003) have suggested an alternative analysis of nickel-containing samples or residues Analysis of nickel-containing soluble fractions were conducted by electrothermal atomic absorption spectrometry (ETAAS**)**. Electrothermal measurements were completed using a Shimadzu AA-660 1G spectrometer with a graphite furnace atomizer (Shimadszu GFA-4B) (Profumo *et al.*, 2003). The limit of detection for nickel with this apparatus (LOD) = 1.0 μg/L; limit of quantification 3 μg/L; linear absorbance-concentration range from 3 to 15 μg/L.

Electrothermal (Graphite furnace) (ETAAS) or acetylene flame (FAAS) Atomic Absorption Spectrometry:

The principle of Ni speciation in a solid sample is based on determination of Ni extracted from the solid after some treatment. Detectable levels of nickel can be measured (1) in a solution or (2) in an insoluble residue of unextractable material. In either case, it is nickel that is registered, not the form of the metal present in the particulate matter that is characterized.

Nickel determination can be performed with various analytical techniques including spectrophotometry, atomic absorption spectrometry (methods differ according to the method of atomization: flame atomic absorption spectrometry [FAAS] and/or electrothermal atomic absorption [ETAAS]), inductively coupled argon plasma optical emission spectrometry (ICP-OES), ICP-MS and voltammetry.

Analysis can also be completed by a less sensitive method employing FAAS **(**Perkin-Elmer 1100B atomic absorption spectrometer). Flame atomic absorption spectrometry is much less sensitive than ETAAS, and gives a much less sensitive detection limit: Linear absorbance-concentration range from 500 to 4000 μg/L (LOD = 0.07 mg/L; LOQ = 0.35 mg/L). Prior to speciation analysis, the total nickel in a sample can be determined after aggressive acidification of a portion of the sample (Profumo *et al.*, 2003). For example, a procedure to determine total nickel was as follows: In a teflon bomb, the nickel standard or sample was dissolved in 1:3 :: HNO_3 (70%): HCl 37% with a “few drops” of HF (48%) at 140 ^oC for 8 h. At the end of the treatment, acid was evaporated until the white fumes disappeared, and the residue dissolved in water volumetrically for analysis.

Metal Speciation Task Force

Minutes of Meeting
November 3, 2004 – 10:00
CEI Offices

Attendees:

INCO	Bruce Conard	Glen Watson
Falconbridge	Denis Kemp	
MOE	Ron Bell	Brendan Birmingham
	Randy Jones	Dave McLaughlin
	Brian McMahon (by phone)	Rusty Moody
	Mary-Ellen Starodub	
SARA Group	Douglas Bryant	Glenn Ferguson
	Suzanne Goldacker (recorder)	Rob Irwin
	Elliot Sigal	Chris Wren

Sudbury District Health Unit (SDHU) – not attending

Agenda:

1. Introduction
2. Objectives of speciation analyses in the context of the Sudbury Soils Study (*e.g.*, relevant metals requiring speciation for HHRA and ERA)
3. Overview of relevant metal speciation options
   - Sequential leach methods (*e.g.*, modified Tessier, NiPERA/Zatka, SM&T extractions)
   - Trace mineral analysis
   - Bulk mineral analyses (*e.g.*, x-ray diffraction analysis, QemSCAN analysis, electron microprobe analysis)
   - X-ray absorption fluorescence spectroscopy (*e.g.*, XANES spectroscopy)
   - Others?
4. Discussion of advantages/disadvantages of each method
5. Recommended speciation protocol for Sudbury Soils Study
6. Adjournment

A record of the discussions and a listing of the presentations that took place during the meeting are provided below, in the approximate order that they happened.

Introductions and general discussion:

Glenn F.	Provided an introduction on behalf of the SARA Group
Elliot	Provided an overview of how metal speciation can be used in HHRA. He pointed out that the usefulness of speciating nickel is fairly clear, but that speciating the other COCs doesn't provide a lot of additional information

	for the HHRA since the toxicological data generally does not distinguish between species of those metals.
	The SDHU has expressed concern over the emphasis on only nickel; therefore the Task Force should discuss the need to speciate the other COCs. Speciation of the other COCs can provide information on their bioavailability, but other planned bioaccessibility studies (*i.e.*, stomach leaching soil metals bioaccessibility, veggie garden study to look at movement into vegetables, modelling of movement of metal species into vegetation) will also provide these data.
Glenn F.	There is a need to distinguish in this meeting between risk assessment and risk management needs. Speciation of the other COCs could be useful in risk management to distinguish between natural and anthropogenic sources, but is not a required element for the HHRA itself.
Bruce	In selecting COCs for speciation, Bruce would prefer to consider the health endpoints of a particular COC, and what the importance of speciation is to that endpoint. For oral intake, speciation is not very important because knowing the bioaccesibility will tell you how much is being taken into the body. For dermal absorption, you need to know the metal species in order to estimate their solubility into sweat, but according to the literature on occupational exposure, dermal exposure is a very minor route. So, from the perspective of dermal exposure, it would be nice but not vital to speciate the COCs. For inhalation exposure you need to consider cancer and non-cancer endpoints in the respiratory system, and these are species specific, particularly for Ni and As. Without speciation of Ni and As, risk assessments tend to assume that the entire exposure is to the most potent form (*e.g.*, nickel subsulfide, arsenic trioxide), and then backtrack to say that part of the exposure was to less potent species when the risk assessment shows an extreme level of risk that is obviously not being experienced. This is not the most compelling way to talk about risk.

Discussion on types of sample to speciate:

Chris	Pointed out the need to resolve which COCs and which samples types it is important to speciate. Air filters are the primary sample type to speciate.
Elliot	Soil and indoor dust samples are next in importance to speciate, although it's uncertain that there will be enough indoor dust sample to speciate. For garden vegetable samples you can assume 100% bioavailability, and there is literature to back this up, so it is not important to speciate.
Bruce	In water you can assume 100% bioavailability, so it is not important to speciate, except to determine organic vs. inorganic As.
MOE	MOE representatives generally agreed with these statements.
Glen W.	Asked how important was it to speciate TSP, since by virtue of its particle size it's not necessarily available.
Bruce	If PM_{10} levels will be used to calculate the amount of dust inhaled, then that fraction should be the one speciated.
Glenn F.	Agreed with Bruce and stated that PM_{10} will be used in the risk assessment.

Mary Ellen	Pointed out that it may be useful to speciate TSP because it's the same size fraction as soil, and there's a relationship between resuspended soil and TSP in air.

Presentation on analytical options for metal speciation (Rob Irwin)

General discussion of speciation techniques

Bruce	Pointed out that communicating the results of chemical analyses to the public is difficult because they expect definitive answers, and we need to address the expectations of the public with regard to certainty. Bruce believes we need a technique that proves the presence or absence of nickel subsulfide.
Rob	Hadn't seen any techniques to separate the nickel sulfides in the literature.
Brendan	Suggested the Wong *et al*. voltametry approach as a method that can distinguish between sulfides in a solid sample. He promised to provide five papers by Wong *et al*. to Bruce.

Bruce felt that the NiPERA/Zatka method should be referred to by a different name, as the method cited by SGS-Lakefield has not been officially endorsed by NiPERA, and is not a public document. The method referred to as the NiPERA/Zatka method in the Metal Speciation Rationale (Draft Version 1.3) and in Rob's presentation, is called "modified Zatka" here. There was some confusion about whether people were talking about Tessier vs. modified Tessier or Zatka vs. modified Zatka. Bruce tended to discuss the original method.

Discussion of the modified Tessier and modified Zatka sequential leaches

Bruce	The Tessier method was developed for sediments, while the Zatka method was developed and validated for workplace air conditions (specifically sulfidic ore processing). Bruce pointed out that the modified Zatka method hasn't been peer reviewed, and that the Zatka method isn't completely infallible (*e.g.,* particle size can influence results).
Rob	The modified Zatka method was validated for a broader array of sample types and operations other than the Zatka method.

Discussion of QemSCAN analysis:

Dennis	QemSCAN has limitations, but is good for analysis of fine materials.

Discussion of the XANES spectroscopy technique

Douglas	XANES is a high energy light source method to speciate metals. The analysis depends on subjective comparisons, so reproducibility is difficult. It is being used by Dr. Mark Lamoureux at St. Marys University in Nova Scotia, but it is *very* time consuming and the equipment is very finicky. A separate run is required for each chemical being speciated. The method is mostly used for soil samples, but has been applied to air samples. Fairly large amounts of sample are required. The sensitivity of the method can't be judged against the sequential leach methods with the information at

	hand. Overall, the method seems more appropriate to a research program than a risk assessment.
Bruce	So far, there is only a very primitive library of “known spectra” (for making the subjective comparisons), but the method promises to be useful in the future. The method could be used as a complimentary technique to add to the weight of evidence in this risk assessment, but more data can lead to more questions. It should have only a very low weight, if it’s used at all.
Dennis	Beam time for XANES should be arranged immediately if the technique is used.
Chris	The SARA Group may not be in favour of XANES analyses if there is no use for the data in the risk assessment. A very few samples won’t be useful.
Rusty	XANES was useful in Port Colborne.

Discussion of Other Methods

Bruce	XRD is not suitable for the types of samples we’re likely to get, and it’s not quantitative.
Mary Ellen	Crystallographic analysis of As in soil (*e.g.*, with the Canadian Light Source method) will provide information on form which could help explain a lack of human health problems. SRM and XRD analyses could provide information on whether the metals are on the inside or outside of particles, or provide additional information on its form. SRM and XRD can measure many metals/compounds simultaneously. Mary Ellen noted that Batonneau *et al*. (2004)[1] developed a method to find relative amounts of metal species on a mass basis. The method could be used to compare/validate data.

Discussion of arsenic speciation

Randy	There may potentially be a need for another sequential leach to speciate arsenic in soil, since Tessier won’t give an adequate detection limit.
Glenn F.	The appropriateness of Tessier for arsenic speciation should be judged based on what information is needed for the risk assessment.
Elliot	It’s unclear how speciating arsenic will improve the risk assessment. The Falconbridge urinary arsenic study is our most powerful tool to determine bioavailability through the comparison with the control community. Elevated levels in Falconbridge relative to the control community would indicate a need for further work to determine where the arsenic is coming from. If levels in Falconbridge residents are not elevated, then we know that the arsenic in soil is not bioavailable.

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[1] Batonneau, Y., Bremard, C., Gengembre, L., Laureyns, J., Le Maguer, A., Le Maguer, D., Perdrix, E., and Sobanska, S. 2004. Speciation of PM_{10} Sources of Airborne Nonferrous Metals within the 3-km Zone of Lead/Zinc Smelters. Environ. Sci. Technol. 38:5281-5289.

Mary Ellen	Due to the short half life of arsenic in the body, the urinary arsenic study will give you a snapshot of arsenic exposure, which may not be representative of the work case or even the average for that individual. Exposure for this snapshot won't be controlled, therefore the information won't be as strong as we'd like. A lot of weight shouldn't be put on the results of this one study. An acid gut extraction for arsenic will likely underestimate bioavailability, since the greatest dissolution of arsenic occurs under alkaline conditions in the small intestine. If we could mathematically determine the percent bioavailability at which we have an unacceptable risk, then the acid + alkaline gut extraction could tell us if we're near the threshold and need to investigate further.
Chris	The urinary arsenic study will be powerful. The community profile will mean that we won't have to look at an individual at a single point in time.
Bruce	The urinary arsenic study can't tell you quantitatively what the exposure was. It will tell you the level of body burden, but not what fraction of arsenic in the stomach is taken up. The study will be of limited use in the risk assessment. Since there is no standard method for arsenic speciation, there are two options 1) develop a method (not recommended due to costs) or 2) take a protective approach and assume that all ingested arsenic will be taken up.
Elliot	Assuming that all the arsenic will be taken up would give predicted cancer rates of well over 1 in 1,000,000. Propose that we use a weight of evidence including the urinary arsenic study and literature data on bioaccessibility.
Glenn F.	The Technical Committee agreed with the proposed bioaccessibility methodology of doing a simulated stomach extraction only, due to the considerable uncertainties inherent in the second phase for the non-lead COCs. Are we now recommending adding small intestine?
Bruce	The small intestine extraction will introduce more uncertainty. There are weaknesses in the Taiwanese and Chinese studies on which the slope factor was based.
All	There are no advantages at this point to speciating arsenic or doing a bioavailability study, since there are no accepted techniques and even the ICP-MS analysis of arsenic is problematic. The Tessier leachate will not be analyzed for arsenic and no additional studies will be added at this time. We can consider adding arsenic speciation or bioavailability studies later if the results warrant it. This treatment of arsenic will have to be carefully communicated to the public.

Selection of speciation technique(s)

Dave	The SEM, XANES and Tessier techniques were used for Port Colborne. You cannot rely on only one technique, and different techniques may be more suitable for difference matrices. We must remember that the time and money spent on multiple tests may not lead to increased understanding.

Rusty	For air filter samples, it may not be possible to use a second speciation technique if both are destructive methods and there is no air filter left.
Glenn F.	We appear to be advocating the Tessier method, based on Bruce's comments on the appropriateness of the Zatka and modified-Zatka methods. However, would the modified Zatka technique, since it was developed with Ni in mind, be more appropriate for Ni speciation, particularly on air filters, than Tessier?
Bruce	By the time it is deposited, emitted Ni is no longer in the same form as it was in the industrial situation, it is closer to the forms found in sediment (the medium for which the Tessier method was developed). Tessier is more likely than Zatka or modified Zatka to show the best information. If Tessier is the base-technique, then for a second technique to be used on perhaps 50% of samples, Bruce would prefer that we not select another sequential leach. XANES could be used on 2-5% of samples as the third technique in the suite. If there is not enough sample to use a suite of techniques, the only solution is to use different samples collected from the same time and place. It is not necessary to use the same technique on both soil and air filter samples, if a benefit of some technique other than Tessier can be demonstrated for air filters. Identifying a technique with a sufficiently low detection limit for arsenic may be a problem.
All	It was decided that: • It is appropriate to use a weight-of-evidence approach to evaluate speciation of metals. • The Tessier sequential leach analyses will be used as the primary method for soil and dust speciation, and air filters where sufficient material have been collected. • QemSCAN or similar bulk mineralogical analyses will be used as a supplemental method for all evaluated samples (10% of samples submitted for sequential leach analyses). Where there is insufficient material in a PM10 filter to complete sequential leach analyses, QemSCAN analyses may be selected as the alternate primary method. • XANES and other "cutting-edge" analytical methodologies will not be pursued at this time, given they are still largely experimental, and also have time and cost limitations. However, if these analyses were pursued outside of the risk assessment, and data were available in time, then the results of these analyses could be used as part of the weight-of-evidence approach.

Discussion on Validation of Analytical Results

Chris	We budgeted to speciate 100 samples. Scientifically, is that a reasonable number? Prefer analysing standard reference materials (SRMs) rather than split sample analyses to validate the lab results.
Rob	SRMs for Tessier are difficult.

Rusty	The SRMs must have been developed with the same analysis used to analyze them here. Failing a split sample analysis, the lab could reanalyze samples 10 times on 10 different days, and also volunteer to participate in a round robin.
Randy	Perhaps the National Institute of Standards and Technology (NIST) lab could do splits, since we're using the same method.

No consensus was reached on this topic.

Discussion on Sample Preparation and Archived *versus* New Sample

Rob	The easiest sample preparation method for the lab is to air dry and screen soil samples. This will result in some modification of the sample. Will we accept that since the method is simple?
Randy	Air drying and screening the 2 mm fraction is probably best. Archived sample could be used.
Bruce	Use of archived samples led to public suspicion over the method in Port Colborne.
All	New (non-archived) samples will be used, as additional samples are currently be collected as part of the indoor dust survey, and only a small amount is needed. Samples will be air dried and screened.

Discussion on SDHU Comments

Elliot	What was agreed here does not quite agree with the comments from SDHU. They want to know why we're focussing on nickel.
All	The focus on nickel for metal speciation will be explained in the Metal Speciation Rationale.

SGS Lakefield Research Limited

A Combined Mineralogical and Analytical Study of Speciation of Chemicals of Concern (COC's) in Soils, Dusts and Air Filters

prepared for

THE SARA GROUP

LR 11007-001 – MI5001-AUG05
August 18, 2005

NOTE:
This report refers to the samples as received.

The practice of this Company in issuing reports of this nature is to require the recipient not to publish the report or any part thereof without the written consent of SGS Lakefield Research Limited.

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Executive Summary

An extensive suite of dust, soil and air-filter samples were submitted to SGS Lakefield Research for sequential, Tessier leach analyses and corroborating mineralogical analysis were performed on a selected number of the samples. Leach work was performed by Analytical Services under the supervision of Mr. R. Irwin and the mineralogical work by Mineral Technologies under the supervision of Mr. C. Hamilton.

An outline of the methods employed as well as complete results are presented in the body and appendices of this report. An attempt at reconciling the mineralogical and analytical results is also presented, along with key findings of the mineralogical study which provide important links between sets of data and, as a consequence, a rational basis for interpreting analytical results.

Despite a few discrepancies and variations, both broad and specific correlations can be drawn and apparent shortcomings are explicable in terms of differences in approach and mineralogical evidence. This combined approach provides a prima facie case and rationale for interpreting COC deportment in Sudbury Area materials.

SGS LAKEFIELD RESEARCH LIMITED

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Introduction

In order to study the deportment of chemicals of concern (COC's), particularly Ni, Pb, Co, Cu and As, in Sudbury Area soils, dusts and airborne particulates, an integrated study was commissioned by C. Wren and Associates under the auspices of the Sudbury Area Risk Assessment (SARA) Study Group. In particular, a Tessier leach method was chosen to partition COC's into categories or groups of species representing bio-available through to sequentially more resistant fractions.

After analytical results were obtained, mineralogical studies were performed on selected samples. In this part of the study, corroborating mineralogical evidence was sought that would assist in the identification and explanation of speciation results. This combined approach was specifically aimed at providing mineralogical evidence for benchmarking purposes.

1. Analytical Procedure

The sequential extraction procedure of Tessier et al (1979) was adopted for the present study with one modification to omit an easily reducible step and generate a reducible fraction in a single aggressive stage (see Table 1, Step 3). The method and nominally defined speciation fractions are outlined in Table 1.

Table 1: Tessier Leach Fractions and Methodology.

Definition	**Fraction Sought**	**Method Used**
1. Exchangeable	Metals bound by sorption/desorption processes. Readily bio-available.	1 M $MgCl_2$ shaken for 1 hr. at neutral pH
2. Carbonate-hosted	COC bound to carbonate. Bio-available subsequent to degradation/dissolution of carbonate.	Residue from 1 leached with sodium acetate (NaOAc) adjusted to pH 5 with acetic acid (HOAc) to completion.
3. Reducible*	Bound to Fe-Mn-Oxides. Complete free Fe-oxide dissolution evaluated.	Residue from 2 leached with 0.04 M $NH_2OH.HCl$ in 25% (v/v) HOAc at 96^{o}C.
4. Organic-bound or Oxidizable.	Bound to organic matter.	Residue from 3 leached with 30% v/v H2O2. 0.02 M HNO3, 85^{o}C. 3.2 M NH_4Ac (20% v/v HNO3) added, shaken for 3 min.
5. Residual	Nitric-acid soluble species. Excludes silicate-bound and thus inert/stable/benign COC’s	Residue from 4 leached with 25% v/v HNO_3 heated to dryness. Then leached in 10% v/v HNO_3.

* A combined leach, rather than 2 steps usually separating an easily and moderately reducible fraction. (E.g. easily reducible targets Mn-Oxides.)

For comparative and reconciliation purposes, a strong acid HNO_3 digestion was also performed on a replicate sample. In most cases this value does not exactly correspond to the cumulative leached COC values but this difference is not considered significant in the light of compound error of precision and accuracy as variance is generally less than 10%. Where these differences are considered significant, special mention is made in the body of the report.

2. Mineralogical Procedure

The mineralogical analyses were carried out by scanning electron microscopy (SEM) using a Leo 440 SEM combined with energy dispersive X-ray spectrometry (EDS) and equipped with both a secondary electron and back-scattered electron detector. The EDS system was a light-element-capable Oxford ISIS unit providing the opportunity of identifying organic matter and easily discriminating sulphate and sulphide species.

Air filter samples were cut and mounted directly on a SEM plate, while soil and dust samples were prepared as “sprinkle-mounts” on 13 mm Cambridge style SEM stubs to which were affixed double-sided round carbon stickers. Sprinkle mounts were prepared by gently placing the sticker-affixed stub into the sample in a 50 ml polypropylene bottle and shaking the bottle until the carbon sticker was covered. A gentle spray with compressed air removed loose material not adhering to the double-sided sticker. After preparation, all samples were carbon-coated to render surfaces conductive under the electron beam.

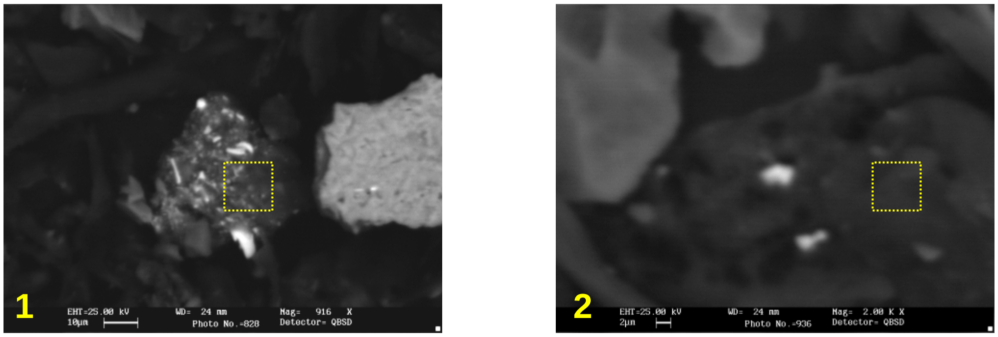
SEM Operating conditions were 25 kV accelerating voltage and 3 nA incident specimen current. Qualitative mineral identifications were made using 10 second counting times and semi-automated, systematic scans of sample surfaces were performed, stopping at candidate particles to identify and characterize grains when COC species were encountered. For each COC particle, measurements, qualitative identifications as well as photomicrographs were taken. For each scan, a target population of 30 occurrences were sought in an allotted 3 hour search period: lower statistics were encountered within the allotted time at low total grades. Relative abundance data of heavy metal species were determined by summing the total area of individual grain species and dividing by the total area of all counted heavy metal grains.

Results – Dust Samples

Appendix 1 provides raw data for all dust samples and Figures 1 and 2 illustrate summarized Tessier and mineralogical data respectively. The following discussion, along with mineralogical and petrographic evidence is devoted to comparing the analytical and mineralogical results to provide an explanation of the Tessier data.

Tessier and mineralogical data reveal the following points:

1. **As** and **Se** data are sparse, with few significant levels of reducible Se whereas organically bound As predominates. Although arsenopyrite (FeAsS) was the dominant mineralogical As-carrier found in this study, there is insufficient As in this form to account for all, and certainly not most As. There is evidence that Se occurs in metallic Pb-bearing species and it is possible that As may similarly be associated with Pb. However, since most mineralogically bound As in the Ni-rich concentrates historically produced in the Sudbury district occurs as Ni-arsenides, and given the smelting behaviour of As, it is not unexpected that As would occur bound to fugitive coke-like emissions. Photomicrographic evidence of porous, carbon-rich particles (Figures1 and 2) has been documented in this study, consistent with coke.



Figures 1 and 2. SEM/BSE photmicrographs **(1.)** A Pb-sulphate-rich particle composed predominantly of organic material rich in K, Al, Ca, S and Si, probably representing slag/coke (584-1308-18). The bright particle at right is a porous Fe-oxide, probably hematite. (**2.)** A partial, high magnification view of a porous, carbon-rich particle hosting two inclusions of Ni-sub-sulphide (Ni_3S_2). (05-51311-5). Yellow boxes denote areas analysed by SEM/EDS yielding detectable Ni and Cu levels.

2. Sequential leach **Pb** results generally show very low (9 ppm on average) residual values and somewhat higher exchangeable (28 ppm on average) and carbonate (78 ppm on average) Pb values. Average reducible and organic values of 187 and 158 respectively show that Pb behaves chemically similarly to As and Se. Mineralogical evidence, of which Figure 1 is fairly representative, demonstrates that a substantial proportion, if not most, Pb is present as Pb-sulphate. It is clear that sulphate-Pb completely enveloped by organic material may be protected from complete reducible leaching. Subsequent organic stripping would liberate this Pb, rendering it amenable to leaching. The proportion of sulphate- to metallic Pb identified mineralogically is consistent with the ratio of combined reducible+organic to residual Pb, suggesting that metallic compounds account for the residual Pb.

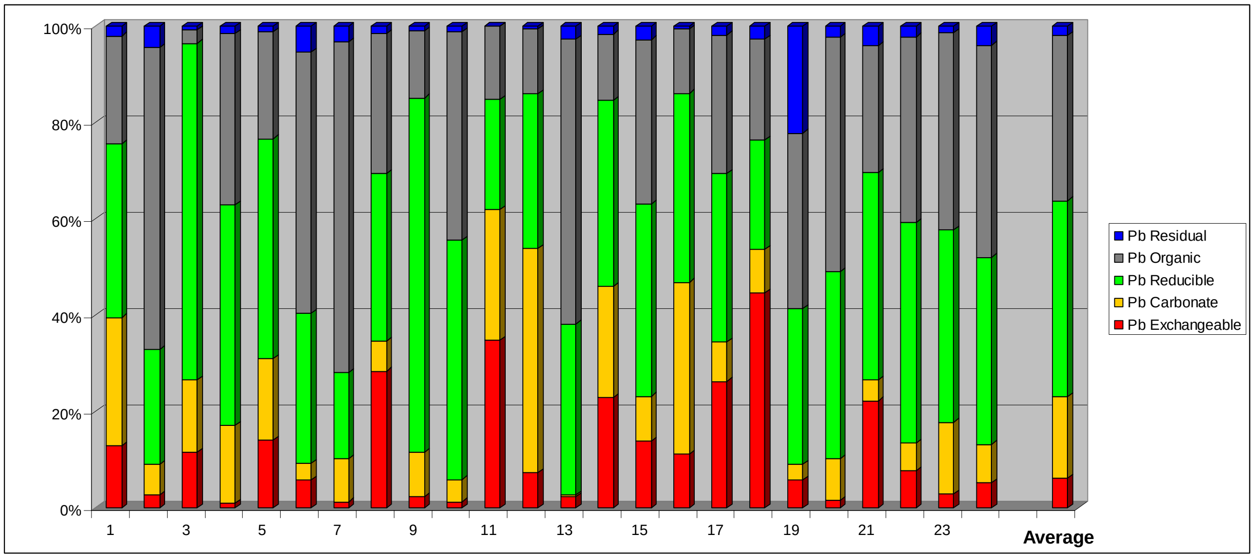


Figure 3. Tessier results for Pb normalized to 100% for all dust samples, with an average at far right.

3. **Cu** data, in contrast to Pb, show exceptionally high organic extractions. On balance, mineralogical data are difficult to reconcile with the sequential leach data, suggesting that a significant proportion of Cu has not been mineralogically accounted for. In an attempt to identify a significant Cu-host that would redress this balance, 5 samples (1, 6, 11, 16 & 21) were briefly examined for the presence of alternative forms of Cu. Results showed that a significant number of organic particles which show no evidence of any oxide,

sulphide or metallic Cu species nevertheless show Cu and Ni contents at the 0.5 % level (Figures 5 and 6).

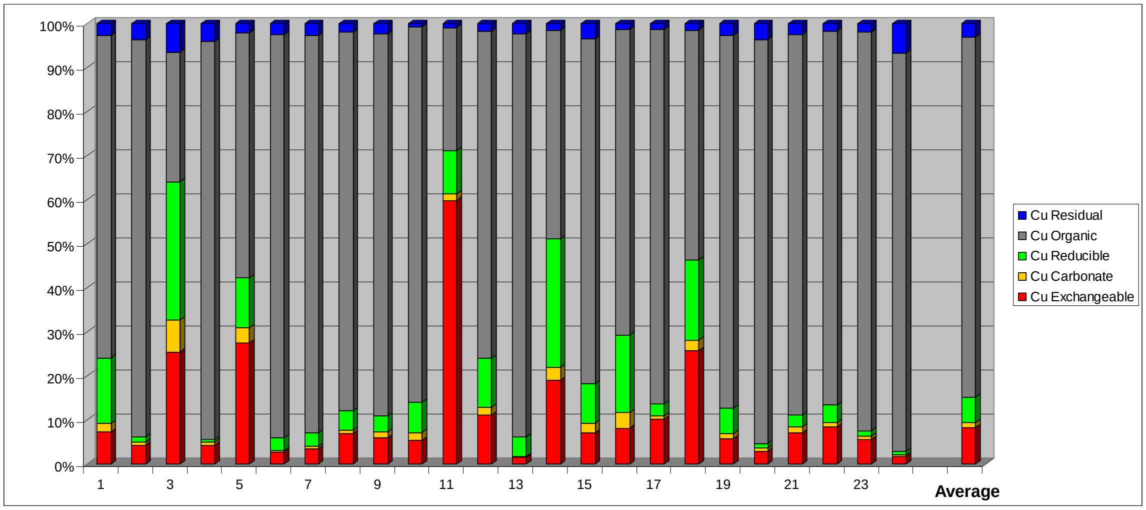
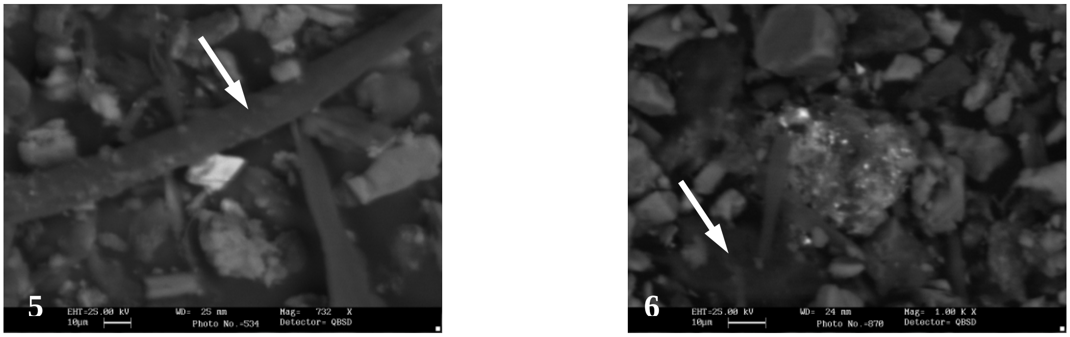


Figure 4. Tessier results for Cu normalized to 100% for all dust samples, with an average at far right.



Figures 5 and 6. SEM/BSE Photomicrographs. **(5)** Fibrous, organic particle (Sample 529-51297) containing detectable Cu and Ni contents. The brighter grain beneath is a pyramidal Fe/Ni-sulphate crystal. **(6)** Apart from the Pb- and Cu-bearing particle in centre view, the particle at the lower left (white arrow) carries significant Cu and Ni contents. (Sample 600-5781)

4. Except for absolute values, Ni and Co sequential leach results are very similar and only **Ni** results are shown in Figure 7. Substantially higher residual extractions than other metals imply persistence of identified Ni-alloy into this fraction.

5. Apart from organically bound Ni discussed regarding Cu above, a highly complex Ni-species assemblage has been noted in several dust samples. In particular, mixed composite particles of metal-oxide, sulphate and metallic and sometimes even sulphides indicate an assemblage usually only witnessed in refinery products. Sulphate species similar to those detected in the air filters were detected in the dust samples.

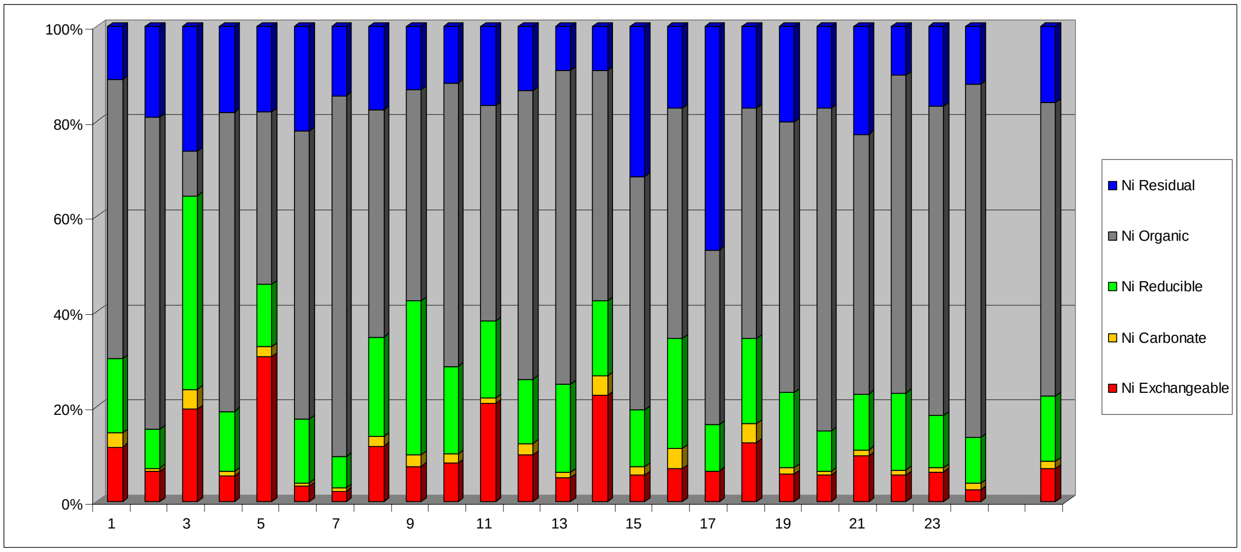


Figure 7. Tessier results for Ni normalized to 100% for all dust samples, with an average at far right.

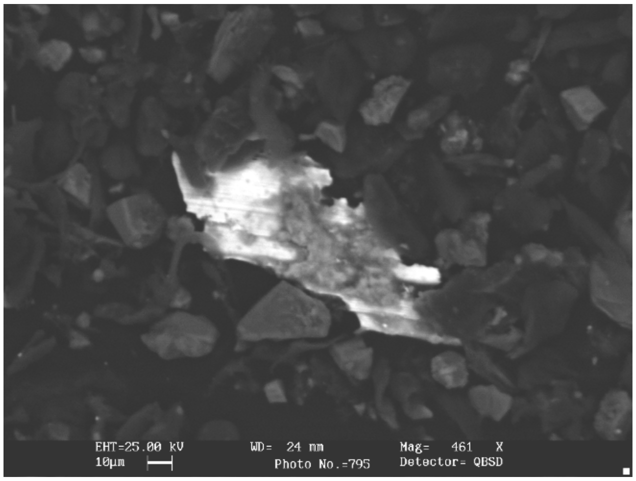


Figure 8.

SEM/BSE Photomicrograph of a striated Ni-alloy particle with a mixture of slag-like material, Ni-oxide and Ni-sulphate.

Results – Air Filter Samples

Appendix 2 provides raw data for all air filter samples and Figures 9 and 10 illustrate summarized Tessier and mineralogical data respectively. As before, analytical, mineralogical and petrographic evidence is presented in the following section to assist in explaining the Tessier data.

Tessier and mineralogical data reveal the following points:

1. As with dust samples, air filter results show sparse **As** data, with detectable exchangeable and organic values only. A single Ni-As grain was detected mineralogically, consistent with low analytical values. By contrast, **Se** data show detectable data for all fractions, with organic fraction hosting highest values on average. No Se-species were detected mineralogically,

2. It is difficult to reconcile or explain the Tessier results except to state that Se is known to correlate with metallic and/or sulphide-Cu species. Although lower-than-detection level results are witnessed in As data, detectable As data appear to show an even spread between exchangeable and organically-bound As. This suggests a similarity to dust data in terms of organically-hosted As, and mineralogically unaccounted-for exchangeable As-species. This is consistent with higher sulphate species in general (Ni and Pb) encountered in the filter mineralogy.

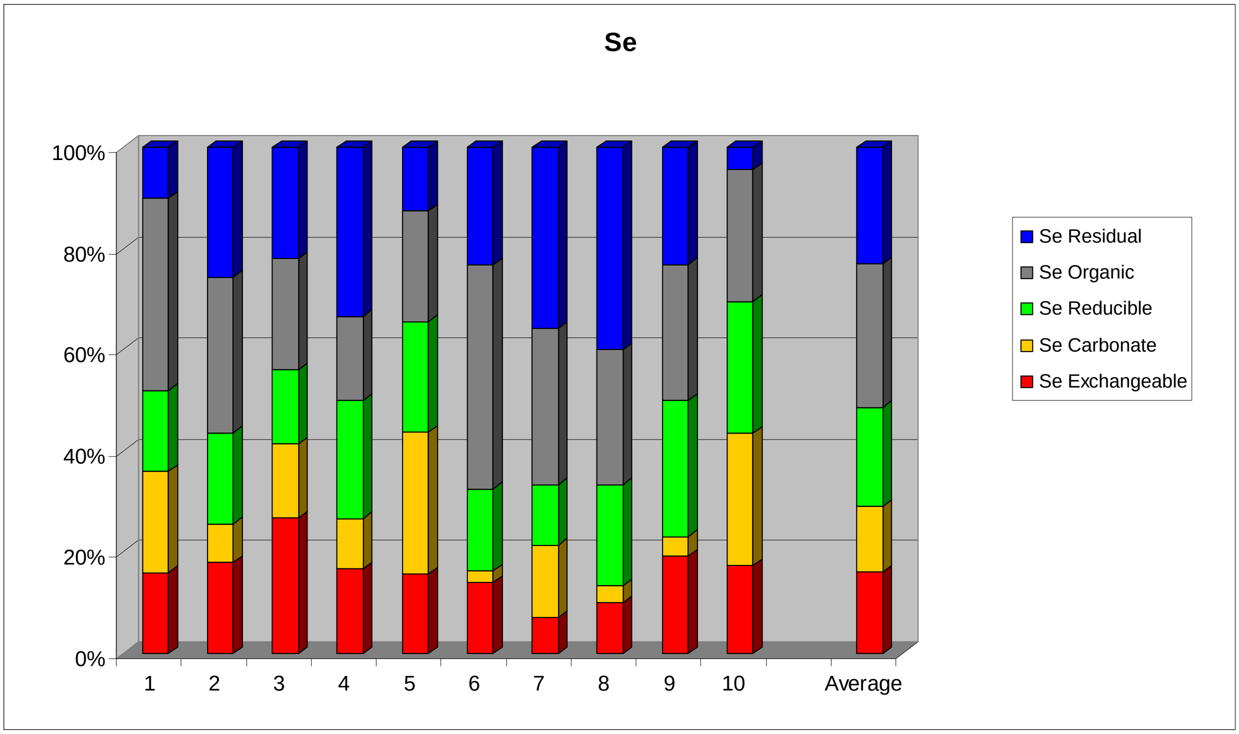


Figure 9. Tessier results for Se normalized to 100% for all filter samples, with an average at far right.

3. Sequential leach **Pb** results for filters also show high exchangeable values (as with As; demonstrating a probable mineralogical affinity of arsenate and sulphate species). An overall systematic increase in residual values with decreasing exchangeable values is witnessed, and is supported Mineralogically in that metallic species are more common in the latter three samples.

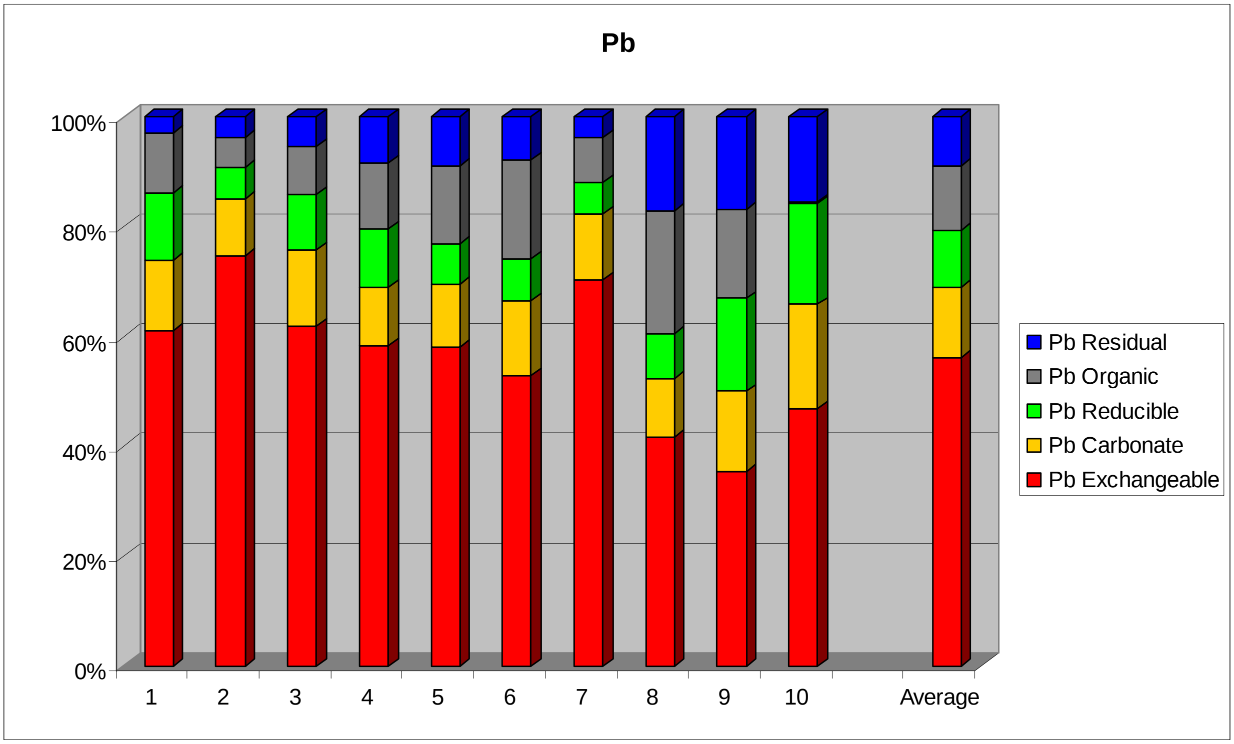


Figure 10. Tessier results for Pb normalized to 100% for all filter samples, with an average at far right.

4. Sequential leach **Cu** results for filters also show a residual Cu fraction increasing in the same order as for Pb, but exchangeable Cu values are erratic.

5. Exchangeable Cu data suggest highly variable and significant sulphate-Cu species but are not consistent with mineralogical data. It is likely that these species were missed in the mineralogical study and to test for this possibility, additional inorganic and organic species were sought separately. Photomicrographs depcted in Figures 12 and 13 reveal difficult-to-resolve yet detectable phases, probably sulphates and similar species which form matted clusters, partial coatings and films which appear to have precipitated or settled on the filters in a different manner than simple entrapment of PM10 particles within filter fibres.

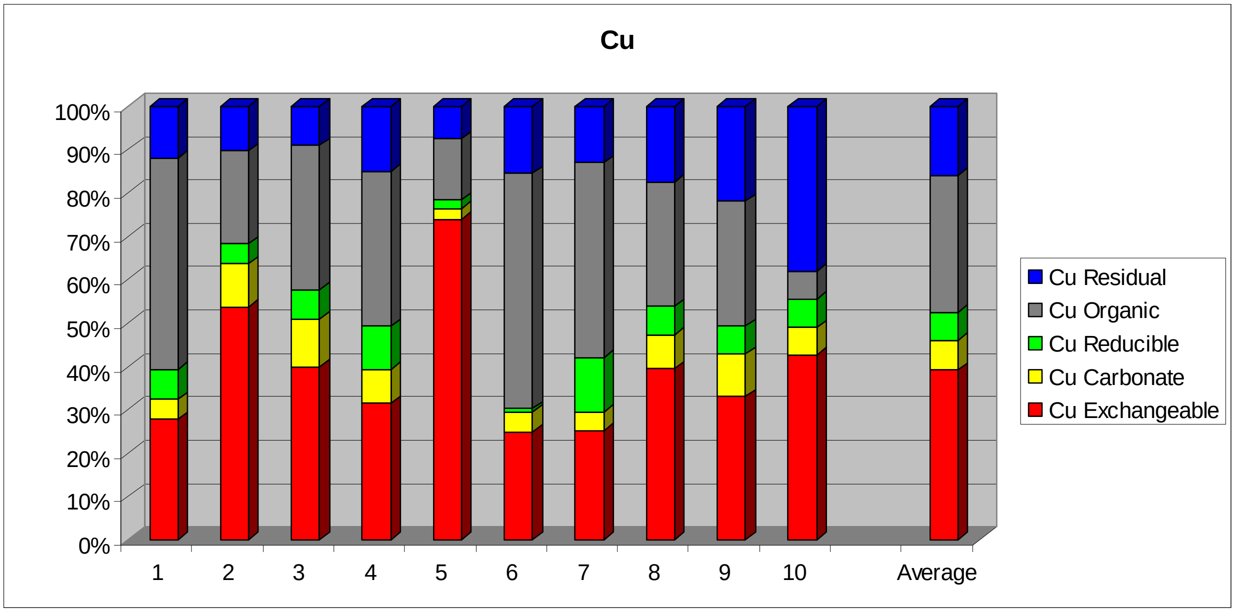
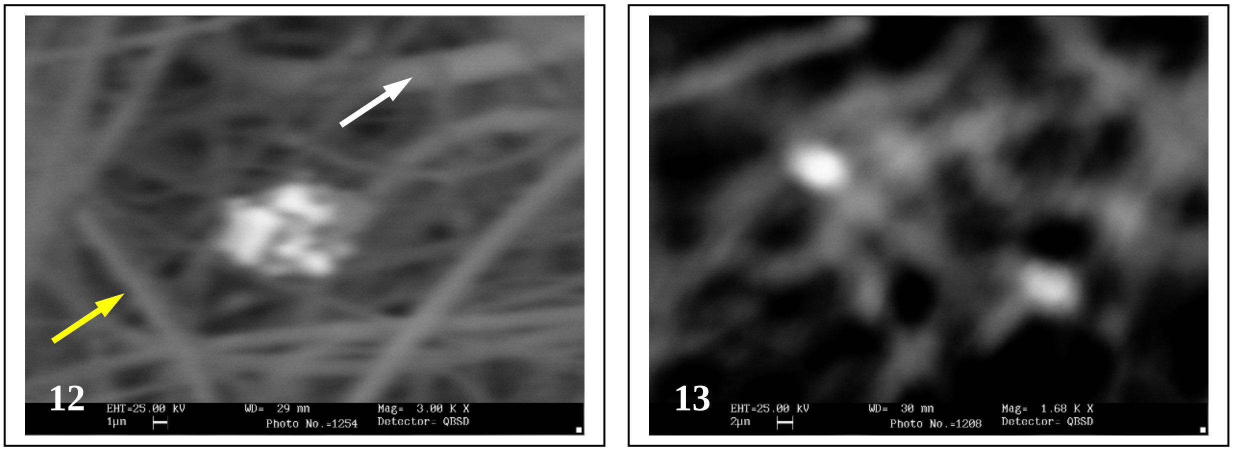


Figure 11. Tessier results for Cu normalized to 100% for all filter samples, with an average at far right.



Figures 12 and 13. SEM/BSE Photomicrographs**.** **(12)** A composite particle of about four Cu-sulphide grains set in a lower BSE intensity Ni-sulphate matrix (Sample 200404810). Despite poor resolution, note also the jagged appearance of some of the filter fibres, providing evidence of a likely surface coating to some fibres (white arrow denotes clear fibre, yellow arrow a coated fibre which shows evidence of elevated Cu and Ni levels). **(13)** Two high-BSE species, a Pb-sulphate and a Cu-sulfide trapped in filter fibres heavily loaded with unresolved species of Cu, Co and Ni, showing both S and O, the latter in excess of oxygen typically associated with Si-fibres.

6. **6.** Tessier Co data (Figure 14) are somewhat similar to Cu data but very little mineralogical data on Co is apparent. High exchangeable values do, however, correlate with the presence of detectable oxides as well as the observation that Mn was noted by EDS with many anglesite and Fe-Ni-oxide grains.

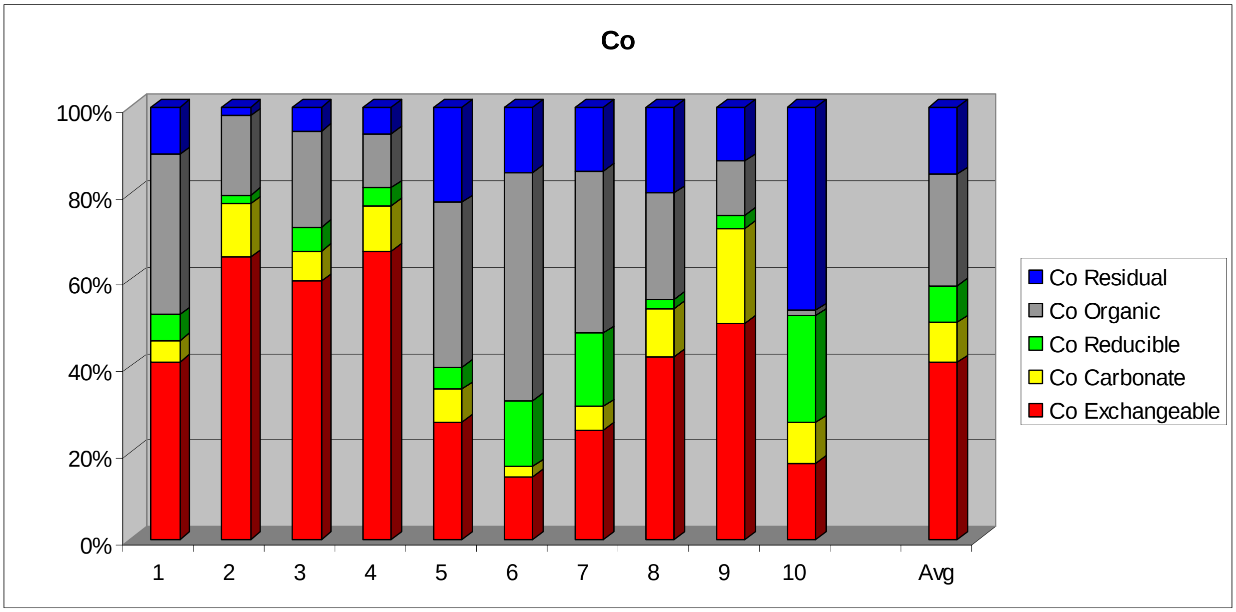


Figure 14. Tessier results for Co normalized to 100% for all filter samples, with an average at far right.

7. **Ni** leach results**,** unlike the soil data, do not directly correlate with Co results, indicating a closer affinity of Co with Cu. This is consistent with a control by refining processes and by inference, probable location to Cu-refining premises.

8. Significantly higher residual Ni values are characteristic of the air filter results relative to Co and Cu. This correlates with somewhat higher pentlandite mineral contents determined mineralogically. Again, residual Ni may be buffered by Ni bound by organics which may be released by the organic leach step (see figure 16)

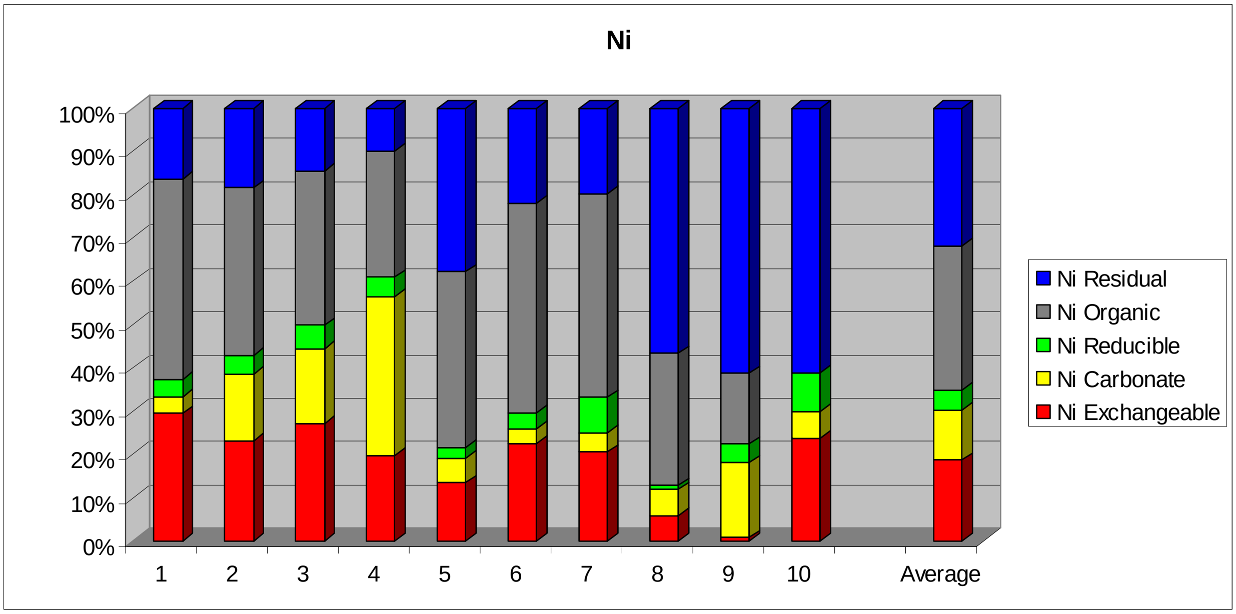
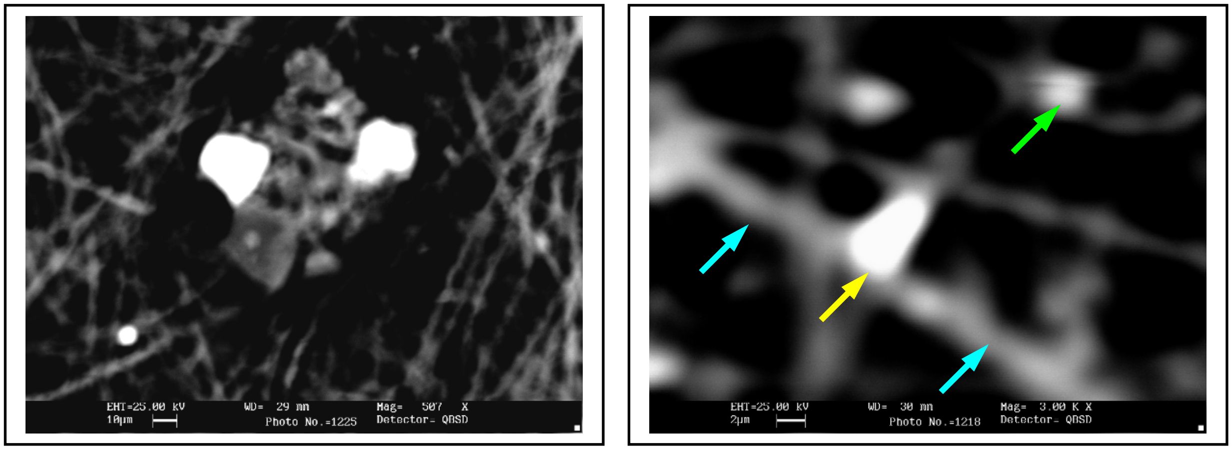


Figure 15. Tessier results for Ni normalized to 100% for all filter samples, with an average at far right.



Figures 16 and 17. SEM/BSE Photomicrographs. **(16)** Two pentlandite grains attached to an ashed coke particle (sample 200404813, location 7). The coke/slag particle also showed detectable Cu contents. **(17)** A large Pb-sulphate grain (yellow arrow) and a Ni-sulphate (green arrow), together with abundant filming on fibres (blue arrows). Sample 200404810, location 6. The fact that these species are of a lower BSE signal intensity than sulphates suggects they are probable sulphates and/or oxy-hydroxy-sulphates or hydroxide species.

Results – Additional TSP Air Filter Samples (2004040811 & 2004040722)

After preliminary review of the data, two additional TSP air filter samples were submitted as part of a due diligence study. SEM results for these samples are presented in Appendix 2. These samples were selected for direct comparison against filters from similar locations and were significantly loaded with particulate material which is coarser than the original filters.

The search on TSP filter 2004040811 yielded no Ni-sub-sulphide.

Results from TSP filter 2004040722 did yield Ni-sub-suphide, consistent with results from filters 20004040724 and 2004040725.

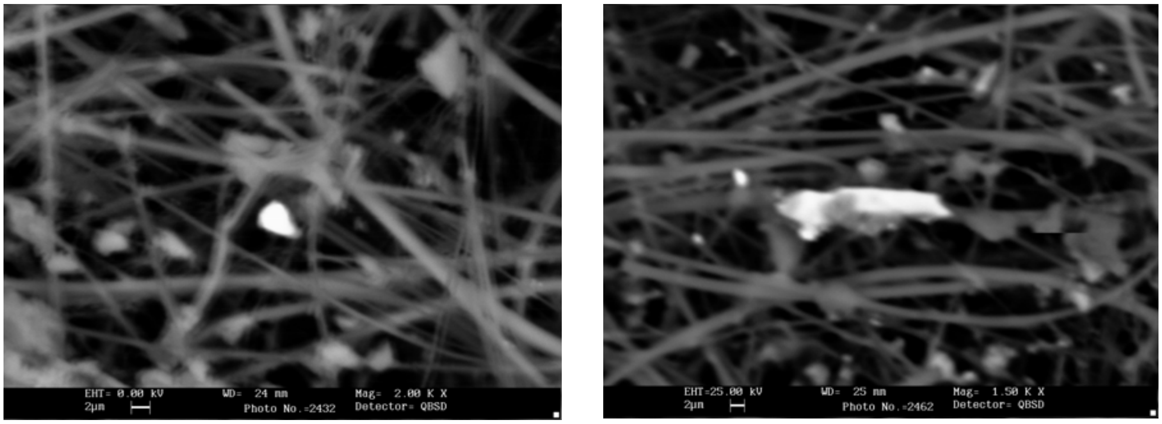


Figure 18. SEM/BSE Photomicrographs of Ni species detected in (A) TSP filter 2004040722 and (B) TSP filter 2004040811. In (A), a small Ni-Sulphide (Ni_3S_2) identified as Ni-sub-sulphide is illustrated. In (b), a large, plate-like millerite (NiS) grain is illustrated.

Results – Soil Samples

Appendix 3 provides raw data for all soil samples and Figures 19 through 24 illustrate summarized Tessier and mineralogical data respectively. The following discussion, along with mineralogical and petrographic evidence is devoted to comparing the analytical and mineralogical results to provide an explanation of the Tessier data. Results indicate:

1. Without detectable exchangeable and carbonate As data not much can be said of As except that organic-bound As predominates. Only rare sulpharsenide species were detected in two soil samples, indicating non-detection of reducible and organic As-hosts. It is inferred once again that fugitive ash/coke/slag materials host most of this As.

2. Pb data indicate lowest exchangeable and carbonate levels in all sample types and organic and reducible values vary sympathetically. Considering the mineralogical data, reducible Pb appears to derive from liberated anglesite, whereas organic Pb derives from both adsorbed and occluded Pb-species in organics/ash.

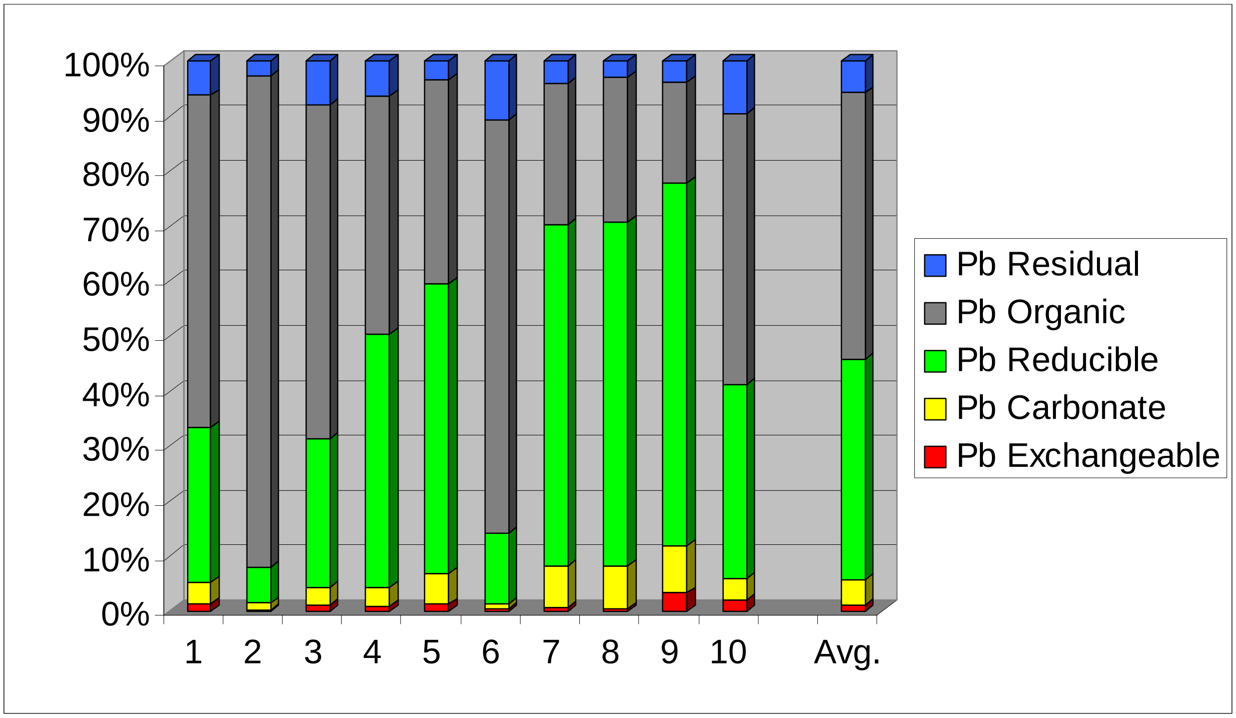


Figure 19. Tessier results for Pb normalized to 100% for all soil samples, with an average at far right.

3. As with Pb, **Cu** shows very little exchangeable and carbonate-values and residual values are conistently low. The highest residual Cu yield (location 6 or sample 522) correlates with mineralogically detectable Cu-alloy, indicating that alloy is least susceptible to acid leaching.

4. An apparent correlation between Tessier organic-Cu data and Cu-sulphides is indicated which if true, may simply reflect the mechanism by which Cu-sulphides are transported as occluded grains within fugitive ash-like emissions. Sulphide Cu levels are too low to account for all Cu and they would be expected to be fairly resistant to the Tessier leach procedure.

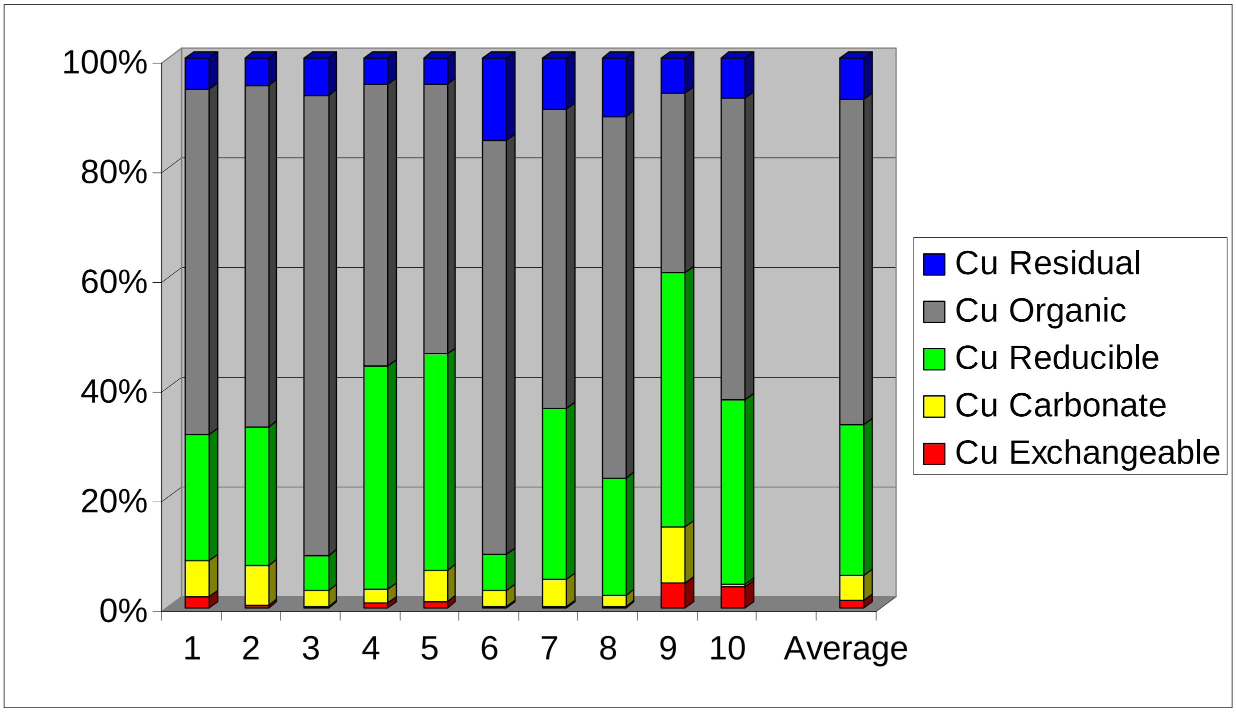


Figure 20. Tessier results for Cu normalized to 100% for all soil samples, with an average at far right.

5. **Ni** data, unlike Cu and Pb, indicate moderate levels of exchangeable and carbonate Ni. For Cu and Pb, the results imply these species do not survive the exterior environment. For Ni, equivalent species are either more resistant or newly formed mobile Ni species form in the environment subsequent to oxidation of released and non-benign Ni-species.

6. The highest Tessier result is in the reducible Ni category, which correlates with a high mineralogically determined oxide group content. This provides direct evidence that oxide phases represent this leach category.

7. A significant drop in organic-Ni relative to filter and dust samples supports the observation that sulphide is finer grained than these alloy/oxide particles and that the association with fugitive emissions is significant (Figure 22). It should also be noted that pentlandite can be derived from either ore materials or from smelter matte.

8. It is believed that some species designated as alloys of Fe, Co, Ni and Cu are likely also oxide species. Figures 23 and 24 represent examples, from which it is evident that a range from metal rich to oxide-rich particles exist.

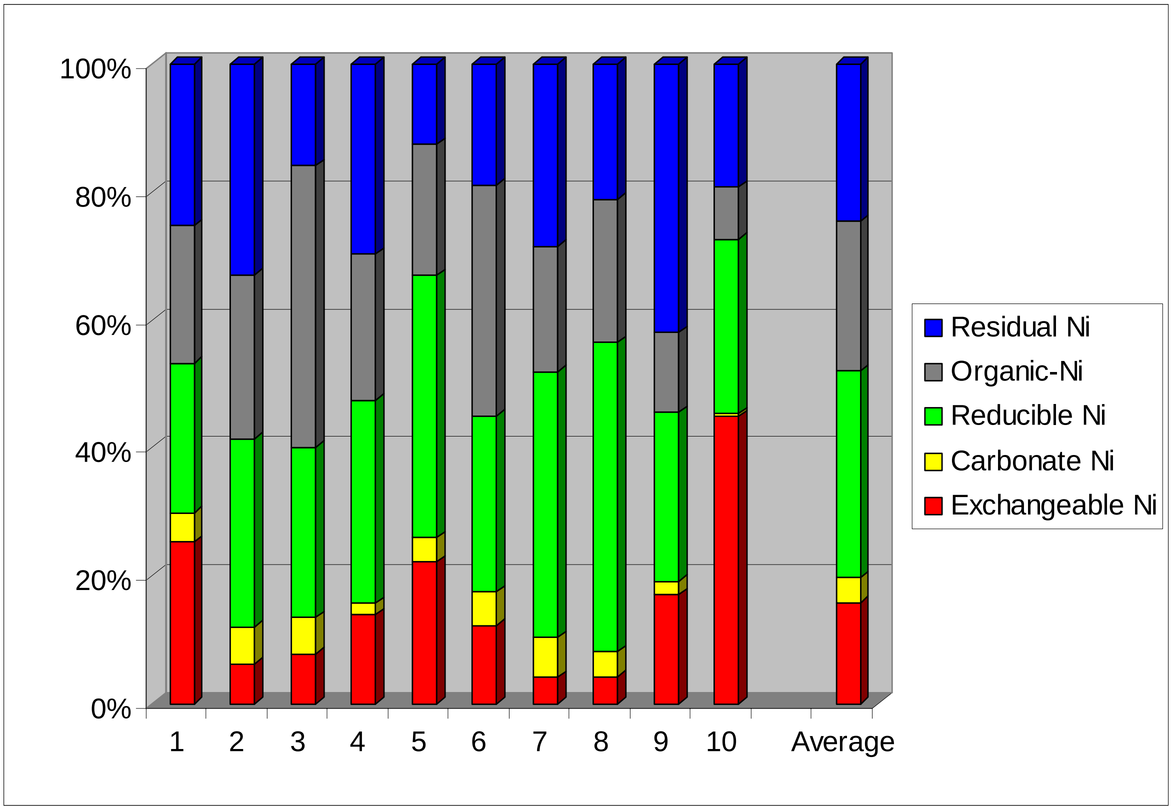


Figure 21. Tessier results for Ni normalized to 100% for all soil samples, with an average at far right.

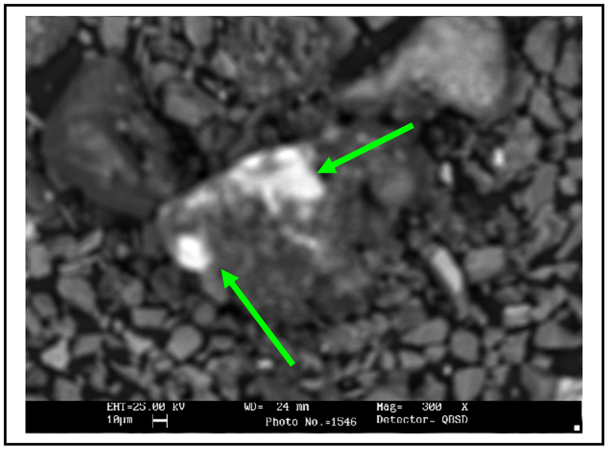
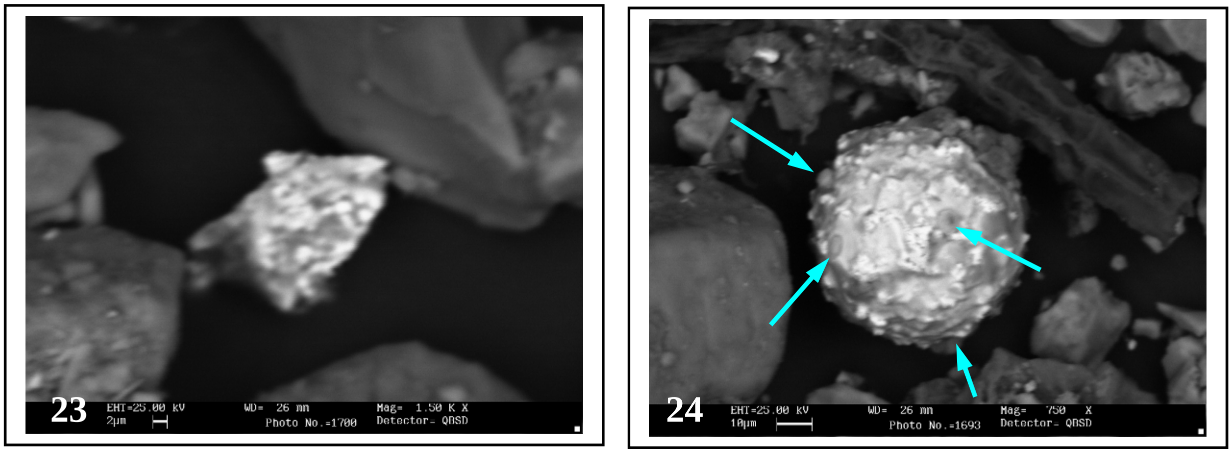


Figure 22.

Pentlandite grains (green arrows) enveloped by a slag/coke-like particle. This is a common associaton which provides evidence that these sulphides have been transported by fugitive coke/slag particles.

Sample 507ss./Location 3



Figures 23 and 24. SEM/BSE Photomicrographs. **(23)** An angular Ni-oxide particle with several protrusions of higher-BSE species, likely metallic (Soil sample 561ss). **(24)** A large rounded Ni-Fe-alloy particle with numerous rounded oxide grains adhering to the periphery (blue arrows).

Conclusions and Recommendations

The following points represent the major findings of this investigation:

1. Data have been presented to reconcile both mineralogical and analytical results of this study. Although difficult to interpret at face value, correlations emerge best when viewed in a between-material (i.e. soil, dust & filter) context. In particular, the following conclusions and inferences can be drawn:

    a. Most mineralogically identified Pb is present as anglesite (Pb-sulphate) and no mineralogical evidence for speciation differences by Tessier leach was apparent. There is clearly a major proportion of mineralogically unaccounted Pb. Some Pb-sulphide may be present but Tessier data reveal exchangeable and carbonate-Pb which is inferred to be oxidic and unaccounted for mineralogically. More sophisticated techniques or methods should be applied to confirm this.

    b. Moreover, for Pb-data, it is interesting that direct nitric leaches extract on average 39% less than the sequential leach. Petrographic evidence of occlusion by organics suggests an interpretation due to liberation of Pb species during the organic step.

    c. Mineralogical Arsenic and Selenium data are sparse; measurement statistics preclude any correlations to be made.

    d. In terms of copper, exchangeable Cu predominates in the filters, reducible and organic Cu in the dusts, and organic and reducible Cu in the soils. Mineralogically, filters were found to contain high and approximately equal proportions of Cu-Fe-sulphide and Cu-sulphide (chalcocite or Cu-matte) and evidence of sub-micrometer sulphates on filter fibres was found. Dust samples showed predominant Cu-sulphide and Cu-oxide, with substantially less Cu-Fe-Sulphide. Soil sample mineralogical results revealed that Cu-Fe-sulphide and Cu-alloy species predominate. Although a distinct Cu species bias appears to mask potential correlations, it is suspected that organic particles carrying fine sulphides also affect speciation results. By virtue of their encapsulation in organic particles, organic Cu values can be taken as evidence of light (i.e. low SG) materials.

e. On average, residual Ni values are higher than all other COC residual values for all data sets. Predominant Ni categories are roughly equal parts of residual and organic-Ni in filters, organic-Ni in dusts, and equal parts of reducible, organic and residual-Ni in the soils. Mineralogically, Ni-sulphides predominate (>66% combined) in the filter mineralogy, with lesser Ni-oxides (16%) and subordinate Ni-sulphates; these results are difficult to correlate with leach data. In dust samples, sulphide values drop on average (42%), with an increase in Ni-sulphate (11%) and oxide (21%) and significantly more metallic/alloy-Ni. These data are particularly difficult to reconcile with Tessier organic-Ni results, from which it is inferred that it is key to understand the mechanisms by which the organic fraction is leached.

2. It is difficult to establish direct correlations between mineralogical and Tessier results for the following reasons:

a. The current mineralogical approach was adapted from a method designed to locate and characterize high atomic number species which normally show as high BSE intensity species under the SEM. As a consequence of the presence of sulphates and organic material hosting COC's, a bias has been introduced and difficulties in interpretation resulted.

b. There is a regrettable lack of information in the literature on the actual response and mineralogical influences on the Tessier leach procedures.

3. Notwithstanding the above, differences in both Tessier and mineralogical data do however show comparable differences between the different materials, allowing certain correlations and inferences to be made. Specifically, filters, dusts and soils show characteristics explicable in terms of speciation effects and likely provenance.

4. Mineral assemblages for most COC’s are apparently common to all samples, but with relative proportions varying between filters, dusts and soils. The differences are consistent with: (1) presence and preservation of sulphates and organic particles (c.f. Figures 1, 2, 16 and 21) in air filters, (2) a high organic fraction in dusts (Figures 5 and 6), indicating a more airborne fraction and, (3) a high proportion of metal-oxide species (64 % combined Ni- Co- Cu-oxides) in the soil samples.

5. To confirm the inferences and correlations, particularly regarding bio-available and mineralogically unaccounted species, it is recommended that select materials be subjected to further leaches, and residues generated in the leach procedure be studied in order to unequivocally establish species categories.

6. After initial reviews of mineralogical data, two additional air filters (TSP filters 2004040722 and 2004040811) were submitted to test for the presence of heazlewoodite (Ni_3S_2). Results from filters in close proximity to these stations indicated the presence of Ni_3S_2. The TSP filter results confirmed the presence of Ni_3S_2 in TSP filter 2004040722 but not in TSP filter 200408040811.

7. Given the statistical representation and the SEM/EDS limitations in the current study protocols, it is recommended that Ni-sub-sulphide be unequivocally confirmed by more sensitive techniques.

APPENDIX 1: Dust Results

Position				1	2	3	4	6	7
Sample COC	**Mineral**	**Qualification/Interpretation**	**Possible Derivation**	**502 57824**	**504 57822**	**510 05-1291**	**512 57826**	**513 05-1292**	**515 57830**
Pb	**anglesite**	PbSO4: May in cases be galena (PbS)	Smelting/Refining(?)	5.7	3.1	10.7	67.1	49.0	2.4
	Pb-Sn	Pb/Sn alloy: either solder or other	Domestic(?)	0.0	0.0	0.0	0.0	0.0	0.0
	Pb-Cl	Chloride a probable smelter emission	Smelting/Refining(?)	0.0	0.0	0.0	0.0	0.0	0.0
	Pb/Te/Se	Possible smelter alloy or oxide/sulphate	Smelting/Refining(?)	0.0	0.0	2.1	0.0	0.0	0.0
Zn	**sphalerite**	ZnS; trace Ore mineral	Ore	59.5	0.0	0.0	0.0	0.0	0.0
As	**arsenopyrite**	FeAsS; trace Ore mineral	Ore	5.2	0.0	0.0	0.0	0.0	0.0
	As-Oxide	Either As-flue species or domestic origin (As could be from ore, coal/coke or protective wood-coating wash)	Smelter emission(?)	0.0	0.0	0.0	0.0	0.0	0.0
Cu	**tetrahedrite(?)**	Cu-Sb-S; trace ore mineral	Ore	0.0	0.0	0.0	0.0	0.0	0.0
	chalcopyrite	Cu-Fe-S; essential ore mineral	Ore	5.8	0.0	0.0	1.7	0.0	0.9
	Cu-matte	Cu2S: matte sulphide/chalcocite-phase	Smelter/matte	2.7	0.3	9.9	0.0	14.4	34.9
	Cu-sulphate	Cu-S-O phase; Cu-refining phase	Refining	0.0	23.3	6.6	0.0	11.7	5.5
	Cu-Oxide	CuO: Cu-refining phase	Refining	0.0	0.0	1.4	1.5	0.0	11.3
	Cu-Metal	CuO: Cu-refining phase	Refining	0.0	0.0	3.7	0.0	0.0	0.0
	brass	Cu>Zn; domestic or miscellaneous	Domestic/Other	0.0	0.0	3.6	0.0	7.1	0.0
Ni,Co	**pentlandite**	Fe-Ni-Sulphide; major ore mineral	Ore	2.7	0.0	0.0	27.1	0.0	0.0
	millerite	NiS	Ore	2.0	0.0	0.0	0.0	0.0	5.5
	heazlewoodite	Ni3S2; nickel subsulphide	Smelter/matte	5.6	26.3	21.8	2.6	0.0	21.7
	Ni-Sulphate	Cu-S-O phase; Cu-refining phase	Refining	0.0	2.3	14.8	0.0	0.0	3.6
	Ni-oxide	NiO: Ni-refining phase	Refining	7.0	17.6	17.9	0.0	17.9	14.2
	Ni-Co-Oxide	NiO: Ni-refining phase	Refining	0.0	0.0	0.0	0.0	0.0	0.0
	Ni-metal	Ni: Ni-refining phase	Refining	0.0	27.1	7.7	0.0	0.0	0.0
	steel	Tramp metal/stainless steel(?)	Miscellaneous	3.7	0.0	0.0	0.0	0.0	0.0
Se	**Se-metal(?)**	Unknown; likely metallic refining residue	Refining(?)	0.0	0.0	0.0	0.0	0.0	0.0
			Total	100.0	100.0	100.0	100.0	100.0	100.0

Chemical Analysis

	502 57824	**504 57822**	**510 05-1291**	**512 57826**	**513 05-1292**	**515 57830**
LEACH ASSAYS						
As Exchangeable	< 5	< 5	< 5	< 5	< 5	< 5
As Carbonate	< 5	< 5	< 5	< 5	< 5	< 5
As Reducible	5	< 5	36	6	21	5
As Organic	17	18	< 5	27	13	20
As Residual	< 5	< 5	< 5	< 5	< 5	< 5
Co Exchangeable	4.8	2.1	4.9	3.2	2.9	1.2
Co Carbonate	< 0.3	0.4	1.0	0.8	0.3	0.7
Co Reducible	12	5.4	23	21	11	11
Co Organic	20	20	3.3	70	10	30
Co Residual	16	6.3	9.7	17	6.4	18
Cu Exchangeable	30	43	130	130	390	59
Cu Carbonate	8.0	6.6	37	21	50	9.9
Cu Reducible	61	12	160	19	160	63
Cu Organic	300	890	150	2700	790	2000
Cu Residual	11	36	33	120	30	56
Ni Exchangeable	55	47	230	140	160	49
Ni Carbonate	14	5	49	24	11	11
Ni Reducible	75	60	480	320	69	200
Ni Organic	280	480	110	1600	190	910
Ni Residual	54	140	310	460	94	330
Pb Exchangeable	15	4.4	25	42	108	8.8
Pb Carbonate	31	10	32	630	130	5.3
Pb Reducible	42	38	150	1800	350	47
Pb Organic	26	100	5.9	1400	170	82
Pb Residual	2.4	7.0	1.8	63	9.5	8.2
Se Exchangeable	< 5	< 5	< 5	< 5	< 5	< 5
Se Carbonate	< 5	< 5	< 5	< 5	< 5	< 5
Se Reducible	7	< 5	< 5	< 5	8	< 5
Se Organic	< 5	< 5	< 5	9	< 5	< 5
Se Residual	< 5	< 5	< 5	< 5	< 5	< 5

5	8	9	10	11	13	14	15	12	16
521 05-1294	**522 05-1295**	**523 57797**	**525 57817**	**529 05-1297**	**533 05-1298**	**534 57834**	**541 05-1300**	**550 05-1301**	**552 05-1302**
3.7	3.3	5.7	63.9	16.0	27.2	18.1	39.5	12.2	34.6
0.0	0.0	0.0	3.5	0.0	2.9	3.5	23.1	0.7	12.3
0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	2.4
0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
0.0	4.5	0.0	0.0	1.7	0.0	0.0	0.0	0.0	12.3
0.0	0.0	0.0	0.0	0.0	0.0	0.0	1.8	0.0	0.0
0.0	0.0	0.0	0.0	0.8	0.0	0.0	0.0	0.0	0.0
0.0	0.0	0.0	0.0	15.3	0.0	0.0	0.0	0.0	0.0
33.6	22.7	36.8	0.0	14.0	26.0	0.0	4.8	7.3	0.0
14.5	23.7	25.4	5.5	0.0	10.3	1.4	10.2	0.5	10.3
1.8	5.0	0.0	19.5	0.0	0.7	34.6	0.0	0.7	3.7
7.5	0.0	0.0	0.0	0.0	0.0	41.5	0.0	30.5	3.8
2.4	3.1	0.0	0.0	2.2	5.1	0.0	12.2	8.4	7.5
0.0	2.0	21.8	0.0	8.4	0.0	0.0	0.0	0.0	0.5
0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
14.3	1.4	9.0	0.0	5.5	0.0	0.0	2.0	37.1	0.0
17.0	17.3	0.9	4.1	16.4	0.0	0.0	0.0	0.1	0.0
4.4	5.3	0.0	3.5	19.6	27.8	0.9	0.0	2.4	0.0
0.0	6.7	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
0.8	0.0	0.0	0.0	0.0	0.0	0.0	3.6	0.0	0.0
0.0	5.0	0.4	0.0	0.0	0.0	0.0	2.8	0.0	10.3
0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	2.4
100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

521 05-1294	522 05-1295	523 57797	525 57817	529 05-1297	533 05-1298	534 57834	541 05-1300	550 05-1301	552 05-1302
< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5
< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5
10	9	8	< 5	< 5	11	< 5	< 5	< 5	10
170	15	5	22	22	12	82	15	6	13
7	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5
1.6	6.5	1.9	3.2	5.5	1.6	2.5	11	< 0.3	1.0
0.6	1.6	1.1	0.9	1.7	< 0.3	0.8	< 0.3	< 0.3	0.4
18	41	18	8.6	8.5	7.5	14	7.0	3.5	5.3
250	90	7.8	20	10	20	60	10	6.6	8.1
150	69	2.5	4.8	9.2	6.6	17	6.8	4.5	3.9
130	67	29	96	730	130	45	170	35	130
21	6.2	6.2	32	18	19	3.5	25	9.9	56
110	42	18	120	120	130	120	260	44	280
3300	820	420	1500	340	860	2500	420	380	1100
98	18	11	15	11	21	66	14	17	21
81	140	37	38	87	73	59	120	16	23
25	24	12	9	5	18	14	22	5	14
230	250	160	87	68	100	220	85	34	77
2700	570	220	280	190	450	780	260	140	160
520	210	66	56	70	100	110	50	90	57
10	40	2.4	10	73	46	7.7	25	9.8	126
71	8.7	9.2	35	57	290	1.5	25	6.5	400
140	49	74	380	48	200	120	42	28	440
540	41	14	330	32	84	200	15	24	150
26	2.2	1.0	9.4	< 0.7	3.9	9.0	1.8	2.0	6.7
< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5
< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5
6	< 5	< 5	< 5	33	5	< 5	20	< 5	6
5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5
< 5	< 5	< 5	< 5	< 5	< 5	< 5	9	< 5	< 5

17	18	19	20	21	22	24	23			
560 05-1303	**572 05-1305**	**582 05-1307**	**584 05-1308**	**600 57810**	**601 05-1310**	**602 05-1311**	**606 05-1312**	**Average**	**COC**	**Mineral**
13.9	11.0	25.2	28.9	6.7	19.0	44.9	0.9	**21.4**	**Pb**	**anglesite**
8.4	3.3	1.8	0.0	0.0	0.0	0.0	0.0	**2.5**		**Pb-Sn**
0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	**0.0**		**Pb-Cl**
0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	**0.2**		**Pb/Te/Se**
0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	**2.5**	**Zn**	**sphalerite**
0.0	0.0	6.0	0.0	16.1	52.8	7.7	0.0	**4.4**	**As**	**arsenopyrite**
0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	**0.1**		**As-Oxide**
0.0	9.1	0.0	0.0	0.0	0.0	0.0	0.0	**0.4**	**Cu**	**Tetrahedrite**
0.0	0.0	0.0	3.4	0.0	0.0	15.7	18.2	**2.5**		**chalcopyrite**
0.0	2.4	2.4	0.3	0.0	0.0	1.6	26.6	**10.0**		**Cu-matte**
4.1	1.1	0.0	5.2	5.3	0.6	3.7	24.2	**8.0**		**Cu-sulphate**
11.0	0.0	0.0	5.0	7.2	11.2	0.0	0.4	**4.8**		**Cu-Oxide**
0.0	0.0	0.0	0.0	0.4	0.3	0.3	0.0	**3.7**		**Cu-Metal**
5.3	6.6	0.0	0.0	19.0	2.7	3.1	0.0	**3.7**		**brass**
0.0	0.0	46.1	15.2	0.0	0.0	2.6	0.0	**5.3**	**Ni,Co**	**pentlandite**
0.0	0.0	0.0	11.1	6.1	0.0	0.4	8.9	**1.4**		**Millerite**
0.0	0.0	18.5	0.0	3.1	0.0	13.6	16.4	**8.3**		**heazlewoodite**
0.0	0.0	0.0	15.5	10.2	0.0	0.0	0.0	**4.3**		**Ni-Sulphate**
0.0	2.2	0.0	6.9	26.0	8.8	2.4	4.5	**7.9**		**Ni-oxide**
0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	**0.3**		**Ni-Co-Oxide**
0.0	51.3	0.0	0.0	0.0	0.0	1.8	0.0	**3.8**		**Ni-metal**
57.4	12.9	0.0	8.5	0.0	4.5	2.1	0.0	**4.5**		**steel**
0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	**0.1**	**Se**	**Se-metal(?)**
100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	**100.0**		**Total**

560 05-1303	**572 05-1305**	**582 05-1307**	**584 05-1308**	**600 57810**	**601 05-1310**	**602 05-1311**	**606 05-1312**	**Average**	
< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	As Exchangeable
< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	As Carbonate
< 5	< 5	< 5	8	< 5	6	< 5	26	12	As Reducible
< 5	10	8	39	14	26	6	130	31	As Organic
< 5	< 5	< 5	< 5	< 5	< 5	< 5	9	< 8	As Residual
0.4	3.1	0.4	1.8	0.8	0.8	0.6	2.9	3	Co Exchangeabl
< 0.3	< 0.3	< 0.3	0.4	< 0.3	< 0.3	< 0.3	1.0	< 0.8	Co Carbonate
1.7	3.4	4.1	8.3	1.7	4.1	3.2	23	11	Co Reducible
3.4	5.7	10	40	7.6	9.4	10	110	35	Co Organic
4.9	2.8	4.9	9.4	3.0	2.6	3.4	22	17	Co Residual
64	94	11	43	32	44	51	99	116	Cu Exchangeabl
4.4	8.6	2.1	10	6.7	5.3	6.6	21	16	Cu Carbonate
17	66	11	14	12	21	11	40	80	Cu Reducible
530	190	160	1300	390	440	810	5070	1140	Cu Organic
8.7	5.4	5.3	51	11	8.6	18	380	44	Cu Residual
12	16	8	63	23	16	36	130	69	Ni Exchangeable
< 1	5	2	7	3	3	5	72	16	Ni Carbonate
18	23	22	94	28	46	63	490	137	Ni Reducible
68	62	79	750	130	190	370	3800	615	Ni Organic
87	22	28	190	54	29	96	620	160	Ni Residual
21	49	2.9	8.2	16	11	5.0	13	28	Pb Exchangeable
6.5	10	1.6	44	3.1	8.3	25	20	78	Pb Carbonate
28	25	16	200	31	65	67	97	187	Pb Reducible
23	23	18	250	19	55	69	110	158	Pb Organic
1.5	3.0	11	12	2.9	3.2	2.3	9.9	9	Pb Residual
< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	Se Exchangeabl
< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	Se Carbonate
< 5	6	< 5	< 5	< 5	< 5	< 5	< 5	< 6	Se Reducible
< 5	< 5	< 5	8	< 5	< 5	< 5	---	< 7	Se Organic
< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 9	Se Residual

APPENDIX 2: Air Filter Results

COC	Compound	Possible derivation	Likely Mineral/Species	2004040724	2004040725	2004031715	2004031716	2004040810
				1	2	3	4	5
Pb	Pb,S,O	Emissions	Anglesite	24.6	2.3	54.2	14.2	4.8
	Pb,S	Ore	Galena	0.0	0.0	0.0	0.0	0.0
	Pb, Sn	Ore/PGM-Residue	Pb-Alloy(?)	0.0	0.0	0.0	0.0	0.0
	Pb,Pd	Ore/PGM-Residue	Pb-Pd-Alloy(?)	0.0	0.0	0.0	0.0	0.0
Cu	Cu,Fe,S	Ore	Chalcopyrite	9.1	32.2	7.6	10.8	15.8
	Cu,S	Matte	Cu-Matte	18.8	2.9	0.0	8.5	20.3
	Cu,S,O	Refining	Cu-Sulphate	0.0	0.0	0.0	0.3	30.7
	Cu,O	Refining	Cu-Oxide	0.0	0.0	3.2	0.5	1.0
	Cu	Refining	Cu-Metal	0.0	0.0	0.0	2.6	0.0
	Cu,Sb,O	Refining	Cu-Sb-Oxide	0.0	0.0	0.0	0.0	0.0
	Cu,Zn	Domestic/refining	Brass	0.0	0.0	0.0	0.0	0.0
	Ag,Sb,Cu,S	Ore/PGM-Residue	Argentotennantite(?)	0.0	0.0	0.0	0.0	0.0
	Ag,Cu	Ore/PGM-Residue	Ag-Cu-Alloy	0.0	0.0	0.0	0.0	0.0
Ni	Ni,Fe,S	Ore	Pentlandite	23.0	23.3	21.1	23.2	18.4
	Co,Ni,Fe,S	Ore	Co-Pentlandite	1.7	0.0	0.0	0.0	0.0
	Ni~S	Ore	Millerite	0.0	1.0	0.0	3.9	0.2
	Fe,S>Ni	Ore	Pyrrhotite	0.0	0.0	0.0	0.0	0.0
	Ni,As,S	Ore	Ni-Arsenide	1.1	0.0	0.0	0.0	0.0
	Ni,O	Refining	Ni-Oxide	0.0	25.1	11.2	2.6	8.6
	Fe,Mn,Ni,O	Refining	Fe/Mn/Ni-Oxide	7.3	0.0	0.0	0.0	0.0
	Ni,Co,O	Refining	Ni-Co-Oxide	3.7	0.0	0.0	0.0	0.0
	Ni3S2	Matte	Ni-Matte	8.3	0.7	0.0	0.0	0.0
	Ni,S,O	Refining	Ni-Suphate	2.5	2.0	2.7	0.8	0.1
	Ni,Co,S,O	Refining	Ni/Co-sulphate	0.0	0.0	0.0	4.7	0.0
	Ni<<Fe,Mg,Si	Matte/Smelting	Ni-Slag	0.0	0.0	0.0	6.2	0.0
	Fe,Cr,Ni	Miscellaneous	Steel	0.0	10.4	0.0	0.0	0.0
Zn	Zn,O	Refining?	Zn-Oxide	0.0	0.0	0.0	6.6	0.0
	Zn,S,O	Refining?	Zn-Sulphate	0.0	0.0	0.0	14.6	0.0
	Zn,Cl	Refining?	Zn-Chloride	0.0	0.0	0.0	0.5	0.0
	Zn>Fe, S	Ore	Sphalerite	0.0	0.0	0.0	0.0	0.1
			Totals	**100**	**100**	**100**	**100**	**100**

Chemical Analysis		**2004040724**	**2004040725**	**2004031715**	**2004031716**	**2004040810**
Co Exchangeable	µg	0.41	0.32	0.43	0.32	0.32
Co Carbonate	µg	0.05	0.06	0.05	0.05	0.09
Co Reducible	µg	0.06	< 0.02	0.04	0.02	0.06
Co Organic	µg	**0.37**	**0.09**	**0.16**	**0.06**	**0.45**
Co Residual	µg	0.11	< 0.02	0.04	0.03	0.26
Cu Exchangeable	µg	3.06	3.11	2.50	1.04	27.8
Cu Carbonate	µg	0.51	0.58	0.69	0.26	0.95
Cu Reducible	µg	0.76	0.27	0.43	0.33	0.72
Cu Organic	µg	**5.36**	**1.24**	**2.08**	**1.18**	**5.29**
Cu Residual	µg	1.32	0.60	0.57	0.50	2.85
Ni Exchangeable	µg	3.21	0.69	1.20	0.50	0.95
Ni Carbonate	µg	0.43	0.46	0.76	0.93	0.40
Ni Reducible	µg	0.43	0.13	0.24	0.11	0.17
Ni Organic	µg	**5.04**	**1.15**	**1.57**	**0.74**	**2.86**
Ni Residual	µg	1.79	0.55	0.64	0.25	2.66
Pb Exchangeable	µg	2.20	1.81	1.05	0.77	2.25
Pb Carbonate	µg	0.47	0.25	0.24	0.14	0.45
Pb Reducible	µg	0.44	0.14	0.17	0.14	0.28
Pb Organic	µg	0.39	0.13	0.15	0.16	0.55
Pb Residual	µg	0.11	0.09	0.09	0.11	0.35
Se Exchangeable	µg	0.8	0.7	1.1	0.5	0.5
Se Carbonate	µg	1.0	0.3	0.6	0.3	0.9
Se Reducible	µg	0.8	0.7	0.6	0.7	0.7
Se Organic	µg	1.9	1.2	0.9	0.5	0.7
Se Residual	µg	0.5	1.0	0.9	1.0	0.4

2004040812	2004040813	2004040815	2004040816	2004072106	Average	
6	7	8	9	10		
7.4	1.3	20.3	53.9	1.3	**18.4**	Anglesite
0.0	0.0	2.5	0.0	0.0	**0.2**	Galena
0.0	0.0	0.0	0.0	9.3	**0.9**	Pb-Alloy(?)
0.0	0.0	0.0	8.7	0.0	**0.9**	Pb-Pd-Alloy(?)
24.0	22.0	34.0	1.5	40.3	**19.7**	Chalcopyrite
28.6	26.2	0.9	10.0	16.1	**13.2**	Cu-Matte
0.0	0.0	0.0	1.9	0.0	**3.3**	Cu-Sulphate
0.0	4.0	7.0	0.0	0.0	**1.6**	Cu-Oxide
0.0	0.0	6.0	0.0	0.0	**0.9**	Cu-Metal
0.0	0.0	0.5	0.0	0.0	**0.0**	Cu-Sb-Oxide
0.0	0.0	11.7	0.0	0.0	**1.2**	Brass
0.0	0.0	0.0	7.1	0.0	**0.7**	Argentotennantite(?)
0.0	0.0	0.0	0.5	0.0	**0.1**	Ag-Cu-Alloy
15.5	37.8	12.5	11.7	22.9	**20.9**	Pentlandite
0.0	0.0	0.0	0.0	0.0	**0.2**	Co-Pentlandite
0.2	1.6	0.0	0.0	8.0	**1.5**	Millerite
0.0	0.0	0.0	0.4	0.0	**0.0**	Pyrrhotite
0.0	0.0	0.0	0.0	0.0	**0.1**	Ni-Arsenide
0.7	7.0	1.8	1.1	1.6	**6.0**	Ni-Oxide
0.0	0.0	0.0	0.0	0.0	**0.7**	Fe/Mn/Ni-Oxide
0.0	0.0	0.0	0.0	0.0	**0.4**	Ni-Co-Oxide
11.0	0.0	0.0	0.0	0.0	**2.0**	Ni-Matte
12.6	0.0	2.9	1.7	0.5	**2.6**	Ni-Suphate
0.0	0.0	0.0	0.0	0.0	**0.5**	Ni/Co-sulphate
0.0	0.0	0.0	0.0	0.0	**0.6**	Ni-Slag
0.0	0.0	0.0	1.0	0.0	**1.1**	Steel
0.0	0.0	0.0	0.0	0.0	**0.7**	Zn-Oxide
0.0	0.0	0.0	0.0	0.0	**1.5**	Zn-Sulphate
0.0	0.0	0.0	0.0	0.0	**0.0**	Zn-Chloride
0.0	0.0	0.0	0.5	0.0	**0.1**	Sphalerite
100	**100**	**100**	**100**	**100**		

2004040812	2004040813	2004040815	2004040816	2004072106
1.28	0.48	0.19	0.16	0.15
0.21	0.10	0.05	0.07	0.08
1.34	0.32	< 0.02	< 0.02	0.21
4.66	**0.71**	**0.11**	**0.04**	**< 0.02**
1.34	0.28	0.09	0.04	0.40
44.8	10.6	6.25	3.49	12.3
8.21	1.82	1.25	1.04	1.84
1.37	5.29	1.04	0.68	1.89
97.5	**18.9**	**4.57**	**3.04**	**1.83**
28.0	5.49	2.77	2.32	11.0
24.3	4.52	0.13	0.01	4.33
3.59	0.96	0.13	0.20	1.12
4.09	1.81	0.02	0.05	1.61
52.2	**10.3**	**0.67**	**0.19**	**0.01**
23.6	4.35	1.24	0.71	11.1
10.8	8.21	0.71	0.46	1.69
2.75	1.40	0.18	0.19	0.68
1.59	0.68	0.14	0.22	0.66
3.66	0.96	0.38	0.21	0.01
1.59	0.43	0.29	0.22	0.56
0.6	0.3	0.3	0.5	0.4
0.1	0.6	0.1	0.1	0.6
0.7	0.5	0.6	0.7	0.6
1.9	1.3	0.8	0.7	0.6
1.0	1.5	1.2	0.6	0.1

Additional TSP Filters for Due Diligence Reference

COC	Inferred Mineral from EDS	Qualification/Interpretation	Possible Derivation	2004040811	2004040722
Pb	**anglesite**	PbSO4: May in cases be galena (PbS)	Smelting/Refining(?)	3.2	3.5
	Pb-Sn	Pb/Sn alloy: either solder or other	Domestic(?)	1.4	-
Zn	**sphalerite**	ZnS; trace Ore mineral	Ore	5.4	-
Cu	**tetrahedrite(?)**	Cu-Sb-S; trace ore mineral	Ore		
	chalcopyrite	Cu-Fe-S; essential ore mineral	Ore	27.8	21.8
	Cu>S	Cu2S: matte sulphide/chalcocite-phase	Smelter/matte/refining	26.7	9.1
	Cu-sulphate	Cu-S-O phase; Cu-refining phase	Refining	-	1.6
	Cu-Oxide	CuO: Cu-refining phase	Refining	-	-
	Cu-Metal	CuO: Cu-refining phase	Refining	-	11.2
	brass	Cu>Zn; domestic or miscellaneous	Domestic/Other	-	-
Ni,Co	**pentlandite**	Fe-Ni-Sulphide; major ore mineral	Ore	19.8	31.5
	millerite	NiS	Ore	9.0	4.8
	Ni>S	Ni3S2; nickel subsulphide	Smelter/matte/refining	-	2.1
	Ni-Sulphate	Cu-S-O phase; Cu-refining phase	Refining	3.1	1.2
	Ni-oxide	NiO: Ni-refining phase	Refining	3.6	13.1
	Total			100.0	100.0

APPENDIX 3: Soil Results

COC	Sample ID	Compound	Probable Origin	502ss	504ss	507ss	512ss	516ss	522ss	561ss	569ss	584ss	597ss
Pb	Anglesite	Pb-S-O	Smelter Fumes	12.4	1.7	1.1	2.0	1.1	2.4	0.2	0.1	11.7	0.5
	Pb-SS	Pb-Sb-Ag	Ore/Refining	7.5	1.7	0.0	1.1	0.3	0.7	0.0	0.0	0.6	0.1
	Galena	PbS	Ore	0.0	0.0	0.0	0.0	0.0	0.1	0.2	0.0	0.9	0.0
As	Arsenopyrite	FeAsS	Ore	4.8	0.6	0.0	0.0	0.0	0.0	0.0	0.8	0.0	0.0
	Enargite	$Cu_{12}AsS_{13}$	Ore	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1
Cu	Brass	Cu-Zn	Miscellaneous	2.0	0.0	0.0	3.9	0.8	0.4	0.0	0.6	8.5	0.5
	Chalcopyrite	$CuFeS_2$	Ore	24.8	2.4	11.2	0.0	3.1	15.6	0.3	2.6	0.0	0.0
	Cu- Matte	Cu_2S	Matte	0.0	0.0	0.0	0.0	0.6	0.0	0.0	0.0	0.0	0.0
	Cu-Alloy	Cu	Refining	0.0	0.0	1.2	2.3	0.0	48.5	7.3	0.0	0.0	1.8
	Cu-Oxide	Cu-O	Refining	2.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	Fe-Cu Oxide	Fe-Cu-O	Refining	0.0	0.0	0.0	1.2	0.0	0.0	0.3	0.0	0.0	37.9
	Cu-Slag	Cu-Fe-Mg-Si-O	Refining/Smelter	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	3.4	0.0
Ni	Pentlandite	$Fe_5Ni_4S_8$	Ore	5.3	7.2	46.8	0.0	31.7	0.7	0.6	2.1	0.0	0.2
	Fe-Ni-Cu Alloy	Fe-Ni-Cu	Refining	0.0	0.0	3.8	0.0	0.0	0.0	13.9	1.9	7.8	0.1
	Ni-Fe-Co Alloy	Ni-Fe-Co	Refining	0.0	0.0	0.0	0.0	0.0	0.0	0.0	16.3	0.0	0.0
	Ni-Fe- Alloy	Ni-Fe	Refining	10.4	4.4	6.2	0.0	7.1	5.5	55.2	0.0	23.8	0.0
	Ni-Co Oxide	Ni-Co-O	Refining	0.0	5.8	0.0	6.9	0.0	0.0	0.0	0.0	0.0	0.0
	Ni-Fe-Oxide	Ni-Fe-O	Refining	30.9	76.2	23.0	76.4	37.3	26.0	1.1	73.2	0.0	49.4
	Ni-Cu-Fe Oxide	Ni-Cu-Fe-O	Refining	0.0	0.0	0.0	3.6	17.9	0.0	20.8	2.4	26.8	9.2
	Ni-Fe Sulphate	Ni-Fe-S-O	Refining	0.0	0.0	0.0	2.7	0.0	0.0	0.0	0.0	0.0	0.0
	Ni Slag	Ni-Fe-Mg-Si-O	Refining/Smelter	0.0	0.0	6.7	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	Stainless Steel	Fe>Cr-Ni	Miscellaneous	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.0	16.5	0.3
	Total			**100**	**100**	**100**	**100**	**100**	**100**	**100**	**100**	**100**	**100**

Chamical Analysis

	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
As Exchangeable	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5
As Carbonate	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5
As Reducible	61	< 5	13	7	< 5	23	7	< 5	15	28
As Organic	73	10	31	16	13	133	7	7	16	21
As Residual	6	< 5	< 5	< 5	< 5	18	< 5	< 5	< 5	< 5
As Total Recoverable	120	18	43	20	12	150	12	< 5	24	52
	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
Co Exchangeable	3.0	< 0.3	1.7	1.2	1.8	5.8	< 0.3	< 0.3	1.6	8.3
Co Carbonate	0.4	< 0.3	0.8	< 0.3	< 0.3	1.8	0.6	< 0.3	< 0.3	< 0.3
Co Reducible	9.5	8.2	16	16	11	27	9.9	6.6	15	8.3
Co Organic	8.5	5.4	27	7.9	5.0	34	4.4	4.5	9.5	5.5
Co Residual	11	8.1	13	11	5.2	23	6.1	5.5	10	12
Co Total Recoverable	31	25	71	27	19	100	17	15	25	38
	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
Cu Exchangeable	17	2.1	1.6	9.1	4.6	3.0	0.3	0.1	32	21
Cu Carbonate	58	50	18	26	23	40	12	4.4	75	2.6
Cu Reducible	200	170	42	430	160	93	74	42	340	190
Cu Organic	550	420	550	540	200	1060	130	130	240	310
Cu Residual	49	33	44	50	19	211	22	21	46	40
Cu Total Recoverable	990	1000	830	1000	420	1500	270	220	780	850
	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
Ni Exchangeable	130	34	59	140	130	200	14	14	110	280
Ni Carbonate	23	32	42	19	22	86	21	13	13	2
Ni Reducible	120	160	200	320	240	450	140	160	170	170
Ni Organic	110	140	330	230	120	590	66	74	80	51
Ni Residual	130	180	120	300	74	310	96	70	270	120
Ni Total Recoverable	600	740	860	890	610	1500	320	360	560	840
	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
Pb Exchangeable	1.4	0.8	0.7	1.1	1.3	0.6	0.6	0.6	6.4	1.0
Pb Carbonate	4	8	2	4	6	1	8	11	17	2
Pb Reducible	29	40	17	55	57	17	66	88	129	18
Pb Organic	62	550	38	52	40	98	27	37	36	25
Pb Residual	6.4	16	5.0	7.5	3.7	14	4.4	4.1	7.4	4.9
Pb Total Recoverable	83	150	56	100	93	79	150	32	150	77

SGS

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Wednesday, October 19, 2005

Date Rec. : 13 April 2005
LR Report : **CA10172-APR05**
Project : Sudbury Soils Phase 2

CERTIFICATE OF ANALYSIS

Final report

Analysis	**1: Analysis Start Date**	**2: Analysis Start Time**	**3: Analysis Approval Date**	**4: Analysis Approval Time**	**5: 2004040724**	**6: 2004040725**	**7: 2004031715**
As Exchangeable [µg]	09-Jun-05	14:06	23-Jun-05	11:01	0.41	0.32	0.43
As Carbonate [µg]	09-Jun-05	14:06	23-Jun-05	11:01	< 0.25	< 0.25	< 0.25
As Reducible [µg]	09-Jun-05	14:06	23-Jun-05	11:01	< 0.25	< 0.25	< 0.25
As Organic [µg]	09-Jun-05	14:06	23-Jun-05	11:01	0.37	< 0.25	< 0.25
As Residual [µg]	09-Jun-05	14:06	23-Jun-05	11:01	< 0.25	< 0.25	< 0.25
Co Exchangeable [µg]	09-Jun-05	14:06	23-Jun-05	11:01	0.41	0.32	0.43
Co Carbonate [µg]	09-Jun-05	14:06	23-Jun-05	11:01	0.05	0.06	0.05
Co Reducible [µg]	09-Jun-05	14:06	23-Jun-05	11:01	0.06	< 0.02	0.04
Co Organic [µg]	09-Jun-05	14:06	23-Jun-05	11:01	0.37	0.09	0.16
Co Residual [µg]	09-Jun-05	14:06	23-Jun-05	11:01	0.11	< 0.02	0.04
Cu Exchanfeable [µg]	09-Jun-05	14:06	23-Jun-05	11:01	3.06	3.11	2.50

Analysis	**8: 2004031716**	**9: 2004040810**	**10: 2004040812**	**11: 2004040813**	**12: 2004040815**	**13: 2004040816**	**14: 2004072106**
As Exchangeable [µg]	0.32	0.32	1.28	0.48	< 0.25	< 0.25	< 0.25
As Carbonate [µg]	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25
As Reducible [µg]	< 0.25	< 0.25	1.34	0.32	< 0.25	< 0.25	< 0.25
As Organic [µg]	< 0.25	0.45	4.66	0.71	< 0.25	< 0.25	< 0.25
As Residual [µg]	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25
Co Exchangeable [µg]	0.32	0.32	1.28	0.48	0.19	0.16	0.15
Co Carbonate [µg]	0.05	0.09	0.21	0.10	0.05	0.07	0.08
Co Reducible [µg]	0.02	0.06	1.34	0.32	< 0.02	< 0.02	0.21
Co Organic [µg]	0.06	0.45	4.66	0.71	0.11	0.04	< 0.02
Co Residual [µg]	0.03	0.26	1.34	0.28	0.09	0.04	0.40
Cu Exchanfeable [µg]	1.04	27.8	44.8	10.6	6.25	3.49	12.3

Analysis	**1: Analysis Start Date**	**2: Analysis Start Time**	**3: Analysis Approval Date**	**4: Analysis Approval Time**	**5: 2004040724**	**6: 2004040725**	**7: 2004031715**
Cu Carbonate [µg]	09-Jun-05	14:06	23-Jun-05	11:01	0.51	0.58	0.69
Cu Reducible [µg]	09-Jun-05	14:06	23-Jun-05	11:01	0.76	0.27	0.43
Cu Organic [µg]	09-Jun-05	14:06	23-Jun-05	11:01	5.36	1.24	2.08
Cu Residual [µg]	09-Jun-05	14:06	23-Jun-05	11:01	1.32	0.60	0.57
Ni Exchangeable [µg]	09-Jun-05	14:06	23-Jun-05	11:01	3.21	0.69	1.20
Ni Carbonate [µg]	09-Jun-05	14:06	23-Jun-05	11:01	0.43	0.46	0.76
Ni Reducible [µg]	09-Jun-05	14:06	23-Jun-05	11:01	0.43	0.13	0.24
Ni Organic [µg]	09-Jun-05	14:06	23-Jun-05	11:01	5.04	1.15	1.57
Ni Residual [µg]	09-Jun-05	14:06	23-Jun-05	11:01	1.79	0.55	0.64
Pb Exchangeable [µg]	09-Jun-05	14:06	23-Jun-05	11:01	2.20	1.81	1.05
Pb Carbonate [µg]	09-Jun-05	14:06	23-Jun-05	11:01	0.47	0.25	0.24
Pb Reducible [µg]	09-Jun-05	14:06	23-Jun-05	11:01	0.44	0.14	0.17
Pb Organic [µg]	09-Jun-05	14:06	23-Jun-05	11:01	0.39	0.13	0.15
Pb Residual [µg]	09-Jun-05	14:06	23-Jun-05	11:01	0.11	0.09	0.09
Se Exchangeable [µg]	09-Jun-05	14:06	23-Jun-05	11:01	0.8	0.7	1.1
Se Carbonate [µg]	09-Jun-05	14:06	23-Jun-05	11:01	1.0	0.3	0.6
Se Reducible [µg]	09-Jun-05	14:06	23-Jun-05	11:01	0.8	0.7	0.6
Se Organic [µg]	09-Jun-05	14:06	23-Jun-05	11:01	1.9	1.2	0.9
Se Residual [µg]	09-Jun-05	14:06	23-Jun-05	11:01	0.5	1.0	0.9

Analysis	**8: 2004031716**	**9: 2004040810**	**10: 2004040812**	**11: 2004040813**	**12: 2004040815**	**13: 2004040816**	**14: 2004072106**
Cu Carbonate [µg]	0.26	0.95	8.21	1.82	1.25	1.04	1.84
Cu Reducible [µg]	0.33	0.72	1.37	5.29	1.04	0.68	1.89
Cu Organic [µg]	1.18	5.29	97.5	18.9	4.57	3.04	1.83
Cu Residual [µg]	0.50	2.85	28.0	5.49	2.77	2.32	11.0
Ni Exchangeable [µg]	0.50	0.95	24.3	4.52	0.13	< 0.02	4.33
Ni Carbonate [µg]	0.93	0.40	3.59	0.96	0.13	0.20	1.12
Ni Reducible [µg]	0.11	0.17	4.09	1.81	0.02	0.05	1.61
Ni Organic [µg]	0.74	2.86	52.2	10.3	0.67	0.19	< 0.02
Ni Residual [µg]	0.25	2.66	23.6	4.35	1.24	0.71	11.1
Pb Exchangeable [µg]	0.77	2.25	10.8	8.21	0.71	0.46	1.69
Pb Carbonate [µg]	0.14	0.45	2.75	1.40	0.18	0.19	0.68
Pb Reducible [µg]	0.14	0.28	1.59	0.68	0.14	0.22	0.66
Pb Organic [µg]	0.16	0.55	3.66	0.96	0.38	0.21	0.01
Pb Residual [µg]	0.11	0.35	1.59	0.43	0.29	0.22	0.56
Se Exchangeable [µg]	0.5	0.5	0.6	0.3	0.3	0.5	0.4
Se Carbonate [µg]	0.3	0.9	< 0.2	0.6	< 0.2	< 0.2	0.6
Se Reducible [µg]	0.7	0.7	0.7	0.5	0.6	0.7	0.6
Se Organic [µg]	0.5	0.7	1.9	1.3	0.8	0.7	0.6
Se Residual [µg]	1.0	0.4	1.0	1.5	1.2	0.6	< 0.2

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Wednesday, October 19, 2005

Date Rec. : 13 April 2005
LR Report : **CA10171-APR05**
Project : Sudbury Soils Phase 2

CERTIFICATE OF ANALYSIS

Final Report

Analysis	**1: Analysis Start Date**	**2: Analysis Start Time**	**3: Analysis Approval Date**	**4: Analysis Approval Time**	**5: 502 57824 Lab Bottle**	**6: 504 57822 Lab Bottle**
As Exchangeable [µg/g]	09-Jun-05	14:36	22-Jun-05	09:29	< 5	< 5

Analysis	**7: 510 05-1291 Whirlpack**	**8: 512 57826 Lab Bottle**	**9: 513 05-1292 Whirlpack**	**10: 515 57830 Lab Bottle**	**11: 521 05-1294 Whirlpack**	**12: 522 05-1295 Whirlpack**
As Exchangeable [µg/g]	< 5	< 5	< 5	< 5	< 5	< 5

Analysis	**13: 523 57797 Lab Bottle**	**14: 525 57817 Lab Bottle**	**15: 529 05-1297 Whirlpack**	**16: 533 05-1298 Whirlpack**	**17: 534 57834 Lab Bottle**	**18: 541 05-1300 Whirlpack**
As Exchangeable [µg/g]	< 5	< 5	< 5	< 5	< 5	< 5

Analysis	**19: 550 05-1301 Whirlpack**	**20: 552 05-1302 Whirlpack**	**21: 560 05-1303 Whirlpack**	**22: 572 05-1305 Whirlpack**	**23: 582 05-1307 Whirlpack**	**24: 584 05-1308 Whirlpack**
As Exchangeable [µg/g]	< 5	< 5	< 5	< 5	< 5	< 5

Analysis	**25: 600 57810 Lab Bottle**	**26: 601 05-1310 Whirlpack**	**27: 602 05-1311 Whirlpack**	**28: 606 05-1312 Whirlpack**	**29: Blk 1**	**30: Blk 2**	**31: SS-1**	**32: STD-Env Rep 10171-6**
As Exchangeable [µg/g]	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5

Analysis	**1: Analysis Start Date**	**2: Analysis Start Time**	**3: Analysis Approval Date**	**4: Analysis Approval Time**	**5: 502 57824 Lab Bottle**	**6: 504 57822 Lab Bottle**
As Carbonate [µg/g]	09-Jun-05	14:36	22-Jun-05	09:29	< 5	< 5
As Reducible [µg/g]	10-Jun-05	07:53	22-Jun-05	09:29	5	< 5
As Organic [µg/g]	09-Jun-05	12:30	22-Jun-05	09:29	17	18
As Residual [µg/g]	09-Jun-05	12:30	22-Jun-05	09:29	< 5	< 5

Analysis	**7: 510 05-1291 Whirlpack**	**8: 512 57826 Lab Bottle**	**9: 513 05-1292 Whirlpack**	**10: 515 57830 Lab Bottle**	**11: 521 05-1294 Whirlpack**	**12: 522 05-1295 Whirlpack**
As Carbonate [µg/g]	< 5	< 5	< 5	< 5	< 5	< 5
As Reducible [µg/g]	36	6	21	5	10	9
As Organic [µg/g]	< 5	27	13	20	170	15
As Residual [µg/g]	< 5	< 5	< 5	< 5	7	< 5

Analysis	**13: 523 57797 Lab Bottle**	**14: 525 57817 Lab Bottle**	**15: 529 05-1297 Whirlpack**	**16: 533 05-1298 Whirlpack**	**17: 534 57834 Lab Bottle**	**18: 541 05-1300 Whirlpack**
As Carbonate [µg/g]	< 5	< 5	< 5	< 5	< 5	< 5
As Reducible [µg/g]	8	< 5	< 5	11	< 5	< 5
As Organic [µg/g]	5	22	22	12	82	15
As Residual [µg/g]	< 5	< 5	< 5	< 5	< 5	< 5

Analysis	**19: 550 05-1301 Whirlpack**	**20: 552 05-1302 Whirlpack**	**21: 560 05-1303 Whirlpack**	**22: 572 05-1305 Whirlpack**	**23: 582 05-1307 Whirlpack**	**24: 584 05-1308 Whirlpack**
As Carbonate [µg/g]	< 5	< 5	< 5	< 5	< 5	< 5
As Reducible [µg/g]	< 5	10	< 5	< 5	< 5	8
As Organic [µg/g]	6	13	< 5	10	8	39
As Residual [µg/g]	< 5	< 5	< 5	< 5	< 5	< 5

Analysis	**25: 600 57810 Lab Bottle**	**26: 601 05-1310 Whirlpack**	**27: 602 05-1311 Whirlpack**	**28: 606 05-1312 Whirlpack**	**29: Blk 1**	**30: Blk 2**	**31: SS-1**	**32: STD-Env Rep 10171-6**
As Carbonate [µg/g]	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5
As Reducible [µg/g]	< 5	6	< 5	26	< 5	< 5	< 5	< 5
As Organic [µg/g]	14	26	6	130	< 5	< 5	31	19
As Residual [µg/g]	< 5	< 5	< 5	9	< 5	< 5	< 5	< 5

Analysis	1: Analysis Start Date	2: Analysis Start Time	3: Analysis Approval Date	4: Analysis Approval Time	5: 502 57824 Lab Bottle	6: 504 57822 Lab Bottle
Co Exchangeable [µg/g]	09-Jun-05	14:36	22-Jun-05	09:29	4.8	2.1
Co Carbonate [µg/g]	09-Jun-05	14:36	22-Jun-05	09:29	< 0.3	0.4
Co Reducible [µg/g]	10-Jun-05	07:53	22-Jun-05	09:29	12	5.4
Co Organic [µg/g]	09-Jun-05	12:30	22-Jun-05	09:29	20	20

Analysis	7: 510 05-1291 Whirlpack	8: 512 57826 Lab Bottle	9: 513 05-1292 Whirlpack	10: 515 57830 Lab Bottle	11: 521 05-1294 Whirlpack	12: 522 05-1295 Whirlpack
Co Exchangeable [µg/g]	4.9	3.2	2.9	1.2	1.6	6.5
Co Carbonate [µg/g]	1.0	0.8	0.3	0.7	0.6	1.6
Co Reducible [µg/g]	23	21	11	11	18	41
Co Organic [µg/g]	3.3	70	10	30	250	90

Analysis	13: 523 57797 Lab Bottle	14: 525 57817 Lab Bottle	15: 529 05-1297 Whirlpack	16: 533 05-1298 Whirlpack	17: 534 57834 Lab Bottle	18: 541 05-1300 Whirlpack
Co Exchangeable [µg/g]	1.9	3.2	5.5	1.6	2.5	11
Co Carbonate [µg/g]	1.1	0.9	1.7	< 0.3	0.8	< 0.3
Co Reducible [µg/g]	18	8.6	8.5	7.5	14	7.0
Co Organic [µg/g]	7.8	20	10	20	60	10

Analysis	19: 550 05-1301 Whirlpack	20: 552 05-1302 Whirlpack	21: 560 05-1303 Whirlpack	22: 572 05-1305 Whirlpack	23: 582 05-1307 Whirlpack	24: 584 05-1308 Whirlpack
Co Exchangeable [µg/g]	< 0.3	1.0	0.4	3.1	0.4	1.8
Co Carbonate [µg/g]	< 0.3	0.4	< 0.3	< 0.3	< 0.3	0.4
Co Reducible [µg/g]	3.5	5.3	1.7	3.4	4.1	8.3
Co Organic [µg/g]	6.6	8.1	3.4	5.7	10	40

Analysis	25: 600 57810 Lab Bottle	26: 601 05-1310 Whirlpack	27: 602 05-1311 Whirlpack	28: 606 05-1312 Whirlpack	29: Blk 1	30: Blk 2	31: SS-1	32: STD-Env Rep 10171-6
Co Exchangeable [µg/g]	0.8	0.8	0.6	2.9	< 0.3	< 0.3	< 0.3	2.8
Co Carbonate [µg/g]	< 0.3	< 0.3	< 0.3	1.0	< 0.3	< 0.3	1.2	0.5
Co Reducible [µg/g]	1.7	4.1	3.2	23	< 0.3	< 0.3	23	6.6
Co Organic [µg/g]	7.6	9.4	10	110	< 0.3	< 0.3	10	20

Analysis	1: Analysis Start Date	2: Analysis Start Time	3: Analysis Approval Date	4: Analysis Approval Time	5: 502 57824 Lab Bottle	6: 504 57822 Lab Bottle
Co Residual [µg/g]	14-Jun-05	08:45	22-Jun-05	09:29	16	6.3
Cu Exchangeable [µg/g]	09-Jun-05	14:36	22-Jun-05	09:29	30	43
Cu Carbonate [µg/g]	09-Jun-05	14:36	22-Jun-05	09:29	8.0	6.6
Cu Reducible [µg/g]	10-Jun-05	07:53	22-Jun-05	09:29	61	12

Analysis	7: 510 05-1291 Whirlpack	8: 512 57826 Lab Bottle	9: 513 05-1292 Whirlpack	10: 515 57830 Lab Bottle	11: 521 05-1294 Whirlpack	12: 522 05-1295 Whirlpack
Co Residual [µg/g]	9.7	17	6.4	18	150	69
Cu Exchangeable [µg/g]	130	130	390	59	130	67
Cu Carbonate [µg/g]	37	21	50	9.9	21	6.2
Cu Reducible [µg/g]	160	19	160	63	110	42

Analysis	13: 523 57797 Lab Bottle	14: 525 57817 Lab Bottle	15: 529 05-1297 Whirlpack	16: 533 05-1298 Whirlpack	17: 534 57834 Lab Bottle	18: 541 05-1300 Whirlpack
Co Residual [µg/g]	2.5	4.8	9.2	6.6	17	6.8
Cu Exchangeable [µg/g]	29	96	730	130	45	170
Cu Carbonate [µg/g]	6.2	32	18	19	3.5	25
Cu Reducible [µg/g]	18	120	120	130	120	260

Analysis	19: 550 05-1301 Whirlpack	20: 552 05-1302 Whirlpack	21: 560 05-1303 Whirlpack	22: 572 05-1305 Whirlpack	23: 582 05-1307 Whirlpack	24: 584 05-1308 Whirlpack
Co Residual [µg/g]	4.5	3.9	4.9	2.8	4.9	9.4
Cu Exchangeable [µg/g]	35	130	64	94	11	43
Cu Carbonate [µg/g]	9.9	56	4.4	8.6	2.1	10
Cu Reducible [µg/g]	44	280	17	66	11	14

Analysis	25: 600 57810 Lab Bottle	26: 601 05-1310 Whirlpack	27: 602 05-1311 Whirlpack	28: 606 05-1312 Whirlpack	29: Blk 1	30: Blk 2	31: SS-1	32: STD-Env Rep 10171-6
Co Residual [µg/g]	3.0	2.6	3.4	22	< 0.3	< 0.3	4.2	5.8
Cu Exchangeable [µg/g]	32	44	51	99	5.7	< 0.1	1.9	58
Cu Carbonate [µg/g]	6.7	5.3	6.6	21	< 0.1	< 0.1	20	6.8
Cu Reducible [µg/g]	12	21	11	40	< 0.1	0.1	250	15

Analysis	1: Analysis Start Date	2: Analysis Start Time	3: Analysis Approval Date	4: Analysis Approval Time	5: 502 57824 Lab Bottle	6: 504 57822 Lab Bottle
Cu Organic [µg/g]	09-Jun-05	12:30	22-Jun-05	09:29	300	890
Cu Residual [µg/g]	14-Jun-05	08:44	22-Jun-05	09:29	11	36
Ni Exchangeable [µg/g]	09-Jun-05	14:37	22-Jun-05	09:29	55	47
Ni Carbonate [µg/g]	09-Jun-05	14:37	22-Jun-05	09:29	14	5

Analysis	7: 510 05-1291 Whirlpack	8: 512 57826 Lab Bottle	9: 513 05-1292 Whirlpack	10: 515 57830 Lab Bottle	11: 521 05-1294 Whirlpack	12: 522 05-1295 Whirlpack
Cu Organic [µg/g]	150	2700	790	2000	3300	820
Cu Residual [µg/g]	33	120	30	56	98	18
Ni Exchangeable [µg/g]	230	140	160	49	81	140
Ni Carbonate [µg/g]	49	24	11	11	25	24

Analysis	13: 523 57797 Lab Bottle	14: 525 57817 Lab Bottle	15: 529 05-1297 Whirlpack	16: 533 05-1298 Whirlpack	17: 534 57834 Lab Bottle	18: 541 05-1300 Whirlpack
Cu Organic [µg/g]	420	1500	340	860	2500	420
Cu Residual [µg/g]	11	15	11	21	66	14
Ni Exchangeable [µg/g]	37	38	87	73	59	120
Ni Carbonate [µg/g]	12	9	5	18	14	22

Analysis	19: 550 05-1301 Whirlpack	20: 552 05-1302 Whirlpack	21: 560 05-1303 Whirlpack	22: 572 05-1305 Whirlpack	23: 582 05-1307 Whirlpack	24: 584 05-1308 Whirlpack
Cu Organic [µg/g]	380	1100	530	190	160	1300
Cu Residual [µg/g]	17	21	8.7	5.4	5.3	51
Ni Exchangeable [µg/g]	16	23	12	16	8	63
Ni Carbonate [µg/g]	5	14	< 1	5	2	7

Analysis	25: 600 57810 Lab Bottle	26: 601 05-1310 Whirlpack	27: 602 05-1311 Whirlpack	28: 606 05-1312 Whirlpack	29: Blk 1	30: Blk 2	31: SS-1	32: STD-Env Rep 10171-6
Cu Organic [µg/g]	390	440	810	5070	< 0.1	< 0.1	860	940
Cu Residual [µg/g]	11	8.6	18	380	< 0.1	< 0.1	16	33
Ni Exchangeable [µg/g]	23	16	36	130	2	< 1	< 1	55
Ni Carbonate [µg/g]	3	3	5	72	< 1	< 1	7	5

Analysis	**1: Analysis Start Date**	**2: Analysis Start Time**	**3: Analysis Approval Date**	**4: Analysis Approval Time**	**5: 502 57824 Lab Bottle**	**6: 504 57822 Lab Bottle**
Ni Reducible [μg/g]	10-Jun-05	08:05	22-Jun-05	09:29	75	60
Ni Organic [μg/g]	09-Jun-05	12:30	22-Jun-05	09:29	280	480
Ni Residual [μg/g]	14-Jun-05	08:44	22-Jun-05	09:29	54	140
Pb Exchangeable [μg/g]	09-Jun-05	14:38	22-Jun-05	09:29	15	4.4

Analysis	**7: 510 05-1291 Whirlpack**	**8: 512 57826 Lab Bottle**	**9: 513 05-1292 Whirlpack**	**10: 515 57830 Lab Bottle**	**11: 521 05-1294 Whirlpack**	**12: 522 05-1295 Whirlpack**
Ni Reducible [μg/g]	480	320	69	200	230	250
Ni Organic [μg/g]	110	1600	190	910	2700	570
Ni Residual [μg/g]	310	460	94	330	520	210
Pb Exchangeable [μg/g]	25	42	108	8.8	10	40

Analysis	**13: 523 57797 Lab Bottle**	**14: 525 57817 Lab Bottle**	**15: 529 05-1297 Whirlpack**	**16: 533 05-1298 Whirlpack**	**17: 534 57834 Lab Bottle**	**18: 541 05-1300 Whirlpack**
Ni Reducible [μg/g]	160	87	68	100	220	85
Ni Organic [μg/g]	220	280	190	450	780	260
Ni Residual [μg/g]	66	56	70	100	110	50
Pb Exchangeable [μg/g]	2.4	10	73	46	7.7	25

Analysis	**19: 550 05-1301 Whirlpack**	**20: 552 05-1302 Whirlpack**	**21: 560 05-1303 Whirlpack**	**22: 572 05-1305 Whirlpack**	**23: 582 05-1307 Whirlpack**	**24: 584 05-1308 Whirlpack**
Ni Reducible [μg/g]	34	77	18	23	22	94
Ni Organic [μg/g]	140	160	68	62	79	750
Ni Residual [μg/g]	90	57	87	22	28	190
Pb Exchangeable [μg/g]	9.8	126	21	49	2.9	8.2

Analysis	**25: 600 57810 Lab Bottle**	**26: 601 05-1310 Whirlpack**	**27: 602 05-1311 Whirlpack**	**28: 606 05-1312 Whirlpack**	**29: Blk 1**	**30: Blk 2**	**31: SS-1**	**32: STD-Env Rep 10171-6**
Ni Reducible [μg/g]	28	46	63	490	< 1	< 1	180	72
Ni Organic [μg/g]	130	190	370	3800	< 1	< 1	100	510
Ni Residual [μg/g]	54	29	96	620	< 1	< 1	5	140
Pb Exchangeable [μg/g]	16	11	5.0	13	< 0.7	0.8	< 0.7	6.5

Analysis	**1: Analysis Start Date**	**2: Analysis Start Time**	**3: Analysis Approval Date**	**4: Analysis Approval Time**	**5: 502 57824 Lab Bottle**	**6: 504 57822 Lab Bottle**
Pb Carbonate [µg/g]	09-Jun-05	14:38	22-Jun-05	09:29	31	10
Pb Reducible [µg/g]	10-Jun-05	08:06	22-Jun-05	09:29	42	38
Pb Organic [µg/g]	09-Jun-05	12:30	22-Jun-05	09:29	26	100
Pb Residual [µg/g]	14-Jun-05	08:44	22-Jun-05	09:29	2.4	7.0

Analysis	**7: 510 05-1291 Whirlpack**	**8: 512 57826 Lab Bottle**	**9: 513 05-1292 Whirlpack**	**10: 515 57830 Lab Bottle**	**11: 521 05-1294 Whirlpack**	**12: 522 05-1295 Whirlpack**
Pb Carbonate [µg/g]	32	630	130	5.3	71	8.7
Pb Reducible [µg/g]	150	1800	350	47	140	49
Pb Organic [µg/g]	5.9	1400	170	82	540	41
Pb Residual [µg/g]	1.8	63	9.5	8.2	26	2.2

Analysis	**13: 523 57797 Lab Bottle**	**14: 525 57817 Lab Bottle**	**15: 529 05-1297 Whirlpack**	**16: 533 05-1298 Whirlpack**	**17: 534 57834 Lab Bottle**	**18: 541 05-1300 Whirlpack**
Pb Carbonate [µg/g]	9.2	35	57	290	1.5	25
Pb Reducible [µg/g]	74	380	48	200	120	42
Pb Organic [µg/g]	14	330	32	84	200	15
Pb Residual [µg/g]	1.0	9.4	< 0.7	3.9	9.0	1.8

Analysis	**19: 550 05-1301 Whirlpack**	**20: 552 05-1302 Whirlpack**	**21: 560 05-1303 Whirlpack**	**22: 572 05-1305 Whirlpack**	**23: 582 05-1307 Whirlpack**	**24: 584 05-1308 Whirlpack**
Pb Carbonate [µg/g]	6.5	400	6.5	10	1.6	44
Pb Reducible [µg/g]	28	440	28	25	16	200
Pb Organic [µg/g]	24	150	23	23	18	250
Pb Residual [µg/g]	2.0	6.7	1.5	3.0	11	12

Analysis	**25: 600 57810 Lab Bottle**	**26: 601 05-1310 Whirlpack**	**27: 602 05-1311 Whirlpack**	**28: 606 05-1312 Whirlpack**	**29: Blk 1**	**30: Blk 2**	**31: SS-1**	**32: STD-Env Rep 10171-6**
Pb Carbonate [µg/g]	3.1	8.3	25	20	< 0.7	< 0.7	5.9	12
Pb Reducible [µg/g]	31	65	67	97	< 0.7	< 0.7	160	47
Pb Organic [µg/g]	19	55	69	110	< 0.7	< 0.7	140	110
Pb Residual [µg/g]	2.9	3.2	2.3	9.9	< 0.7	< 0.7	8.1	6.8

Analysis	**1: Analysis Start Date**	**2: Analysis Start Time**	**3: Analysis Approval Date**	**4: Analysis Approval Time**	**5: 502 57824 Lab Bottle**	**6: 504 57822 Lab Bottle**
Se Exchangeable [µg/g]	09-Jun-05	14:38	22-Jun-05	09:29	< 5	< 5
Se Carbonate [µg/g]	09-Jun-05	14:38	22-Jun-05	09:29	< 5	< 5
Se Reducible [µg/g]	10-Jun-05	07:54	22-Jun-05	09:29	7	< 5
Se Organic [µg/g]	09-Jun-05	12:30	22-Jun-05	09:29	< 5	< 5

Analysis	**7: 510 05-1291 Whirlpack**	**8: 512 57826 Lab Bottle**	**9: 513 05-1292 Whirlpack**	**10: 515 57830 Lab Bottle**	**11: 521 05-1294 Whirlpack**	**12: 522 05-1295 Whirlpack**
Se Exchangeable [µg/g]	< 5	< 5	< 5	< 5	< 5	< 5
Se Carbonate [µg/g]	< 5	< 5	< 5	< 5	< 5	< 5
Se Reducible [µg/g]	< 5	< 5	8	< 5	6	< 5
Se Organic [µg/g]	< 5	9	< 5	< 5	5	< 5

Analysis	**13: 523 57797 Lab Bottle**	**14: 525 57817 Lab Bottle**	**15: 529 05-1297 Whirlpack**	**16: 533 05-1298 Whirlpack**	**17: 534 57834 Lab Bottle**	**18: 541 05-1300 Whirlpack**
Se Exchangeable [µg/g]	< 5	< 5	< 5	< 5	< 5	< 5
Se Carbonate [µg/g]	< 5	< 5	< 5	< 5	< 5	< 5
Se Reducible [µg/g]	< 5	< 5	33	5	< 5	20
Se Organic [µg/g]	< 5	< 5	< 5	< 5	< 5	< 5

Analysis	**19: 550 05-1301 Whirlpack**	**20: 552 05-1302 Whirlpack**	**21: 560 05-1303 Whirlpack**	**22: 572 05-1305 Whirlpack**	**23: 582 05-1307 Whirlpack**	**24: 584 05-1308 Whirlpack**
Se Exchangeable [µg/g]	< 5	< 5	< 5	< 5	< 5	< 5
Se Carbonate [µg/g]	< 5	< 5	< 5	< 5	< 5	< 5
Se Reducible [µg/g]	< 5	6	< 5	6	< 5	< 5
Se Organic [µg/g]	< 5	< 5	< 5	< 5	< 5	8

Analysis	**25: 600 57810 Lab Bottle**	**26: 601 05-1310 Whirlpack**	**27: 602 05-1311 Whirlpack**	**28: 606 05-1312 Whirlpack**	**29: Blk 1**	**30: Blk 2**	**31: SS-1**	**32: STD-Env Rep 10171-6**
Se Exchangeable [µg/g]	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5
Se Carbonate [µg/g]	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5
Se Reducible [µg/g]	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5
Se Organic [µg/g]	< 5	< 5	< 5	---	< 5	< 5	< 5	6

Analysis	1: Analysis Start Date	2: Analysis Start Time	3: Analysis Approval Date	4: Analysis Approval Time	5: 502 57824 Lab Bottle	6: 504 57822 Lab Bottle
Se Residual [μg/g]	14-Jun-05	08:44	22-Jun-05	09:29	< 5	< 5

Analysis	7: 510 05-1291 Whirlpack	8: 512 57826 Lab Bottle	9: 513 05-1292 Whirlpack	10: 515 57830 Lab Bottle	11: 521 05-1294 Whirlpack	12: 522 05-1295 Whirlpack
Se Residual [μg/g]	< 5	< 5	< 5	< 5	< 5	< 5

Analysis	13: 523 57797 Lab Bottle	14: 525 57817 Lab Bottle	15: 529 05-1297 Whirlpack	16: 533 05-1298 Whirlpack	17: 534 57834 Lab Bottle	18: 541 05-1300 Whirlpack
Se Residual [μg/g]	< 5	< 5	< 5	< 5	< 5	9

Analysis	19: 550 05-1301 Whirlpack	20: 552 05-1302 Whirlpack	21: 560 05-1303 Whirlpack	22: 572 05-1305 Whirlpack	23: 582 05-1307 Whirlpack	24: 584 05-1308 Whirlpack
Se Residual [μg/g]	< 5	< 5	< 5	< 5	< 5	< 5

Analysis	25: 600 57810 Lab Bottle	26: 601 05-1310 Whirlpack	27: 602 05-1311 Whirlpack	28: 606 05-1312 Whirlpack	29: Blk 1	30: Blk 2	31: SS-1	32: STD-Env Rep 10171-6
Se Residual [μg/g]	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5

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Wednesday, October 19, 2005

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Project : Sudbury Soils Phase 2

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Final Report

Analysis	1: Analysis Start Date	2: Analysis Start Time	3: Analysis Approval Date	4: Analysis Approval Time	5: 501ss-0.5cm-split SG Apr8/05	6: 502ss-0.5cm-split SG Apr8/05	7: 504ss-0.5cm-split SG Apr8/05	8: 505ss-0.5cm-split SG Apr8/05	9: 506ss-0.5cm-split SG Apr8/05	10: 507ss-0.5cm-split SG Apr8/05	11: 509ss-0.5cm-split SG Apr8/05
As Exchangeable [µg/g]	25-Apr-05	14:00	27-Jun-05	11:20	< 5	< 5	< 5	< 5	< 5	< 5	< 5
As Carbonate [µg/g]	25-Apr-05	14:00	27-Jun-05	11:20	< 5	< 5	< 5	< 5	< 5	< 5	< 5
As Reducible [µg/g]	25-Apr-05	14:00	27-Jun-05	11:20	12	61	< 5	6	6	13	< 5
As Organic [µg/g]	25-Apr-05	14:00	27-Jun-05	11:20	23	73	10	8	14	31	< 5
As Residual [µg/g]	25-Apr-05	14:00	27-Jun-05	11:20	< 5	6	< 5	< 5	< 5	< 5	< 5
As Total Recoverable [µg/g]	25-Apr-05	14:00	26-Apr-05	08:39	34	120	18	9	13	43	< 5
Co Exchangeable [µg/g]	25-Apr-05	14:00	27-Jun-05	11:20	3.0	3.0	< 0.3	0.6	1.8	1.7	< 0.3
Co Carbonate [µg/g]	25-Apr-05	14:00	27-Jun-05	11:20	0.7	0.4	< 0.3	< 0.3	0.4	0.8	< 0.3
Co Reducible [µg/g]	25-Apr-05	14:00	27-Jun-05	11:20	12	9.5	8.2	6.9	13	16	4.4
Co Organic [µg/g]	25-Apr-05	14:00	27-Jun-05	11:20	11	8.5	5.4	4.6	11	27	3.5
Co Residual [µg/g]	25-Apr-05	14:00	27-Jun-05	11:20	12	11	8.1	8.5	16	13	5.2
Co Total Recoverable [µg/g]	25-Apr-05	14:00	26-Apr-05	08:39	30	31	25	16	22	71	8.7
Cu Exchangeable [µg/g]	25-Apr-05	14:00	27-Jun-05	11:20	4.9	17	2.1	3.1	19	1.6	4.2
Cu Carbonate [µg/g]	25-Apr-05	14:00	27-Jun-05	11:20	26	58	50	48	200	18	37
Cu Reducible [µg/g]	25-Apr-05	14:00	27-Jun-05	11:20	76	200	170	150	630	42	120
Cu Organic [µg/g]	25-Apr-05	14:00	27-Jun-05	11:20	300	550	420	520	920	550	150
Cu Residual [µg/g]	25-Apr-05	14:00	27-Jun-05	11:20	36	49	33	37	71	44	12

Analysis	**1: Analysis Start Date**	**2: Analysis Start Time**	**3: Analysis Approval Date**	**4: Analysis Approval Time**	**5: 501ss-0.5cm-sp lit SG Apr8/05**	**6: 502ss-0.5cm-sp lit SG Apr8/05**	**7: 504ss-0.5cm-sp lit SG Apr8/05**	**8: 505ss-0.5cm-sp lit SG Apr8/05**	**9: 506ss-0.5cm-sp lit SG Apr8/05**	**10: 507ss-0.5cm-sp lit SG Apr8/05**	**11: 509ss-0.5cm-sp lit SG Apr8/05**
Cu Total Recoverable [µg/g]	25-Apr-05	14:00	26-Apr-05	08:39	390	990	1000	850	1400	830	340
Ni Exchangeable [µg/g]	25-Apr-05	14:00	27-Jun-05	11:20	120	130	34	52	180	59	50
Ni Carbonate [µg/g]	25-Apr-05	14:00	27-Jun-05	11:20	30	23	32	26	52	42	18
Ni Reducible [µg/g]	25-Apr-05	14:00	27-Jun-05	11:20	150	120	160	100	240	200	110
Ni Organic [µg/g]	25-Apr-05	14:00	27-Jun-05	11:20	110	110	140	110	260	330	61
Ni Residual [µg/g]	25-Apr-05	14:00	27-Jun-05	11:20	120	130	180	210	420	120	67
Ni Total Recoverable [µg/g]	25-Apr-05	14:00	26-Apr-05	08:39	470	600	740	480	680	860	280
Pb Exchangeable [µg/g]	25-Apr-05	14:00	27-Jun-05	11:20	0.8	1.4	0.8	0.7	< 0.7	0.7	0.8
Pb Carbonate [µg/g]	25-Apr-05	14:00	27-Jun-05	11:20	1	4	8	6	4	2	1
Pb Reducible [µg/g]	25-Apr-05	14:00	27-Jun-05	11:20	10	29	40	27	24	17	5.8
Pb Organic [µg/g]	25-Apr-05	14:00	27-Jun-05	11:20	18	62	550	48	41	38	5
Pb Residual [µg/g]	25-Apr-05	14:00	27-Jun-05	11:20	3.3	6.4	16	6.8	7.7	5.0	4.0
Pb Total Recoverable [µg/g]	25-Apr-05	14:00	26-Apr-05	08:39	28	83	150	88	56	56	11
Se Exchangeable [µg/g]	25-Apr-05	14:00	27-Jun-05	11:20	< 5	< 5	< 5	< 5	< 5	< 5	< 5
Se Carbonate [µg/g]	25-Apr-05	14:00	27-Jun-05	11:20	< 5	< 5	< 5	< 5	< 5	< 5	< 5
Se Reducible [µg/g]	25-Apr-05	14:00	27-Jun-05	11:20	< 5	< 5	< 5	< 5	< 5	< 5	< 5
Se Organic [µg/g]	25-Apr-05	14:00	27-Jun-05	11:20	< 5	< 5	< 5	< 5	7	< 5	< 5
Se Residual [µg/g]	25-Apr-05	14:00	27-Jun-05	11:20	< 5	< 5	< 5	< 5	< 5	< 5	< 5
Se Total Recoverable [µg/g]	25-Apr-05	14:00	26-Apr-05	08:39	< 5	< 5	< 5	< 5	< 5	< 5	< 5

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Final Report

Analysis	12: 510ss-0.5cm-split SG Apr8/05	13: 511ss-0.5cm-split SG Apr8/05	14: 512ss-0.5cm-split SG Apr8/05	15: 513ss-0.5cm-split SG Apr8/05	16: 514ss-0.5cm-split SG Apr8/05	17: 515ss-0.5cm-split SG Apr8/05	18: 516ss-0.5cm-split SG Apr8/05	19: 517ss-0.5cm-split SG Apr8/05	20: 518ss-0.5cm-split SG Apr8/05	21: 519ss-0.5cm-split SG Apr8/05
As Exchangeable [µg/g]	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5
As Carbonate [µg/g]	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5
As Reducible [µg/g]	< 5	< 5	7	< 5	17	< 5	< 5	15	7	6
As Organic [µg/g]	7	8	16	< 5	37	< 5	13	28	10	22
As Residual [µg/g]	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5
As Total Recoverable [µg/g]	11	< 5	20	< 5	57	< 5	12	45	16	26
Co Exchangeable [µg/g]	< 0.3	< 0.3	1.2	0.6	2.9	< 0.3	1.8	< 0.3	< 0.3	< 0.3
Co Carbonate [µg/g]	< 0.3	< 0.3	< 0.3	< 0.3	0.8	< 0.3	< 0.3	0.3	< 0.3	< 0.3
Co Reducible [µg/g]	6.0	4.4	16	3.6	25	2.2	11	10	6.8	9.5
Co Organic [µg/g]	3.8	4.8	7.9	4.5	42	3.3	5.0	7.7	5.5	9.6
Co Residual [µg/g]	5.4	5.5	11	3.6	14	3.7	5.2	5.6	5.4	5.8
Co Total Recoverable [µg/g]	12	9.2	27	6.5	100	5.5	19	18	15	23
Cu Exchangeable [µg/g]	2.1	3.6	9.1	4.9	0.8	< 0.1	4.6	0.6	1.5	0.2
Cu Carbonate [µg/g]	28	24	26	0.3	4.7	0.4	23	10	11	1.5
Cu Reducible [µg/g]	89	85	430	12	54	5.8	160	52	56	25
Cu Organic [µg/g]	240	130	540	25	630	23	200	150	160	150
Cu Residual [µg/g]	21	17	50	2.9	46	2.3	19	22	15	10

Analysis	12: 510ss-0.5cm-sp lit SG Apr8/05	13: 511ss-0.5cm-sp lit SG Apr8/05	14: 512ss-0.5cm-sp lit SG Apr8/05	15: 513ss-0.5cm-sp lit SG Apr8/05	16: 514ss-0.5cm-sp lit SG Apr8/05	17: 515ss-0.5cm-sp lit SG Apr8/05	18: 516ss-0.5cm-sp lit SG Apr8/05	19: 517ss-0.5cm-sp lit SG Apr8/05	20: 518ss-0.5cm-sp lit SG Apr8/05	21: 519ss-0.5cm-sp lit SG Apr8/05
Cu Total Recoverable [µg/g]	440	220	1000	42	940	31	420	290	280	210
Ni Exchangeable [µg/g]	42	25	140	7	84	1	130	11	41	9
Ni Carbonate [µg/g]	29	6	19	< 1	34	< 1	22	19	19	5
Ni Reducible [µg/g]	130	45	320	10	310	17	240	140	120	90
Ni Organic [µg/g]	82	45	230	20	480	14	120	100	110	100
Ni Residual [µg/g]	96	74	300	17	130	12	74	52	62	39
Ni Total Recoverable [µg/g]	360	140	890	42	1300	38	610	330	380	240
Pb Exchangeable [µg/g]	0.7	1.0	1.1	3.9	< 0.7	0.8	1.3	< 0.7	0.7	< 0.7
Pb Carbonate [µg/g]	2	5	4	3	1	2	6	2	2	2
Pb Reducible [µg/g]	7.1	27	55	21	14	7.9	57	16	11	8.0
Pb Organic [µg/g]	9	17	52	13	33	5	40	14	19	14
Pb Residual [µg/g]	4.0	3.6	7.5	4.6	4.2	3.4	3.7	3.5	3.8	5.3
Pb Total Recoverable [µg/g]	17	31	100	41	55	11	93	40	30	19
Se Exchangeable [µg/g]	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5
Se Carbonate [µg/g]	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5
Se Reducible [µg/g]	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5
Se Organic [µg/g]	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5
Se Residual [µg/g]	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5
Se Total Recoverable [µg/g]	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5

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Final Report

Analysis	**22: 520ss-0.5cm-sp lit SG Apr8/05**	**23: 521ss-0.5cm-sp lit SG Apr8/05**	**24: 522ss-0.5cm-sp lit SG Apr8/05**	**25: 523ss-0.5cm-sp lit SG Apr8/05**	**26: 524ss-0.5cm-sp lit SG Apr8/05**	**27: 525ss-0.5cm-sp lit SG Apr8/05**	**28: 526ss-0.5cm-sp lit SG Apr8/05**	**29: 528ss-0.5cm-sp lit SG Apr8/05**	**30: 529ss-0.5cm-sp lit SG Apr8/05**	**31: 530ss-0.5cm-sp lit SG Apr8/05**
As Exchangeable [µg/g]	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5
As Carbonate [µg/g]	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5
As Reducible [µg/g]	< 5	7	23	31	< 5	< 5	< 5	11	< 5	< 5
As Organic [µg/g]	< 5	12	133	83	6	7	< 5	15	< 5	< 5
As Residual [µg/g]	< 5	< 5	18	6	< 5	< 5	< 5	< 5	< 5	< 5
As Total Recoverable [µg/g]	< 5	16	150	110	7	10	< 5	33	6	10
Co Exchangeable [µg/g]	< 0.3	1.3	5.8	4.5	< 0.3	< 0.3	< 0.3	0.9	0.3	1.4
Co Carbonate [µg/g]	< 0.3	< 0.3	1.8	1.8	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3
Co Reducible [µg/g]	2.7	11	27	25	4.2	4.0	2.2	14	1.6	5.4
Co Organic [µg/g]	3.2	6.4	34	43	3.3	3.7	2.6	14	2.5	3.2
Co Residual [µg/g]	3.3	9.2	23	24	3.4	4.8	3.2	15	3.0	5.1
Co Total Recoverable [µg/g]	6.6	24	100	56	12	11	5.7	50	6.2	12
Cu Exchangeable [µg/g]	0.2	13	3.0	1.5	< 0.1	0.3	< 0.1	1.0	< 0.1	12
Cu Carbonate [µg/g]	0.5	44	40	16	2.3	7.6	< 0.1	14	< 0.1	31
Cu Reducible [µg/g]	7.8	220	93	65	14	36	3.3	61	3.6	130
Cu Organic [µg/g]	82	580	1060	540	110	110	30	310	34	170
Cu Residual [µg/g]	4.8	39	211	59	9.3	13	2.7	45	4.1	15

Analysis	22: 520ss-0.5cm-sp lit SG Apr8/05	23: 521ss-0.5cm-sp lit SG Apr8/05	24: 522ss-0.5cm-sp lit SG Apr8/05	25: 523ss-0.5cm-sp lit SG Apr8/05	26: 524ss-0.5cm-sp lit SG Apr8/05	27: 525ss-0.5cm-sp lit SG Apr8/05	28: 526ss-0.5cm-sp lit SG Apr8/05	29: 528ss-0.5cm-sp lit SG Apr8/05	30: 529ss-0.5cm-sp lit SG Apr8/05	31: 530ss-0.5cm-sp lit SG Apr8/05
Cu Total Recoverable [µg/g]	98	1100	1500	740	180	180	45	610	51	530
Ni Exchangeable [µg/g]	12	130	200	190	11	8	4	51	11	93
Ni Carbonate [µg/g]	2	22	86	108	11	9	2	15	2	9
Ni Reducible [µg/g]	30	160	450	510	65	64	25	110	14	84
Ni Organic [µg/g]	40	150	590	460	62	58	21	150	15	76
Ni Residual [µg/g]	31	220	310	140	38	51	14	110	22	91
Ni Total Recoverable [µg/g]	92	700	1500	1200	210	190	65	560	73	410
Pb Exchangeable [µg/g]	0.9	< 0.7	< 0.7	< 0.7	< 0.7	< 0.7	< 0.7	< 0.7	< 0.7	< 0.7
Pb Carbonate [µg/g]	2	3	1	1	1	1	< 0.7	1	1	2
Pb Reducible [µg/g]	9.6	15	17	21	7.6	8.8	4.7	15	4.7	16
Pb Organic [µg/g]	14	35	98	53	15	13	7	21	6	15
Pb Residual [µg/g]	3.6	6.1	14	5.4	2.5	4.4	3.5	2.6	< 0.7	4.5
Pb Total Recoverable [µg/g]	23	59	79	76	26	23	13	54	12	38
Se Exchangeable [µg/g]	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5
Se Carbonate [µg/g]	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5
Se Reducible [µg/g]	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5
Se Organic [µg/g]	< 5	6	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5
Se Residual [µg/g]	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5
Se Total Recoverable [µg/g]	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5

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Wednesday, October 19, 2005

Date Rec. : 13 April 2005
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Project : Sudbury Soils Phase 2

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CERTIFICATE OF ANALYSIS

Final Report

Analysis	**32: 531ss-0.5cm-sp lit SG Apr8/05**	**33: 532ss-0.5cm-sp lit SG Apr8/05**	**34: 533ss-0.5cm-sp lit SG Apr8/05**	**35: 534ss-0.5cm-sp lit SG Apr8/05**	**36: 541ss-0.5cm-sp lit SG Apr8/05**	**37: 542ss-0.5cm-sp lit SG Apr8/05**	**38: 546ss-0.5cm-sp lit SG Apr8/05**	**39: 547ss-0.5cm-sp lit SG Apr8/05**	**40: 550ss-0.5cm-sp lit SG Apr8/05**	**41: 551ss-0.5cm-sp lit SG Apr8/05**
As Exchangeable [µg/g]	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5
As Carbonate [µg/g]	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5
As Reducible [µg/g]	< 5	45	6	35	< 5	< 5	< 5	< 5	< 5	< 5
As Organic [µg/g]	< 5	134	7	70	< 5	< 5	< 5	< 5	< 5	< 5
As Residual [µg/g]	< 5	11	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5
As Total Recoverable [µg/g]	< 5	210	16	120	< 5	< 5	< 5	< 5	< 5	< 5
Co Exchangeable [µg/g]	< 0.3	4.3	0.3	1.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3
Co Carbonate [µg/g]	< 0.3	0.4	< 0.3	0.6	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3
Co Reducible [µg/g]	2.3	19	9.4	16	1.8	0.5	1.1	2.2	3.4	1.6
Co Organic [µg/g]	2.2	23	4.7	18	2.7	1.8	2.1	3.4	3.6	2.2
Co Residual [µg/g]	3.4	15	9.3	12	3.4	2.5	3.3	3.7	3.6	2.5
Co Total Recoverable [µg/g]	5.2	70	23	44	4.8	2.0	3.4	5.6	6.2	6.1
Cu Exchangeable [µg/g]	< 0.1	3.6	4.3	1.3	< 0.1	< 0.1	< 0.1	< 0.1	0.3	< 0.1
Cu Carbonate [µg/g]	0.9	28	42	24	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Cu Reducible [µg/g]	11	150	260	76	4.9	1.5	2.2	2.9	7.6	2.6
Cu Organic [µg/g]	35	700	380	500	23	11	18	29	28	13
Cu Residual [µg/g]	4.7	87	46	67	2.1	1.3	2.6	2.8	3.1	1.4

Analysis	32: 531ss-0.5cm-sp lit SG Apr8/05	33: 532ss-0.5cm-sp lit SG Apr8/05	34: 533ss-0.5cm-sp lit SG Apr8/05	35: 534ss-0.5cm-sp lit SG Apr8/05	36: 541ss-0.5cm-sp lit SG Apr8/05	37: 542ss-0.5cm-sp lit SG Apr8/05	38: 546ss-0.5cm-sp lit SG Apr8/05	39: 547ss-0.5cm-sp lit SG Apr8/05	40: 550ss-0.5cm-sp lit SG Apr8/05	41: 551ss-0.5cm-sp lit SG Apr8/05
Cu Total Recoverable [µg/g]	77	1200	1200	810	35	13	24	38	46	22
Ni Exchangeable [µg/g]	3	170	52	57	3	2	1	4	7	3
Ni Carbonate [µg/g]	2	25	12	31	< 1	< 1	< 1	< 1	< 1	< 1
Ni Reducible [µg/g]	17	270	140	270	12	4	8	16	11	8
Ni Organic [µg/g]	13	210	100	320	13	7	10	17	16	9
Ni Residual [µg/g]	28	190	230	140	16	7	15	14	20	8
Ni Total Recoverable [µg/g]	73	1100	600	830	40	15	29	44	46	28
Pb Exchangeable [µg/g]	< 0.7	< 0.7	< 0.7	< 0.7	< 0.7	< 0.7	< 0.7	< 0.7	0.7	< 0.7
Pb Carbonate [µg/g]	1	2	2	3	1	1	1	1	1	1
Pb Reducible [µg/g]	5.0	21	16	27	3.7	2.4	3.9	4.9	3.7	6.2
Pb Organic [µg/g]	5	59	22	59	4	4	6	6	5	7
Pb Residual [µg/g]	3.8	6.7	6.0	5.7	4.4	3.6	4.4	2.9	4.1	2.6
Pb Total Recoverable [µg/g]	11	100	72	120	7.0	5.1	9.5	9.7	7.6	12
Se Exchangeable [µg/g]	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5
Se Carbonate [µg/g]	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5
Se Reducible [µg/g]	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5
Se Organic [µg/g]	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5
Se Residual [µg/g]	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5
Se Total Recoverable [µg/g]	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5

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CERTIFICATE OF ANALYSIS

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Analysis	42: 552ss-0.5cm-sp lit SG Apr8/05	43: 553ss-0.5cm-sp lit SG Apr8/05	44: 554ss-0.5cm-sp lit SG Apr8/05	45: 557ss-0.5cm-sp lit SG Apr8/05	46: 559ss-0.5cm-sp lit SG Apr8/05	47: 560ss-0.5cm-sp lit SG Apr8/05	48: 561ss-0.5cm-sp lit SG Apr8/05	49: 562ss-0.5cm-sp lit SG Apr8/05	50: 563ss-0.5cm-sp lit SG Apr8/05	51: 564ss-0.5cm-sp lit SG Apr8/05
As Exchangeable [µg/g]	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5
As Carbonate [µg/g]	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5
As Reducible [µg/g]	< 5	< 5	6	< 5	< 5	< 5	7	< 5	< 5	< 5
As Organic [µg/g]	< 5	< 5	12	< 5	< 5	< 5	7	< 5	< 5	< 5
As Residual [µg/g]	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5
As Total Recoverable [µg/g]	5	6	21	< 5	< 5	< 5	12	< 5	8	< 5
Co Exchangeable [µg/g]	< 0.3	< 0.3	0.4	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3
Co Carbonate [µg/g]	< 0.3	< 0.3	0.4	< 0.3	< 0.3	< 0.3	0.6	< 0.3	< 0.3	< 0.3
Co Reducible [µg/g]	2.9	4.1	8.1	4.3	1.7	1.7	9.9	1.4	6.0	2.1
Co Organic [µg/g]	4.6	3.2	6.4	5.0	2.2	3.0	4.4	2.1	3.0	3.7
Co Residual [µg/g]	3.7	3.8	6.4	3.4	3.4	3.5	6.1	2.9	5.3	4.2
Co Total Recoverable [µg/g]	12	10	17	15	4.3	5.1	17	3.3	13	6.6
Cu Exchangeable [µg/g]	< 0.1	< 0.1	3.1	< 0.1	< 0.1	< 0.1	0.3	< 0.1	4.1	< 0.1
Cu Carbonate [µg/g]	< 0.1	0.4	48	0.8	0.6	< 0.1	12	< 0.1	18	0.6
Cu Reducible [µg/g]	3.6	20	130	4.0	4.6	3.5	74	3.3	120	7.6
Cu Organic [µg/g]	70	64	200	42	22	23	130	13	180	34
Cu Residual [µg/g]	7.0	8.2	22	4.1	3.8	2.8	22	1.6	24	5.7

Analysis	42: 552ss-0.5cm-split SG Apr8/05	43: 553ss-0.5cm-split SG Apr8/05	44: 554ss-0.5cm-split SG Apr8/05	45: 557ss-0.5cm-split SG Apr8/05	46: 559ss-0.5cm-split SG Apr8/05	47: 560ss-0.5cm-split SG Apr8/05	48: 561ss-0.5cm-split SG Apr8/05	49: 562ss-0.5cm-split SG Apr8/05	50: 563ss-0.5cm-split SG Apr8/05	51: 564ss-0.5cm-split SG Apr8/05
Cu Total Recoverable [µg/g]	120	110	510	130	40	34	270	19	420	64
Ni Exchangeable [µg/g]	7	4	69	6	5	1	14	< 1	49	4
Ni Carbonate [µg/g]	8	3	59	4	1	2	21	< 1	15	2
Ni Reducible [µg/g]	41	60	200	37	14	17	140	9	94	22
Ni Organic [µg/g]	80	36	110	31	9	12	66	7	30	18
Ni Residual [µg/g]	28	32	74	17	21	15	96	12	92	26
Ni Total Recoverable [µg/g]	220	140	570	150	45	41	320	24	270	70
Pb Exchangeable [µg/g]	< 0.7	< 0.7	< 0.7	< 0.7	< 0.7	< 0.7	< 0.7	< 0.7	0.8	< 0.7
Pb Carbonate [µg/g]	1	1	2	1	2	1	8	< 0.7	1	1
Pb Reducible [µg/g]	4.4	7.2	19	3.9	14	6.8	66	5.6	15	8.8
Pb Organic [µg/g]	11	9	19	7	6	5	27	4	9	8
Pb Residual [µg/g]	2.7	3.0	3.7	3.0	4.7	3.2	4.4	3.5	3.2	2.0
Pb Total Recoverable [µg/g]	21	19	41	14	29	9.8	150	6.6	28	18
Se Exchangeable [µg/g]	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5
Se Carbonate [µg/g]	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5
Se Reducible [µg/g]	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5
Se Organic [µg/g]	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5
Se Residual [µg/g]	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5
Se Total Recoverable [µg/g]	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5

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Project : Sudbury Soils Phase 2

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CERTIFICATE OF ANALYSIS

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Analysis	**52: 565ss-0.5cm-sp lit SG Apr8/05**	**53: 566ss-0.5cm-sp lit SG Apr8/05**	**54: 567ss-0.5cm-sp lit SG Apr8/05**	**55: 568ss-0.5cm-sp lit SG Apr8/05**	**56: 569ss-0.5cm-sp lit SG Apr8/05**	**57: 570ss-0.5cm-sp lit SG Apr8/05**	**58: 571ss-0.5cm-sp lit SG Apr8/05**	**59: 572ss-0.5cm-sp lit SG Apr8/05**	**60: 573ss-0.5cm-sp lit SG Apr8/05**	**61: 574ss-0.5cm-sp lit SG Apr8/05**
As Exchangeable [µg/g]	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5
As Carbonate [µg/g]	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5
As Reducible [µg/g]	< 5	< 5	< 5	12	< 5	10	17	< 5	8	< 5
As Organic [µg/g]	< 5	< 5	< 5	53	7	6	21	< 5	15	< 5
As Residual [µg/g]	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5
As Total Recoverable [µg/g]	< 5	< 5	< 5	45	< 5	15	46	< 5	21	< 5
Co Exchangeable [µg/g]	< 0.3	< 0.3	< 0.3	2.7	< 0.3	< 0.3	0.5	< 0.3	0.8	< 0.3
Co Carbonate [µg/g]	< 0.3	< 0.3	< 0.3	0.7	< 0.3	< 0.3	0.6	< 0.3	< 0.3	< 0.3
Co Reducible [µg/g]	4.2	4.7	3.1	44	6.6	6.1	10	1.1	5.2	2.1
Co Organic [µg/g]	3.2	4.7	5.5	109	4.5	2.7	11	1.7	6.8	3.6
Co Residual [µg/g]	5.2	3.9	6.2	17	5.5	7.0	7.8	2.2	5.6	4.3
Co Total Recoverable [µg/g]	7.9	10	5.6	89	15	16	44	2.8	21	5.6
Cu Exchangeable [µg/g]	1.4	0.8	< 0.1	2.0	< 0.1	0.3	< 0.1	< 0.1	< 0.1	< 0.1
Cu Carbonate [µg/g]	5.9	12	0.6	28	4.4	13	9.6	< 0.1	< 0.1	1.6
Cu Reducible [µg/g]	69	66	8.2	30	42	110	51	2.9	9.7	5.4
Cu Organic [µg/g]	120	55	26	660	130	130	220	11	130	23
Cu Residual [µg/g]	12	7.1	3.4	111	21	27	55	2.2	25	2.7

Analysis	52: 565ss-0.5cm-sp lit SG Apr8/05	53: 566ss-0.5cm-sp lit SG Apr8/05	54: 567ss-0.5cm-sp lit SG Apr8/05	55: 568ss-0.5cm-sp lit SG Apr8/05	56: 569ss-0.5cm-sp lit SG Apr8/05	57: 570ss-0.5cm-sp lit SG Apr8/05	58: 571ss-0.5cm-sp lit SG Apr8/05	59: 572ss-0.5cm-sp lit SG Apr8/05	60: 573ss-0.5cm-sp lit SG Apr8/05	61: 574ss-0.5cm-sp lit SG Apr8/05
Cu Total Recoverable [µg/g]	160	200	47	750	220	590	500	19	220	38
Ni Exchangeable [µg/g]	11	9	< 1	110	14	8	28	1	41	4
Ni Carbonate [µg/g]	3	5	1	39	13	14	36	< 1	< 1	6
Ni Reducible [µg/g]	37	88	25	180	160	97	160	9	78	16
Ni Organic [µg/g]	19	55	19	490	74	30	150	6	64	13
Ni Residual [µg/g]	61	31	19	220	70	160	100	10	55	14
Ni Total Recoverable [µg/g]	87	210	50	850	360	400	710	23	290	47
Pb Exchangeable [µg/g]	< 0.7	< 0.7	< 0.7	< 0.7	< 0.7	< 0.7	< 0.7	< 0.7	< 0.7	< 0.7
Pb Carbonate [µg/g]	3	2	1	2	11	2	2	1	2	2
Pb Reducible [µg/g]	32	8.6	6.9	31	88	21	17	4.5	10	10
Pb Organic [µg/g]	16	5	6	46	37	9	15	4	13	6
Pb Residual [µg/g]	2.9	2.9	2.8	4.3	4.1	5.1	4.3	1.6	3.8	3.2
Pb Total Recoverable [µg/g]	31	31	11	64	32	44	45	5.7	26	12
Se Exchangeable [µg/g]	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5
Se Carbonate [µg/g]	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5
Se Reducible [µg/g]	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5
Se Organic [µg/g]	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5
Se Residual [µg/g]	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5
Se Total Recoverable [µg/g]	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5

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CERTIFICATE OF ANALYSIS

Final Report

Analysis	**62: 577ss-0.5cm-sp lit SG Apr8/05**	**63: 580ss-0.5cm-sp lit SG Apr8/05**	**64: 581ss-0.5cm-sp lit SG Apr8/05**	**65: 582ss-0.5cm-sp lit SG Apr8/05**	**66: 584ss-0.5cm-sp lit SG Apr8/05**	**67: 585ss-0.5cm-sp lit SG Apr8/05**	**68: 586ss-0.5cm-sp lit SG Apr8/05**	**69: 588ss-0.5cm-sp lit SG Apr8/05**	**70: 589ss-0.5cm-sp lit SG Apr8/05**	**71: 590ss-0.5cm-sp lit SG Apr8/05**
As Exchangeable [µg/g]	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5
As Carbonate [µg/g]	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5
As Reducible [µg/g]	6	5	21	< 5	15	8	11	< 5	< 5	< 5
As Organic [µg/g]	6	< 5	34	< 5	16	9	12	< 5	< 5	< 5
As Residual [µg/g]	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5
As Total Recoverable [µg/g]	9	< 5	53	< 5	24	10	16	< 5	< 5	< 5
Co Exchangeable [µg/g]	0.3	1.1	1.4	< 0.3	1.6	0.5	0.5	0.3	< 0.3	< 0.3
Co Carbonate [µg/g]	< 0.3	< 0.3	0.4	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3
Co Reducible [µg/g]	8.4	2.4	7.6	3.2	15	8.4	6.1	9.6	3.4	2.7
Co Organic [µg/g]	9.0	2.1	5.7	4.3	9.5	3.8	7.0	3.7	2.9	2.3
Co Residual [µg/g]	9.8	4.4	7.1	3.4	10	8.4	14	7.5	4.6	3.8
Co Total Recoverable [µg/g]	24	7.3	22	7.7	25	14	18	12	9.6	6.1
Cu Exchangeable [µg/g]	0.1	3.1	0.7	0.7	32	3.5	14	5.0	< 0.1	< 0.1
Cu Carbonate [µg/g]	3.4	2.7	6.1	0.7	75	21	39	12	< 0.1	< 0.1
Cu Reducible [µg/g]	20	26	29	7.7	340	160	540	230	15	2.8
Cu Organic [µg/g]	270	210	130	21	240	130	710	190	44	22
Cu Residual [µg/g]	59	18	30	3.0	46	32	61	16	4.9	2.2

Analysis	62: 577ss-0.5cm-sp lit SG Apr8/05	63: 580ss-0.5cm-sp lit SG Apr8/05	64: 581ss-0.5cm-sp lit SG Apr8/05	65: 582ss-0.5cm-sp lit SG Apr8/05	66: 584ss-0.5cm-sp lit SG Apr8/05	67: 585ss-0.5cm-sp lit SG Apr8/05	68: 586ss-0.5cm-sp lit SG Apr8/05	69: 588ss-0.5cm-sp lit SG Apr8/05	70: 589ss-0.5cm-sp lit SG Apr8/05	71: 590ss-0.5cm-sp lit SG Apr8/05
Cu Total Recoverable [µg/g]	360	230	250	29	780	380	1400	570	94	38
Ni Exchangeable [µg/g]	42	47	47	6	110	49	79	46	4	5
Ni Carbonate [µg/g]	13	3	16	< 1	13	9	11	7	< 1	< 1
Ni Reducible [µg/g]	150	56	98	12	170	94	130	130	33	12
Ni Organic [µg/g]	170	30	52	37	80	38	160	55	24	11
Ni Residual [µg/g]	110	84	58	14	270	160	530	95	25	12
Ni Total Recoverable [µg/g]	510	170	320	37	560	320	670	350	89	51
Pb Exchangeable [µg/g]	< 0.7	< 0.7	< 0.7	0.8	6.4	1.3	< 0.7	1.0	< 0.7	< 0.7
Pb Carbonate [µg/g]	2	2	1	< 0.7	17	4	2	3	2	1
Pb Reducible [µg/g]	9.8	8.7	11	4.2	129	48	30	40	20	2.8
Pb Organic [µg/g]	14	10	13	4	36	20	52	17	11	3
Pb Residual [µg/g]	2.7	4.0	3.1	2.7	7.4	12	6.2	4.2	4.5	2.7
Pb Total Recoverable [µg/g]	23	16	24	6.7	150	78	73	33	41	4.7
Se Exchangeable [µg/g]	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5
Se Carbonate [µg/g]	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5
Se Reducible [µg/g]	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5
Se Organic [µg/g]	< 5	< 5	< 5	< 5	< 5	< 5	7	< 5	< 5	< 5
Se Residual [µg/g]	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5
Se Total Recoverable [µg/g]	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5

Rob Irwin B.Sc., C.Chem
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Wednesday, October 19, 2005

Date Rec. : 13 April 2005
LR. Ref. : **CA10170-APR05**
Project : Sudbury Soils Phase 2

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CERTIFICATE OF ANALYSIS

Final Report

Analysis	**72: 591ss-0.5cm-sp lit SG Apr8/05**	**73: 592ss-0.5cm-sp lit SG Apr8/05**	**74: 593ss-0.5cm-sp lit SG Apr8/05**	**75: 594ss-0.5cm-sp lit SG Apr8/05**	**76: 596ss-0.5cm-sp lit SG Apr8/05**	**77: 597ss-0.5cm-sp lit SG Apr8/05**	**78: 598ss-0.5cm-sp lit SG Apr8/05**	**79: 599ss-0.5cm-sp lit SG Apr8/05**	**80: 600ss-0.5cm-sp lit SG Apr8/05**	**81: 601ss-0.5cm-sp lit SG Apr8/05**
As Exchangeable [µg/g]	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5
As Carbonate [µg/g]	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5
As Reducible [µg/g]	< 5	< 5	< 5	< 5	< 5	28	13	< 5	< 5	< 5
As Organic [µg/g]	< 5	< 5	< 5	< 5	< 5	21	12	< 5	< 5	< 5
As Residual [µg/g]	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5
As Total Recoverable [µg/g]	< 5	< 5	< 5	< 5	< 5	52	29	< 5	< 5	< 5
Co Exchangeable [µg/g]	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	8.3	1.5	< 0.3	< 0.3	< 0.3
Co Carbonate [µg/g]	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3
Co Reducible [µg/g]	1.8	2.3	2.7	1.3	5.6	8.3	17	2.0	1.3	1.3
Co Organic [µg/g]	2.7	2.0	2.8	2.0	4.9	5.5	8.6	2.4	1.7	1.6
Co Residual [µg/g]	4.2	4.1	3.6	3.2	15	12	7.6	3.7	3.0	3.1
Co Total Recoverable [µg/g]	4.2	6.0	7.8	3.8	7.4	38	23	6.5	3.6	3.4
Cu Exchangeable [µg/g]	< 0.1	< 0.1	< 0.1	< 0.1	0.7	21	0.9	< 0.1	< 0.1	< 0.1
Cu Carbonate [µg/g]	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	2.6	< 0.1	< 0.1	< 0.1	< 0.1
Cu Reducible [µg/g]	1.0	8.6	3.1	2.3	20	190	32	4.1	3.0	2.9
Cu Organic [µg/g]	25	50	8.7	13	110	310	190	48	7.7	11
Cu Residual [µg/g]	3.6	4.1	0.8	1.5	18	40	28	8.4	1.0	1.6

Analysis	72: 591ss-0.5cm-sp lit SG Apr8/05	73: 592ss-0.5cm-sp lit SG Apr8/05	74: 593ss-0.5cm-sp lit SG Apr8/05	75: 594ss-0.5cm-sp lit SG Apr8/05	76: 596ss-0.5cm-sp lit SG Apr8/05	77: 597ss-0.5cm-sp lit SG Apr8/05	78: 598ss-0.5cm-sp lit SG Apr8/05	79: 599ss-0.5cm-sp lit SG Apr8/05	80: 600ss-0.5cm-sp lit SG Apr8/05	81: 601ss-0.5cm-sp lit SG Apr8/05
Cu Total Recoverable [µg/g]	36	75	18	20	140	850	250	73	16	18
Ni Exchangeable [µg/g]	2	9	3	< 1	19	280	72	< 1	1	< 1
Ni Carbonate [µg/g]	< 1	< 1	< 1	< 1	< 1	2	< 1	< 1	< 1	< 1
Ni Reducible [µg/g]	11	19	5	8	36	170	230	22	6	9
Ni Organic [µg/g]	17	13	9	8	31	51	140	22	7	7
Ni Residual [µg/g]	18	28	9	10	68	120	80	20	9	12
Ni Total Recoverable [µg/g]	36	67	25	24	100	840	440	73	22	23
Pb Exchangeable [µg/g]	< 0.7	< 0.7	< 0.7	< 0.7	< 0.7	1.0	< 0.7	< 0.7	< 0.7	< 0.7
Pb Carbonate [µg/g]	2	2	1	2	2	2	3	3	3	2
Pb Reducible [µg/g]	2.2	6.1	2.3	7.8	9.4	18	9.0	6.0	2.9	3.7
Pb Organic [µg/g]	5	7	3	5	13	25	11	8	3	4
Pb Residual [µg/g]	4.2	4.9	3.0	4.4	5.0	4.9	2.6	4.4	3.5	4.4
Pb Total Recoverable [µg/g]	7.5	18	3.1	13	15	77	19	17	5.0	5.9
Se Exchangeable [µg/g]	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5
Se Carbonate [µg/g]	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5
Se Reducible [µg/g]	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5
Se Organic [µg/g]	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5
Se Residual [µg/g]	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5
Se Total Recoverable [µg/g]	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5

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Wednesday, October 19, 2005

Date Rec. : 13 April 2005
LR. Ref. : **CA10170-APR05**
Project : Sudbury Soils Phase 2

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CERTIFICATE OF ANALYSIS

Final Report

Analysis	82: 602ss-0.5cm-split SG Apr8/05	83: 606ss-0.5cm-split SG Apr8/05	84: 607ss-0.5cm-split SG Apr8/05	85: 608ss-0.5cm-split SG Apr8/05	86: 611ss-0.5cm-split SG Apr8/05	87: 612ss-0.5cm-split SG Apr8/05	88: 613ss-0.5cm-split SG Apr8/05
As Exchangeable [µg/g]	< 5	< 5	< 5	< 5	< 5	< 5	< 5
As Carbonate [µg/g]	< 5	< 5	< 5	< 5	< 5	< 5	< 5
As Reducible [µg/g]	< 5	< 5	< 5	< 5	< 5	< 5	32
As Organic [µg/g]	6	< 5	< 5	< 5	< 5	< 5	66
As Residual [µg/g]	< 5	< 5	< 5	< 5	< 5	< 5	< 5
As Total Recoverable [µg/g]	12	< 5	< 5	< 5	< 5	< 5	110
Co Exchangeable [µg/g]	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	1.8
Co Carbonate [µg/g]	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3
Co Reducible [µg/g]	5.7	1.3	2.5	4.9	2.7	1.2	15
Co Organic [µg/g]	3.8	1.8	2.8	2.9	2.2	1.9	10.0
Co Residual [µg/g]	6.0	3.3	3.5	5.1	3.6	2.9	7.1
Co Total Recoverable [µg/g]	25	3.7	6.7	7.3	6.0	4.2	59
Cu Exchangeable [µg/g]	2.6	< 0.1	2.7	< 0.1	< 0.1	< 0.1	2.9
Cu Carbonate [µg/g]	0.8	< 0.1	13	0.3	0.2	0.2	2.8
Cu Reducible [µg/g]	150	4.0	85	6.2	1.9	3.4	78
Cu Organic [µg/g]	240	34	76	17	13	21	290
Cu Residual [µg/g]	20	2.0	5.0	3.3	1.8	3.0	23

Analysis	**82: 602ss-0.5cm-sp lit SG Apr8/05**	**83: 606ss-0.5cm-sp lit SG Apr8/05**	**84: 607ss-0.5cm-sp lit SG Apr8/05**	**85: 608ss-0.5cm-sp lit SG Apr8/05**	**86: 611ss-0.5cm-sp lit SG Apr8/05**	**87: 612ss-0.5cm-sp lit SG Apr8/05**	**88: 613ss-0.5cm-sp lit SG Apr8/05**
Cu Total Recoverable [µg/g]	980	27	260	32	21	32	580
Ni Exchangeable [µg/g]	39	4	16	5	< 1	2	92
Ni Carbonate [µg/g]	< 1	< 1	6	< 1	< 1	< 1	3
Ni Reducible [µg/g]	110	30	51	18	17	13	160
Ni Organic [µg/g]	71	50	29	13	11	10	130
Ni Residual [µg/g]	120	11	33	13	12	17	70
Ni Total Recoverable [µg/g]	940	36	150	43	32	39	620
Pb Exchangeable [µg/g]	< 0.7	< 0.7	< 0.7	0.8	< 0.7	< 0.7	< 0.7
Pb Carbonate [µg/g]	2	2	1	2	3	3	3
Pb Reducible [µg/g]	10	3.3	6.0	3.1	3.2	4.6	24
Pb Organic [µg/g]	14	3	5	3	4	5	21
Pb Residual [µg/g]	5.3	4.2	4.9	4.0	5.7	3.2	4.1
Pb Total Recoverable [µg/g]	56	5.3	14	5.1	8.1	9.7	59
Se Exchangeable [µg/g]	< 5	< 5	< 5	< 5	< 5	< 5	< 5
Se Carbonate [µg/g]	< 5	< 5	< 5	< 5	< 5	< 5	< 5
Se Reducible [µg/g]	< 5	< 5	< 5	< 5	< 5	< 5	< 5
Se Organic [µg/g]	< 5	< 5	< 5	< 5	< 5	< 5	< 5
Se Residual [µg/g]	< 5	< 5	< 5	< 5	< 5	< 5	< 5
Se Total Recoverable [µg/g]	< 5	< 5	< 5	< 5	< 5	< 5	< 5

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MEMORANDUM

To Glenn Ferguson, Cantox Environmental Inc.

From Fred Ford Date September 16, 2005

Subject Review of Lakefield Research Ni Speciation Results

Background

Lakefield Research is examining soil, dust and air filter samples from the Sudbury area to determine the type of Ni-bearing species present (Ni as metallic, oxide, sulphide or sulphate). They are using an SEM equipped with an X-ray spectrometer to conduct the chemical typing of the various particles. In the course of their study, Lakefield has determined that some of the Ni in some of these samples is present as the mineral Heazlewoodite (Ni_3S_2). I visited Lakefield Research September 15, 2005 to review their techniques and confirm their identification of Heazlewoodite.

Method and Equipment

Lakefield Research is conducting their study using the QEMSEM scanning electron microscope equipped with a light element energy dispersive X-ray detector (EDS). The EDS detector is capable of analyzing elements heavier than Boron (can determine carbon and oxygen).

The samples are introduced into the SEM using two types of sample mounts. Air filter samples are introduced as ~1cm square pieces cut from the original air filter. Soil and dust samples are sprinkled as loose powder on ~1cm diameter round stubs. Both sample varieties are coated with a thin layer of carbon to provide a grounding path for the electron beam.

Ni-bearing particles are detected using an automated scanning method, which moves the samples under the electron beam in a systematic manner. Greyscale images are obtained from each field of view. The brighter particles in each picture are most likely those that are Ni-bearing. An operator revisits these particles manually and an X-ray spectrum is obtained. The chemistry of each bright particle is determined in this manner and a mineral name is assigned.

Discussion

There are two limitations to the chemical typing of sulphide particles using X-ray microbeam techniques that should be noted.

First, the EDS detector cannot determine the presence of hydrogen, so hydroxide or hydroxyl groups (if present) cannot be identified. This limitation exists for all analytical techniques measuring X-ray production, since hydrogen is not capable of producing X-rays.

The second limitation concerns the resolution of the electron beam when producing X-rays in the SEM. When the electron beam strikes a particle, X-rays are produced within a spherical region called the interaction volume. This is generally on the order of 3 to 5 microns in diameter, and while this may seem small, the bright particles I observed in the dust filter samples were generally 1 to 2 microns in diameter. This means that X-rays are being generated outside of the particle in question, by the filter paper and surrounding particles for example. It is difficult to calculate the contribution that these extraneous X-rays are contributing to the overall chemistry signal obtained for a very small particle (Total X-rays signal = X-rays from the target particle + some unknown contribution from the surroundings). This greatly increases the uncertainty of chemical typing.

Review of Ni-Sulphide Mineralogy

There are two stable Ni sulphide compounds that would have similar X-ray spectra in the scanning electron microscope (the spectra should contain only S and Ni, and be devoid of Fe and Cu). These are Millerite (NiS) and Heazlewoodite (Ni_3S_2). Millerite occurs naturally in Sudbury ore. Heazlewoodite is normally the Ni-bearing sulphide phase in smelter matte. To distinguish between these two phases by X-ray spectrometry, one needs to quantify the X-ray spectrum and compare the results against the ideal mineral chemistry summarized in Table 1 below. If the Ni-sulphide particle in question contains 65% Ni, it is Millerite, if the particle contains 72% Ni, it is Heazlewoodite.

Table 1: Ni Sulfide Mineral Chemistry

Mineral	**Ni Assay (Wt.%)**	**S Assay (Wt.%)**
Millerite (NiS)	65	35
Heazlewoodite (Ni_3S_2)	72	27

Lakefield Results – Air Filter Samples

I reviewed five particles on filter paper that Lakefield personnel had identified as possible occurrences of Heazlewoodite. The X-ray spectrum obtained from these particles had Ni and S peaks, however, in each case, the spectrum also contained additional X-ray peaks. As mentioned previously in the discussion concerning X-ray interaction volume, it is assumed that these additional peaks are produced outside of the target particle due to the small particle size. For example, the presence of silicon and oxygen peaks in the X-ray spectrum is usually attributed to the surrounding filter paper. However, each of the possible Heazlewoodite particles examined also contained minor peaks for Fe and Cu. The presence of these elements in the X-ray spectrum could possibly be explained by X-ray generation in surrounding particles, however, the amount of Fe and Cu I observed in each of the possible Heazlewoodite particles appeared to be relatively constant (not what you would expect for a random sampling of surrounding material).

There are two additional challenges that complicate the examination of particulate matter trapped in filter paper in the SEM. The first is the non-planar geometry of the particle, whereby particles are typically trapped at any angle by the filter paper. The routines that are used to quantify X-ray spectra assume that the beam impinges on the sample at a 90-degree angle. Any deviation from this geometry increases the uncertainty in the quantitative analysis, making the identification of Millerite from Heazlewoodite discussed above more difficult. The second challenge is caused by uneven application of carbon coating (for sample grounding) due to filter paper shadowing. This uneven coating of carbon can contribute to negative charge build-up on the target particle, preferentially decreasing the production of more energetic X-rays like Ni (alters the Ni:S ratio). Also, the quantitative routines assume that the entire sample has a uniform coating of carbon resulting in a uniform absorption of X-rays.

All of the factors discussed above make the identification of Heazlewoodite in trapped filter paper particulate an uncertain undertaking. The quantitative analysis required to differentiate Millerite from Heazlewoodite cannot be accurately undertaken with such small particles in a three dimensional geometry. The particles I examined at Lakefield might have been Heazlewoodite, or they might have been something else (Millerite, Metallic Ni with a Sulphate coating?).

Lakefield Results – Dust Samples

I reviewed five dust particles on stubs that Lakefield personnel had identified as possible occurrences of Heazlewoodite. The particles were much larger than the air filter particulate, typically on the order of 5 to 10 microns. The X-ray spectrum obtained from these larger particles was much cleaner than the spectrum from the air filter particulate, containing only Ni and S peaks (no other extraneous X-ray peaks). Quantitative results from the X-ray spectra produced Ni assays between 70 and 80 weight percent (indicating Heazlewoodite). I am 90% certain that the particles I observed in the dust samples have been correctly identified as Heazlewoodite (Ni_3S_2).

Recommendations

1) The fine size of the air filter particulate represents the largest challenge to the accurate identification of the Ni-sulphide species present. Higher resolution scanning electron microscopes (i.e. field emission SEM or transmission electron microscope - TEM) with smaller probing beams are available and should be used to better resolve the X-ray spectrum of the Ni-sulphide particles.

2) Mount the dust and soil samples in epoxy impregnated mounts and polish the surface. The particles are sufficiently large in some cases that it will be possible to do a full quantitative analysis using an electron microprobe. This should resolve any ambiguity whether the Ni-sulphide present is Heazlewoodite or Millerite. Even if the particles were too small for microprobe analysis, this mounting technique would eliminate geometric uncertainty in the quantitative X-ray analysis programs, providing more reliable X-ray analysis in the SEM.

Canadian Light Source
Centre canadien de rayonnement synchrotron

Glenn Ferguson
Program director/Senior Scientist
Cantox Environmental

23-November-05

Dear Glenn,

Please find enclosed a report on the measurements carried out for air filter samples at the National Synchrotron Light Source (NSLS, [http://www.nsls.bnl.gov/]) at Brookhaven National Laboratory (BNL) in October 2005 and at the Synchrotron Radiation Center (SRC, [http://www.src.wisc.edu/]) at the University of Wisconsin-Madison, in November, 2005. A description of all sample and reference compounds, as well as the measurement parameters are listed in Tables 1 and 2 with further details in the text.

The measurements were focused on identifying the nickel and sulfur speciation in the air filter samples provided using X-ray Absorption Near-Edge Structure (XANES) spectroscopy.

If you have questions about the report or if there is any further information you require please do not hesitate to contact me.

Sincerely,

Jeff Warner

Jeff Warner, Ph.D
Industrial Liaison Scientist
Canadian Light Source, Inc.
tel. 306.657.3568
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Introduction

X-ray absorption spectroscopy is capable of probing *in-situ* a particular element in a complex sample in any physical state.

X-rays and charged particle beams (like electrons) interact with matter in a number of distinct ways. The interactions typically involve excitation of, or scattering with, the medium. X-ray photons in the energy range 500 electron volts (eV) to 50 keV, corresponding to wavelengths from 25 angstroms (Å) to 0.25 Å interact with matter mainly through the photoelectric excitation process. In this regime, energies correspond to the binding energies of tightly bound atomic core electrons. Since every atom has core-level electrons with well-defined binding energies, it is possible to select the element to probe by tuning the x-ray energy to an appropriate absorption edge. Oxidation state and chemical bonding have small but detectable effects on the potential or binding energy of these core electrons, which manifests as a shift in the position of the x-ray absorption edge. This is the basis for x-ray absorption near-edge structure (XANES) spectroscopy.

X-ray absorption near-edge structure (XANES) spectra can be divided into two regions. The pre-edge region, where the incident photon energy is less than the binding energy of the core level electron, and the main edge region, where transitions occur from a core level to unoccupied bound states or to continuum states (Brown et al., 1988). In the pre-edge region transitions are limited to low probability localized transitions of the K level (1*s*) electrons to the lowest energy unoccupied or partially occupied levels. For the first row transition elements a pre-edge peak corresponds to a 1*s*-3*d* transition and is diagnostic for determination of the site symmetry of the absorbing atom and in some cases for the oxidation state as well. The total XANES region typically extends approximately 50 eV above the absorption edge. Analysis of the shape, which is determined by the relative intensities and widths of these low lying "bound state" transitions, and position of the absorption edge can reveal details of the metal site symmetry, oxidation state and the nature of the surrounding ligands. As the electronegativity of the ligands increase or as the oxidation state of the metal increases, the absorption edge moves to higher energy. This shift can be as large as 5 eV per unit oxidation state change but is typically around 1 or 2 eV.

Background

The experimental and theoretical details of x-ray absorption near edge structure (XANES) spectroscopy and extended x-ray absorption fine structure (EXAFS) spectroscopy have been extensively described in the literature (Stern and Heald, 1983). These techniques have risen in popularity recently due to increased accessibility to synchrotron radiation and advances in the state of EXAFS theory and data analysis methods. Currently, with the development in *ab initio* theories, which better account for multiple scattering from electrons, precise knowledge of coordination numbers and bond distances can be obtained within a distance of 8 angstroms of the central absorbing atom.

Unfortunately, the analytical power of the above techniques is diminished when the system under investigation is a heterogeneous mixture of species. In this situation, each absorbing element may have different local coordination environments. This complicates the analysis because the number of structural parameters needed to describe the data properly may exceed the number of independent data points in the experimental spectrum. One method which has been developed to analyze complex mixtures is least squares linear combinations of model compound spectra to fit an unknown sample spectrum (O'Day, et al., 2004; Ressler, 2000).

Synchrotron-based S K-edge XANES spectroscopy has been previously used to identify and quantify sulfur in environmental samples (Solomon et al. (2003) and references therein).

Sample Descriptions

The standard and unknown Ni K-edge samples were collected on beamline X11A at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory, NY in October, 2005. Sulfur K-edge spectra were collected on the Double Crystal Monochromator (DCM) beamline at the Synchrotron Radiation Center (SRC) at the University of Wisconsin, Madison, WI in November, 2005.

Ni K-edge XANES measurements were made on three unknown samples (Table 1) consisting of air-filtered nickel-bearing particulates at different locations. Portions of the air filter not exposed to particulates were used as blanks. Several samples were not shipped in time to be measured at the NSLS. These samples were sent to the NSLS after our return and after our official beamtime and will be measured during Beamline Scientist discretionary time.

Sulfur K-edge measurements were made on several unknown aerosol samples on filter paper (Table 2), including a sample (54057822) labeled as lab bottle.

Materials and Methods

Ni K-edge (8333 eV) spectra were recorded on beamline X11A at the NSLS at Brookhaven National Laboratory. The storage ring was operating at 2.8 GeV with a current of 280 mA. Beamline X11A utilizes a 1.36 T bending magnet as a source. The beamline was equipped with a Si(111) double crystal monochromator. Higher harmonics of the incident beam were rejected by detuning the second monochromator crystal by 50% for nickel. Entrance slits defined the beam size at 0.9x9.5 mm.

Transmission data were collected from powder samples diluted with boron nitride (~1:20) under ambient pressure and temperature. Unknown compound spectra were collected using a fluorescence ion chamber detector (Lytle et al., 1984) filled with argon gas and employing a Co (3 μ absorbance) filter and Soller slits to minimize unwanted elastic scattering. X11A was calibrated using Ni foil, defining the Ni K-edge at 8333 eV (McMaster et al., 1969).

Sulfur K-edge (2472 eV) spectra were recorded on the high vacuum DCM beamline at the SRC located at the University of Wisconsin, Madison. The storage ring, Aladdin, was operating at 800 MeV with a current of 160 mA. The DCM beamline utilizes Si(111) monochromator crystals over the energy range 1500 – 4000 eV. Spectra were collected in fluorescence mode using a 9 element Ge detector. The DCM was calibrated using elemental sulfur defining the edge position at 2472 eV.

Air filter samples were prepared by carefully cutting strips of air filter (~3x12 mm) while wearing gloves and loading these in a Teflon sample holder contained using kapton tape. Spectra contained in this report were obtained on five such strips layered together.

Raw Ni K-edge and S K-edge data were processed using the program *Athena* (v. 0.8.045; Ravel and Newville, 2005). Least squares linear combination fits were applied to the XANES spectra using the program SixPack (Webb, 2002). Ni K-edge linear combination fitting was applied over the range 8325-8375 eV for all standards and sample unknowns. Linear combination fitting of the sulfide peak was performed over the range 2465–2474 eV. Peak heights of sulfide were determined at 2471.5 eV and correlated against the actual concentration from the mechanical mixtures of NiS and $NiSO_4.6H_2O$.

Results and Discussion

Figure 1 (top) shows an experimental schematic of an X-ray Absorption experiment. The bottom picture in Figure 1 is an actual experimental set-up at beamline X11a at the National Synchrotron Light Source (NSLS).

Figure 2 shows the normalized nickel K-edge XANES spectra for all the nickel model reference compounds measured in this investigation, nickel oxide (NiO), nickel chloride ($NiCl_2$), nickel carbonate ($NiCO_3$), nickel sulfate ($NiSO_4.6H_2O$), pentlandite ($(Fe,Ni)_9S_8$), nickel sulfide (NiS), nickel sulfide (NiS_2), nickel subsulfide (Ni_3S_2), as well as the three air filter samples that were measured. Each of the model reference compounds was tested as an appropriate component of the three unknown air filter samples. It was found that the best fits included the species, NiO, NiS and $NiSO_4.6H_2O$ for all three unknown air filter samples. Other fits were attempted with different sets of components but none agreed with the data based on values of the reduced chi square (χ^2) coefficient. The total and component fits of the air filter spectra are shown in Figure 3. The poorest fit quality was with filter 724, which had the lowest nickel concentration.

Table 3 lists the amounts of nickel species determined for the unknown air filter samples measured using Ni K-edge XANES with least squares linear combination analysis. Table 3 also shows the results of fits to the interior dust sample (lb50457822) of organic sulfur species using sulfur K-edge XANES spectroscopy, discussed further below.

Figure 9 is presented to illustrate the difference in the XANES spectra of nickel sulfide and nickel subsulfide (top). There is a small 1 eV difference in the inflection point of the main edge as shown in the bottom plot and changes in shapes of some of the other features in the post-edge region.

Sulfur K-edge XANES

Sulfur K-edge XANES spectra of sulfur standard compounds and unknown air filter samples are shown in Figure 4. The air filter samples all show large peaks consistent with the presence of sulfate, as demonstrated with the nickel sulfate reference compound. Filter samples 811 and 812 also show small peaks at 2471.5 eV that correspond to a sulfide peak (Figure 5). The other air filter samples do not have peaks in the sulfide region. At these low concentrations of sulfide it is difficult to assign these peaks to either sulfide or subsulfide. As shown by drop lines in Figure 5, nickel sulfide and nickel subsulfide have a small 0.2 eV difference in their S K-edge peak maxima. The peak position of the sulfide peak in filters 811 and 812 corresponds more closely to that of sulfide.

The lab bottle sample (50457822) spectrum has peak maxima at 2482.8 eV (sulfate) and at 2473.6 eV. No sulfide appears to be present but the peak at 2473.6 most likely corresponds to an organic sulfur species. This sample was compared to existing data collected for various organic sulfur species with the result of fitting shown in Table 3. As shown in Table 3, the interior dust sample (lb50457822) is adequately fit with nickel sulfate and either thiol, organic sulfide, disulfide or thiophene. It cannot be fit with nickel sulfide or subsulfide and based on the derivative spectrum in Figure 7 (bottom), which is more sensitive to small inflections and changes in peak shape, there is no indication of the presence of nickel subsulfide. The fits of the sulfur XANES indicate sulfate and the organic species are approximately both present at 50% levels.

Figure 6 (top) shows a series of S K-edge XANES spectra of mechanical mixtures of nickel sulfide and nickel sulfate. Actual concentrations of these mixtures are listed in Table 4. The bottom plot in Figure 6 shows the deviations of the linear combination fitted mechanical mixtures from the actual concentrations used in the mixtures. The solid black lines represent the actual concentrations and the red and blue lines are the fitted values of nickel sulfate and nickel sulfide, respectively. In order to try and improve on the predicted linear combination fit percentage values, the mixtures were used to develop a calibration curve for the amount of sulfide based on the peak at 2471.5 eV (Figure 8). The calibration curve was linear at low concentrations of sulfide. Percentage values of the amount of sulfide from linear combination fitting and a curve based on the sulfide peak height gave values for filter 811 of 14.0% and 17.8% and for filter 812 of 8.1% and 14.2%, respectively. Based on previous analyses, we assume an error of 3% on these low concentration values.

Conclusions

Fitting of the Ni K-edge XANES spectra (Table 3) result in the following speciation results;
filter 724: 23% NiO, 0% NiS, 77% $NiSO_4.6H_2O$
filter 811: 30% NiO, 20% NiS, 50% $NiSO_4.6H_2O$
filter 812: 20% NiO, 14% NiS, 66% $NiSO_4.6H_2O$
Uncertainty values are at the ±3% level.
The remaining samples did not arrive at the NSLS in time for measurement but are currently at the beamline (X11A) and will be measured sometime after U.S. Thanksgiving.

The sulfur K-edge measurements indicate that, except for sample 811, 812, and the lab bottle sample (#50457822), the unknown air filters contain only sulfur in the sulfate form (Table 4). Samples 811 and 812 also contain sulfur in the sulfide form. From a series of mechanical mixtures, we were able to obtain two independent determinations of the amount of sulfide (Table 4). The averaged values for these are,
filter 811: 16% sulfide, 84% sulfate
filter 812: 11% sulfide, 89% sulfate
Uncertainty values are at the ±3% level.

It should be noted that sulfide concentrations determined from the Ni K-edge XANES and S K-edge XANES are in close agreement, including the 0% NiS fit value in filter 724.

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Table 1. Description of samples measured at the Ni K-edge at Beamline X11A (NSLS)

pure reference compounds (Ni K-edge)				
sample	**formula**	**# scans**	**detection mode**	**source**
nickel sulfide	NiS	2	transmission	Alfa Aesar
nickel metal	Ni	2	transmission	NiPERA repository
nickel carbonate	$NiCO_3$	2	transmission	Alfa Aesar
nickel subsulfide	Ni_3S_2	2	transmission	NiPERA repository
nickel sulfate	$NiSO_4.6H_2O$	2	transmission	Alfa Aesar
nickel carbonate	$NiCO_3$	2	transmission	Alfa Aesar
nickel chloride	$NiCl_2$	2	transmission	Alfa Aesar
nickel oxide	NiO	2	transmission	Sigma-Aldrich
unknown samples				
sample	**form**	**# scans**	**detection mode**	**source**
2004040812	air filter	9	fluorescence	MI5007-JUL05
2004040811	air filter	7	fluorescence	MI5021-SEP05
2004040724	air filter	11	fluorescence	MI5007-JUL05

Table 2. Description of samples measured at the S K-edge at the CSRF DCM (SRC)

pure reference compounds (S K-edge)				
sample	**formula**	**# scans**	**detection mode**	**source**
nickel sulfide	NiS	2	electron yield	Alfa Aesar
elemental sulfur	S	2	electron yield	NiPERA repository
nickel sulfate	$NiSO_4.6H_2O$	2	electron yield	Alfa Aesar
sodium sulfite	Na_2SO_3	2	electron yield	Alfa Aesar
sodium thiosulfate	$Na_2S_2O_3$	2	electron yield	Alfa Aesar
unknown samples				
sample	**form**	**# scans**	**detection mode**	**source**
filter306	air filter station 15525	4	electron yield	May 1, 2005 filter lot 002283
filter812	air filter 2004040812	6	electron yield	MI5007-JUL05
filter811	air filter 2004040811	3	electron yield	MI5021-SEP05
filter724	air filter 2004040724	3	electron yield	MI5007-JUL05
filter722	air filter 2004040722	2	electron yield	MI5021-SEP05
lab bottle	powder	2	electron yield	MI5009-APR05

Table 3. Ni K-edge XANES spectra of unknown air filter samples with linear combination (LC) fitted values.

sample	LC fits (mole %)						
	NiO	NiS	$NiSO_4$	**$NiSO_4$/ S**H (alkyl)	**$NiSO_4$/** R-**S**-R (alkyl)	**$NISO_4$/** R-**S-S**-R (disulfide)	**$NISO_4$/** cyclic **S** (thiophene)
nickel K-edge							
unknown (filter 724)	23	0	77				
unknown (filter 811)	30	20	50				
unknown (filter 812)	20	14	66				
sulfur K-edge							
lab bottle MI5009-APR05				49/51	53/47	45/55	46/54

Table 4. S K-edge XANES spectra of mechanical mixtures of NiS and $NiSO_4.6H_2O$ with linear combination (LC) fitted values. Fitted percentages are also given for filters 811 and 812, which showed intensity at the sulfide peak. Linear regression values were determined only at low sulfide concentration. The sulfide peak occurs at 2471.5 eV and the sulfate peak at 2482.8 eV.

sample	**composition (mole %)**		**normalized peak height**	**LC fits (mole %)**		**linear regression fit (mole %)**	
	NiS	**$NiSO_4$**		**NiS**	**$NiSO_4$**	**NiS**	**$NiSO_4$**
NiSO4	0	100	n/a	n/a	n/a	0	100
10NiS	10.3	89.7	0.03	9.5	90.5	12.0	88.0
20NiS	18.5	81.5	0.06	13.9	86.1	17.1	82.9
30NiS	27.2	72.8	0.11	19.6	80.4	25.7	74.3
40NiS	34.7	65.3	0.17	26.3	73.1	35.9	64.1
50NiS	42.5	57.5	0.25	32.6	67.4	n/a	n/a
60NiS	49.6	50.4	0.24	32.1	67.9	n/a	n/a
70NiS	56.1	43.9	0.34	48.4	51.6	n/a	n/a
80NiS	62.7	37.3	0.32	48.6	51.4	n/a	n/a
90niS	68.6	31.4	0.69	75.7	24.3	n/a	n/a
NiS	100	0	n/a	n/a	n/a	100	0
unknown samples							
unknown (filter 811)	n/a	n/a	0.064	14.0	86.0	17.8	82.2
unknown (filter 812)	n/a	n/a	0.043	8.1	91.9	14.2	85.8

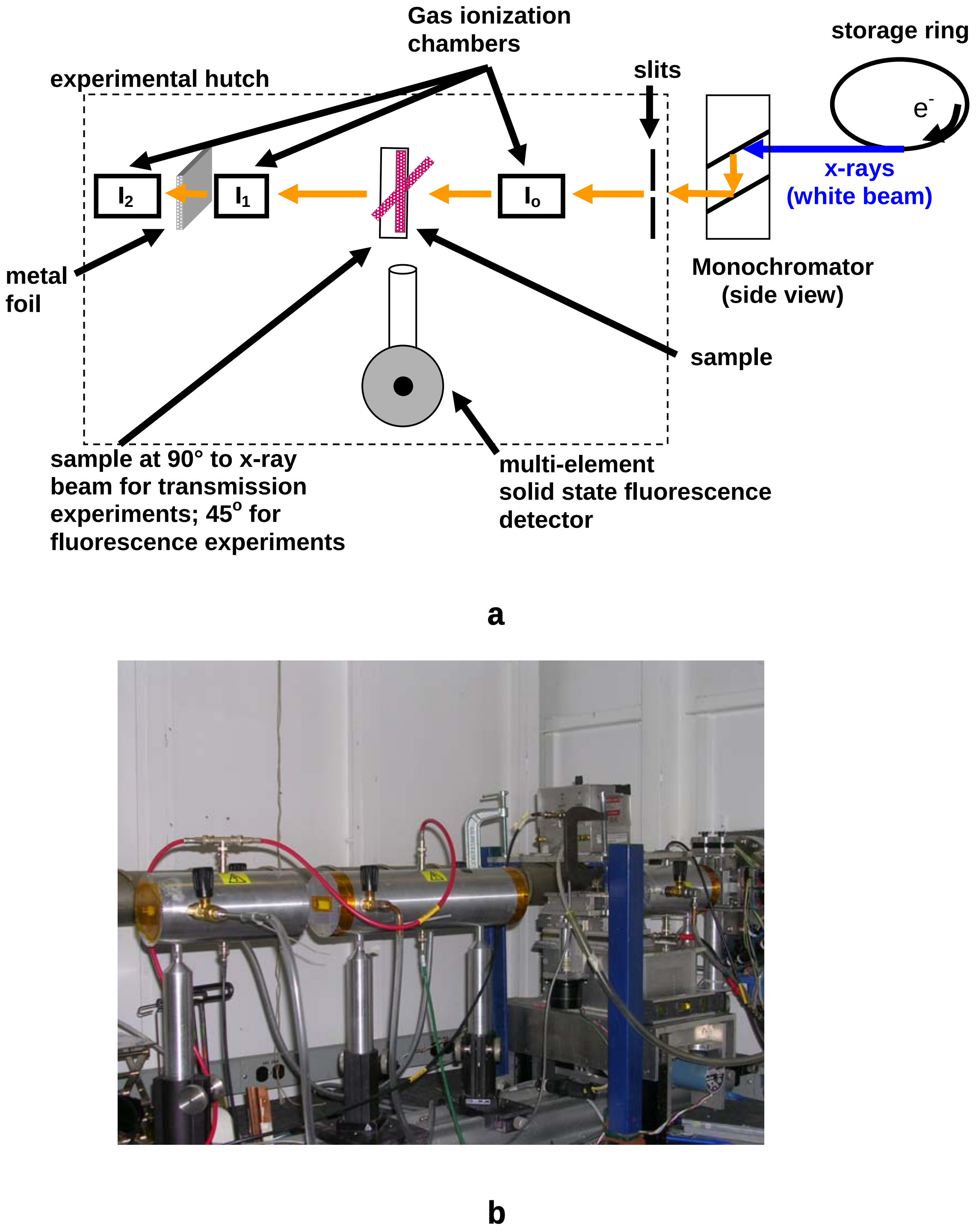


Figure 1. Schematic setup of an x-ray absorption experiment (a) and picture of the experimental arrangement at X11A with the x-ray beam entering from the right.

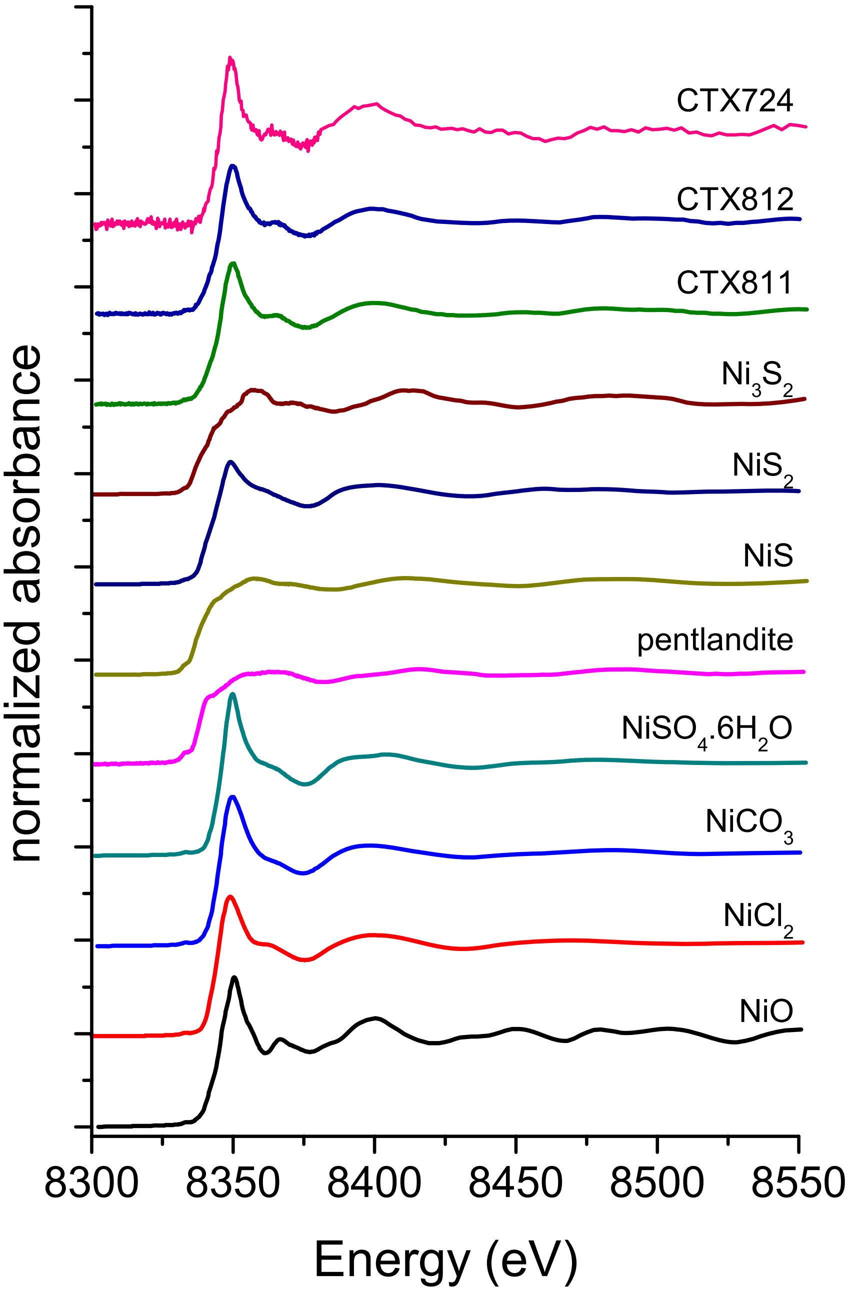


Figure 2. Pre-edge subtracted and normalized XANES spectra of nickel reference compounds and air filters measured at the Ni K-edge.

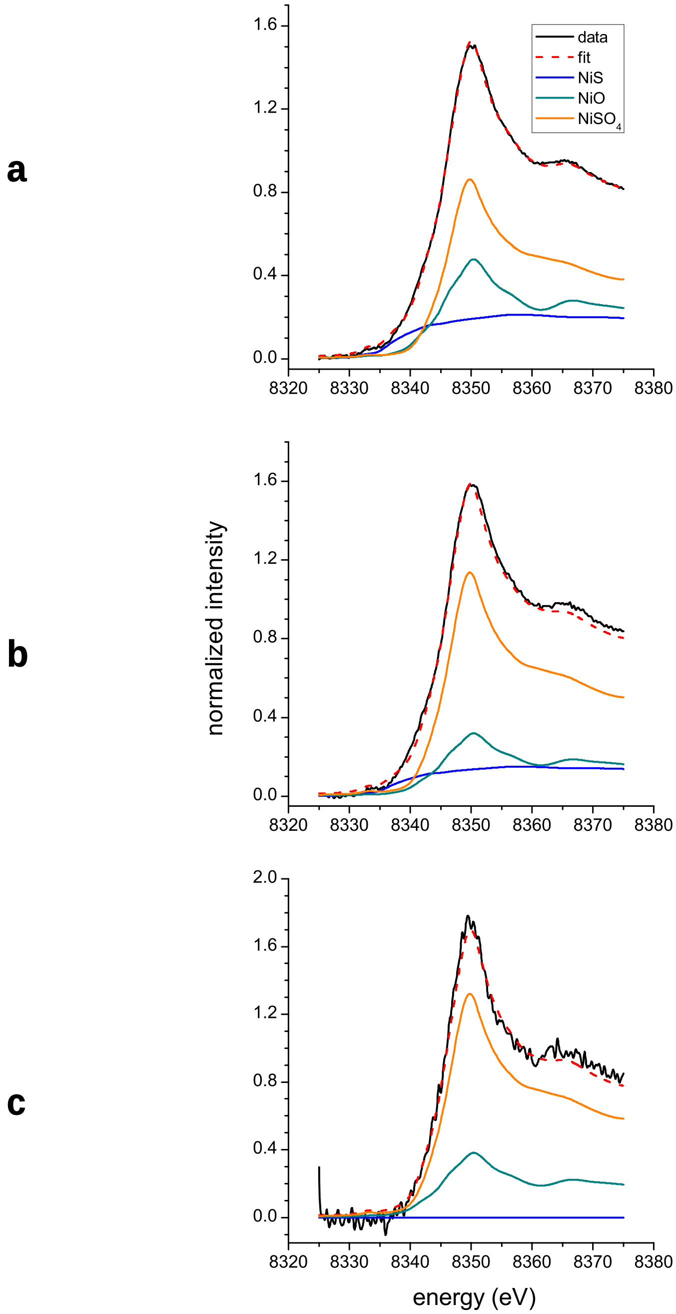


Figure 3. Least squares linear combination XANES fits of the three air filter samples (filter 811 (**a**), filter 812 (**b**) and filter 724 (**c**)) measured at the Ni K-edge. The black line is the measured XANES spectrum, the red dashed line is the total fit and the other lines represent the component percentages (Table 3) of NiO, NiS and $NiSO_4.6H_2O$.

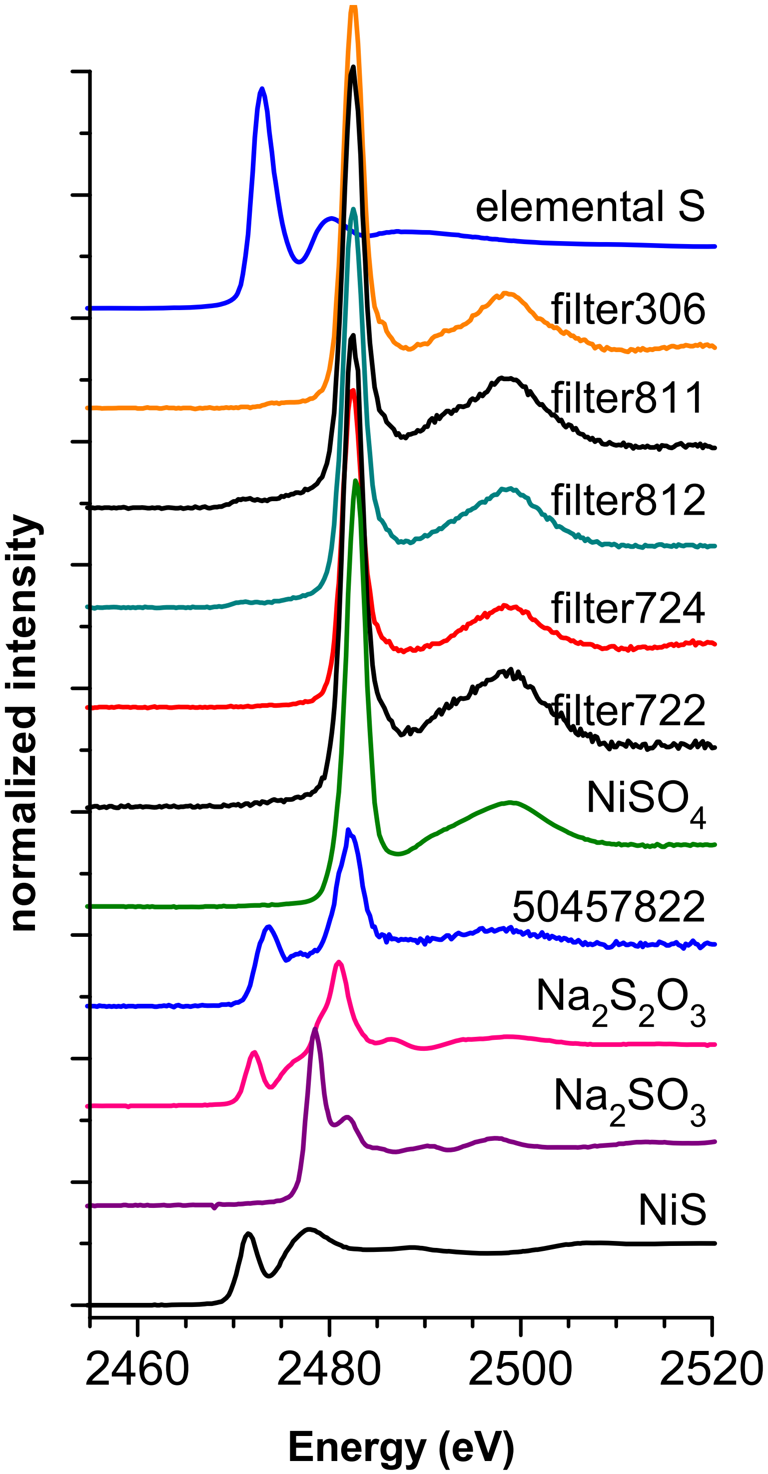


Figure 4. S K-edge XANES spectra of reference and unknown air filter samples.

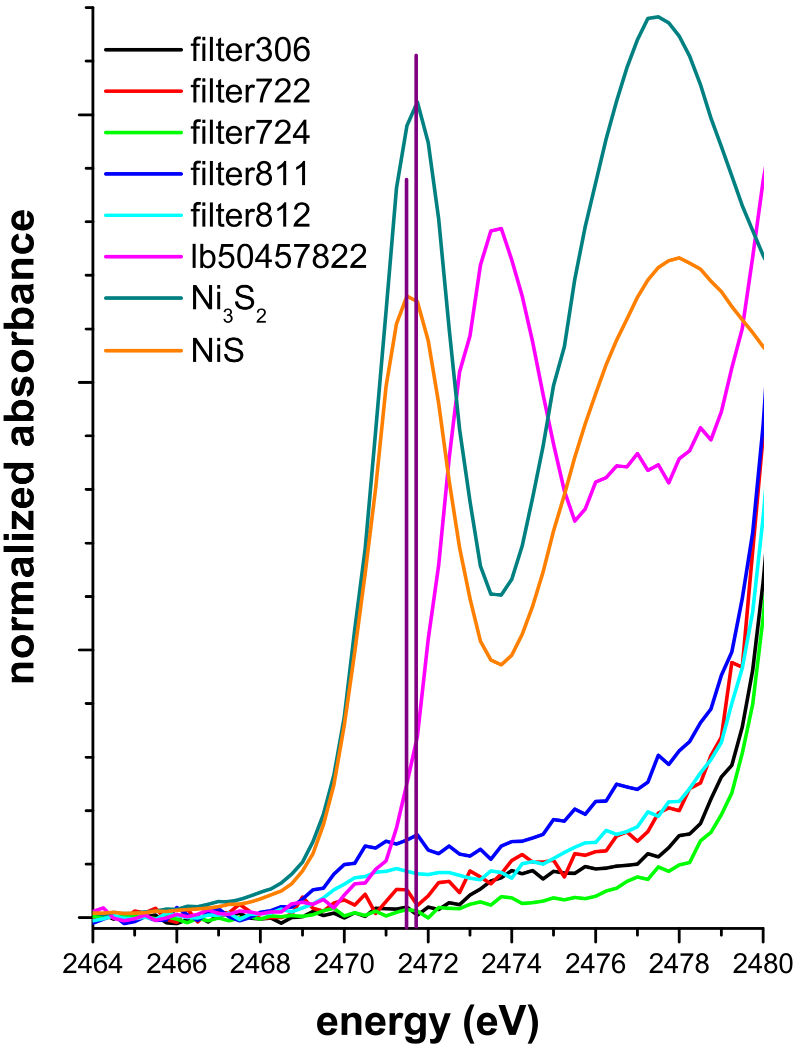
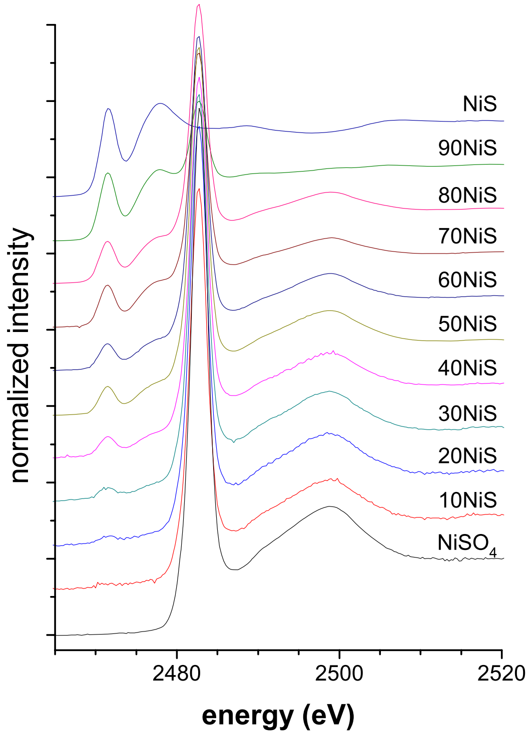


Figure 5. S K-edge XANES spectra showing in closer detail the region before the main sulfate peak of the unknown aerosol samples on air filters. Filters 811 (blue) and 812 (cyan) show small peaks that correspond to either subsulfide or sulfide.



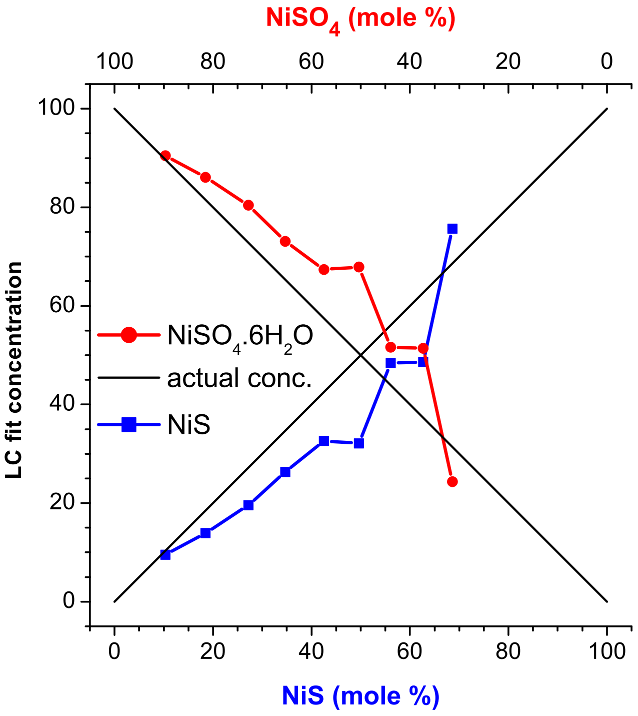


Figure 6. Sulfur K-edge XANES of a series of mechanical mixtures of NiS and $NiSO_4.6H_2O$, actual concentrations are listed in Table 4 (top) and, the linear combination fit deviations (red and blue lines) from the actual concentration values of NiS and $NiSO_4.6H_2O$ (bottom).

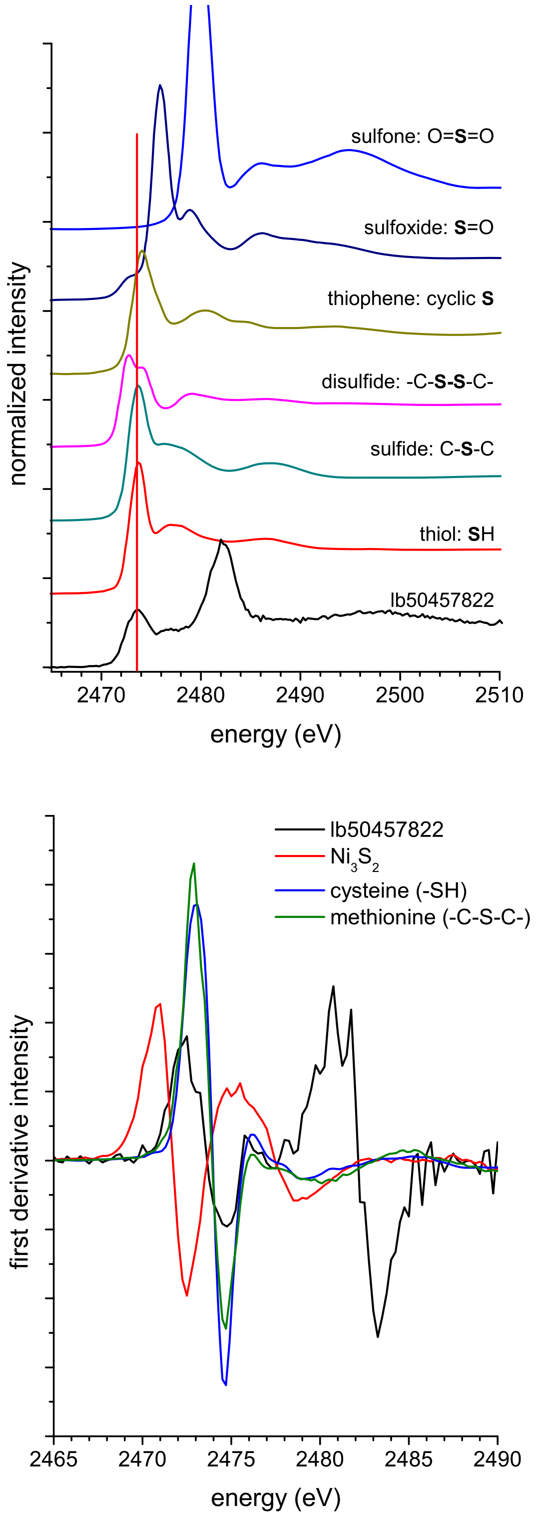


Figure 7. Comparison of the sulfur K-edge XANES spectra of the unknown sample lb50457822 to various organic sulfur species (top), the first derivative absorption spectra of various sulfur-containing species showing the difference between Ni_3S_2 and the sample.

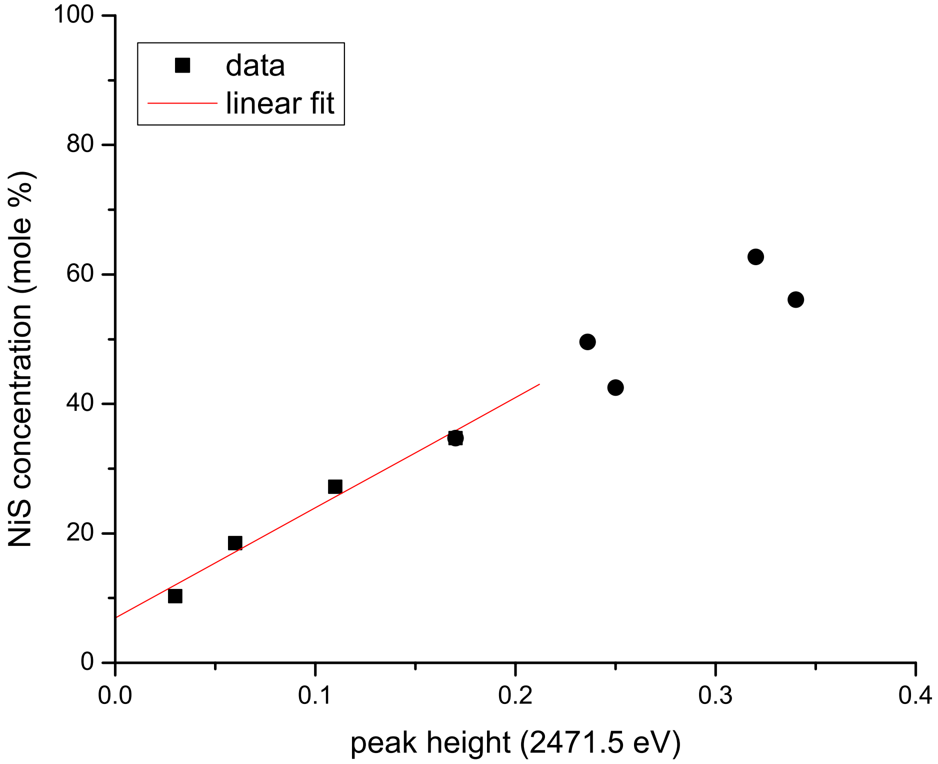


Figure 8. Linear regression line (y=6.9213 + 170.31x) of the sulfide peak height and actual sulfide concentration for a series of mechanical mixtures of NiS and $NiSO_4.6H_2O$. The relationship was not linear at high concentrations of sulfide.

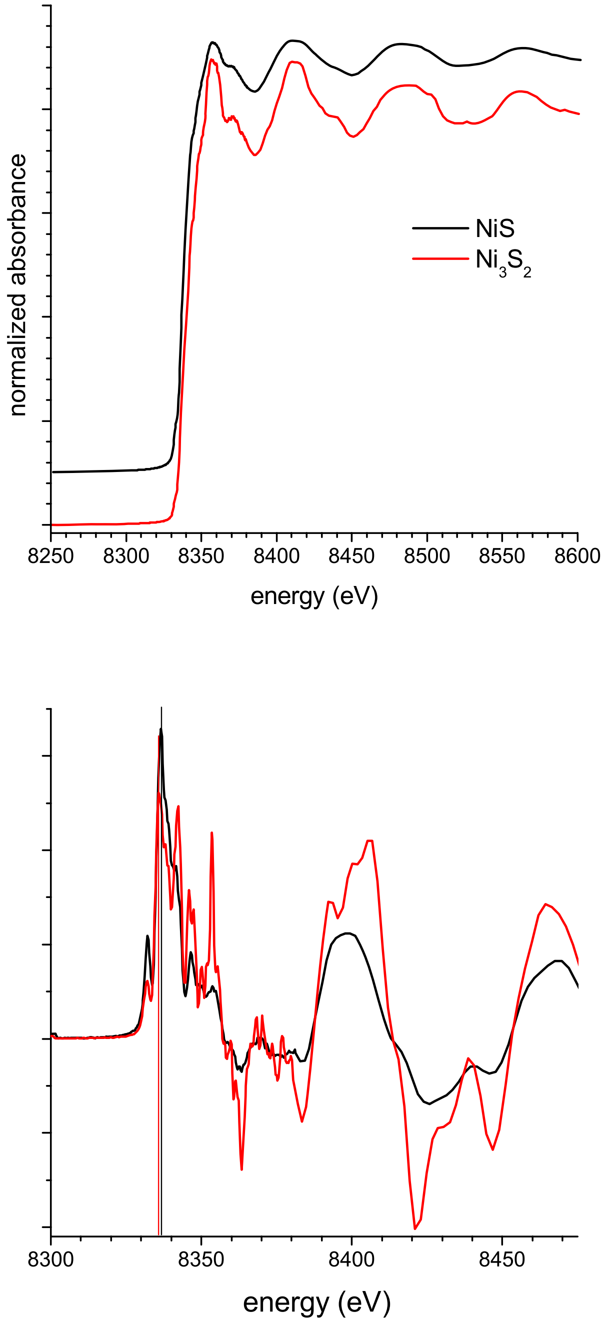


Figure 9. Normalized Ni K-edge XANES Spectra of nickel sulfide (NiS) and nickel subsulfide (Ni_3S_2) (top). The bottom plot shows the corresponding first derivative absorbance spectra, small differences can be noted in the position of the edge and certain post edge features in the spectrum.

Report on nickel (Ni) speciation in particulate matter collected on filters

Presented to

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Abstract

The Ni speciation in particulate matter (PM) collected on filters was determined using x-ray absorption fine structure (XAFS) spectroscopy analysis. The XAFS spectra of PM samples were analyzed using Principal Component Analysis and Target Transformation to identify the most probable Ni species in the samples. The XAFS spectra were fitted using a Least-Squares Regression analysis procedure using a combination of most probable Ni species, which generally included $NiSO_4$, NiO green, and Ni metal. The calculated, average oxidation state of Ni species in the PM samples is nearly +2. The DELTA E fit results were in good agreement with the experimentally determined DELTA E for all samples. Fit and weight percentage were determined for the relevant Ni species, i.e., $NiSO_4$, NiO green, and Ni metal. The presence of NiO green and $NiSO_4$ was found in all samples by inspecting the Fourier Transform of the k-weighted XAFS spectra of each sample. Also, FT analysis showed that Ni_3S_2 was absent from all samples.

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Introduction

The following report is prepared for Ontario Ministry of the Environment by Dr. Marc Lamoureux (ENVIROANALYTIX SERVICES Ltd.). This report is for work done up to October 1st, 2005.

The report consists of XAFS spectra of 7 samples, 1 filter blank, 7 Ni standards for the analysis of nickel species associated with particulate matter collected on membrane filters (glass fibre or quartz) using X-Ray Absorption Fine Structure (XAFS) Spectroscopy. All filter samples and blank were provided by the Ontario Ministry of the Environment (MOE) or their associates. The purpose of this work is to determine the speciation of nickel in particulate matter collected on filters.

XAFS theory

The following is a brief description of the operating principle of X-ray Absorption Fine Structure Spectroscopy (XAFS). A more extensive review of the theory of XAFS can be found in the excellent book edited by D.C. Koningsberger, and R. Prins[1]. Figure 1 shows the XAFS spectrum of some Mn compounds. The qualitative description that follows using Fig. 1 applies equally to Ni XAFS spectra. Each XAFS spectrum (see Fig. 1) represents the x-ray absorption signal (y-axis) as a function of the incident x-ray energy (x-axis). The absorption edge corresponds to the absorption of an x-ray photon by a core electron from the target analyte. This is a quantized event (quantum mechanic) and thus the edge energy is characteristic to the element of interest (i.e., no other elements can absorb that photon). The intensity of the absorption process (edge jump) is proportional to the concentration of the target element in the sample (this is analogous to Beer's Law in absorption spectroscopy). The oscillations observed about the x-ray absorption signal (see Figure 1) are referred to as the "x-ray absorption fine structure". The fine structures together with the absorption edge represent a fingerprint of an individual species. Thus, the combination of XAFS spectrum from appropriate standards (those that are present in the unknown sample) allows one to replicate the XAFS spectrum of an unknown sample. Figure 1 is a typical representation of an XAFS spectrum, which shows a plot of the normalized absorption (a.u.) spectrum for any samples or standards vs x-ray energy (KeV).

For this work, the region of interest for the Least-Squares Regression analysis (the fitting region) is the X-ray Absorption Near Edge Structure (XANES) and it includes the region just before the absorption edge, the absorption edge, and approximately the first 130 eV after the absorption edge. As well, the Extended X-Ray Absorption Fine Structure (EXAFS) for this work comprised the region that extended about 500 eV after the Ni K-edge (8.333 KeV). The presence of Cu (Cu K-edge 8.979 KeV) in the particulate matter prevented the possibility of measuring the EXAFS beyond 500 eV.

Experimental

All XAFS spectra were measured at the Stanford Synchrotron Radiation Laboratory (SSRL) in California. XAFS spectra were collected in fluorescence mode using SSRL beam line 10-2. Beam line 10-2 has insertion devices (wigglers) and provide therefore more photon flux (thus more sensitivity) than bending magnet only beam line (e.g., beam line 2-3). The monochromator on beam line 10-2 was de-tuned by 50% to reject secondary harmonics. The dimension of the x-ray beam that irradiated the surface of the sample on beam line 10-2 was about 1.0 mm^2 (0.1 x 10 mm). The detectors used for the data collection was a solid state detector, a 30-element Ge detector. The Ge detector is more sensitive than the Lytle detector (gas ionization detector), thus the signal is more intense when measured with the Ge detector. The XAFS spectra for all Ni standards, blank and samples were measured with a Ge detector. All spectra were referenced (energy calibration) to a Ni foil located between I1 and I2 gas ionization chambers. All blank and sample filters were fitted individually on an sample holder (made of aluminium, 1 mm thickness with a 5 x 20 mm window) using double sided sticky tape (only the sample edges were taped). Blank and sample filters were covered with a piece of thin x-ray film (6 µm thickness polypropylene film), and the sample holder was then fitted on a cryostat sample rod. The sample rod was positioned at a 45° angle from the incident x-ray beam and the Ge-detector. The cryostat was maintained to 100 K to minimize both the thermal noise and possible radiation damage to the sample.

XAFS spectra were collected using SSRL data collection software XAS_Collect. XAFS data reduction was done using EXAFSPAK (written by Graham George, SSRL). The Principal Component Analysis (PCA) and Least-Squares Regression analysis were carried out using the software WinXAS v3.1 (written by Thornsten Ressler). All Ni standards and PM samples were treated the same way during data reduction. Specifically, all spectra were inspected and weak or bad Ge-detector channels were removed, spectrum were then averaged and energy calibrated (with respect to the Ni foil K-edge energy - 8.333 KeV), blank subtracted, all spectra were clipped to keep the XAFS signal between 8.24 and 8.80 KeV, post-edge background was removed using a cubic spline and normalized to a common energy point (8.350 KeV). XAFS spectra were fitted by combining XAFS signals from standards using the linear least-squares regression fitting algorithm in WinXAS. The Least-Squares Regression fit allowed both the concentration and the position of the absorption edge to be automatically modified at each successive iteration until no further fit improvement was achieved. Prior to fitting unknown samples with standards, all samples were subjected to Principal Component Analysis (PCA) to identify the most probable components in the mixture. PCA attempts to determine how many different Ni reference compounds or standards are needed to fit the samples adequately. Another feature of PCA is Target Transformation, which attempts to determine which Ni standards are probable species in the unknown sample. More details on the principle and use of PCA and Target Transformation can be obtained from Ref. 2 and 3.

Materials

The suite of nickel standards used for the linear least square fitting of the unknown samples includes a series of oxides-hydroxides (NiO green, NiO black, $Ni(OH)_2$), sulfur-containing nickel species (NiS, NiS_2, Ni_3S_2, and $NiSO_4•6H_2O$), and nickel metal (as a foil).

The choice of the above-mentioned suite of Ni compounds is based on previous work done by this researcher on similar samples for the benefit of MOE and in the course of his own research program at Saint Mary's University. Many anthropogenic activities such as coal power plants and smelters can be a significant source of Ni sulfate and sulfides. Ni oxides (NiO green and black) and hydroxides and be naturally occurring or man-made. The possibility that some wind blown dust could be collected by the PM-10 samplers and consequently that a Ni-containing silicate compound would be among the possible Ni species in the particulate matter could not be tested because a well defined Ni-silicates was not available at the time of analysis.

The sample ID, such as "ni_coppercliff1", was constructed to reflect the existing sample labeling at MOE (or their associates). The letter "ni" indicates that Ni was the targeted metal for x-ray absorption analysis. The series of letters and number after the underscore identifies the sampling location (i.e., copper cliff), and the number (e.g.1) was extracted from the sample label as provided by MOE.

Criteria for successful Least-Squares Regression analysis

For all PM samples, PCA analysis showed that the first 3 Principal Components were enough to fit 95% or more of all sample XAFS spectra. Target Transformation showed that $NiSO_4$ hexahydrate (hexahydrate will be omitted from hereon), NiO green (abbreviated NiOgrn from hereon), and $Ni(OH)_2$ were present in most samples at varying concentration.

In order to achieve a meaningful, successful fit (i.e., a fit that makes sense from a physico-chemical point of view), one needs to adopt a set of rules (criteria) when performing PCA and Least-squares Regression analysis. Failure to do this or to observe the adopted rules can result into a very good fit that is meaningless. In other words, it is possible to combine linearly XAFS spectra of standards such that it can fit the XAFS spectrum of an unknown even though the analyte standards are known not to be present (as ascertained by other analytical methods) in the sample! This is equivalent to using geometry to piece together geometric forms to represent another, different geometric form, even though the geometric forms used initially have no relationship with the targeted geometric form.

The following are the rules that were imposed onto the fitting procedure:

1. All fits began with $NiSO_4$, NiOgrn, and $Ni(OH)_2$ as indicated by PCA and Target Transformation, and then refined as required. The fitting procedure is an iterative process that attempts to minimize the residual (i.e., what is left unfitted) and (CHI)'2 ((the sum of the deviation squared between the fit and experimental spectra) values. In general, the best fit has the smallest residual and CHI'2 values.
2. The fit parameters are concentration and edge energy shift. Valid concentration values had to be between 0 and 100%. A fit resulting in one or more standards having a negative concentration indicated that these Ni standards were not probable Ni species in the unknown sample under investigation and, therefore, were removed from future fit iterations of that unknown sample. Nickel standards that yielded a concentration value of 5% or less were also removed from future fit iterations. The rational is that the

estimated noise level is in the order of 5% of the normalized XAFS signal, and thus standards with a concentration value of 5% or less can easily be confused with noise. Variation in edge energy (E0 shift) was constrained by ± 0.0034 KeV, which corresponds to an average deviation of ± 0.5 Ni oxidation state for Ni species having an oxidation state between 0 (Ni metal) and +2 ($NiSO_4$, $Ni(OH)_2$, and NiO). It was estimated that the error in the determination of the edge energy (after energy calibration) of any Ni standard was less than ± 0.0034 KeV, and that the variation in edge energy for a given oxidation state (due to variation in ligand or coordinating atoms) was also less than ± 0.0034 KeV. Edge energy shift greater than ± 0.0034 KeV would be equivalent to practicing geometry with XAFS spectra of standards.

3. Fit iterations were continued until the residual from the energy edge (~ 8.33 KeV) to the end of the energy range (8.80 KeV) was 5% or less, 5% being the estimated noise level for most unknown samples.
4. If two fits generated using a different combination of Ni standards were nearly identical (i.e., visually, and residual and CHI'2 values), the fit that reproduced the energy edge (the rising portion or energy step of the XAFS signal) the most accurately was deemed the best fit. The edge energy of the fit spectra was compared with the edge energy of the experimental spectra and good agreement had to be verified. If this did not resolve which is the best fit, the one with the smallest sum of edge energy shift of all Ni species present was then deemed the best fit.
5. The inclusion of an additional Ni compound in the Least-Squares Regression fit is justified only if it reduces the residual and the (CHI)'2 values of the fit by 10% or more. The rational for this is that the noise itself is estimated at 5% and consequently, inclusion of another Ni compound must at least reduce the residual and the (CHI)'2 values by the noise level percentage. This would be analogous to adopting a 95% confidence level (2σ) for the fit.
6. Visual inspection that the most important features and general shape of the targeted XAFS spectrum are reproduced by the fit spectrum.

Results and Discussion

The normalized XAFS spectra (with offsets for presentation purpose) of all nickel standards used for this work are shown in Figs. 2a and 2b (Appendix A), whereas Fig.3 (Appendix A) shows the normalized XAFS spectra (with offsets for presentation purpose) for the filter blank and sample PM on filter. Figure 3 also shows that Ni concentration as an impurity in the filter substrate is small, but was never-the-less removed from all PM samples (thus blank corrected). The XAFS spectrum of NiO green and NiO black were indistinguishable and, therefore, results for NiO green only are reported from hereon. Similarly, the XAFS spectrum of Ni sub-sulfides (i.e. NiS, NiS_2 and Ni_3S_2) were indistinguishable from each other and, therefore, results for Ni_3S_2 only are reported from hereon. Sample homogeneity was tested by analyzing two sub-samples of the same filter and results were identical for all samples within experimental error. On occasion, significant diffraction lines (i.e., intense) were observed on certain channels of the Ge detector due to the presence of one or more Ni-containing crystalline compounds. This was remedied by repositioning the sample such that the incident x-ray beam would not interact with any significant amount of the Ni-containing crystalline compound(s). If this did not correct the problem, then the detector channels that were affected were simply removed during the data reduction such that these channels would not be part of the average XAFS spectrum used for the rest of the analysis.

Figures 4A and 4B (Appendix B) show typical outputs of a Principal Component Analysis (PCA). Figure 4A shows that spectrum No. 5 (Falco4) is not completely reconstructed when using two components whereas Figure 4B shows that 3 components are sufficient to reproduce more than 95% of spectrum No. 5. Principal Component Analysis showed that 3 principal components was sufficient to reconstruct 95% or more of every PM sample XAFS measured during this work. Consequently, it is expected that no more than three Ni standards are required to reconstruct any of the unknown samples. Figure 5 shows examples of Target Transformation. The Target Transformation of Ni_3S_2 was unsuccessful (Fig 5A), i.e., the Ni_3S_2 XAFS (red line) cannot be recovered by features in unknown samples (blue line) and, consequently, Ni_3S_2 is not a probable candidate for the Least-Squares Regression analysis. On the other hand, Fig. 5B shows that Target Transformation of NiO green was successful as the NiO green XAFS spectrum (red line) was nearly completely recovered by features in unknown samples (blue line) and, consequently, NiO green is a probable candidate for the Least-Squares Regression analysis.

Appendix C shows Target Transformation results and Least-Squares Regression fits for the seven samples measured in this work. The Target Transformation section begins with a list of sample filenames (i.e. samples measured during this work), followed by the name of the Ni standard onto which Target Transformation is performed, and finally a numerical output (R-value), which is an indicator of the degree of success of Target Transformation. The Ni standard with the smallest Target Transformation R-value has the highest probability of being present in the set of seven samples, the Ni standard with the second smallest R-value would be the second most probable Ni species to be present in the set and so forth. The Target Transformation results show that NiO green has the lowest R-value (1.38, in bold) and thus has the highest probability of being present in the set of samples, followed by $NiSO_4$ (1.52, in bold) and $Ni(OH)_2$ (1.85, in bold). One need to exercise caution when using Target Transformation because Ni standards with similar features tend to produced similar R-values. This is the case for NiO green and $Ni(OH)_2$. Least-squares fitting that included both NiO green and $Ni(OH)_2$ did not yield a successful fit, i.e., either large energy shift or negative concentration (or both) were obtained for $Ni(OH)_2$. The inclusion of Ni sub-sulfides (NiS, NiS_2, or Ni_3S_2) in the least-squares fitting procedure always resulted in either large energy shift or negative concentration (or both) for these Ni species. It was found that Ni metal could be included to four samples (coppercliff2, falco4, garson6, skead7) to generate a successful fit. In agreement with the Target Transformation results, Ni metal had a low probability of being presence in the set of seven samples, i.e. it is only found in 4 out of 7 samples and it is always the Ni component with the smallest weight percentage.

The fit results for the seven samples analyzed in this work follows the Target Transformation section. Each least-squares fit result shows the sample filename, followed by the "(CHI)'2" and "Residual" results, which are indicators of the quality of the fit. Both (CHI)'2 and Residual results are to be minimized by successive fit iterations until no further improvement can be obtained with additional fit iterations. The name of each Ni standard used in the fit process is listed together with the corresponding fit % result (called "partial c") and energy shift (called "E0 shift). The measured spectrum (in red) and the fit spectrum (in blue) are shown together with the XAFS spectrum of each Ni standard (in magenta) used in the fit process. The residual (the unfitted XAFS signal) is shown in green below each measured and fit spectra. The Absorption Correction section for LC XANES Fit shows the partial concentration (c'), the x-ray mass attenuation coefficient (mue), and the weight % of the Ni standard of interest in the sample. The fit percentage obtained by Least-Squares Regression analysis is not necessarily equal to the weight percentage of the Ni species in the sample. One can convert from fit percentage to weight percentage using the x-ray mass attenuation coefficient (μ/ρ) of each Ni species of interest. The x-ray mass attenuation coefficient for a given Ni species can be determined experimentally if the thickness of the sample is known or it can be calculated using tabulated values of the mass attenuation coefficient of the elements[6] and the weight fraction of each element in the Ni compound of interest. Table 1 (Appendix D) shows the fit% results, the calculated x-ray mass attenuation coefficient for different Ni species found in particulate matter, and the corresponding weight % results for all PM samples.

Table 2 (Appendix E) shows the Ni K-edge energy of the Ni standards and samples analyzed in this work. The Ni K-edge energy was determined from the experimentally measured and fitted XAFS spectra. Table 2 shows the DELTA E, which is the edge energy, as measured from the first maximum in the first derivative of the rising portion of the energy edge of each sample, minus the edge energy of Ni metal (Ni K-edge is at 8.333 KeV). The Ni K-edge energy for a given Ni oxidation state (e.g., +2) is sensitive to its chemical environment, more specifically the number and type of coordinating atoms. Table 2 shows the average DELTA E and the corresponding standard deviation of both the experimentally measured and fitted XAFS spectra. All DELTA E calculated from the first derivative of the sample spectra are in good agreement with those determined from fit spectra. This is consistent with the fact that samples with smallest DELTA E (falco3 and falco4) have the largest concentration of NiO green (DELTA E is 10.5 eV) whereas samples with largest DELTA E (garson6 and skead7) have the largest concentration of $NiSO_4$ (DELTA E is 12.6 eV). The average DELTA E determined from both experimentally and fitted data indicates that the average Ni oxidation state in all samples is essentially +2. The impact Ni metal has on the average oxidation state is small either because the Ni metal fit % in the sample is small (e.g. skead7) or because the DELTA E value for Ni metal is compensated by a large contribution of $NiSO_4$, which increases the DELTA E value.

Performing a Fourier Transform (FT) on a k-weighted XAFS spectrum (k is the wavenumber and is proportional to square root of DELTA E) converts the information from an energy dependent space to a radial distance dependent space. In other words, the FT procedure on an XAFS spectrum yields a pseudo-radial distribution of near neighbour atoms around the target analyte (the x-ray excited analyte). Figure 6 (Appendix F) shows the XAFS Fourier Transform of some Ni standards and the 7 samples analyzed in this work. The peaks in Figure 7 represent coordination shells where near neighbour atoms are located. These shells have not been phase-corrected and therefore their true distance from the origin is about 0.2 to 0.5 Å further away. The distance between these shells and the origin (the x-ray absorbing Ni is at the origin - distance 0 Å) can often represent bond length between the target analyte and a coordinating atom or ligand.

A few important shells in Figure 7 will be discussed. The first one is at about 1.6 Å and is present in both $NiSO_4$ and NiO green. The second shell of importance is at about 2.57 Å and is present only in NiO, and the peak intensity ratio of shell 2.57 Å to shell 1.6 Å is about 2.9. The presence of NiO is clearly observable in the FT of all samples due to the presence of the double peaks at 1.6 and 2.57 Å (e.g. sample “falco3"). The presence of $NiSO_4$ causes the intensity of the shell at 1.6 Å to increase such that the peak intensity ratio between shell 2.57 and 1.6 Å decreases (not linearly) as the concentration of $NiSO_4$ increases. Hence, the presence of $NiSO_4$ can be identified in all samples by observing a decrease in the peak intensity ratio between shell 2.57 and 1.6 Å. The Fourier Transform of the Ni_3S_2 XAFS spectrum shows only one important shell at about 2.00 Å. This shell was not observed in any of the samples analyzed in this work. This shell would be located, if present, in the valley between the two above mentioned shells at about 1.6 and 2.57 Å, and any appreciable amount (more than 10% in the fit) of Ni_3S_2 would tend to make the valley disappear. Therefore, it is unlikely that Ni_3S_2 is present in any of the samples analyzed in this work. This result is consistent with the fact that Target Transformation did not identify Ni_3S_2 as a candidate having a high probability of being present in any of the samples and the Least-Square Regression fitting procedure gave unreasonable fit results (e.g., negative concentration) for Ni_3S_2. The FT of the Ni metal XAFS spectrum shows an intense shell at about 2.18 Å. It is difficult to ascertain the presence of Ni metal using the FT results because of the lower abundance of Ni metal in the samples. It should noted that the shell peak intensity in the FT pseudo-radial distribution depends on many factors such as the number of atoms inside the shell, the x-ray scattering power of the atoms in the shell, bond length, etc.

In summary, the XAFS analysis shows that all seven samples have an average Ni oxidation state of +2, that the most important Ni species are $NiSO_4$ and NiO, with occasionally a minor contribution of Ni metal.

Conclusions

The Ni speciation in particulate matter (PM) collected on filters was determined using x-ray absorption fine structure (XAFS) spectroscopy analysis. The XAFS spectra of PM samples were analyzed using Principal Component Analysis and Target Transformation to identify the most probable Ni species in the samples. The XAFS spectra were fitted using a Least-Squares Regression analysis procedure using a combination of most probable Ni species, which generally included $NiSO_4$, NiO green, and Ni metal. The calculated, average oxidation state of Ni species in the PM samples is nearly +2. The DELTA E fit results were in good agreement with the experimentally determined DELTA E for all samples. Fit and weight percentage were determined for the relevant Ni species, i.e., $NiSO_4$, NiO green, and Ni metal. The presence of NiO green and $NiSO_4$ was found in all samples by inspecting the Fourier Transform of the k-weighted XAFS spectra of each sample. Also, FT analysis showed that Ni_3S_2 was absent from all samples. The work herein demonstrates the ability of XAFS to provide qualitative and quantitative Ni speciation in airborne particulate matter.

Finally, the results reported herein are based on the assumption that sample integrity has been preserved from time of sampling to time of XAFS analysis. Also, the results also depend on the availability of reference standards at the time of analysis and the analytical concentration results provided by MOE. EnviroAnalytix Services Ltd. (c/o Dr. Marc Lamoureux) cannot guarantee the exactness of the reported results because of the lack of certified reference materials (CRM) with certified concentration values for specific Ni species (and not just total Ni concentration). There are no commercial CRMs for metal speciation work that exist at this time. However, the XAFS analyses, including the data reduction and fitting procedure used by Dr. Lamoureux, have been carried out using standard XAFS analysis procedure [1, 2, 4, 5] and all spectra have consistently been analyzed using the same protocol.

Marc Lamoureux

Dr. Marc Lamoureux
EnviroAnalytix Services Ltd.

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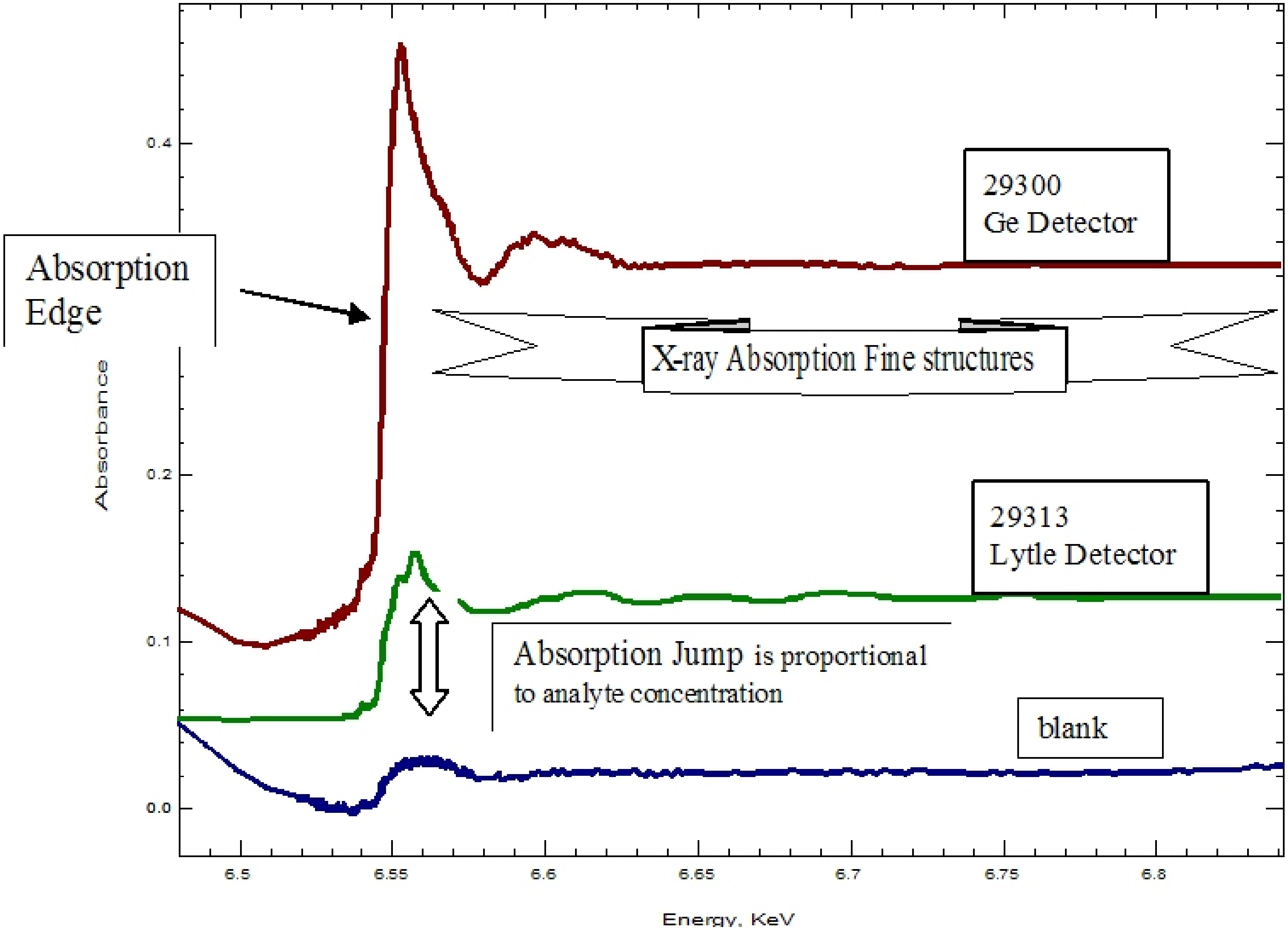
Figure 1. Typical XAFS spectra of some manganese compounds.



Appendix A - XAFS Spectra of standards, blank filter and PM on filter

Figure 2. XAFS spectra of some Ni standards.

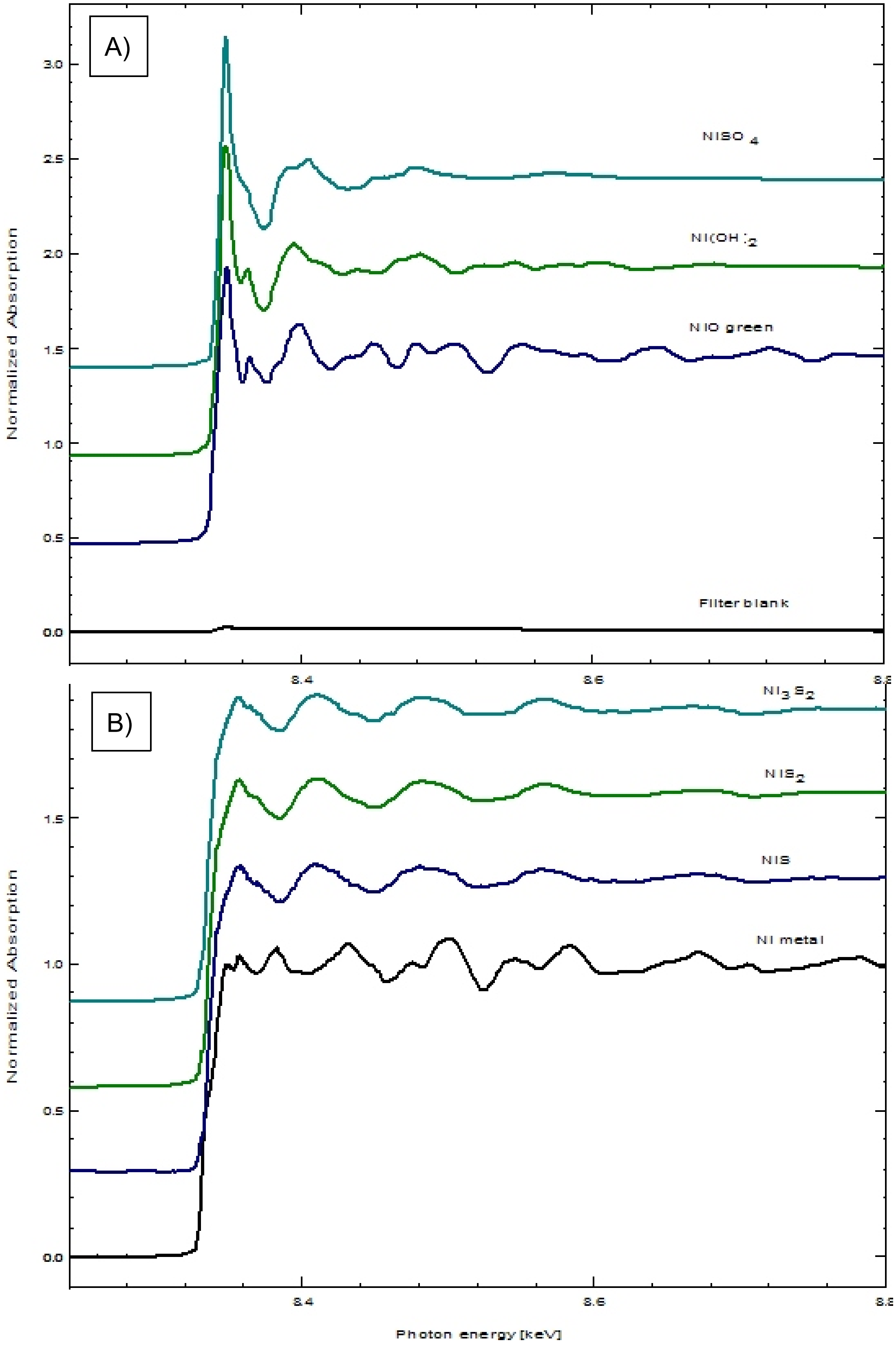
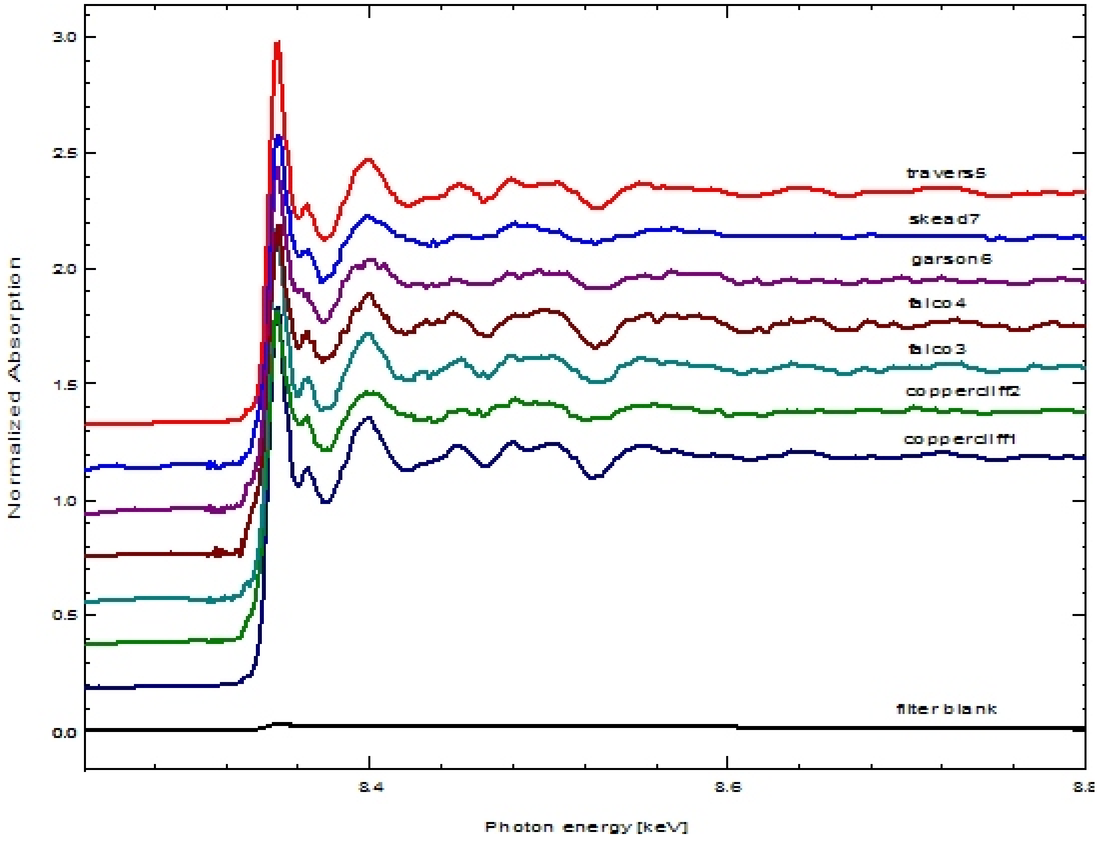
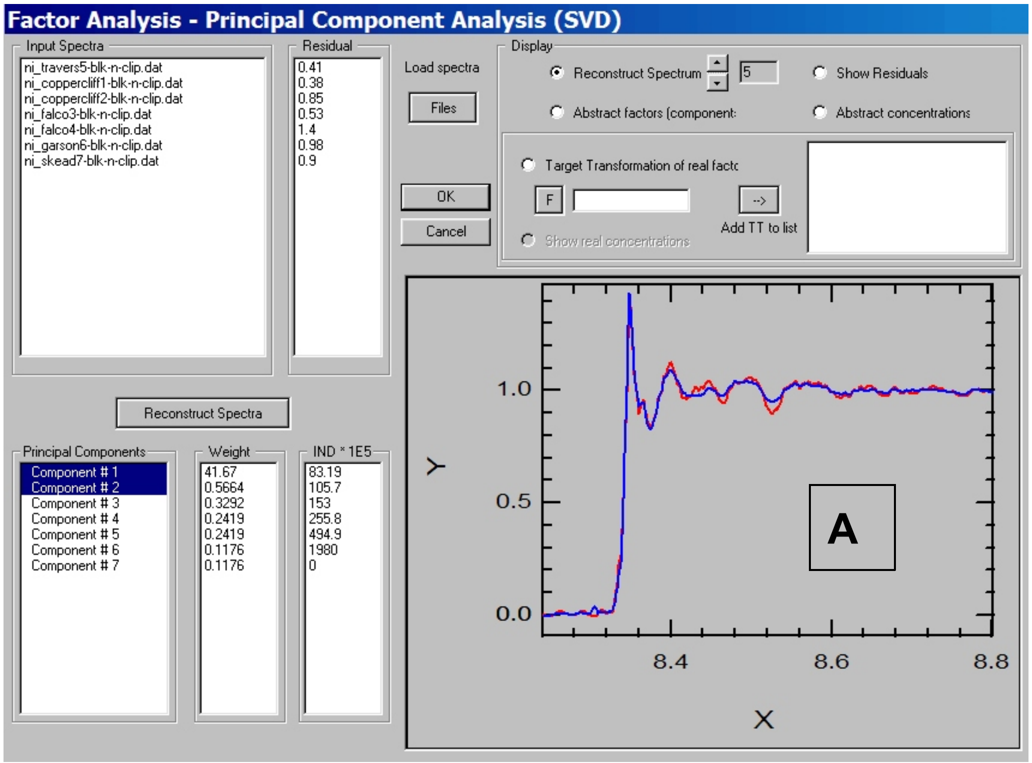


Figure 3. XAFS spectra of filter blank and PM on filter.



Appendix B - Example of PCA and Target Transformation

Figure 4. Example of PCA output.

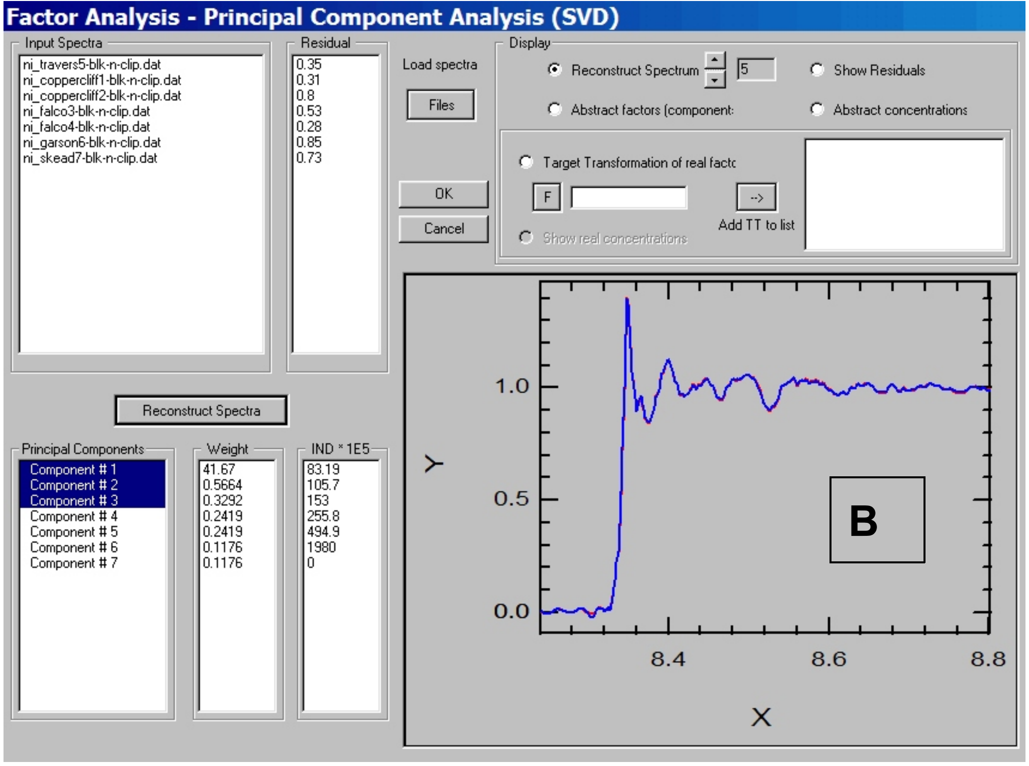


Factor Analysis - Principal Component Analysis (SVD)

Input Spectra	Residual
ni_travers5-blk-n-clip.dat	0.41
ni_coppercliff1-blk-n-clip.dat	0.38
ni_coppercliff2-blk-n-clip.dat	0.85
ni_falco3-blk-n-clip.dat	0.53
ni_falco4-blk-n-clip.dat	1.4
ni_garson6-blk-n-clip.dat	0.98
ni_skead7-blk-n-clip.dat	0.9

Principal Components	Weight	IND * 1E5
Component # 1	41.67	83.19
Component # 2	0.5664	105.7
Component # 3	0.3292	153
Component # 4	0.2419	255.8
Component # 5	0.2419	494.9
Component # 6	0.1176	1980
Component # 7	0.1176	0

● Reconstruct Spectrum 5



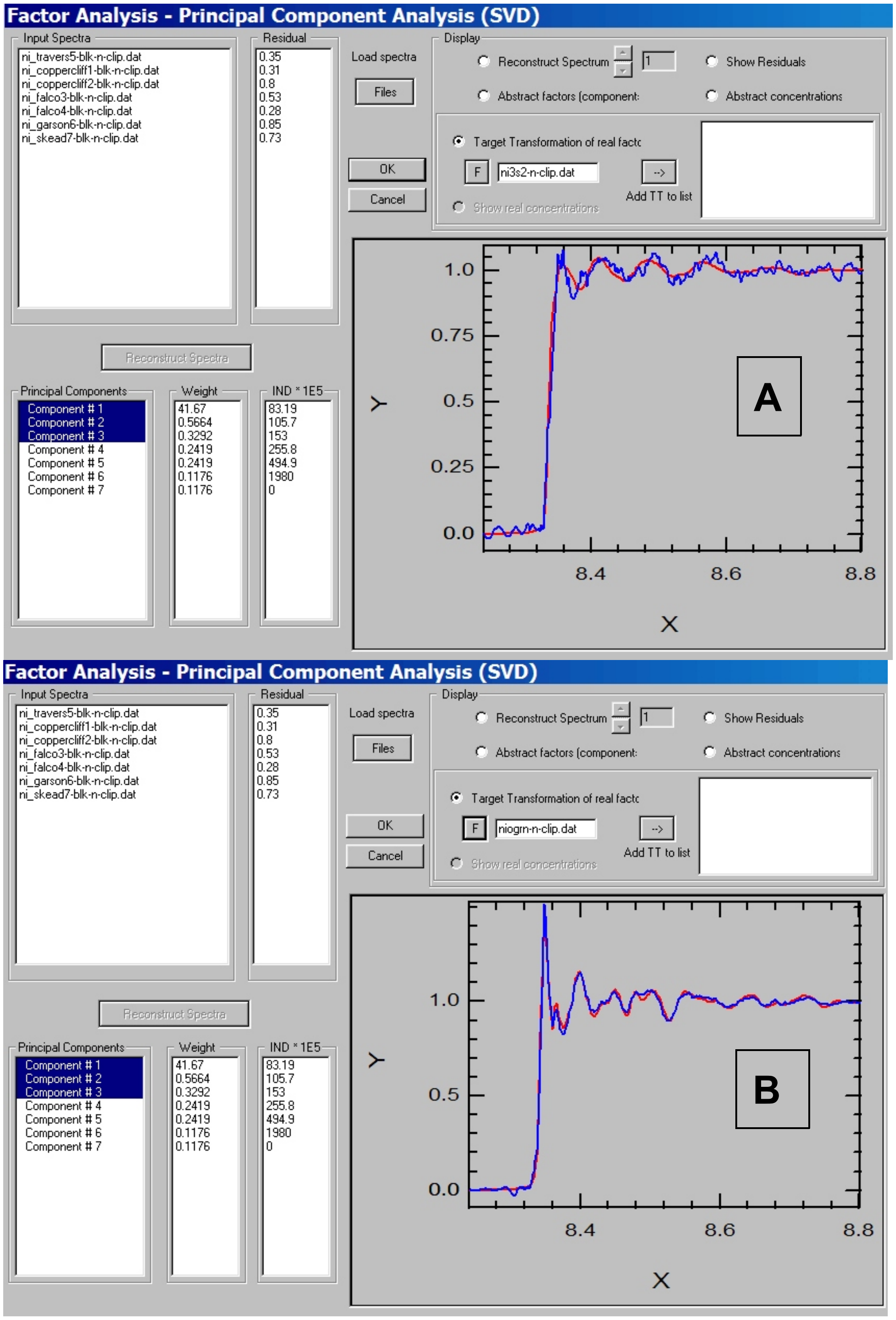
Factor Analysis - Principal Component Analysis (SVD)

Input Spectra	Residual
ni_travers5-blk-n-clip.dat	0.35
ni_coppercliff1-blk-n-clip.dat	0.31
ni_coppercliff2-blk-n-clip.dat	0.8
ni_falco3-blk-n-clip.dat	0.53
ni_falco4-blk-n-clip.dat	0.28
ni_garson6-blk-n-clip.dat	0.85
ni_skead7-blk-n-clip.dat	0.73

Principal Components	Weight	IND * 1E5
Component # 1	41.67	83.19
Component # 2	0.5664	105.7
Component # 3	0.3292	153
Component # 4	0.2419	255.8
Component # 5	0.2419	494.9
Component # 6	0.1176	1980
Component # 7	0.1176	0

● Reconstruct Spectrum 5

Figure 5. Target Transformation comparison of Ni-containing samples with Ni standards



Input Spectra	Residual
ni_travers5-blk-n-clip.dat	0.35
ni_coppercliff1-blk-n-clip.dat	0.31
ni_coppercliff2-blk-n-clip.dat	0.8
ni_falco3-blk-n-clip.dat	0.53
ni_falco4-blk-n-clip.dat	0.28
ni_garson6-blk-n-clip.dat	0.85
ni_skead7-blk-n-clip.dat	0.73

Principal Components	Weight	IND * 1E5
Component # 1	41.67	83.19
Component # 2	0.5664	105.7
Component # 3	0.3292	153
Component # 4	0.2419	255.8
Component # 5	0.2419	494.9
Component # 6	0.1176	1980
Component # 7	0.1176	0

F: ni3s2-n-clip.dat

Input Spectra	Residual
ni_travers5-blk-n-clip.dat	0.35
ni_coppercliff1-blk-n-clip.dat	0.31
ni_coppercliff2-blk-n-clip.dat	0.8
ni_falco3-blk-n-clip.dat	0.53
ni_falco4-blk-n-clip.dat	0.28
ni_garson6-blk-n-clip.dat	0.85
ni_skead7-blk-n-clip.dat	0.73

Principal Components	Weight	IND * 1E5
Component # 1	41.67	83.19
Component # 2	0.5664	105.7
Component # 3	0.3292	153
Component # 4	0.2419	255.8
Component # 5	0.2419	494.9
Component # 6	0.1176	1980
Component # 7	0.1176	0

F: niogrn-n-clip.dat

Appendix C - Target Transformation and Least-Squares Regression fit results

```
       Principal Components Analysis - Results
 ---------------------------------------------

  Reference files (grid: 300 dp):
  File # 1 :  ni_travers5-blk-n-clip.dat
  File # 2 :  ni_coppercliff1-blk-n-clip.dat
  File # 3 :  ni_coppercliff2-blk-n-clip.dat
  File # 4 :  ni_falco3-blk-n-clip.dat
  File # 5 :  ni_falco4-blk-n-clip.dat
  File # 6 :  ni_garson6-blk-n-clip.dat
  File # 7 :  ni_skead7-blk-n-clip.dat


  Target Transformation of   ni3s2-n-clip.dat
  Target Transformation R-value:   2.42858 %
----------------------

  Target Transformation of   ni-n-clip.dat
  Target Transformation R-value:   2.95358 %
----------------------

  Target Transformation of   niogrn-n-clip.dat
  Target Transformation R-value:   1.37957 %
----------------------

  Target Transformation of   Ni(OH)2-n-clip.dat
  Target Transformation R-value:   1.852   %
----------------------

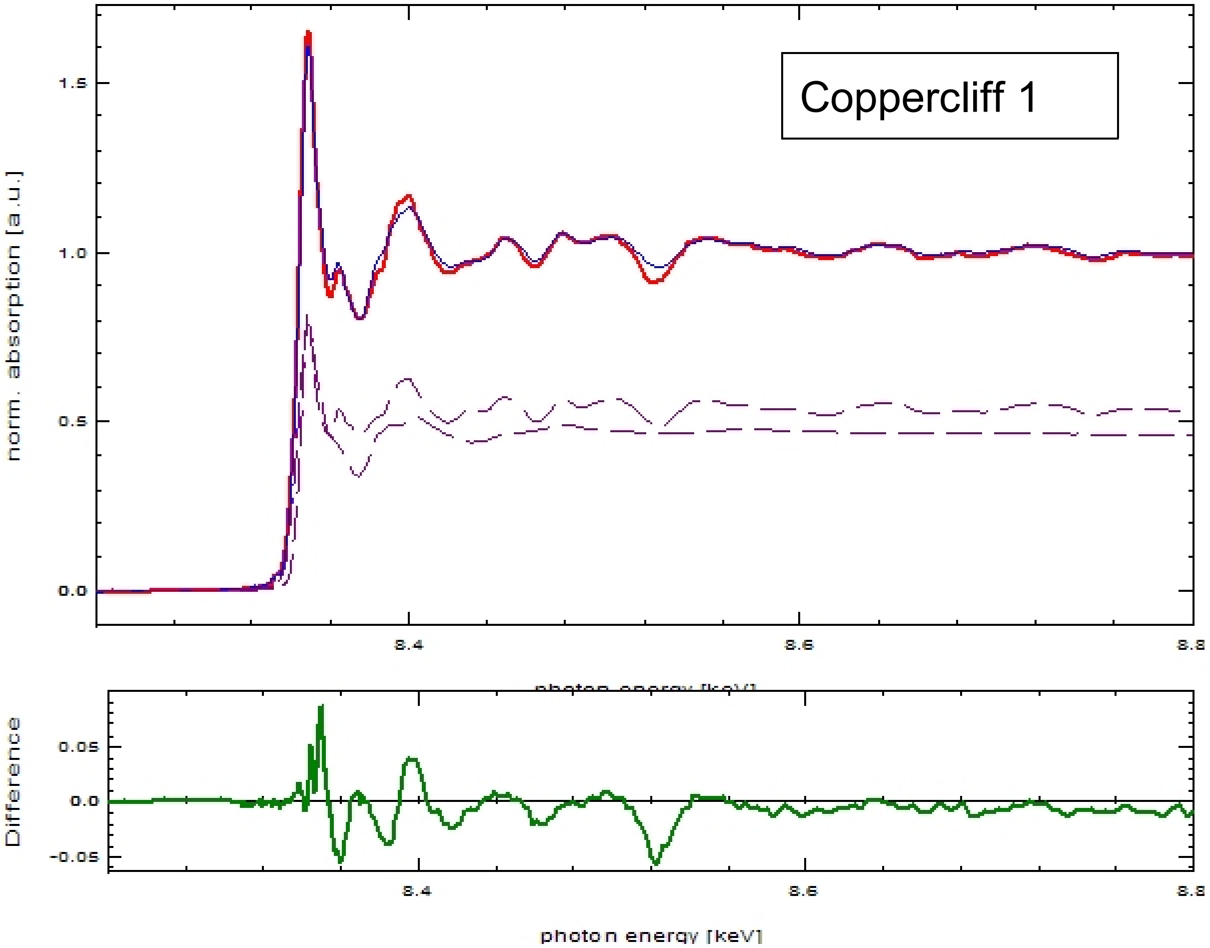
  Target Transformation of   nis2-n-clip.dat
  Target Transformation R-value:   2.33202 %
----------------------

  Target Transformation of   nis-n-clip.dat
  Target Transformation R-value:   2.52417 %
----------------------

  Target Transformation of   niso4-n-clip.dat
  Target Transformation R-value:   1.5211  %
```

```
--LEAST-SQUARES FIT     ( active : 1 )
-- FILE :  ni_coppercliff1-blk-n-clip.dat

Iterations:    13
(CHI)'2:      22520.8
Residual:      1.7351124
F-Test:       0.99998
data points:   330
-----------------------------
 LC xanes  - niso4-n-clip
.............................
#1  partial c.:  0.4674667 +- 0.0019775
#2  E0 shift:  0.0001289  +- 1.003E-005
-----------------------------
 LC xanes  - niogrn-n-clip
.............................
#3  partial c.:  0.5397814  +- 0.0020009
#4  E0 shift:  -0.00017352 +- 1.399E-005
-----------------------------
```

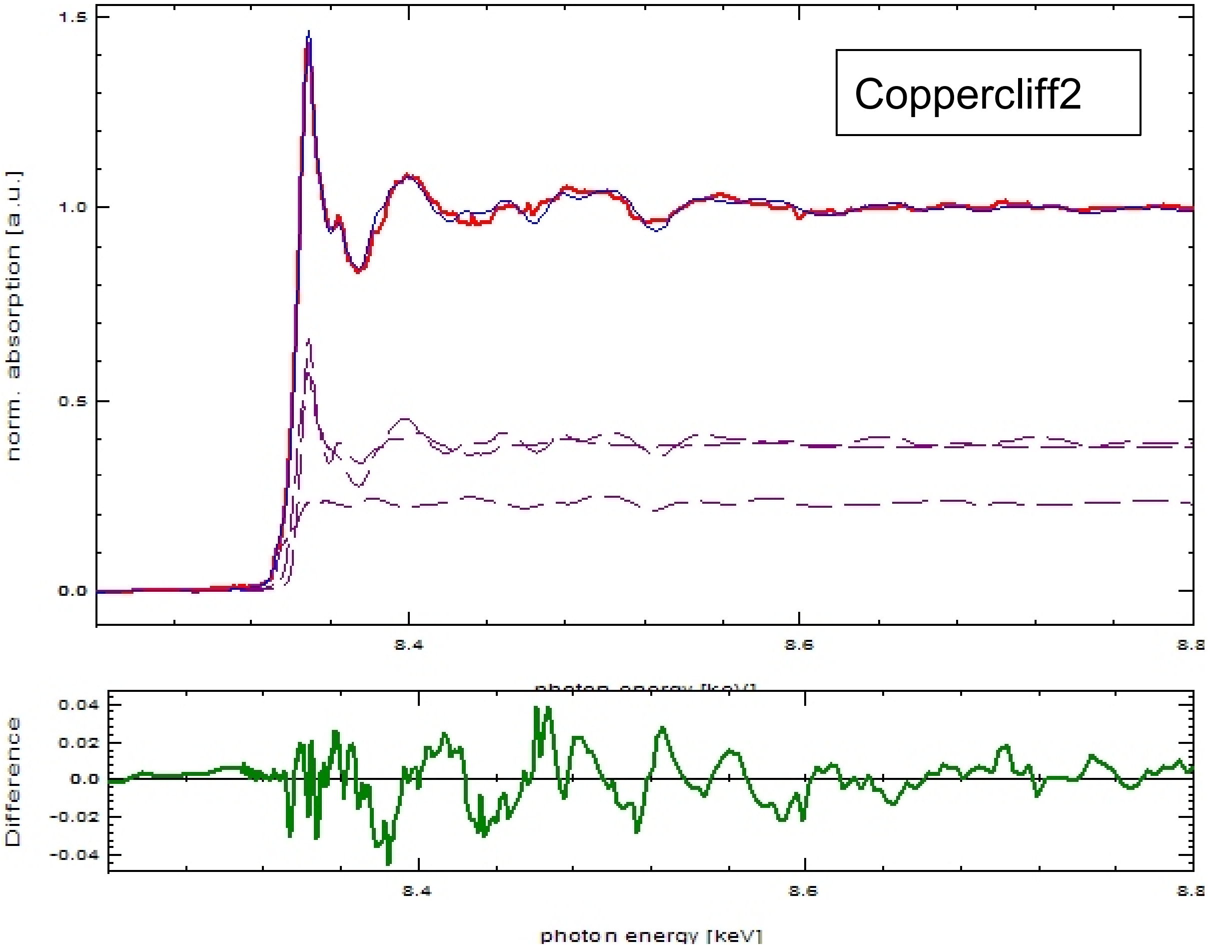


Absorption Correction for LC XANES Fit

```
 Specie #1 [niso4-n-clip]: c'(1)= 0.46747   mue(1)= 147.6     c(1)= 60.514  Weight-%
 Specie #2 [niogrn-n-clip]: c'(2)= 0.53978   mue(2)= 261.2     c(2)= 39.486  Weight-%
```

```
--LEAST-SQUARES FIT     ( active : 1 )
-- FILE :  ni_coppercliff2-blk-n-clip.dat

Iterations:    17
(CHI)'2:       5144.7495
Residual:      1.3569184
F-Test:        0.99997
data points:   330
-----------------------------
 LC xanes  - niso4-n-clip
.............................
#1  partial c.:  0.378550  +- 0.002970
#2  E0 shift:  0.0003454  +- 1.795E-005
-----------------------------
 LC xanes  - ni-n-clip
.............................
#3  partial c.:   0.231114  +- 0.001655
#4   E0 shift:   5.57984E-005 +-  1.0E-010
-----------------------------
 LC xanes  - niogrn-n-clip
.............................
#5  partial c.:   0.3900807  +- 0.003694
#6  E0 shift: -0.0005155  +- 2.963E-005
```

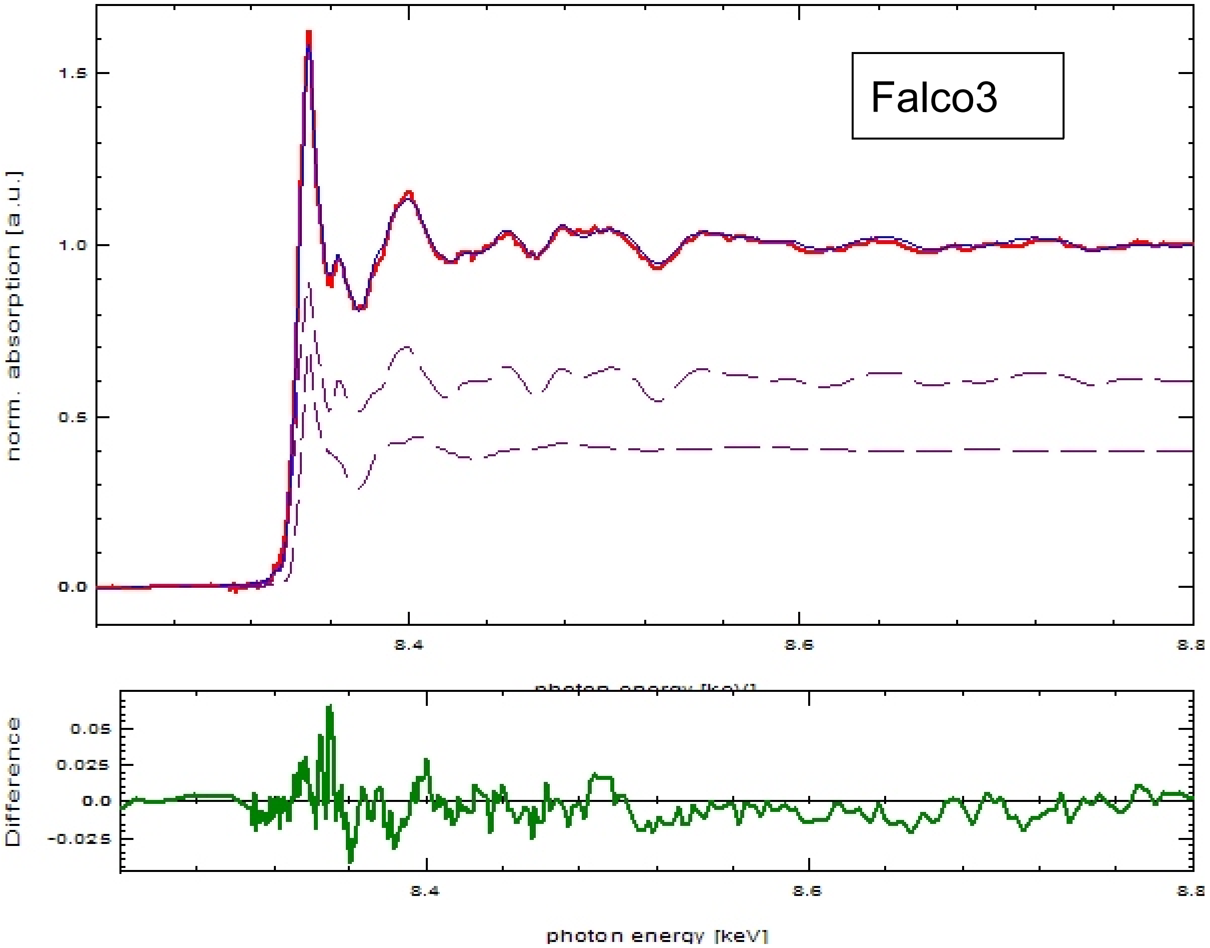


```
Absorption Correction for LC XANES Fit

 Specie #1 [niso4-n-clip]: c'(1)= 0.37855   mue(1)= 147.6     c(1)= 53.878  Weight-%
 Specie #2 [ni-n-clip]: c'(2)= 0.23111   mue(2)= 329.2     c(2)= 14.748  Weight-%
 Specie #3 [niogrn-n-clip]: c'(3)= 0.39008   mue(3)= 261.2     c(3)= 31.373  Weight-%
```

```
--LEAST-SQUARES FIT     ( active : 1 )
-- FILE :  ni_falco3-blk-n-clip.dat

Iterations:    8
(CHI)'2:       5331.8041
Residual:      1.5433627
F-Test:        1
data points:   330
-----------------------------
 LC xanes  - niso4-n-clip
............................
#1  partial c.:   0.400199   +- 0.00335362
#2  E0 shift:  0.0002864  +- 1.8207E-005
-----------------------------
 LC xanes  - niogrn-n-clip
............................
#3  partial c.:   0.6054619  +- 0.00338531
#4  E0 shift:  -0.000398  +- 2.141E-005
-----------------------------
```



```
Absorption Correction for LC XANES Fit

 Specie #1 [niso4-n-clip]: c'(1)= 0.4002    mue(1)= 147.6     c(1)= 53.911  Weight-%
 Specie #2 [niogrn-n-clip]: c'(2)= 0.60546   mue(2)= 261.2     c(2)= 46.089  Weight-%
```

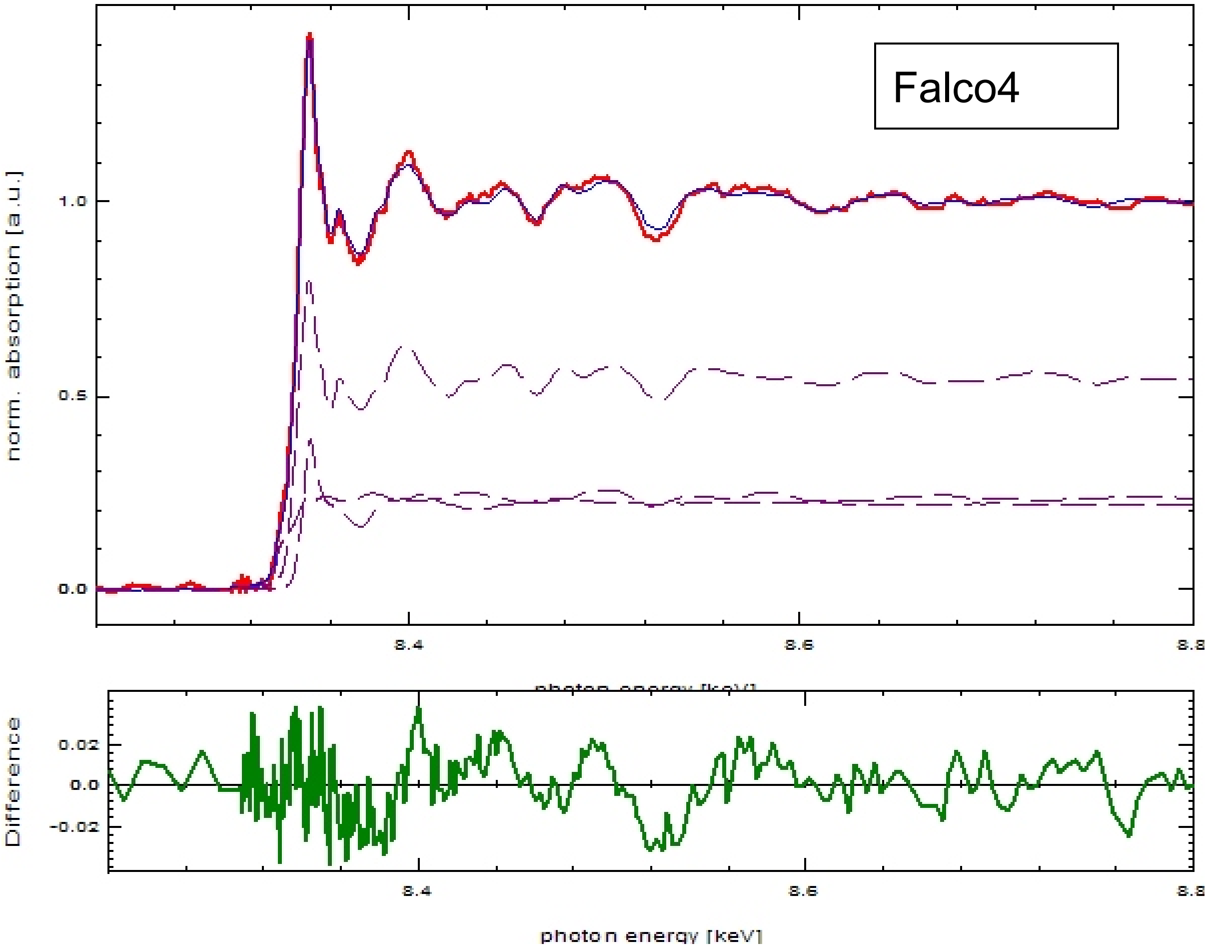
--LEAST-SQUARES FIT   (active : 1)
-- FILE : ni_falco4-blk-n-clip.dat

Iterations: 8
(CHI)'2:   1471.1352
Residual: 1.6573473
F-Test: 1
data points: 330

LC xanes - niso4-n-clip
....
#1 partial c.:   0.220878 +- 0.006672
#2 E0 shift: 0.001185   +- 6.40173E-005

LC xanes - ni-n-clip
....
#3 partial c.:   0.235931 +- 0.003593
#4 E0 shift: -0.0001315 +- 8.980E-005

LC xanes - niogrn-n-clip
....
#5 partial c.:   0.5423595 +- 0.007953
#6 E0 shift: -3.976E-006 +- 1.0E-010

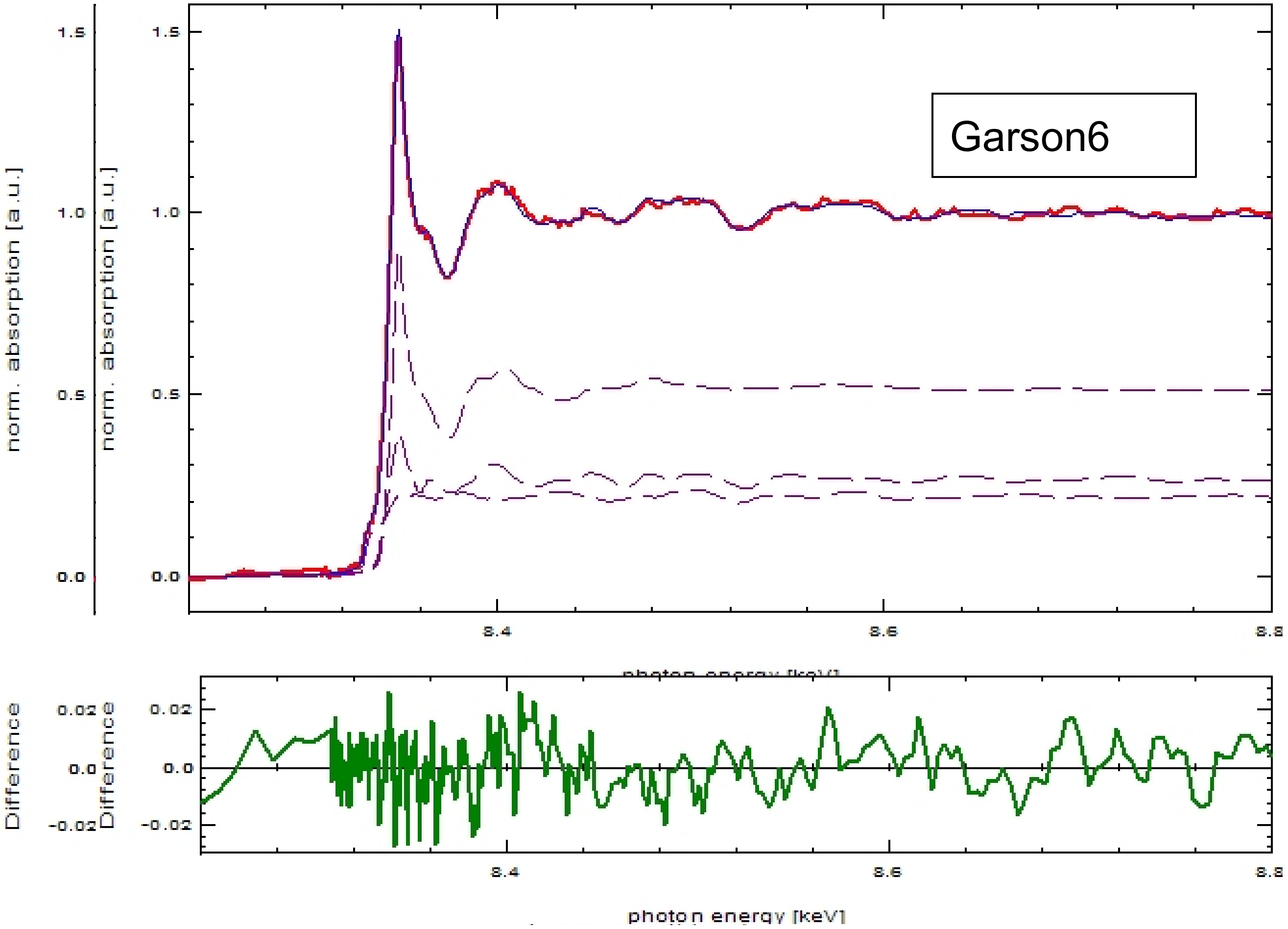


Absorption Correction for LC XANES Fit

Specie #1 [niso4-n-clip]: c'(1)= 0.22088   mue(1)= 147.6   c(1)= 34.89   Weight-%
Specie #2 [ni-n-clip]: c'(2)= 0.23593   mue(2)= 329.4   c(2)= 16.699 Weight-%
Specie #3 [niogrn-n-clip]: c'(3)= 0.54236   mue(3)= 261.2   c(3)= 48.411 Weight-%

```
--LEAST-SQUARES FIT     ( active : 1 )
-- FILE :  ni_garson6-blk-n-clip.dat

Iterations:    8
(CHI)'2:       787.73796
Residual:      1.0418503
F-Test:        1
data points:   330
------------------------------
 LC xanes  - niso4-n-clip
..............................
#1  partial c.:  0.51563  +- 0.00533044
#2  E0 shift: 0.0002026  +- 2.383E-005
------------------------------
 LC xanes  - ni-n-clip
..............................
#3  partial c.:   0.2176254  +- 0.002935
#4  E0 shift: -4.238222E-005 +- 1.0E-010
------------------------------
 LC xanes  - niogrn-n-clip
..............................
#5  partial c.: 0.266231  +- 0.00700368
#6  E0 shift:  4.97046E-005 +- 1.0E-010
```

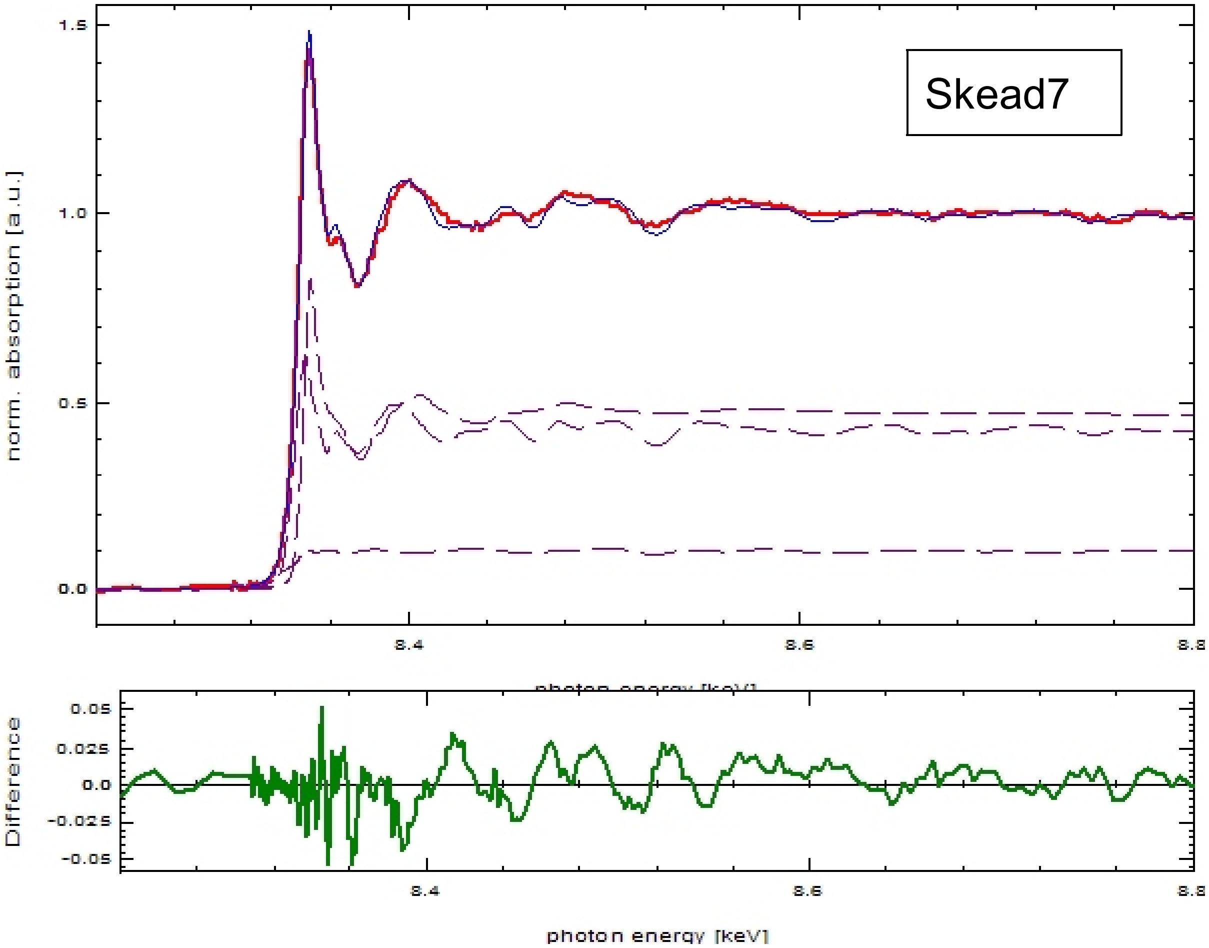


Absorption Correction for LC XANES Fit

```
 Specie #1 [niso4-n-clip]: c'(1)= 0.51564   mue(1)= 147.6     c(1)= 67.528  Weight-%
 Specie #2 [ni-n-clip]: c'(2)= 0.21763   mue(2)= 329.4     c(2)= 12.771  Weight-%
 Specie #3 [niogrn-n-clip]: c'(3)= 0.26623   mue(3)= 261.2     c(3)= 19.702  Weight-%
```

```
--LEAST-SQUARES FIT     ( active : 1 )
-- FILE :  ni_skead7-blk-n-clip.dat

Iterations:    8
(CHI)'2:       2463.7929
Residual:      1.6333296
F-Test:        1
data points:   330
-----------------------------
 LC xanes  - niso4-n-clip
.............................
#1  partial c.:  0.4726934   +- 0.005198
#2  E0 shift:  0.0013786  +- 1.99E-005
-----------------------------
 LC xanes  - ni-n-clip
.............................
#3  partial c.:  0.0989013 +- 0.003344
#4  E0 shift:  0.00029764 +- 0.0001727
-----------------------------
 LC xanes  - niogrn-n-clip
.............................
#5  partial c.:  0.425334  +- 0.005587
#6  E0 shift: -0.0017431 +- 5.0674E-005
```



```
Absorption Correction for LC XANES Fit

 Specie #1 [niso4-n-clip]: c'(1)= 0.47269   mue(1)= 147.61    c(1)= 62.412  Weight-%
 Specie #2 [ni-n-clip]: c'(2)= 0.098901  mue(2)= 329.4     c(2)= 5.8517  Weight-%
 Specie #3 [niogrn-n-clip]: c'(3)= 0.42533   mue(3)= 261.2     c(3)= 31.737  Weight-%
```

```
--LEAST-SQUARES FIT     ( active : 1 )
-- FILE :  ni_travers5-blk-n-clip.dat

Iterations:    8
(CHI)'2:      16283.846
Residual:      1.3107962
F-Test:        1
data points:   330
-----------------------------
 LC xanes  - niso4-n-clip
.............................
#1  partial c.:   0.543244   +- 0.001662
#2  E0 shift:  0.00011424  +- 7.399E-006
-----------------------------
 LC xanes  - niogrn-n-clip
.............................
#3  partial c.:   0.4614692  +- 0.001683
#4  E0 shift: -7.013E-005  +- 1.367E-005
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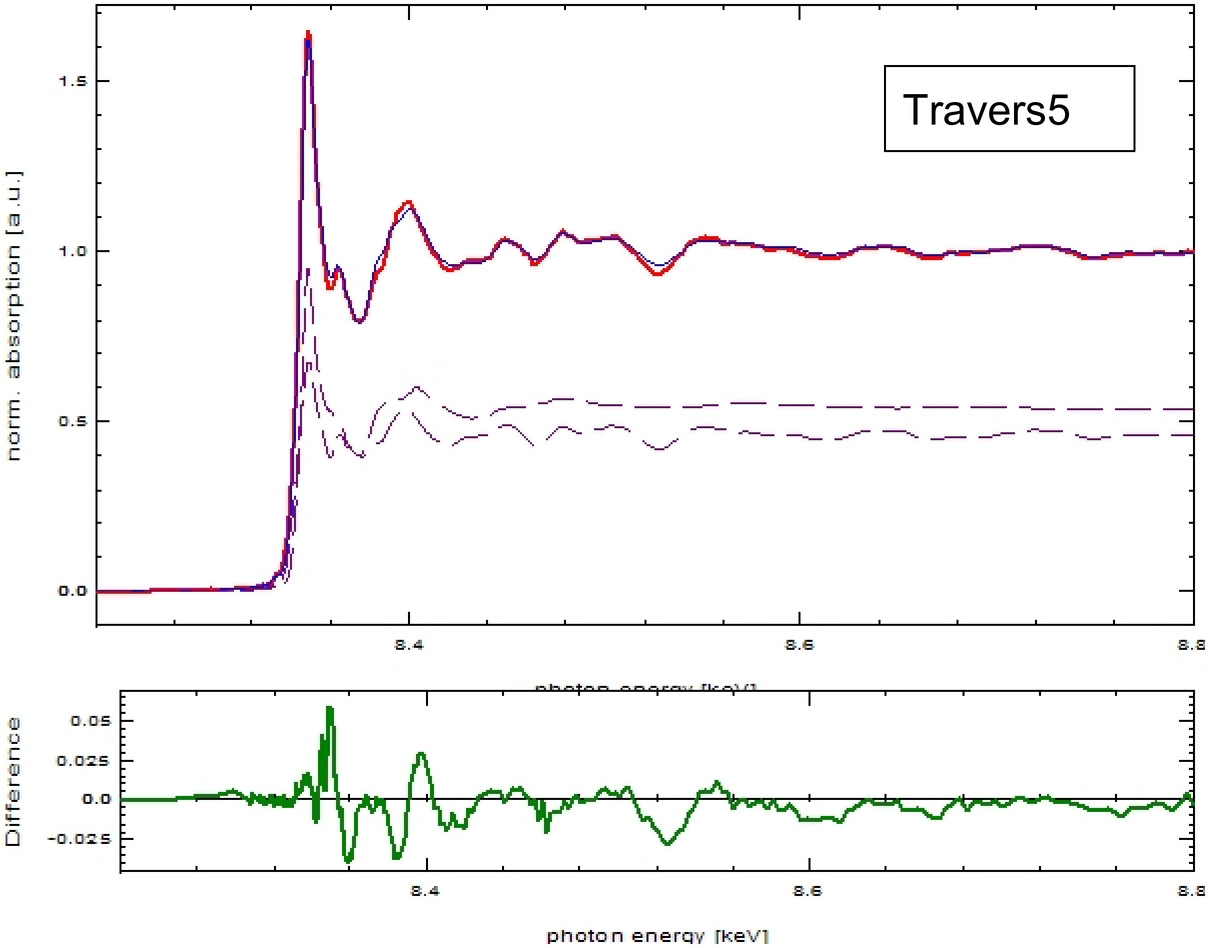


```
Absorption Correction for LC XANES Fit

 Specie #1 [niso4-n-clip]: c'(1)= 0.54324   mue(1)= 147.6     c(1)= 67.567  Weight-%
 Specie #2 [niogrn-n-clip]: c'(2)= 0.46147   mue(2)= 261.2     c(2)= 32.433  Weight-%
```

Appendix D. Summary of results from Least Squares Regression Analysis (% Fit)

Table 1. Least-squares fit and weight % results.

	Fit %		
	% $NiSO_4$	% NiO green	% Ni metal
ni_coppercliff1	47%	54%	
ni_coppercliff12	38%	39%	23%
ni_falco3	40%	61%	
ni_falco4	22%	54%	24%
ni_garson6	52%	27%	22%
ni_skead7	47%	42%	10%
ni_travers5	54%	46%	
	Weight %		
	% $NiSO_4$ ($\mu = 147.6\ cm^2/g$)	% NiO green ($\mu = 261.2\ cm^2/g$)	% Ni metal ($\mu = 329.4\ cm^2/g$)
ni_coppercliff1	61%	39%	
ni_coppercliff12	54%	31%	15%
ni_falco3	54%	46%	
ni_falco4	35%	48%	17%
ni_garson6	67%	20%	13%
ni_skead7	62%	32%	6%
ni_travers5	68%	32%	

μ is the x-ray mass attenuation coefficient

Appendix E - DELTA E - edge energy difference

Table 2. K-edge energy difference of Ni standards and PM samples.

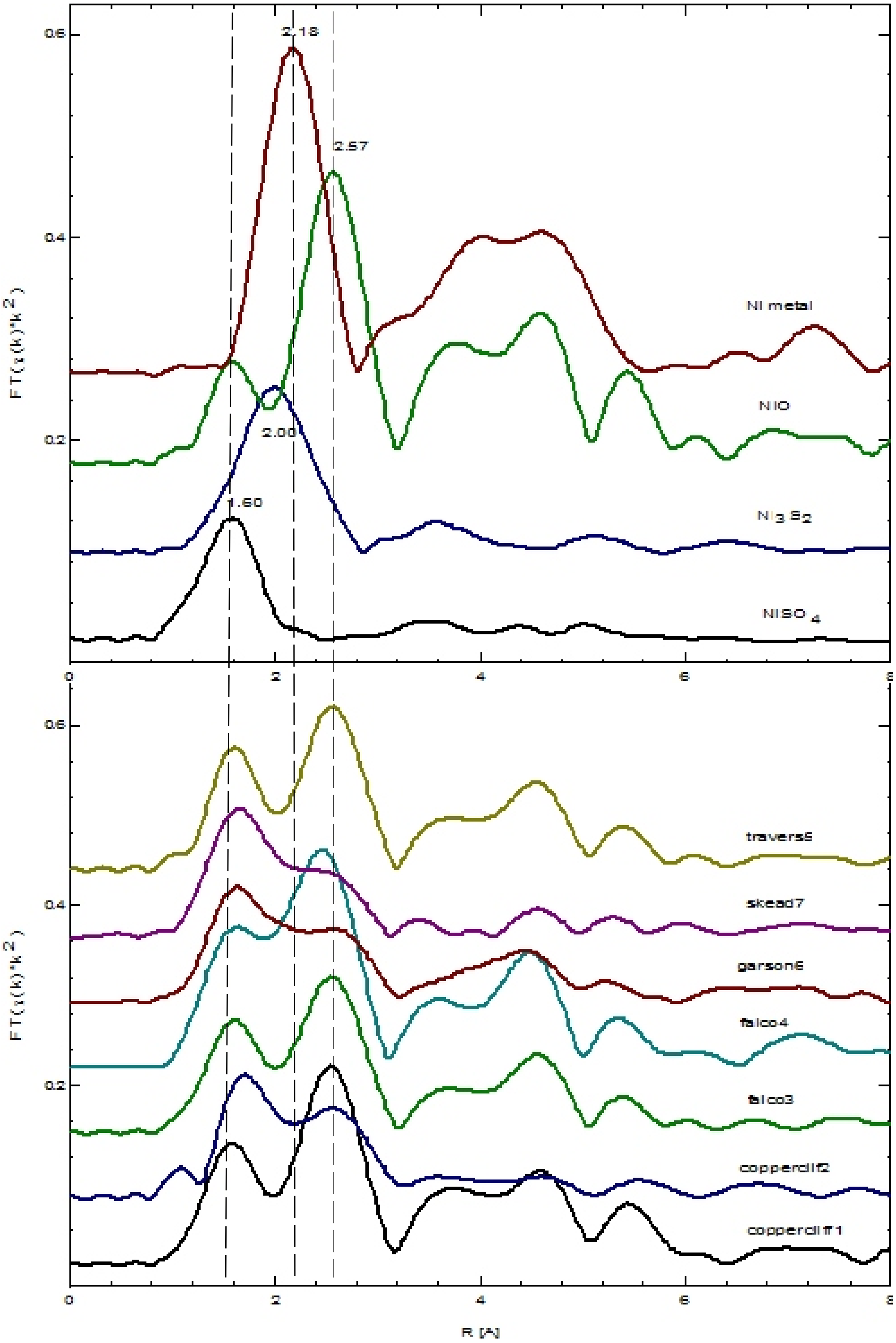
		Experimental data		Fit data	
Sample ID	Ni {Ox}	Delta E_{expt} (eV)	Mean Delta E (± σ)	Delta E_{fit} (eV)	Mean Delta E (± σ)
NiO green	(+2)	10.5	11.8 ± 1.1		
$Ni(OH)_2$	(+2)	12.2			
$NiSO_4 \cdot 6H_2O$	(+2)	12.6			
Ni metal	(0)	0.0			
ni_coppercliff1		11.2	11.2 ± 0.7	11.3	11.5 ± 0.9
ni_coppercliff12		11.6		11.0	
ni_falco3		10.4		10.4	
ni_falco4		10.2		10.6	
ni_garson6		11.8		12.4	
ni_skead7		11.9		12.9	
ni_travers5		11.4		11.8	

"Delta E" stands for the edge energy difference between the measured edge energy of the sample and the Ni metal edge energy (8.333 KeV).

"Ni {Ox}" stands for Nickel Oxidation State.

Appendix F - Fourier Transform of XAFS spectra

Figure 6. Fourier Transform of XAFS spectra of some Ni standards and Ni-containing samples



Metal Speciation Task Force

Minutes of Follow up Meeting

January 20, 2006 1 – 3:30 pm

CEI Offices

Attendees:

Inco	Bruce Conard Mike Dutton (by phone)
Inco Research Labs	Fred Ford
MOE	Dave McLaughlin Rusty Moody (by phone)
SARA Group	Glenn Ferguson
SGS Research	Rob Irwin and Chris Hamilton (by phone)
CLS	Jeff Warner (by phone)
EnviroAnalytix	Marc Lamoureux (by phone)

A summary of the key discussions that took place during the meeting is provided below, in the approximate order that they happened. A package containing the reports representing all speciation work conducted to date was circulated to the participants in advance of the conference call/meeting.

Introductions and general discussion:

Glenn Provided an introduction on behalf of the SARA Group.

Goal of the meeting was to evaluate speciation analytical work conducted to date for the Sudbury Soils Study, discuss the implications of the results, determine what conclusions (if any) can be drawn from these results, and propose any necessary follow up analytical work to reduce uncertainties going forward. Due to the results of the preliminary speciation work and clarifications required, these discussions will focus more on the speciation of the COCs within air filters and dust samples.

Glenn provided an overview of the analytical work conducted to date. A summary of this overview is attached to the current minutes. Each of the researchers was then asked to expand upon the discussion concerning their particular analyses, and provide any additional insights they may have.

Analysis by SGS Research

Rob Wanted to emphasize that the Tessier leach analyses is not designed to identify specific minerals in the sample, just the availability and mobility of the metals present within the sample. So putting nickel subsulphide into one of the categories would be very difficult. The analyses were fairly routine, and the only surprising aspect was that some of the fractions were shifting to the organic phase likely due to the presence of a carbonaceous material observed by the SEM analyses.

Glenn	This is where we observed that metal species that would normally leach out in one of the earlier sequential leaches got carried through to the later organic phase leach due to the presence of this organic material.
Bruce	Was this only observed in the air filters?
Chris	There was a lot more organic and nickel association in the dust samples. In the air filter samples, the particulates were very fine. The larger of the particulates were positively identified as nickel sulfide (millerite) or NiS. Anytime an oxygen was detected with millerite, it was interpreted as some kind of oxide coating on the millerite. Which raises the question of oxide and sulphate potential coatings on other nickel species, which might give a mixed spectrum resembling nickel subsulphide. However, when the subsulphide identification was made, confirmations that there was no oxygen present were made. However, as indicated by Dr. Ford, this can be difficult due to not only electron beam size, but a dynamic resolution issue. With respect to the carbonaceous materials, there are particles within the dust samples that are very low electron back-scatter signal species, and in some cases carry nickel inclusions. SEM inspection supports the presence of nickel sulphate & possible organo-sulphates, and certainly supports an emission derivation. Another important point is that there are four x-ray detectors pointing at the samples, so they are averaging out the effects of any local environmental x-ray detection. So if there are relief effects (*i.e.*, uneven or irregular surfaces), which is an issue with samples like this, the four detectors irons out problems related to this.
Bruce	Wants to make sure we separate discussions of air filters from dust samples, due to the different exposure pathways related to these media. In particular, he would like to see if the bioaccessibility leach is telling us the same thing as the Tessier leach analyses are telling us.
Glenn	That will likely be a separate meeting to discuss bioaccessibility, and we can bring Rob Irwin into the discussion. We can definitely separate out the dust and air filter samples in our discussions, though. We'll put dust aside for now, and focus on air.

Bruce	In the SGS analyses, for the air results we appear to find this ubiquitous carbon coating?
Chris	The coating appeared to be present in most samples. Though it is difficult to determine whether it was carbonaceous material coating sulphates, or *vice versa*.
Bruce	There is some work by Pat Rasmussen of Health Canada that indicates that sulphates can be highly bound to organic phases, so it may not be so much of a coating than an association. If there is carbon material in the air from other sources, when sulphate particles gravitate and find themselves in close proximity to one of those carbon particles they can “glom on” and become tightly bound. This might explain these observations of these “associations”. Nickel sulphate is very “friendly” to carbonaceous materials. So it may be in a Tessier leach or even a bioaccessibility leach that the sulphate is so tightly bound so it cannot be coaxed off as normal sulphate, and that you really have to dissolve the organic phase before the sulphate can be freed up.
Rob/Chris	This seems to reflect their findings.
Marc	Wanted clarification on the source of the dust material.
Glenn	The dust was collected as part of an indoor dust survey conducted in residences throughout Sudbury. A high volume vacuum cleaner was used to collect dust that individuals would be exposed to as part of their daily life.
Bruce	Had an issue with the carbonaceous material being called slag or coke-like material.
Chris	Agreed that is should have been called a porous carbonaceous material.

<u>Analysis by Dr. Fred Ford</u>

Fred	As Glenn indicated, there are limitations to the SEM method, particularly in three dimensional samples where you are looking at materials trapped in air filters. There is much more potential for interference. This is compounded by the size of the x-rays being used for the analyses, which are coarser than the particles being viewed.
	One of the things he was most concerned about in the air sample filters nominally identified to contain nickel subsulphide was the presence of an iron and a copper peak. It is highly unusual for hazelwoodite (nickel subsulphide) to partition iron and copper into the mineral structure. If you

	look at mattes, hazelwoodite will have some iron and copper, but really at trace levels. Not at the peak heights observed in the x-ray spectrum from the air filters. As a result, he thought the identification of nickel subsulphide in the air filters was tentative at best.
	He felt the dust sample identification was much clearer. There was not the problem with the x-ray interaction volume observed in the air filter particulates. As such, he was fairly certain of the identification of nickel subsulphide. About the only way to be 100% certain would be to dislodge the particulate into an epoxy mount, section it, polish it flat, and remove any sort of difficulty you may have from a three dimensional analyses of it.
Bruce	Would it be possible that the iron, copper, and nickel observed simultaneously on the particle, could they be mixed sulphates on another particle.
Fred	It can be any sort of combination that you could foresee. Yes.
Bruce	So you see a particle, but it doesn’t seem to be conglomerate of several particles. It seems to be a single particle.
Fred	But you have no idea if it is a particle of nickel that has been coated sulphate, or some sort of sulphur. He was not sure exactly what it is.
Chris	It could be a binary particle which you are hitting at the top, and the section beneath which you cannot see is being excited as well.
Bruce	Could it be an oxide particle? Or a mixed oxide particle?
Fred	Yes.

Analysis by CLS

Jeff	Jeff gave a brief overview of the analytical methodology and results. Principle components analyses, coupled with linear combination fittings (least squares method), were used to fit reference spectra to a given sample spectrum. With the nickel K-edge analyses, nickel oxide and nickel sulphate were detected in all the samples. Nickel sulphide was also detected in two of the samples, but not the Copper Cliff sample. With the sulphur K-edge, there is some sulphide present in the Travers Street filters. But the dust sample shows a completely different profile than the air filters. There also appeared to be good agreement between the results of the nickel and sulphur K-edges.

Bruce	We have to be careful that if we decide to use the percentages provided in this report that they are mole percent, and not weight percent.
Marc	If there was iron and/or copper sulphide present in the sample, how would it show in your K-edge analyses?
Jeff	Though we didn't run a copper or iron sulphide standard, it would probably show up in that sulphide peak.

Analyses by Dr. Lamoureaux

Marc	Essentially the technique Marc used was the same as that used by CLS. Principle component analyses, along with target transformation analyses, were used to identify the species. Essentially you compare the unknown directly with your library of standards, and you attempt to find features in the unknown that overlap with those in the standard. This increases your confidence that particular standard is a probable candidate for your subsequent fitting technique. The fitting technique was a least squares regression approach. Calibration curves were also generated to confirm identifications. Results of Dr. Lamoureaux's analyses indicated that nickel oxide and nickel sulphate were present in all samples. Nickel subsulphide was not observed in any of the samples. Nickel metal was observed in a small number of cases. A lot of iron and copper was detected in the all the samples. Therefore, if any of the iron is as iron sulphide, it could get convoluted with nickel sulphide. So what you see with the sulphur K-edge, you could get the fingerprint of iron sulphide being taken as nickel sulphide. He indicated that this is speculation until we do the necessary analytical work.
Bruce	Thought the comment about iron sulphide was very critical. Sudbury ore is an iron sulphide ore, which happens to have nickel and copper sulphide. If you are looking at air samples originating from either Inco's or Falconbridge's operations, the iron sulphide and iron oxide would be a very significant component. Therefore, whatever techniques we are using, if there is any chance the results are influenced by the presence of iron, we should take steps to run some iron sulphide and iron oxide samples.

General Discussion

There was some discussion of the objectives of the XANES work. The original work was to distinguish between nickel oxide, sulphate, and subsulphide. Bruce was concerned that a conservative approach may be to toxicologically assume all detected sulphides are subsulphide, as there are no toxicological studies on sulphides. Therefore, if this approach is selected, it is critical to distinguish whether the sulphides are present as nickel sulphide, or if they are iron or copper sulphides (which are not considered carcinogens).

Fred Questioned whether some of the nickel sulphide may be overlapping with pentlandite. He indicated that he thought it was unusual to see such levels of NiS, but that pentlandite (which appeared to have a very similar curve in the report figures) would be quite possible and very common.

Jeff The pentlandite source was not used in the fitting operation because he was sure it was contaminated.

Bruce It’s very difficult to get a pure pentlandite.

Fred indicated he might be able to get a purer pentlandite source for future analyses.

Glenn What further work can we do to better clarify the nature of the sulphides present?

Marc Asked if it is possible for CLS to do L-edge analyses (a finer form of analyses).

Jeff CLS is able to do it at their facility, and he has recently completed some nickel L-edge analyses.

Marc Conducting some iron and copper L-edge work may resolve the issue.

Jeff Agreed.

There was some discussion of the potential source of pentlandite, whether it was from the slag crushing operations, or the tailing piles.

Marc Would it be possible to use solid state NMR analyses? Ni-61 is NMR active. However, he wasn’t sure there was sufficient material to get a sufficient spectrum. But it would be a separate analysis that may be able to shed some light on the nickel sulphide and subsulphide within the samples.

It was generally thought that it would be difficult to collect enough material to complete the analysis.

Glenn How feasible is it to complete the L-edge work time-wise? What is the availability of beam-time at CLS for L-edge analyses?

Jeff I don't think there would be much problem obtaining beam-time here at anytime in the future.

There was concensus that this seemed to be an appropriate approach to help clarify the sulphide issue.

Glenn Why did the SEM identify nickel subsulphide in the dust samples, but not in the CLS analyses?

Bruce What filters were used in the vacuum system?

Glenn I believe it was equipped with a Hepa filter, but I would have to check on that. [ed: It was not HEPA-certified. The filter was rated at 10 µm].

Bruce It would be useful to know what fraction of the particulate ends up in the jar *versus* the vacuum filter.

Glenn I will follow up on that.

Are we concluding that the beam specificity issue for the SEM is hampering the identification of the nickel subsulphide?

Bruce The results of Fred's analysis indicated that he agreed with SGS that the particles in dust were nickel subsulphide.

Fred "A" particle in dust was nickel subsulphide. It's an important distinction. I have no idea of what the population of particles are.

Bruce But did you look at several sulphide-like particles, and were they all the same?

Fred No.

Bruce One of the problems I find as a chemist, is that the very good technical people on the SEM would find an extremely interesting particle and focus on that, yet it would be an insignificant particle in terms of the overall sample. It is a problem finding an interesting particle and then to find if it is prevalent.

Chris Agreed. When we've done our searches, as a result of time, we have limited the statistics to a certain number of occurrences which may be less than 50 grains. As such, the quantitative aspects of this are open to some question because of statistics, compounded with the issues Fred has raised.

Glenn	Only one dust sample has been analyzed by CLS. It would be useful to submit additional dust samples from a couple of different locations to CLS for follow up work, with parallel analyses with SEM by SGS. Would it be fair to say that the XANES approach, because it can gather different layers, rather than focusing on one specific layer like SEM, would provide a better indication of the presence of nickel subsulphide versus sulphides versus other species?
Fred	I think you should get the same answer. However, if you're going to use SEM, you need a good statistically significant dataset. And evaluating 50 particles is not a statistically significant dataset. Something more on the order of 500 particles would be more statistically significant.
Glenn	SGS is that possible?
Chris	Yes. We can do an actual polished section, where we actually look through the plane of a particle. Because both optically and SEM, we can confirm the presence of nickel subsulphide.

A question was asked as to the detection limit of the XANES approach, and whether SEM would be more sensitive than XANES, or would they be more equivalent. Marc indicated he believed that the XANES would be more sensitive than SEM because you have a lot more photons on a given spot.

Chris	Another option would be to look specifically at the residues from each of the Tessier leach steps using SEM. So you could potentially isolate an organic fraction that can be more specifically analyzed.
Glenn	That would be very useful, so that we could make a better correlation for our entire set of samples analyzed by Tessier.
Jeff	Would heartily endorse this approach for XANES as well.
Glenn	Would it be useful to conduct some sampling at different sampling times? Different wind directions, *etc*.?
Bruce	Yes, this would be useful to create a composite of what individuals are exposed. Rather than simply using one snapshot in time, it would be useful to evaluate what is in the air over different seasons and different wind directions. And does it make sense from where it is coming from. Is there something there, from a risk management point of view, that can be controlled … either the emission or the resuspension if it is windblown.
Glenn	Does anyone have any other issues?

Bruce	From his point of view, the air samples are more important than the dust samples because the dust samples are adjusted by the bioaccessibility. However, in air, the unit risks for respiratory cancer are quite significantly different between the various nickel species. So you can get radically different answers which influence radically different risk management plans, depending on whether you have identified the species correctly.
Mike	We need to clarify the discrepancy with the dust. Whether it is using polished sections or another analysis technique.
Glenn	Agreed. I will put together the path/strategy going forward, and submit the draft to everyone. This will then be passed by the TC for their approval. Thank you to all those involved in the meeting.

Meeting adjourned.

OVERVIEW OF SPECIATION ISSUES

The following "weight-of-evidence" analytical approach was conducted for air filter, soil, and dust samples collected during Phase II of the HHRA (see relevant sections in this chapter):

1. All selected samples were analyzed using a modified Tessier sequential leach extraction technique, which quantifies the mass fraction of each COC within the sample which leaches out in sequentially more aggressive digestion procedures; and,

2. All dust and air filter samples were analyzed using mineralogical analyses, such as soil trace mineral search techniques and soil bulk mineralogical analyses (*i.e.*, using a scanning electron microscopy). A subset of the soil samples analysed using the sequential leach extraction (approximately 10%) were also analysed using these mineralogical techniques.

Number of Samples Analyzed using each Speciation Technique

Analytical Technique	Total Samples Analyzed		
	Soil	Air Filter	Dust
Sequential leach	84	10	25
Mineralogical analyses	10	10	25

Soil Samples

A total of 84 soil samples were analyzed using the sequential leach technique, including 19 samples from Copper Cliff, 21 samples from Falconbridge, 18 samples from Coniston, 16 samples from Sudbury central, and 10 samples from Hanmer.

Of these 84 samples, 10 were selected for additional mineralogical analyses using the SEM (4 from Falconbridge, 3 from Copper Cliff, and 3 from Coniston). These particular samples were selected for the additional analyses by SEM due to their locations in the three original smelting communities and the presence of elevated nickel concentrations detected in the samples.

Air Filters

A total of 10 air filters were selected for evaluation by both sequential leach and SEM analyses. These included: a PM10 and PM2.5 filter from each of the Copper Cliff, Falconbridge, Windy Lake, and Travers Street stations, as well as a PM10 filter from the Hanmer Station (no PM2.5 was collected at this site) and an additional PM10 filter from the Travers Street station (different date from the other samples). All filters, with the exception of the additional Travers Street station PM10 filter (collected September 24th, 2004), were obtained on June 8th, 2004.

Dust Samples

A total of 25 indoor dust samples were selected for evaluation by both sequential leach and SEM analyses. These included 4 from Falconbridge, 7 from Copper Cliff, 4 from Sudbury (centre), 5 from Coniston, and 3 from Hanmer.

Speciation Results

Speciation results for soil, air filter, and dust samples indicate emissions from smelting and refining sources have impacted each of the sample media.

- Speciation fingerprint noted in the leach analyses indicated similar species were present in each of the COIs throughout the GSA;
- Nickel and copper were the two predominant COCs detected;
- Nickel oxide appears to be ubiquitous throughout each of the COIs, in each of the sample media, in particular soil and dust samples;
- Lead paint flakes were not detected in any of the media, including dust samples taken from residences throughout the GSA;
- Species present in dust samples are similar to those observed in air filters, indicating that the metals present within the dust likely originated from airborne emission sources, rather than being tracked in from outdoor soil sources.
- Much of the species present in the air filters appears to be coated by an organic carbonaceous layer, likely related to coke material.
- Nickel subsulphide (Ni3S2) was detected in a number of air filter and indoor dust samples taken throughout the GSA. Only the Copper Cliff and the Travers Street stations showed the presence of Ni3S2, while Ni3S2 was observed in nearly all of the dust samples.

As there was some uncertainty associated with the presence of nickel subsulphide in both the air and dust samples, a series of conformational steps were undertaken. Dr. Fred Ford of Inco Technical Services, who has experience working with nickel matte, was contracted by the SARA Group to review the SGS SEM mounts and provide an opinion as to the validity of their analyses and confirmation of the possible presence of nickel subsulphide.

Results of Dr. Ford's analyses indicated that, while SGS was correctly using appropriate techniques to conduct their analyses, due to the nature of the equipment and sample, it was difficult to absolutely confirm the presence of nickel subsulphide. In brief, there are two limitations to chemical typing of sulphide particules using X-ray microbeam techniques:

1. The EDS detector cannot determine the presence of hydrogen, so hydroxide or hydroxyl groups cannot be identified; and,
2. The beam used for the current SEM analyses may be to large to accurately identify the species present in very small particles, such as those on the air filter samples and some of the dust samples.

These uncertainties make it increasingly difficult to accurately distinguish between nickel subsulphide (*i.e.*, Heazlewoodite) and nickel sulphide (*i.e.*, Millerite). Dr. Ford concluded that the particles on the air filters he examined may have been nickel subsulphide, or might have been something else, like nickel sulphide or metallic nickel with a sulphate coating. However, he was more certain that the particles observed in the dust samples were correctly identified as nickel subsulphide.

As a result of this uncertainty, it was decided to submit a number of samples for X-ray Absorption Near-Edge Structure (XANES) spectroscopy analysis.

- Six (6) additional samples were sent to Canadian Light Source (CLS) for analysis.
    - The TSP and PM10 air filters from the Travers Street location for June 8th
    - The TSP and PM10 air filters from the Copper Cliff station for June 8th
    - A dust sample from Falconbridge which was previously reported by SEM to contain nickel subsulphide
    - An air filter from an urban Ontario city during a higher particulate day, for comparison purposes

Results of the CLS analyses indicated:

- There is no nickel subsulphide present in the dust sample. The sulphur structures present appear to be sulphates and an organic sulphur species (e.g., a thiol, disulphide, or thiophene).
- The majority of the sulphur present in the air filters is in sulphate form.
- Only the TSP and PM10 filters from the Travers Street station showed the presence of sulphide. The Copper Cliff station did not show any sulphide present.
- Analyses of the sulphide present in the Travers Street samples (11 to 16% of total) indicates it more closely resembles nickel sulphide than nickel subsulphide.

Dr. Lamoureux's Analyses

- Seven (7) air filters from the Sudbury Soils Study were submitted by the MOE to Dr. Lamoureux for XANES spectroscopic analysis. These samples were selected based upon elevated levels of nickel present, while providing good coverage of the various sampling sites across the GSA.
    - The PM10 and PM2.5 air filters from the Copper Cliff station for March 10th (2 filters)
    - The PM10 air filters from the Travers Street, Garson, and Skead stations for March 10th (3 filters)
    - The PM10 and PM2.5 air filters from the Falconbridge station for October 18th (2 filters)

Results of Dr. Lamoureux's analyses indicated:

- The presence of nickel oxide and nickel sulphate was detected in all seven samples.

- However, no nickel subsulphide was found in any of the seven samples.

SGS Lakefield Research Limited

A Mineralogical Study of Speciation of Ni in two Dust- and five Air-Filter Samples: SARA Project

prepared for

THE SARA GROUP

LR 11060-004 – MI5001-MAR06
March 17, 2006

NOTE:
This report refers to the samples as received.

The practice of this Company in issuing reports of this nature is to require the recipient not to publish the report or any part thereof without the written consent of SGS Lakefield Research Limited.

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Executive Summary

Two dust samples previously analysed by SEM-techniques as surface-mounted particulates on carbon tape were re-submitted for analysis in **polished section**. The objective was to confirm whether or not Nickel-sub-sulphide ($Ni_3S_{2;}$ or Heazlewoodite) was present, as analysis in surface-mounted samples may be compromised by irregular surfaces and other influences on X-ray signal attenuation, as well as lack of discrimination of the complexity candidate particles by bombarding exteriors of particles only. In addition, five air filters were submitted to establish the variability of Ni-species collected over periods of known prevailing wind direction.

Results of the polished section investigation confirmed the presence of heazlewoodite in both dust samples. In sample 582-05-1307, a single Ni sub-sulphide grain was detected as a complex particle attached to a mixed base-metal sulphate. In decreasing order of particle frequency, accompanying Ni species included pentlandite (8), discrete base-metal sulphate particles (4), and Ni-oxides (3). In sample 602-05-1311, a single liberated heazlewoodite particle was detected, along with pentlandite (7) and Ni-oxides (5).

Heazlewoodite was encountered in three of the five air filter samples and distinctly different Ni-species assemblages were encountered.

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Introduction

Two dust samples were submitted for SEM investigation to confirm the presence of Ni-sub-sulphide (Ni_3S_2) in polished section to compare results against a previous, surface-mounted protocol. In addition, five PM10 Air filters were submitted to establish the variability of Ni-species collected over periods of known prevailing wind directions.

Procedures

The mineralogical analyses were carried out by scanning electron microscopy (SEM) using a Leo 440 SEM combined with energy dispersive X-ray spectrometry (EDS) and equipped with both a secondary electron and back-scattered electron detector. The EDS system was a light-element-capable Oxford ISIS unit providing the opportunity of identifying organic matter and easily discriminating sulphate and sulphide species.

Air filter samples were cut and mounted directly on a SEM plate, while soil and dust samples were prepared as polished sections. Two polished sections of each dust sample were prepared by mixing samples in chlorinated epoxy resin and ground and polished using diamond pastes on different cloths to avoid cross-contamination. After preparation, all samples were carbon-coated to render surfaces conductive under the electron beam.

SEM Operating conditions were 25 kV accelerating voltage and 3 nA incident specimen current. Qualitative mineral identifications were made using 10 second counting times and semi-automated, systematic scans of sample surfaces were performed, stopping at candidate particles to identify and characterize grains when Ni species were encountered. For each particle, measurements, qualitative identifications as well as photomicrographs were taken. For each scan, a target population of 30 occurrences were sought in an allotted 3 hour search period.

Results – Dust Samples

Appendix 1 provides raw data for the dust samples and Figures 1 and 2 illustrate particles of interest supporting the presence of Ni-sub-sulphide. Figure 1 specifically shows heazlewoodite in association with a complex, mixed base-metal sulphate particle (Fig. 1A) and discrete base-metal sulphate particle (Fig 1B) in sample 582-05-1307. Figure 2 shows liberated heazlewoodite (Fig. 2A) and a particle of Ni-oxide with an attached Cu-Sulphide (of composition approximating Cu_2S) in sample 602-05-1311. No sulphates were found in the latter sample and the association of Ni-oxide and Cu-sulphide is consistent with derivation from smelter emissions. (In this regard, Cu_2S and heazlewoodite are the primary sulphides formed in smelting.)

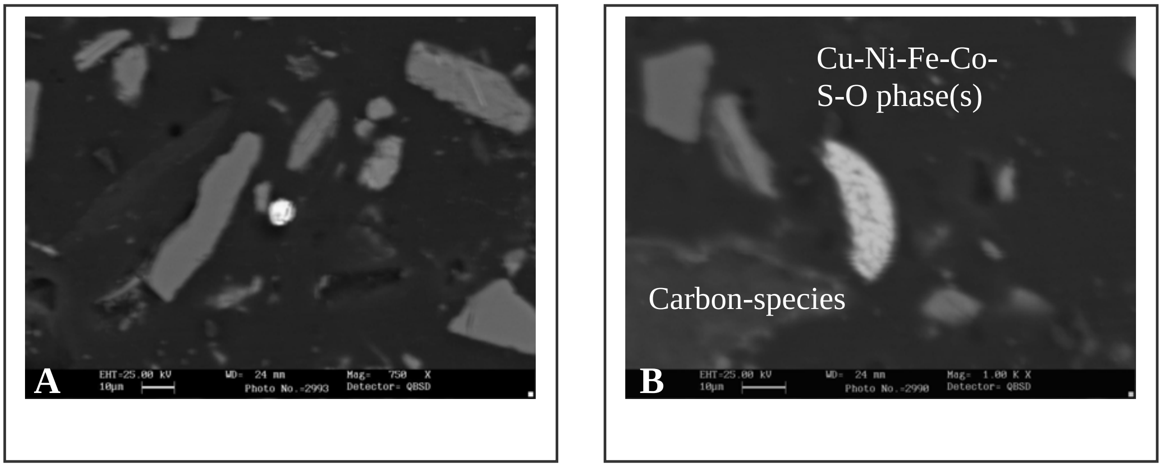

Figure 1. SEM/BSE photomicrographs of: (A) Ni_3S_2 (bright, rounded grain) and (B) A complex, Cu-Fe-Ni-Co-sulphate: **Sample 582-05-1307**. Note the arcuate shape of the latter particle, as well as the lower BSE signal intensity relative to the heazlewoodite.

Appendix 2 shows high-magnification views of the two heazlewoodite grains found in the dust samples, along with EDS spectra and compositional evidence in support of the identification of Ni_3S_2.

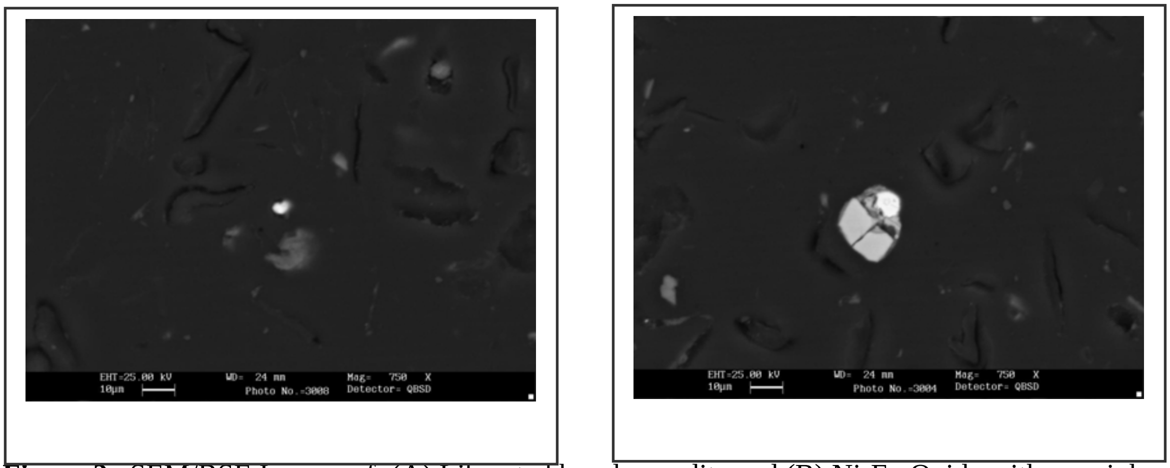

Figure 2. SEM/BSE Images of: (A) Liberated heazlewoodite and (B) Ni-Fe-Oxide with a peripheral inclusion of sub-rounded Cu_2S: **Sample 602-05-1311**. Note the similar BSE signal intensity of the Ni-sulphide and Cu-sulphide.

Results – Air Filter Samples

Air filter sample data are presented in Appendix 3 and data are summarized in Table 1. To assist in correlating between the Ni-assemblage and the nature of particulate matter, Figure 3 shows photomicrographs of arbitrarily selected regions of the filters to demonstrate loadings of particulates on filters.

Table 1. Summary of Ni-species detected in the analysed air filter samples. Candidate Ni-sub-sulphides in doubt are noted in parentheses. Ni-oxides include true, simple oxides with and without Fe and may include species of doubtful chemistry, while the "Ni-other" category includes Cu-Ni-O species which may include undetected light elements. MS denotes mixed-metal-sulphides without oxygen, possibly sulphide-matte.

Air Filter Sample	**Ni_3S_2**	**Pentlandite**	**MS**	**Mixed Sulphates**	**Ni-Sulphates**	**Ni-Oxide**	**Ni-Other**
TRA-JAN 04.04	n.d	n.d.		24	6	n.d.	n.d.
TRA-MAR 10.04	3	5		6	7	4	3
TRA-JUL 02.04	n.d.	12		11	3	3	1
TRA-NOV 29.03	2(1)	18		n.d.	n.d.	7	n.d.
TRA-SEP 30.04	7	2	13	n.d.	n.d.	5	

Ranked in the same sample sequence as tabulated, other points of interest are as follows:

Sample TRA-JAN 04.04:

1. Chlorine was detected in, or accompanying, many of the sulphate particles, as well as thin films of unresolved chlorides on silica-fibres.
2. The average particle size of quantified sulphate species was 2.2 micrometers.
3. Two broad compositional groups of sulphate were found, one predominantly Ni-bearing with traces of Co, Fe and Cu, and the other with Cu and Ni in significant, but variable proportions. The latter group is clearly a mixed sulphate unresolvable in this SEM study.

Sample TRA-MAR 10.04:

4. Chlorine was also detected along with several sulphate particles.
5. The average particle size of quantified sulphate species was 3.4 micrometers.
6. Two broad compositional groups of Ni-sulphate were also found and Ni- and Ni-Cu species with oxygen detected. Variable carbon signals were witnessed, it is not possible to positively identify these species as simple oxides, carbonyls or otherwise.

Sample TRA-JUL 02.04:

7. Ni- and other sulphates have a distinctly rhombic and twinned morphology.
8. Levels of Cu are low but ubiquitous in most sulphates.
9. Fe levels are higher in general relative to previous samples.
10. The average size of analysed particles was 3 micrometers.
11. No Chlorine was detected in analysed particles.

Sample TRA-NOV 29.03:

12. No discrete sulphates were detected, nor any chlorides.
13. Cu-sulphide was also detected, with a composition close to Cu_2S.
14. The first candidate heazlewoodite is very small and lies at depth in the filter. No oxygen was detected, but a mineral chemistry of Ni_3S_2 was returned by SEM/EDS. The second candidate heazlewoodite was confirmed as a sulphide mineral and had a distinct Ni-sulphate attachment.
15. Relative to all other samples, the mineral assemblage is predominantly concentrate-mineral rich.

Sample TRA-SEP 30.04:

16. Cu-metal and Cu-sulphide (Cu_2S) were detected, indicative of smelter-derivation. Fayalite and magnetite were also common, supporting the above, since Fe_2SiO_4 and Fe_3O_4 are known smelter products. In this respect, it is unsurprising that this sample represents the sample with the highest number of heazlewoodite grains.

17. Mixed metal sulphides are dominant in this sample, with substantially variable metal compositions and with no oxygen. Cobalt is present in this sulphide material at about 1% by semi-quantitative SEM/EDS analysis. This is considered to be a sulphide matte species (Figure 3).

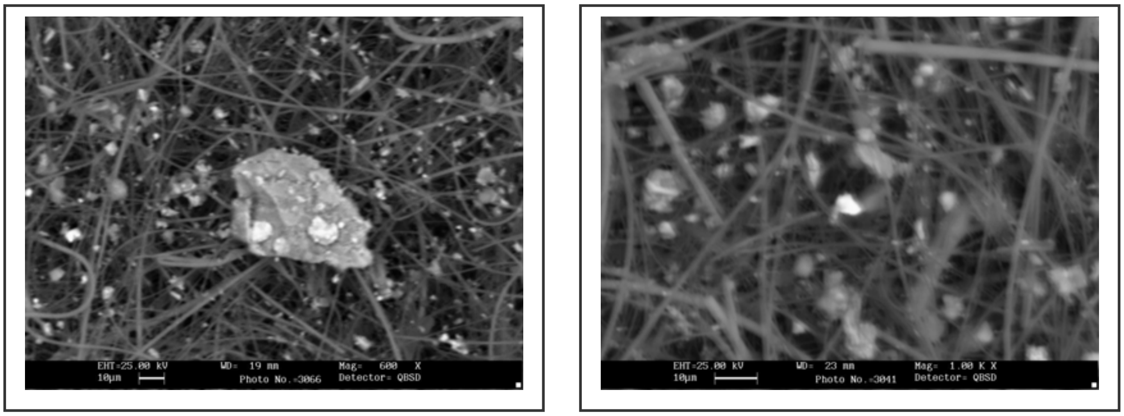

Figure 3. SEM/BSE Images of: (A) Unresolved metal-sulphides, probably matte, at the surface of an angular Fe-silicate particle with duller Fe-oxides relative to sulphide. (B) Probable heazlewoodite with abundant accompanying Fe-oxides. Sample **TRA-SEP-30-04 PM10**.

Conclusions

The present investigation revealed the following results:

1. A single grain of heazlewoodite, or Ni-sub-sulphide (Ni_3S_2) was detected in polished section analysis of both dust samples, confirming the presence as suggested by previous SEM analysis.

2. Using the surface-based SEM analysis method directly on the submitted PM10 air filters, heazlewoodite was found in three of the five submitted samples.

3. In addition, though limited by statistical constraints, air filter results demonstrate distinct overall differences in average Ni-species and presence of Cu_2S correlates with that of heazlewoodite.

APPENDIX 1 : Summary Data for SEM Candidate Particles

(Based on 3-hour scan time or 30 candidate particle-threshold)

SAMPLE **582-05-1307**

Site #	Gr #	Loc. (SEM)		Photo ID	Grain Data												Host Particle Data			
		X	Y		Occurrence	Association	Major	Mod	Minor	ID	Meas. X (um)	Meas. Y (um)	area (um2)	Grain ECD (um)	% distr	Host Phase	Meas. X (um)	Meas Y (um)	Meas area (um2)	ECD. (um)
1	1	12.62	11.09	21031-1	Liberated		As, Fe, S			Arsenopyrite	4.8	4.8	22.8	5.4	1.2					
2	1	14.76	11.25	21031-2	Liberated		Ni, Fe, S			Pentlandite	4.4	5.4	23.9	5.5	1.3					
3	1	15.24	11.14	21031-3	Liberated		Fe	O	Ni, Si	Fe>Ni-Oxide	9.6	8.8	83.9	10.3	4.5					
4	1	19.95	11.11	21031-4	Liberated		Cu		O	Cu-O	3.8	5.2	19.5	5.0	1.0					
5	1	20.11	13.45		Liberated		Fe, Ni, S			Pentlandite	11.1	5.0	55.1	8.4	3.0					
6	1	21.22	14.44		Liberated		Fe, Ni, S			Pentlandite	11.9	7.3	86.6	10.5	4.7					
7	1	19.3	15.05		Liberated		Pb, S		O	Anglesite(?)	6.8	2.7	18.0	4.8	1.0					
8	1	19.48	15.85		Liberated		S,Fe,Cu			Chalcopyrite	9.8	9.2	89.9	10.7	4.8					
9	1	14.52	19.7	21031-5	Liberated		Fe, O	Ni		Fe>Ni-Oxide	23.0	14.2	326.9	20.4	17.6					
10	1	19.04	20.04	21031-6	Liberated		Fe, O	NI		Fe>Ni-Oxide	16.5	16.9	278.7	18.8	15.0					
11	1	14.8	21.51	21031-7	Liberated		Fe, Ni, S			Pentlandite	4.6	4.9	22.5	5.4	1.2					
12	1	15.08	23.23	21031-8	Liberated		Fe, Ni, S			Pentlandite	4.7	6.1	28.5	6.0	1.5					
13	1	50.3	10.89	21037-1	Liberated		Fe, Cu	S	Ni,O,Co	BM-Sulphate	33.2	11.7	387.4	22.2	20.9					
14	1	50.52	16.09	21037-2	Liberated		Fe, Cu, S		Ni,O,Co	BM-Sulphate	8.1	7.8	62.9	9.0	3.4					
15	1	47.9	18.25	21037-3	Liberated		Fe, Ni, S			Pentlandite	5.4	9.0	48.5	7.9	2.6					
16	1	54.43	18.66	21037-4	Attached/Complex grain		Ni, S	Fe		Ni3S2	7.2	2.7	19.4	5.0	1.0					
	2	54.43	18.66	21037-4	Attached/Complex grain		Ni,Cu,Fe	S	O,Co	BM-Sulphate	7.7	5.1	39.2	7.1	2.1					
17	1	47.84	20.88	21037-5	Liberated		Ni	Fe	O	Ni>Fe-Oxide	2.7	3.1	8.2	3.2	0.4					
18	1	49.54	22.24	21037-6	Attached to Cr-Fe-Nd-Oxide		Fe, Ni, S	Cu,O	Co	BM-Sulphate	12.5	6.7	83.9	10.3	4.5	Cr, Fe, Nd, O	13.4	12.27	164.42	14.5
19	1	45.86	23.33	21037-7	Liberated		Fe, Ni, S			Pentlandite	10.3	7.7	78.7	10.0	4.2					
20	1	45.87	23.34	21037-8	Liberated		Fe, Ni, S			Pentlandite	9.7	7.4	71.4	9.5	3.8					
										Sum/Avg.			1856.2	9.3	100.0					

SAMPLE **602-05-1311**

Site #	Gr #	Loc. (SEM)		Photo ID	Grain Data											Host particle Data				
		X	Y		Occurrence	Association	Major	Mod	Minor	ID	Meas. X (um)	Meas. Y (um)	area (um2)	Grain ECD (um)	% distr	Host Phase	Meas. X (um)	Meas Y (um)	Meas area (um2)	ECD. (um)
1	1	85.12	9.54	21032-1	Liberated		Ni		O	Ni-Oxide	7.84	7.54	59.1	8.7	3.0					
2	1	84.06	9.94	21032-2	Liberated		Fe, Ni, S			Pentlandite	14.97	4.24	63.5	9.0	3.2					
3	1	77.88	11.06	21032-3	Liberated		Fe, Ni, S			Pentlandite	6.88	6.22	42.8	7.4	2.1					
4	1	88.74	13.65	21032-4	Liberated		Ni		O	Ni-Oxide	8.12	15.52	126.0	12.7	6.3					
5	1	83.66	13.62	21032-5	Liberated		Fe, Ni, S			Pentlandite	6.36	9.9	63.0	9.0	3.2					
6	1	85.21	13.94	21032-6	Inclusion		Fe	O	Ni	Fe.Ni-Oxide	20.6	17.21	354.5	21.3	17.8	Cu2S	6.65	4.06	27.00	5.9
7	1	83.78	15.42	21032-7	Liberated		Fe, Ni, S			Pentlandite	9.04	9.45	85.4	10.4	4.3					
8	1	79.58	15.82	21032-8	Liberated		Fe, Ni, S			Pentlandite	7.15	5.66	40.5	7.2	2.0					
9	1	87.4	16.2	21032-9	Liberated	Ni (99), Fe (1)	Ni	O	Fe	Ni>Fe-Oxide	10.89	11.6	126.3	12.7	6.3					
10	1	82.71	16.32	21032-10	Liberated		Ni, S			Ni3S2	4.02	5.05	20.3	5.1	1.0					
11	1	83.85	20.13	21032-11	Liberated		Fe, Ni, S			Pentlandite	29.11	13.47	392.1	22.3	19.7					
12	1	77.03	21.94	21032-12	Liberated		Ni		O	Ni-Oxide	10.85	7.19	78.0	10.0	3.9					
13	1	83.65	13.62	21038-1	Liberated		Fe, Ni, S			Pentlandite	6.79	9.47	64.3	9.1	3.2					
14	1	83.86	20.13	21038-2	Liberated		Fe, Ni, S			Pentlandite	29.15	16.36	476.9	24.6	23.9					
										Sum/Avg.			1992.7	12.1	100.0					

SAMPLE **TRA JAN 04.04 PM10**

Site #	Gr #	Loc. (SEM)		Photo ID	Species/Particle Data											Host Particle Data				
		X	Y		Occurance	Association	Major	Mod	Minor	ID	Meas. X (um)	Meas. Y (um)	area (um2)	Grain ECD (um)	% distr	Host Phase	BMS ESD (um)	Host Meas X (um)	Host Meas Y (um)	Host Meas area (um2)
1	1	76.72	70.36	JAN04-1			Ni	Cu	Fe, S, O	BM-Sulphate	1	2	2.0	1.6	1.1					
2	1	76.89	70.31	JAN04-2			Ni	O	Cu, Fe	BM-Sulphate	2	3	6.0	2.8	3.4					
2	2	76.89	70.31	JAN04-2			Ni		S, O	Ni- Sulphate	1	1	1.0	1.1	0.6					
2	3	76.89	70.31	JAN04-2			Ni		S, O	Ni- Sulphate	1	1	1.0	1.1	0.6					
3	1	77.04	70.26	JAN04-3			Ni, O	Cu	Fe, S	BM-Sulphate	4	4	16.0	4.5	9.0					
4	1	77.38	70.24	JAN04-4			Ni	Cu, O	Fe, S	BM-Sulphate	2	2	4.0	2.3	2.2					
4	2	77.38	70.24	JAN04-4			Ni, O	Cu	Fe, S	BM-Sulphate	2	2	4.0	2.3	2.2					
5	1	77.92	70.34	JAN04-5			Ni, O		Cu, Fe, S	BM-Sulphate	1	1	1.0	1.1	0.6					
6	1	79.16	70.75	JAN04-6			Ni, O		Cu, Fe, S	BM-Sulphate	1	1	1.0	1.1	0.6					
6	2	79.16	70.75	JAN04-6			Ni, Cu, O	S	Fe	BM-Sulphate	1	1	1.0	1.1	0.6					
7	1	77.5	70.67	JAN04-7			Ni, O		Cu, S	BM-Sulphate	1	1	1.0	1.1	0.6					
7	2	77.5	70.67	JAN04-7			Ni, O		Cu, S	BM-Sulphate	2	2	4.0	2.3	2.2					
8	1	76.91	70.73	JAN04-8			Ni, O	Cu	Fe, S	BM-Sulphate	2	2	4.0	2.3	2.2					
8	2	76.91	70.73	JAN04-8			Ni, O	Cu	Fe, S	BM-Sulphate	2	2	4.0	2.3	2.2					
9	1	76.43	70.59	JAN04-9			Ni, O		S,Fe, Cu	Ni- Sulphate	2	3	6.0	2.8	3.4					
10	1	76.65	70.9	JAN04-10			Ni, O	Cu	Fe, S	BM-Sulphate	2	2	4.0	2.3	2.2					
11	1	76.81	70.93	JAN04-11			Ni, O		Cu, Fe, S	Ni- Sulphate	2	2	4.0	2.3	2.2					
11	1	76.81	70.93	JAN04-11			Ni, O		Cu, Fe, S	Ni- Sulphate	1	1	1.0	1.1	0.6					
12	1	77.79	70.9	JAN04-12			Ni, O		Cu, Fe, S	Ni- Sulphate	1	2	2.0	1.6	1.1					
13	1	83.96	70.9	JAN04-13			Ni, O	Cu	Fe, S	BM-Sulphate	1	1	1.0	1.1	0.6					
14	2	84	70.92	JAN04-14			Ni, O	Cu	Fe, S	BM-Sulphate	1	6	6.0	2.8	3.4					
14	1	84	70.92	JAN04-14			Ni, O	Cu	Fe, S	BM-Sulphate	1	1	1.0	1.1	0.6					
15	2	81.9	71.27	JAN04-15			Ni, O	Cu	Fe, S	BM-Sulphate	2	2	4.0	2.3	2.2					
15	1	81.9	71.27	JAN04-15			Ni, O	Cu	Fe, S	BM-Sulphate	1	1	1.0	1.1	0.6					
16	1	80.85	71.31	JAN04-16			Ni	O, Cu	Fe, S	BM-Sulphate	2	2	4.0	2.3	2.2					
17	1	80.16	71.14	JAN04-17			Ni, O	Cu	Fe, S	BM-Sulphate	1	2	2.0	1.6	1.1					
18	1	76.31	71.39	JAN04-18			Ni	O, Cu	Fe, S	BM-Sulphate	3	6	18.0	4.8	10.1					
19	1	76.43	71.38	JAN04-19			Ni, O	Cu	Fe, S	BM-Sulphate	2	2	4.0	2.3	2.2					
20	2	76.47	71.45	JAN04-20			Ni	Cu	Fe, O, S	BM-Sulphate	3	5	15.0	4.4	8.4					
20	1	76.47	71.45	JAN04-20			Ni, O	Cu	Fe, S	BM-Sulphate	2	2	4.0	2.3	2.2					
21	1	77.62	71.61	JAN04-21			Ni	Cu	Fe, S	BM-Sulphate	2	2	4.0	2.3	2.2					
22	1	78.82	71.44	JAN04-22			Ni, O	S, Cu	Fe	BM-Sulphate	2	2	4.0	2.3	2.2					
23	1	81.96	71.54	JAN04-23			Ni, O, Cu	S	Fe	BM-Sulphate	1	3	3.0	2.0	1.7					
24	1	81.89	71.61	JAN04-24			Ni,O	Cu, S	Fe,Co,Cl	Co,Fe,Cu,Ni-Sulphate+Cl	3	4	12.0	3.9	6.7					
25	1	82.52	71.54	JAN04-25			Ni	Cu	Fe, S	BM-Sulphate	4	3	12.0	3.9	6.7					
26	1	83.84	71.55	JAN04-26			Ni, O	Cu	S, Fe	BM-Sulphate	2	2	4.0	2.3	2.2					
27	1	84.6	71.51	JAN04-27			Ni	O, Cu	S	BM-Sulphate	2	2	4.0	2.3	2.2					
28	1	85.51	71.81	JAN04-28			Ni, O	Cu, S	Fe	BM-Sulphate	2	2	4.0	2.3	2.2					
29	1	82.82	71.76	JAN04-29			Ni, O	Cu	S, Fe	BM-Sulphate	2	2	4.0	2.3	2.2					
30	1	82.65	71.75	JAN04-30			Ni	O, Cu	S, Fe	BM-Sulphate	2	4	8.0	3.2	4.5					
										Sum/Avg.			178.0	2.2	100.0					

LIMS **DATE**

SAMPLE **TRA JUL 02.04 PM10**

Site #	Gr #	Loc. (SEM)		Photo ID	Particle Data											Host Particle Data					
		X	Y		Occurrence	Association	Major	Mod	Minor	ID	X (um)	Y (um)	area (um2)	Grain ECD (um)	% distr	Host Phase	BMS ESD (um)	Host Meas. X (um)	Host Meas Y (um)	Host Meas area (um2)	Host ECD. (um)
1	1	41.71	40.21				Ni, Fe, S			Pentlandite	8	6	48.0	7.8	17.1						
2	1	42.02	40.18				Ni, Fe, S			Pentlandite	2	2	4.0	2.3	1.4						
3	1	53.87	40.56				Fe, Cu	Ni	O,S	BM-Sulphate	4	4	16.0	4.5	5.7						
4	1	49.78	40.64				Fe, S	O	Ni	BM-Sulphate	2	2	4.0	2.3	1.4						
5	1	54.33	40.81	JUL02-1			Ni		O	Ni Oxide	2	2	4.0	2.3	1.4						
6	1	54.45	40.91				Cu	Fe, Ni, S	O	BM-Sulphate	1	14	14.0	4.2	5.0						
7	1	54.61	40.88				Pb, S			Pb-Sulphate	5	5	25.0	5.6	8.9						
8	1	55.78	40.99				Ni		Cu,Co,Fe,O	Ni-BM-O(?)	1	1	1.0	1.1	0.4						
9	1	55.35	41.02				Ni, Fe, S			Pentlandite	3	2	6.0	2.8	2.1						
10	1	51.61	41.07				Ni, Fe, S			Pentlandite	1	2	2.0	1.6	0.7						
11	1	49.41	41.04				Fe, S		Ni, O	BM-Sulphate	1	2	2.0	1.6	0.7						
12	1	46.55	41				Fe, S		Ni	Pent/Po	1	2	2.0	1.6	0.7						
13	1	46.24	41.08				Ni, Fe, S			Pentlandite	1	1	1.0	1.1	0.4						
14	1	45.16	40.99				Fe, Ni	Cu	S, O	Sulphate	2	3	6.0	2.8	2.1						
15	1	44.94	41.01				Ni, Fe, S			Pentlandite	2	4	8.0	3.2	2.9						
16	1	43.93	40.98				Ni		O	Ni-Oxide	2	1	2.0	1.6	0.7						
17	1	42.62	41.18				Fe	Cu,S	O,Ni	BM-Sulphate	1	1	1.0	1.1	0.4						
18	1	45.55	41.32				Fe	Cu,S	O,Ni	BM-Sulphate	2	2	4.0	2.3	1.4						
19	1	48.22	41.39				Cu, Ni	S	Fe, O	BM-Sulphate	2	2	4.0	2.3	1.4						
20	1	49.22	41.4				Fe, Ni	Cu, S, O		BM-Sulphate	5	5	25.0	5.6	8.9						
21	1	53.99	41.33				Ni, Fe, S			Pentlandite	1	1	1.0	1.1	0.4						
22	1	54.01	41.48				Ni, Fe, S			Pentlandite	2	2	4.0	2.3	1.4						
23	1	55.94	41.3	JUL02-2			Ni		Cu, S, O	Ni_Sulphate	5	5	25.0	5.6	8.9						
24	1	55.94	41.3				Ni		O	Ni-Oxide	3	3	9.0	3.4	3.2						
25	1	54.01	41.48				Ni, Fe, S			Pentlandite	3	2	6.0	2.8	2.1						
26	1	54.01	41.54	JUL02-3			Ni, S		O	Ni-Sulphate	2	2	4.0	2.3	1.4						
27	1	52.74	41.51				Cu	Fe, S	Ni, O	BM-Sulphate	2	4	8.0	3.2	2.9						
28	1	51.46	41.58	JUL02-4			Ni, S		O	Ni-Sulphate	2	2	4.0	2.3	1.4						
29	1	50.84	41.6				Ni, Fe, S			Pentlandite	4	4	16.0	4.5	5.7						
30	1	50.69	41.65				Ni, Fe, S			Pentlandite	4	6	24.0	5.5	8.6						
										Sum/Avg.			280.0	3.0	100.0						

LIMS **DATE**

SAMPLE **TRA MAR 10.04 PM10**

Site #	**Gr #**	**oc. (SEM)**		**Photo ID**	**Particle Data**											**Host Particle Data**					
		X	**Y**		**Occurrence**	**Association**	**Major**	**Mod**	**Minor**	**ID**	**Meas. X (um)**	**Meas. Y (um)**	**area (um2)**	**Grain ECD (um)**	**% distr**	**Host Phase**	**BMS ESD (um)**	**Host Meas. X (um)**	**Host Meas Y (um)**	**Host Meas area (um2)**	**Host ECD. (um)**
1	1	76.11	37.63	MAR10-1			Ni	S	O,Fe,Cu	Ni/>Fe-Sulphate	2	2	4.0	2.3	0.8						
2	1	76.39	37.56				Fe, Ni, S			Pentlandite	1	1	1.0	1.1	0.2						
3	1	76.74	37.5				Ni		Cu, O	Ni-Cu-O(?)	1	2	2.0	1.6	0.4						
4	1	77.28	37.67	MAR10-2			Ni	O	S, Cu	Ni-Sulphate	2	2	4.0	2.3	0.8						
5	1	77.36	37.73				Ni	O	S, Cu	Ni-Sulphate	1	1	1.0	1.1	0.2						
6	1	77.26	37.77				Ni, O		Cu	Ni-Sulphate	1	2	2.0	1.6	0.4						
7	1	79.26	37.54	MAR10-3			Ni, S, O			Ni-Sulphate	3	1	3.0	2.0	0.6						
8	1	90.36	37.85	MAR10-4			Ni, O			Ni-Oxide(?)	2	1	2.0	1.6	0.4						
9	1	83.35	37.97	MAR10-5			Ni, S, O			Ni-Sulphate	2	2	4.0	2.3	0.8						
10	1	75.48	37.93				Ni, O	Cu, S, Pb	Fe	BM-Sulphate	2	4	8.0	3.2	1.6						
11	1	76.77	38.41	MAR10-6			Ni		O	Ni-Oxide(?)	4	3	12.0	3.9	2.4						
12	1	78.42	38.66	MAR10-7			Ni	Cu, S	O,Pb, Fe	BM-Sulphate	2	2	4.0	2.3	0.8						
13	1	78.88	38.78				Fe, Ni, S			Pentlandite	15	15	225.0	16.9	45.0						
14	1	82.2	38.68	MAR10-8			Ni, S	O	Fe	Ni.Fe-Sulphate]	8	8	64.0	9.0	12.8						
15	1	83.17	38.69	MAR10-9			Ni, S			**Ni3S2**	2	5	10.0	3.6	2.0						
16	1	84.29	38.64	MAR10-10			Ni		O	Ni-Oxide(?)	4	2	8.0	3.2	1.6						
17	1	90.36	38.68	MAR10-11			Ni, S	Cu, Pb	Fe	BM-Sulphate	2	2	4.0	2.3	0.8						
18	1	90.04	39.11				Cu, S			Cu2S	4	4	16.0	4.5	3.2						
19	1	82.08	38.98	MAR10-12			Ni, O		Fe	Ni>Fe-Oxide	2	2	4.0	2.3	0.8						
20	1	80.24	38.94				Cu, Ni		O,Pb, S	Ni-Cu-O(?)	2	2	4.0	2.3	0.8						
21	1	78.36	39.11				Ni, Pb		Cl, S	BM-Sulphate	6	6	36.0	6.8	7.2						
22	1	77.88	39.31	MAR10-13			Ni, S			**Ni3S2**	1	1	1.0	1.1	0.2						
23	1	86.02	39.47				Fe, Ni, S			Pentlandite	3	6	18.0	4.8	3.6						
24	1	84.03	39.64				Cu, S			Cu2S	1	3	3.0	2.0	0.6						
25	1	78.75	39.63	MAR10-14			Ni, S			**Ni3S2**	2	2	4.0	2.3	0.8						
26	1	74.87	39.55				Fe, Ni, S			Pentlandite	2	2	4.0	2.3	0.8						
27	1	75.7	39.79				Fe	Ni, S	O,Cu	BM-Sulphate	4	2	8.0	3.2	1.6						
28	1	76.36	39.78				Fe, Ni, S			Pentlandite	6	6	36.0	6.8	7.2						
29	1	76.86	39.83				Ni		O,Cu	Ni-Cu-Ox(?)	2	2	4.0	2.3	0.8						
30	1	78.32	39.94	MAR10-15			Ni, S		Fe,O, Cu	BM-Sulphate	2	2	4.0	2.3	0.8						
										Sum/Avg.			500.0	3.4	100.0						

SAMPLE **TRA NOV 29.03 PM10**

Site #	Gr #	Loc. (SEM)		Photo ID	Particle Data											Host Particle Data				
		X	Y		Occurrence	Association	Major	Mod	Minor	ID	Meas. X (um)	Meas. Y (um)	area (um2)	Grain ECD (um)	% distr	Host Phase	Host Meas. X (um)	Host Meas Y (um)	Host Meas area (um2)	Host ECD. (um)
1	1	43.2	72.8	NOV29-1			Ni	O	Fe	Ni>Fe-Oxide	4	4	16.0	4.5	2.7					
2	1	43.2	72.89				Fe, Ni, S			Pentlandite	4	4	16.0	4.5	2.7					
3	1	44.7	72.86	NOV29-2			Ni, S			**Ni3S2**	1	2	2.0	1.6	0.3					
4	1	44.6	72.96				Fe, Ni, S			Pentlandite	8	8	64.0	9.0	10.9					
5	1	44.9	72.75				Ni, Cu		S, Fe, Cl	MS(C)l?	4	4	16.0	4.5	2.7					
6	1	46.9	72.87				Fe, Ni, S			Pentlandite	3	3	9.0	3.4	1.5					
7	1	46.5	73				Fe, Ni, S			Pentlandite	6	4	24.0	5.5	4.1					
8	1	50.6	72.82	NOV29-3			Ni		O	Ni-Oxide	10	6	60.0	8.7	10.3					
9	1	54.2	72.71				Fe	Ni	Cu, S	CuS/Fe-Ni-Ox	4	4	16.0	4.5	2.7					
10	1	54.4	72.73	NOV29-4			Ni		O	Ni-Oxide	6	6	36.0	6.8	6.2					
11	1	54.9	72.6				Fe, Ni, S			Pentlandite	2	2	4.0	2.3	0.7					
12	1	56.1	72.79				Fe, Ni, S		Cu	Pentlandite + Cp?	2	2	4.0	2.3	0.7					
13	1	57.3	72.74				Fe, Ni, S			Pentlandite	2	2	4.0	2.3	0.7					
14	1	56.3	73.01				Fe, Ni, S			Pentlandite	1	1	1.0	1.1	0.2					
15	1	56.3	73.01	NOV29-5			Ni		O	Ni-Oxide	2	2	4.0	2.3	0.7					
16	1	56.3	73.08				Fe, Ni, S			Pentlandite	1	4	4.0	2.3	0.7					
17	1	52.4	73.16				Fe, Ni, S			Pentlandite	4	4	16.0	4.5	2.7					
18	1	49.8	73.02				Fe, Ni, S			Pentlandite	2	2	4.0	2.3	0.7					
19	1	49.1	73.07				Fe, Ni, S			Pentlandite	2	2	4.0	2.3	0.7					
20	1	44.6	72.96				Fe, Ni, S			Pentlandite	10	10	100.0	11.3	17.1					
21	1	42.8	73.08				Fe, Ni, S			Pentlandite	6	10	60.0	8.7	10.3					
22	1	45.4	73.49	NOV29-6			Se	Cu	O	Cu-Se-O	2	2	4.0	2.3	0.7					
23	1	46.1	73.3				Fe, Ni, S			Pentlandite	1	1	1.0	1.1	0.2					
24	1	46.9	73.28				Fe, Ni, S			Pentlandite	2	2	4.0	2.3	0.7					
25	1	49.9	73.36				Cu, S			Cu2S	2	2	4.0	2.3	0.7					
26	1	57.2	73.44	NOV29-7			Ni		O	Ni-Oxide	2	4	8.0	3.2	1.4					
27	1	57	73.72				Fe, Ni, S			Pentlandite	2	4	8.0	3.2	1.4					
28	1	56.4	73.6	NOV29-8			Ni		O	Ni-Oxide	6	6	36.0	6.8	6.2					
29	1	55.8	73.69				Fe, Ni, S			Pentlandite	4	4	16.0	4.5	2.7					
30	1	53.8	73.57	NOV29-9			Ni, S		Co	**Ni3S2**	6	6	36.0	6.8	6.2					
30	2	53.8	73.57	NOV29-9			Ni		O	Ni-Oxide	2	2	4.0	2.3	0.7					
										Sum/Avg.			585.0	4.2	100.0					

LIMS **DATE**

SAMPLE **TRA SEP 0.04 PM10** FRACTION

Site #	Gr #	Loc. (SEM)		Photo ID	Particle Data											Host Particle Data				
		X	Y		Occurrence	Association	Major	Mod	Minor	ID	Meas. X (um)	Meas. Y (um)	area (um2)	Grain ECD (um)	% distr	Host Phase	Host Meas. X (um)	Host Meas Y (um)	Host Meas area (um2)	Host ECD. (um)
1	1	9.06	75.51				Cu	Fe, S	Ni	MS	1	2	2.0	1.6	0.2					
2	1	9.75	75.59	SEP30-1			Ni, S			**Ni3S2**	2	2	4.0	2.3	0.4					
3	1	971	75.7				Cu, S	Fe	Ni	MS	6	6	36.0	6.8	3.2					
4	1	9.71	75.7				Cu, S	Fe	Ni	MS	2	2	4.0	2.3	0.4					
5	1	10.21	75.5	SEP30-2			Ni		O	Ni- Oxide	30	25	750.0	30.9	66.4					
6	1	10.49	75.45				Cu, S			Cu2S	6	4	24.0	5.5	2.1					
7	1	10.77	75.59				Fe, Cu, S	Ni		MS	2	2	4.0	2.3	0.4					
8	1	12	75.45				Fe, Ni, S			Pentlandite	2	2	4.0	2.3	0.4					
9	1	11.88	75.38				Cu, S			Cu2S	6	6	36.0	6.8	3.2					
10	1	12.08	75.53	SEP30-3			Ni		O	Ni-Oxide	2	2	4.0	2.3	0.4					
11	1	12.58	75.55	SEP30-4			Ni, S		Fe	**Ni3S2**	3	3	9.0	3.4	0.8					
12	1	12.86	75.45				Fe, Ni, S		Cu	MS	10	10	100.0	11.3	8.8					
13	1	13.15	75.53				Fe	Cu	Ni, S	MS/Mt	2	2	4.0	2.3	0.4					
14	1	13.32	75.62				Fe	Ni, S	Cu	MS/Mt	5	5	25.0	5.6	2.2					
15	1	14.56	75.39				Cu, S	Fe	Ni	MS	1	2	2.0	1.6	0.2					
16	1	15.49	75.44				Cu, Ni	Fe, S		MS	2	2	4.0	2.3	0.4					
17	1	17.7	75.45	SEP30-5			Ni		O	Ni-Oxide	2	2	4.0	2.3	0.4					
18	1	17.67	75.49				Cu, S			Cu2S	2	2	4.0	2.3	0.4					
19	1	19.17	75.5	SEP30-6			Ni, S		Fe	**Ni3S2**	4	2	8.0	3.2	0.7					
20	1	19.92	75.49				Cu	Fe, S	Ni	MS	4	2	8.0	3.2	0.7					
21	1	20.36	75.54	SEP30-7			Ni, S	O	Fe	**Ni3S2**	2	2	4.0	2.3	0.4					
22	1	20.36	75.54	SEP30-8			Ni, S		Fe	**Ni3S2**	2	2	4.0	2.3	0.4					
23	2	20.78	75.5				Cu			Metal	4	4	16.0	4.5	1.4					
23	1	20.78	75.5	SEP30-9			Ni, S		Fe	**Ni3S2**	2	2	4.0	2.3	0.4					
24	1	23.16	75.43				Cu, S	Fe	Ni	MS	3	2	6.0	2.8	0.5					
25	1	24.08	75.4	SEP30-10			Ni	O	Fe	Ni-Oxide	4	2	8.0	3.2	0.7					
26	1	25	75.37				Cu, S	Fe	Ni	MS	2	2	4.0	2.3	0.4					
27	1	25.73	75.49				Ni, Fe, S			Pentlandite	2	2	4.0	2.3	0.4					
28	1	22.65	75.87				Fe, Ni, Cu, S			MS	4	4	16.0	4.5	1.4					
29	1	19.2	75.79	SEP30-11			Ni, S		Fe	**Ni3S2**	6	4	24.0	5.5	2.1					
30	1	14.54	75.69	SEP30-12			Ni		O	Ni-Oxide	2	2	4.0	2.3	0.4					
										Sum/Avg.			1130.0	4.3	100.0					

Glenn Ferguson
Program director/Senior Scientist
Cantox Environmental

Canadian Light Source
Centre canadien de rayonnement synchrotron

17-April-06

Dear Glenn,

Please find enclosed a report on the measurements carried out on dust and air filter samples at the National Synchrotron Light Source (NSLS, [http://www.nsls.bnl.gov/]) at Brookhaven National Laboratory (BNL) in April, 2006 and at the Synchrotron Radiation Center (SRC, [http://www.src.wisc.edu/]) at the University of Wisconsin-Madison, in March, 2006. A description of all sample and reference compounds, as well as the measurement parameters are listed in Tables 1 and 2.

The measurements were focused on identifying the sulfur nickel speciation in the air filter samples provided using X-ray Absorption Near-Edge Structure (XANES) spectroscopy at the Ni and S K-edge.

Aerosol sample 722 and dust sample 822 were previously measured at the sulfur K-edge (last report).

Briefly, it was found that the air filter samples contained large quantities of sulfate and the primary mineral pyrrhotite. The dust samples were a little more complicated with respect to their sulfur and nickel speciation. The dust contained sulfur in sulfate form and sulfur in organic forms. Most of the nickel in the dust and air filter samples was present as nickel oxide and nickel sulfate.

If you have questions about the report or if there is any aspect of the report you would like clarified or expanded upon please contact me.

Sincerely,

Jeff Warner

Jeff Warner, Ph.D
Industrial Liaison Scientist
Canadian Light Source, Inc.
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Speciation of 10 Interior Dust and Air Filter Samples using Ni and S K-edge XANES Spectroscopy

April 17, 2006

Introduction

The experimental and theoretical details of x-ray absorption near edge structure (XANES) spectroscopy have been described in the literature (Stern and Heald, 1983). The technique has gained popularity recently due to increased accessibility to synchrotron radiation and advances in the state of XAS theory and data analysis methods.

Unfortunately, the analytical power of the above techniques is diminished when the system under investigation is a heterogeneous mixture of species. In this situation, each absorbing element may have different local coordination environments. This complicates the analysis because the number of structural parameters needed to describe the data properly may exceed the number of independent data points in the experimental spectrum. One method which has been developed to analyze complex mixtures is least squares linear combinations of model compound spectra to fit an unknown sample spectrum (O'Day, et al., 2004; Ressler, 2000).

Sample Descriptions

The standard and unknown samples were measured at the S K-edge and at the Ni K-edge samples. Sulfur K-edge measurements were measured at the CSRF double crystal beamline (1500-4000 eV) at the Synchrotron Radiation Center (SRC), University of Wisconsin, Madison. The SRC operates at 800 MeV with currents of 260 mA. Nickel K-edge measurements were measured on beamline X11A at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory, NY. The NSLS operates at 2.8 GeV with currents of 280 mA.

XANES measurements were made on a total of twelve unknown samples (Tables 1 and 2) consisting of five nickel-bearing air-filter samples with designations TRA JUL02.04PM10, TRA MAR10.04PM10, TRA SEP30.04PM10, TRA NOV29.03PM10. TRA JAN04.04PM10, and air filter sample [200 4040722]. In adddition, five dust samples with designations, 502 57824, 523 57797, 582 05-1307, 600 57810, 602 05-1311 and dust sample [540 57822] were measured. Portions of the air filter not exposed to particulate were used as blanks.

Materials and Methods

Ni K-edge (8333 eV) spectra were recorded on beamline X11A at the NSLS at Brookhaven National Laboratory. The storage ring was operating at 2.8 GeV with a current of 280 mA. Beamline X11A utilizes a 1.36 T bending magnet as a source. The beamline was equipped with a Si(111) double crystal monochromator. Higher harmonics of the incident beam were rejected by detuning the second monochromator crystal by 50% for nickel. Entrance slits defined the beam size at 0.8x9 mm.

Transmission data were collected from powder samples diluted with boron nitride (~1:20) under ambient pressure and temperature. Unknown compound spectra were collected using a fluorescence ion chamber detector (Lytle et al., 1984) filled with argon gas and employing a Co (3 μ absorbance) filter and Soller slits to minimize unwanted elastic scattering. X11A was calibrated using Ni foil, defining the Ni K-edge at 8333 eV (McMaster et al., 1969).

Sulfur K-edge (2472 eV) spectra were recorded on the high vacuum DCM beamline at the SRC located at the University of Wisconsin, Madison. The storage ring, Aladdin, was operating at 800 MeV with a current of 260 mA. The DCM beamline utilizes InSb monochromator crystals over the energy range 1500 – 4000 eV. Spectra were collected in fluorescence mode using a 9 element Ge detector. The DCM was calibrated using freshly cleaved pyrite.

Air filter samples were prepared by carefully cutting strips of air filter (~3x10 mm) while wearing gloves and loading these in a Teflon sample holder contained using kapton tape. Spectra contained in this report were obtained on five such strips layered together.

Raw Ni K-edge and S K-edge data were processed using the program *Athena* (v. 0.8.045; Ravel and Newville, 2005). Least squares linear combination fits were applied to the XANES spectra also using the program SixPack (Webb, 2002).

PCA and LC Fitting

Least squares linear combination fitting was used to identify the species in the unknown samples. This technique fits the unknown spectra with weighted mixtures of model compounds. We have mentioned in previous reports that it is limited by the presence of unique spectral features in either the unknown or the model compounds. This can often limit the technique to an accuracy of ±10% depending on the number and identity of species present.

The technique was applied over two separate data ranges for the sulfur K-edge data. The unknown data could be divided into two ranges; 2464-2477 eV and 2477 to 2486 eV. Various sulfur model compounds were used to aid in identifying the sulfur speciation (Table 1). The nickel K-edge data were fit over the range 8325-8375 eV.

The data was carefully calibrated and therefore energy position of the models was not allowed to vary during the fits. The only constraint applied to the data was to fit with positive numbers. For both series of fits the reduced chi square was used to monitor the quality of the fit.

Results and Discussion

Figure 1 (top) shows the experimental beamline at the SRC. Prominent in the picture is the multi-element detector used for measuring fluorescence radiation from the unknown samples. The bottom picture in Figure 1 is the experimental set-up at beamline X11a at the National Synchrotron Light Source (NSLS).

Figure 2 shows the normalized sulfur K-edge XANES spectra for all the sulfur reference compounds measured in this investigation pentlandite ($(Fe,Ni)_9S_8$), pyrrhotite ($Fe_{1-x}S$), chalcopyrite ($CuFeS_2$), nickel sulfate ($NiSO_4.6H_2O$), nickel sulfide (NiS), nickel subsulfide (Ni_3S_2). Each of the reference compounds was tested as an appropriate component of the unknown air filter samples.

Principal component analysis (PCA) was applied to the sulfur K-edge XANES measurements. If it is assumed that the aerosols contain the same components then PCA indicates that there are two or three unique chemical species in the samples. One of the components is a sulfate species. PCA was not sensitive enough to indicate what the second or third species might be. Results from PCA applied to the dust samples resulted in more uncertainty in the number of components (as indicated by the IND function) but seemed to indicate three or four components. These results are supported by visual inspection of the aerosol and dust S K-edge spectra. The interior dust samples have more complicated spectra, in general.

PCA was also applied to the aerosol and dust Ni K-edge spectra but in general the results were more difficult to interpret. There is less variation in the energy position (chemical shift) of species at the Ni K-edge compared to the S K-edge.

Sulfur K-edge XANES

Two of the aerosol samples (Ajan0404 and Amar1004) showed no evidence for any species being present other than sulfate (Figures 3 and 4). Samples Anov2903 and Asep3004 had a small peak in the S K-edge XANES (Figures 3 and 4) at about 2470 eV. Sample Ajul0204 also shows a possible peak in this area of the spectrum but the data is noisy.

Fits of these spectra are listed in Table 3. Best fits of all the unknown aerosol samples were with sulfate and pyrrhotite ($Fe_{1-x}S$). The pyrrhotite is responsible for the small peak around 2470 eV. Several other species were tested for fits in this region including NiS, Ni_3S_2, chalcopyrite and pentlandite. Pyrrhotite gave the lowest reduced chi-square value $(\chi^2)_{red}$, a measure of the quality of the fit. The fractional weight percent of species were determined by fitting the spectra over the range 2464 to 2477 eV. The pyrrhotite fit to the data was significantly better than either nickel sulfide or nickel subsulfide.

The dust samples do not have significant absorption at 2470 eV but all show a peak centered at 2472.5 eV and some samples (D824, D307 and D797) have an additional small peak at 2475.5 eV. Sample D307 does have a shoulder around 2470 eV. The 2472.5 eV peaks fits as some form of organic sulfur, either thiophene, thiol, sulfoxide, or disulfide. In Table 3 these are grouped under thiosalicylic acid, which had approximately the same peak position as the thiophene and L-cystine model compounds used. The peak at 2475.5 eV is not represented by any of the mineral or organic model compounds measured (including pyrrhotite, chalcopyrite or the nickel sulfides – pentlandite, Ni_3S_2 or NiS) but there is significant organic sulfur present.

Sample D307 (Table 3 and Figure 5) is different from the other dust samples in that it has a low energy shoulder located at about 2470 eV. This small feature coincides with peaks characteristic of sulfides. The best fit (shown in Figure 5) is with nickel subsulfide. The total fit of D307 does not match the amplitude of the experimental data resulting in a poor fit (Figure 5), possibly due to the lack of model compounds (other sulfates, etc.) that may contribute to the total spectrum. The shape determined by the fit in Figure 5 however, does mimic the experimental data quite well. Spectral fits using nickel sulfide (NiS) and primary minerals like pentlandite, pyrrhotite and chalcopyrite had a much higher chi-squared value.

Nickel K-edge XANES

Nickel K-edge XANES spectra of model compounds are shown in Figure 6 and the unknown aerosol and dust samples in Figure 7. Results of fitting these spectra are listed in Table 4.

The Ni K-edge XANES of the aerosol and dust samples are quite similar. There is not much shifting of the main peak at 8350 eV, the major difference seems to be the peak at 8366 eV. The model compounds vary significantly more with the sulfides being quite flat and relatively featureless. As a result of this, a main feature of the fitting procedure was to add a linear component to the fits to see if this compensated for normalization differences among the compounds. Although normalization was done very carefully, slight differences in the background of the unknowns, which occurs frequently depending on their concentration, can affect the overall amplitude of the fit. Featureless spectra (like the sulfides) can then deceive the fit by merely adding amplitude and not actually being a component of the sample. Another feature of linear combination fitting (and fitting in general) is that by adding more parameters it is easier to get a better fit but this comes at the expense of surpassing the actual information content of the spectra. In most cases with tha unknown samples (Table 4), adding such a linear component eliminated the need of adding another chemical component. A wide data range, 8300 – 8407 eV, was used to fit the data because certain of the model compounds have broad peaks in the region of 8390 eV.

Table 4 lists the fitted percentages of model components to the air and dust samples as well as the reduced chi-square value for the fit. The reduced chi-square is a useful guide for choosing the appropriate fit but the lowest value is not necessarily the true fit. In Table 4 the fit with the lowest reduced chi-square is shown, if another fit was within 20% of the best fit then its fit is also shown in Table 4 (in square brackets).

The air filter samples generally contained nickel oxide and nickel sulfate. Sample Nov29.03 was also fit with nickel sulfide. The dust samples were more varied, four were fit with NiS, one with Ni_3S_2, and one (D311) did not contain any sulfate.

The fit to D822 was consistent with nickel oxide, sulfate and nickel sulfide. The S K-edge fits (last report) on this sample indicated it was about 50/50 sulfate and organic sulfur species. That fit was verified during the analysis of this data set. These results can only be made consistent with knowledge of the total amounts of Ni and S in the sample. For example it is possible that a large portion of the Ni is bound as a sulfide but this represents only a small portion of the total sulfur.

The Ni K-edge XANES spectral fit of sample D307 indicates the presence of nickel sulfide rather than nickel subsulfide. This suggests that the S K-edge fit (Table 3) that uses nickel sulfide might be the more accurate fit. Two fits are shown in Table 3 because these could not be distinguished in terms of one being better than the other.

Conclusions

Linear combination fitted values for component percentages of sulfur and nickel species are found in Tables 3 and 4, respectively. Aerosol sample 722 and dust sample 822 were previously measured at the sulfur K-edge (last report).

It was found that the air filter samples contained large quantities of sulfate and the primary mineral pyrrhotite. Dust samples contained sulfur in sulfate form and sulfur in organic forms. Most of the nickel in the dust and air filter samples was present as nickel oxide and nickel sulfate and in some cases nickel sulfide.

Acknowledgements

Use of the National Synchrotron Light Source, Brookhaven National Laboratory, was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-98CH10886.

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Table 1. Description of samples measured at the Ni K-edge at Beamline X11A (NSLS)

pure reference compounds (Ni K-edge)				
sample	**formula**	**# scans**	**detection mode**	**source**
nickel sulfide	NiS	2	transmission	Alfa Aesar
nickel metal	Ni	2	transmission	NiPERA repository
nickel carbonate	$NiCO_3$	2	transmission	Alfa Aesar
nickel subsulfide	Ni_3S_2	2	transmission	NiPERA repository
nickel sulfate	$NiSO_4.6H_2O$	2	transmission	Alfa Aesar
nickel chloride	$NiCl_2$	2	transmission	Alfa Aesar
pentlandite	$(Fe,Ni)_9S_8$	4	transmission	ITSL process mineralogy (Ford)
nickel oxide	NiO	2	transmission	Sigma-Aldrich
unknown samples				
sample	**form**	**# scans**	**detection mode**	**comments**
502 57824	dust sample	6	fluorescence	D824
523 57797	dust sample	6	fluorescence	D797
582 1307	dust sample	8	fluorescence	D307
600 57810	dust sample	8	fluorescence	D810
504 57822	dust sample	3	fluorescence	D822
602 05-1311	dust sample	10	fluorescence	D311
200 4040722	dust sample	8	fluorescence	A722
TRA JUL02.04	air filter	8	fluorescence	Ajul0204
TRA MAR10.04	air filter	8	fluorescence	Amar1004
TRA SEP30.04	air filter	5	fluorescence	Asep3004
TRA NOV29.03	air filter	8	fluorescence	Anov2903
TRA JAN04.04	air filter	8	fluorescence	Ajan0404

Table 2. Description of samples measured at the S K-edge at the CSRF DCM (SRC)

pure reference compounds (S K-edge)				
sample	**formula**	**# scans**	**detection mode**	**source**
nickel sulfide	NiS	2	fluorescence	Alfa Aesar
elemental sulfur	S	2	fluorescence	Aldrich
nickel subsulfide	Ni3S2	2	fluorescence	NiPERA repository
pentlandite	$(Fe,Ni)_9S_8$	3	fluorescence	ITSL process mineralogy (Ford)
pyrrhotite	$Fe_{1-x}S$	2	fluorescence	ITSL process mineralogy (Ford)
chalcopyrite	$CuFeS_2$	1	fluorescence	ITSL process mineralogy (Ford)
thiosalicylic acid	$C_7H_6O_2S$	1	fluorescence	Aldrich
L-cystine	$C_6H_{12}O_4N_2S_2$	1	fluorescence	Aldrich
nickel sulfate	$NiSO_4.6H_2O$	2	fluorescence	Alfa Aesar
sodium sulfite	Na_2SO_3	2	fluorescence	Alfa Aesar
sodium thiosulfate	$Na_2S_2O_3$	2	fluorescence	Alfa Aesar
unknown samples				
sample	**form**	**# scans**	**detection mode**	**comments**
502 57824	dust sample	4	fluorescence	D824
523 57797	dust sample	2	fluorescence	D797
582 1307	dust sample	1	fluorescence	D307
600 57810	dust sample	2	fluorescence	D810
602 05-1311	dust sample	2	fluorescence	D311
TRA JUL02.04	air filter	3	fluorescence	Ajul0204
TRA MAR10.04	air filter	2	fluorescence	Amar1004
TRA SEP30.04	air filter	3	fluorescence	Asep3004
TRA NOV29.03	air filter	2	fluorescence	Anov2903
TRA JAN04.04	air filter	3	fluorescence	Ajan0404

Table 3. S K-edge XANES spectra of unknown air filter and dust samples with linear combination (LC) fitted values.

sample	**linear combination fits (wt %)**					
	SO_4^{2-}	**pyrrhotite**	**thio-salicylic acid**	**S-S**	**NiS**	**Ni_3S_2**
D824 [502 57824]	22	---	78	---	---	---
D797[523 57797]	91	---	9	---	---	---
D307[582 1307]	53 [53]	---	26 [34]	---	0 [13]	21 [0]
D810 [600 57810]	83	---	17	---	---	---
D311 [602 05-1311]	53	---	47	---	---	---
D822 [504 57822]#	48	---	52	---	---	---
A722 [200 4040722]#	---	---	---	---	---	---
Ajul0204 [TRA JUL02.04]	61	39	---	---	---	---
Amar1004 [TRA MAR10.04]	>99	<1	---	---	---	---
Asep3004 [TRA SEP30.04]	54	46	---	---	---	---
Anov2903 [TRA NOV29.03]	71	29	---	---	---	---
Ajan0404 [TRA JAN04.04]	>99	<1	---	---	---	---

* chalcopyrite ($CuFeS_2$), pentlandite ($(Fe,Ni)_9S_8$, pyrrhotite ($Fe_{1-x}S$), S-S denotes disulfide

the S K-edge spectra of these samples was done in the last report
Note that numbers in brackets represent alternate fits

Table 4. Ni K-edge XANES spectra of unknown air filter and dust samples with linear combination (LC) fitted values.

sample	**linear combination fits (wt %)**			
	NiO	**NiS**	**Ni_3S_2**	**$NiSO_4$**
D824 [502 57824] $(\chi^2)_{red}$=	35	35	0	29
D797[523 57797] $(\chi^2)_{red}$=0.0007	22	54	0	24
D307[582 1307] $(\chi^2)_{red}$=0.0015	54	37	0	9
D810 [600 57810] $(\chi^2)_{red}$=0.0029	23	0	0	27
D311 [602 05-1311] $(\chi^2)_{red}$=0.0009 $(\chi^2)_{red}$=0.0010	69 [68]	0 [32]	31 [0]	0 0
D822 [504 57822] $(\chi^2)_{red}$=0.0005	25	40	0	35
A722 [200 4040722] $(\chi^2)_{red}$=0.0019	40	0	0	60
Ajul0204 [TRA JUL02.04] $(\chi^2)_{red}$=0.0036	87	0	0	13
Amar1004 [TRA MAR10.04] $(\chi^2)_{red}$=0.0022	50	0	0	50
Asep3004 [TRA SEP30.04] $(\chi^2)_{red}$=0.0013	93	0	0	7
Anov2903 [TRA NOV29.03] $(\chi^2)_{red}$=0.0003	41	27	0	32
Ajan0404 [TRA JAN04.04] $(\chi^2)_{red}$=0.0017	100	0	0	0

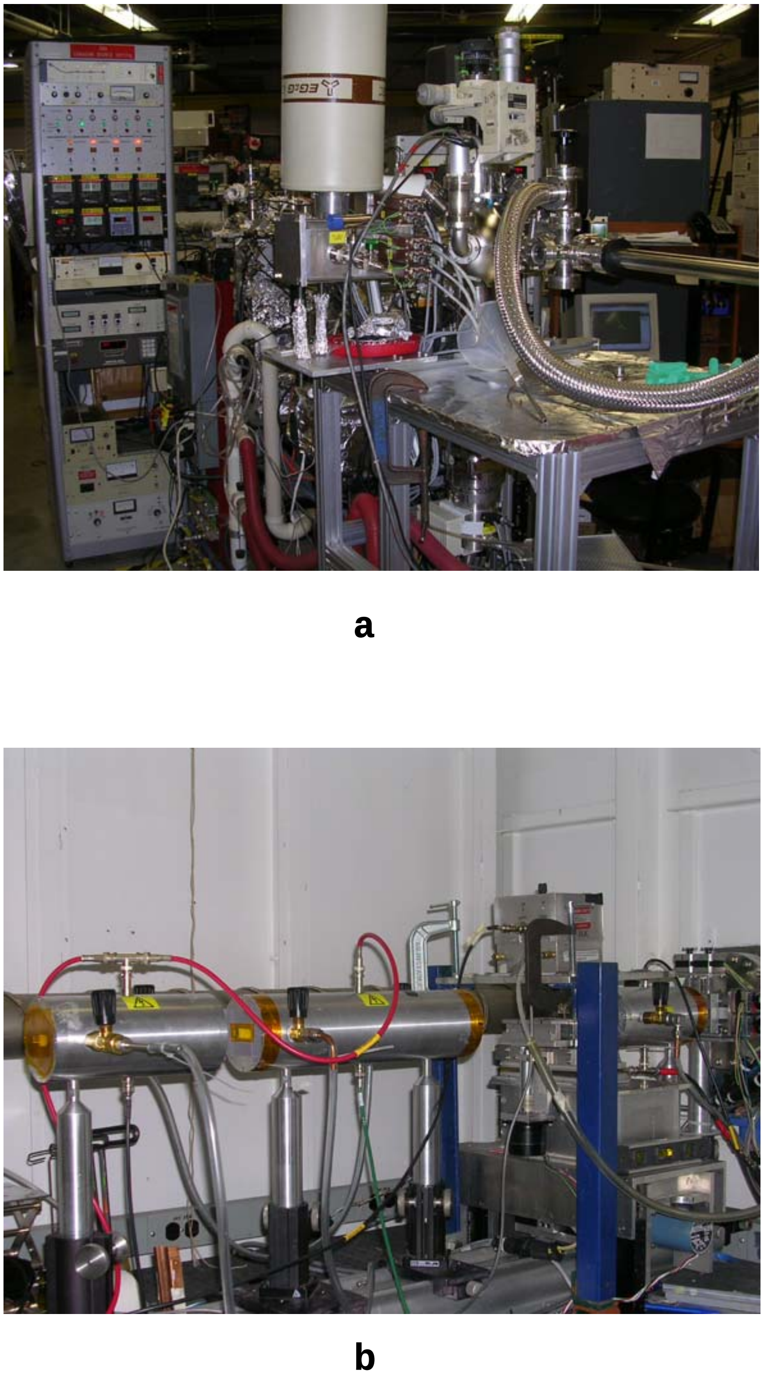


Figure 1. The DCM beamline for measurement of the sulfur K-edge at the SRC in Madison, WI (a) and a picture of the experimental arrangement at X11A at the NSLS at Brookhaven National Laboratory.

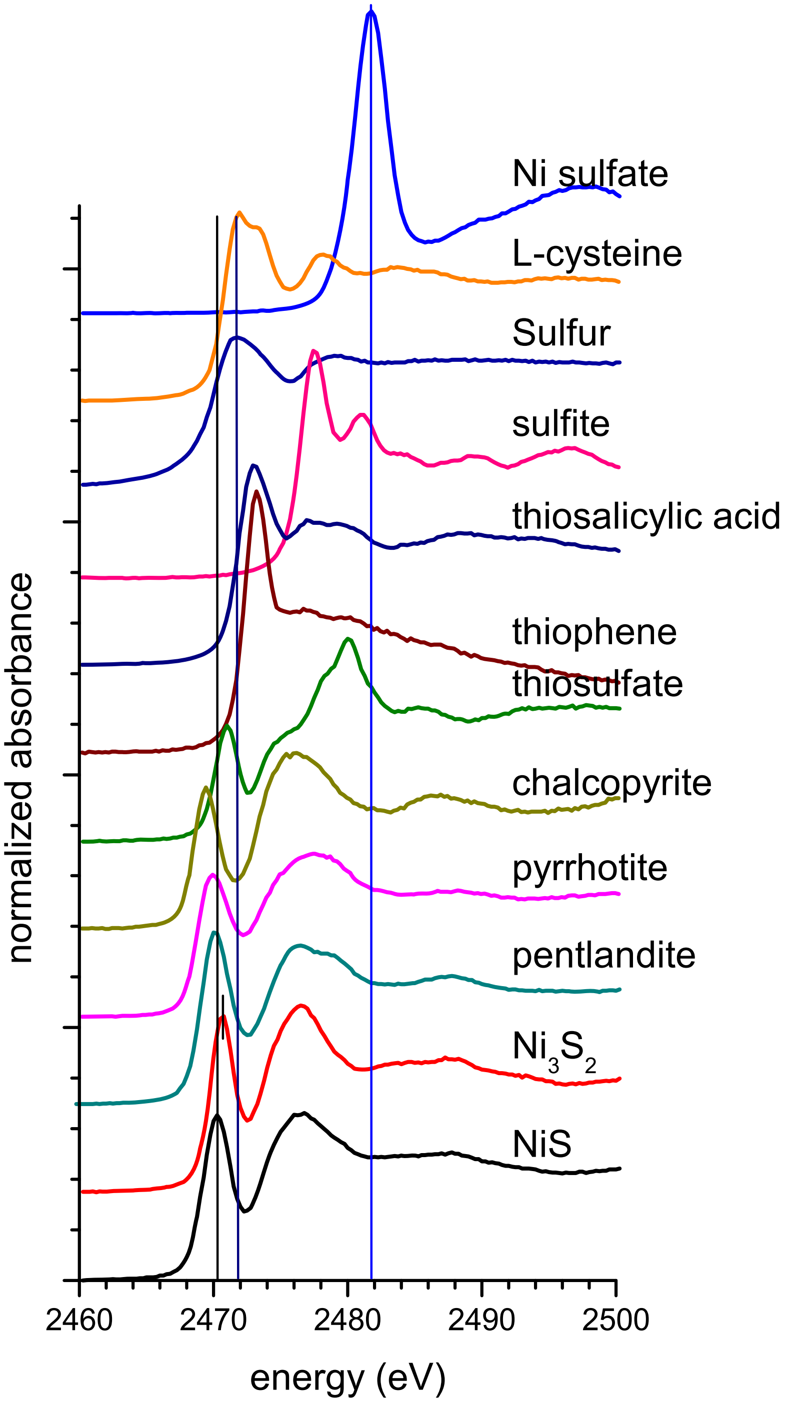


Figure 2. Pre-edge subtracted and normalized XANES spectra of reference compounds measured at the sulfur K-edge. Note that the decreasing absorbance of thiophene was caused by volatilization under the x-ray beam.

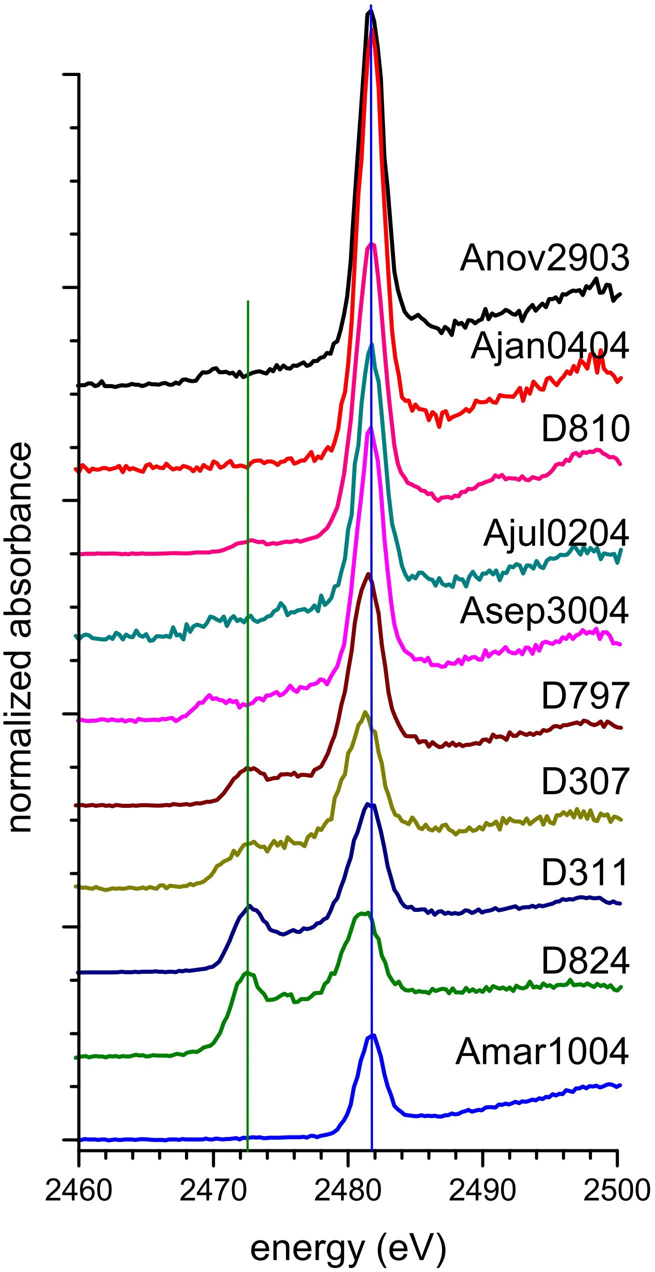


Figure 3. Pre-edge subtracted and normalized XANES spectra of unknown samples measured at the sulfur K-edge.

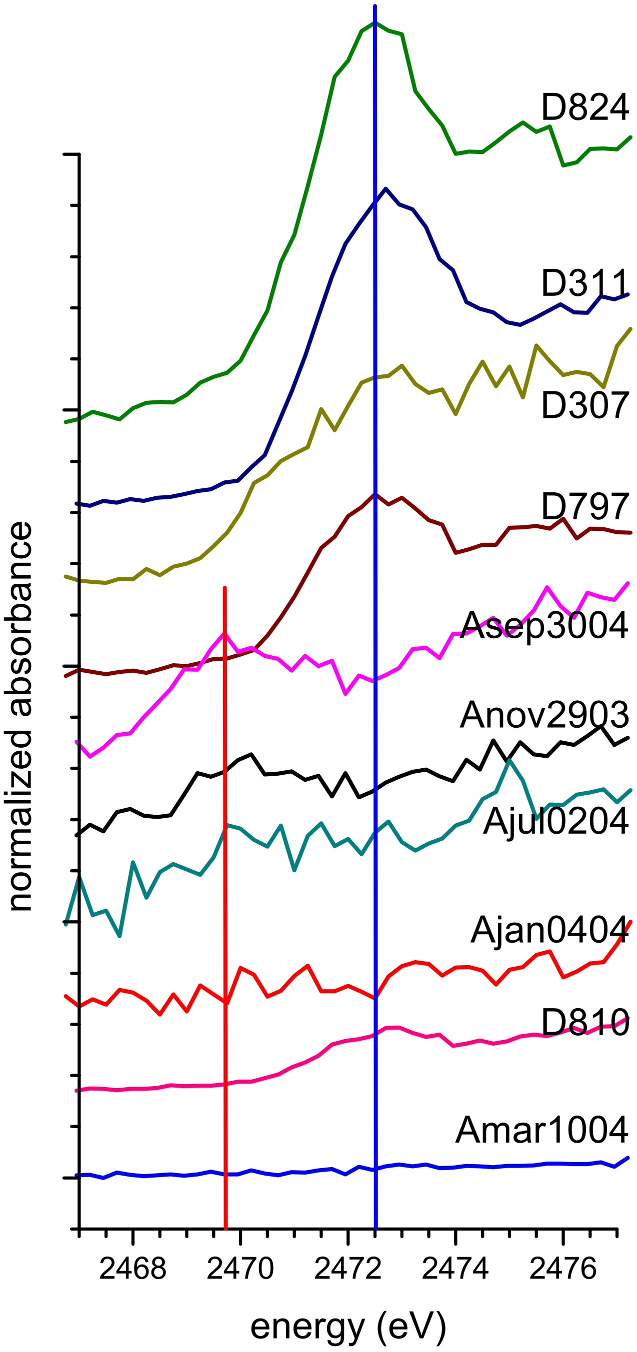


Figure 4. Expanded region of Figure 3 between energies 2467 and 2477 eV containing pre-edge subtracted and normalized XANES spectra of sample unknowns measured at the sulfur K-edge.

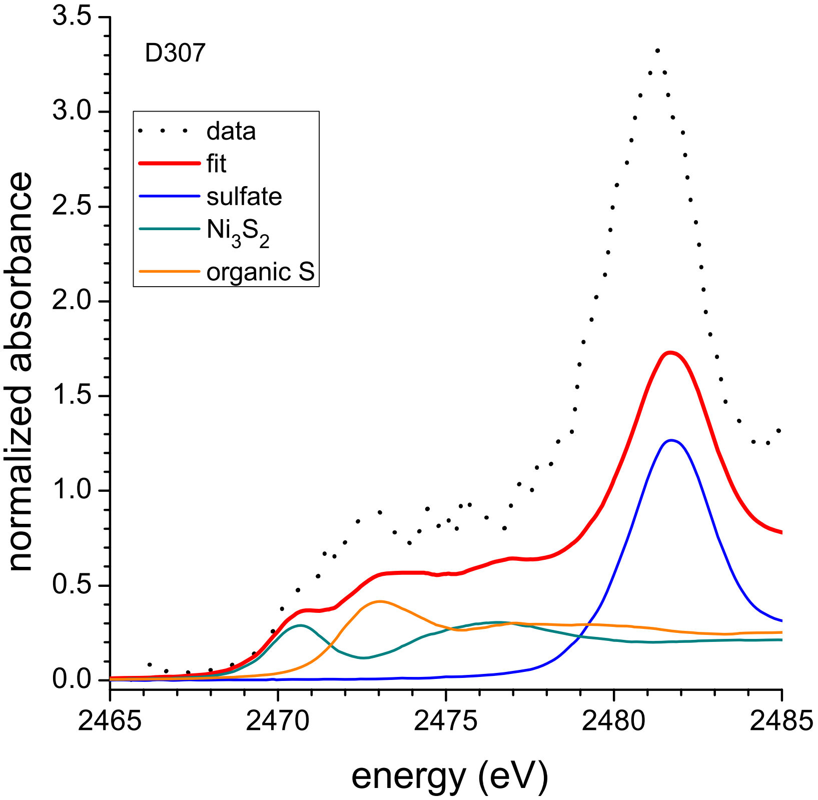


Figure 5. Least squares linear combination XANES fit of sample D307. The black dotted line is the measured XANES spectrum, the red dashed line is the total fit and the other lines represent the component percentages (Table 3) of NiO, NiS and $NiSO_4.6H_2O$.

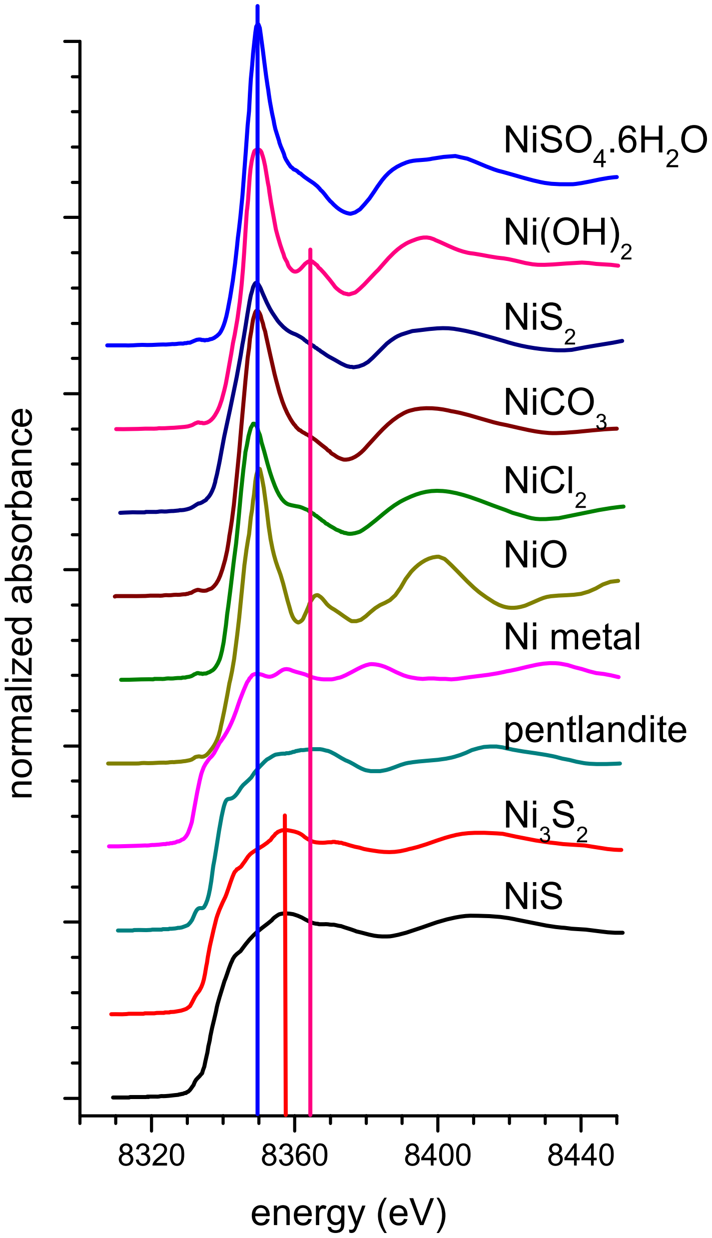


Figure 6. Pre-edge subtracted and normalized XANES spectra of reference compounds measured at the nickel K-edge.

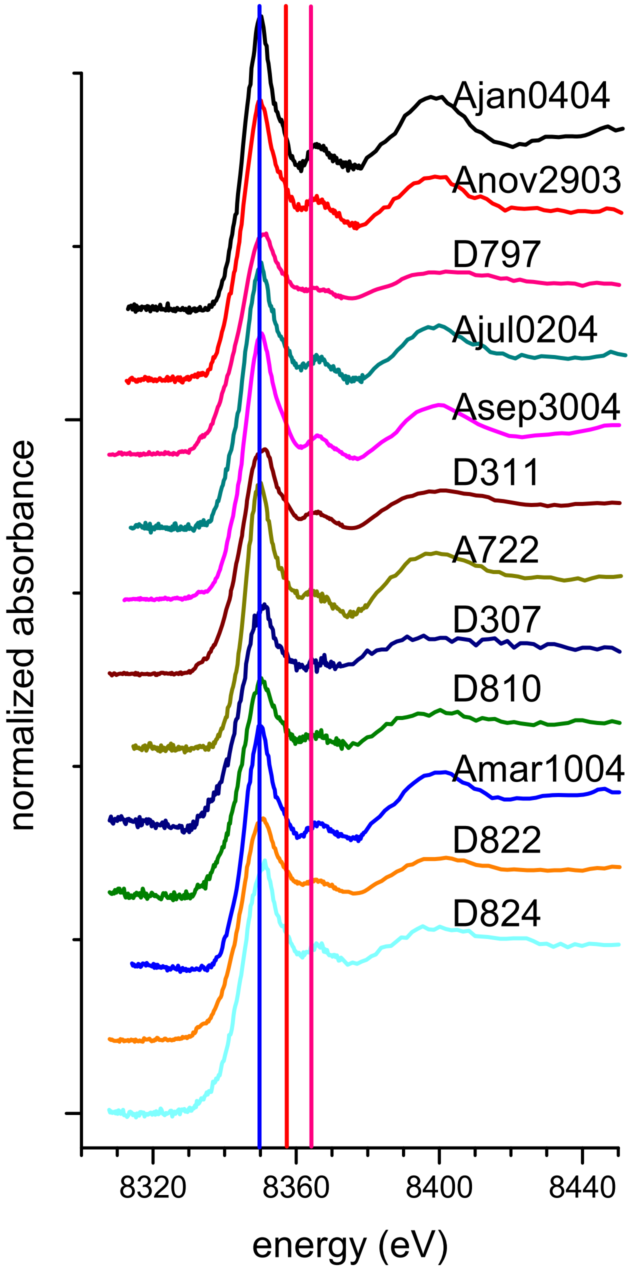


Figure 7. Pre-edge subtracted and normalized XANES spectra of unknown samples measured at the nickel K-edge.

SARA
GROUP

Metal Speciation Task Force

Minutes of Second Speciation Conference Call

May 8, 2006   10 – 11:30 pm

Participants:

Inco	Bruce Conard and Glen Watson (observer)
Falconbridge	Marc Butler (observer)
MOE	Rusty Moody
SARA Group	Glenn Ferguson
SGS Research	Chris Hamilton
SDHU	Evert Niebor and Ido Vettoretti (observer)

A summary of the key discussions that took place during the meeting is provided below, in the approximate order that they happened. A package containing the reports representing all speciation work conducted to date was circulated to the participants in advance of the conference call/meeting.

Introductions and general discussion:

Glenn Provided an introduction on behalf of the SARA Group.

Goal of the meeting was to discuss the latest round of speciation analytical work conducted for the Sudbury Soils Study, and determine what conclusions (if any) can be drawn from these results.

Based on the previous round of discussions, the following additional speciation analyses have been conducted by both Canadian Light Source (CLS) and SGS:

- Five new PM10 filters from the Travers Street monitoring station (this station has been the primary focus of the second round of speciation analyses) were submitted to both SGS and CLS for further speciation analyses (SEM and XAFS, respectively). These samples were taken at different times of the year, and corresponded to differing wind directions: January 4th – wind blowing from north; March 10th – from south-southwest; July 2nd – from north and east; September 30th – from south-southwest; and, November 29th – from west and north.
- Five indoor dust samples, previously identified as containing Ni3S2 by SGS were submitted to CLS for XAFS analyses.
- Two indoor dust samples previously identified as containing Ni3S2 by SGS were reanalyzed by SGS using a polished section investigation (as recommended in the previous task force meetings).

As a guide, the following questions were put forward to the group:

1. Is there any Ni3S2 present in the air filters at Travers Street? If so, can the overall percentage of Ni3S2, in relation to other nickel species (*i.e.*, nickel sulphate, oxides of nickel, *etc*.), be quantified?
2. If the percentage of Ni3S2 cannot necessarily be quantified, can the percentage of nickel sulphides be quantified (using either SEM or XAFS approaches)?
3. Is there Ni3S2 present in dust samples analyzed in the most recent round of analyses?
4. Are there any discrepancies in the results of the two forms of analytical approaches? If so, does this provide us with any additional information?
5. Is any additional analytical work warranted/necessary/helpful at this time?

Analysis by SGS Research

Chris — As part of the polished section analyses, we only found single grain cross-section, that though very small, and was confirmed to be Ni3S2. Overall the grains were 3 microns and smaller. Results of photo-micrographs and observations of optical properties confirmed identification.

Bruce — Has no doubt that the particle you found in the polished section was Ni3S2. The question becomes, how much of the particulate nickel weight is Ni3S2 based upon that one particule in the field examined by SGS. If the number is very small, the question becomes whether CLS can see something that small. In Bruce’s opinion, the two types of analyses don’t necessarily disagree … it is a matter of how sensitive you are going to be in your approach. The SGS approach of looking for grains is very sensitive, whereas the CLS approach of looking at the entire sample and trying to do linear combination of spectra to reveal a combination of compounds that could lead to the observed spectra is less sensitive. Each technique has advantages and disadvantages.

Evert — Would like Chris to comment on the number of particules examined relative to the total number of particles on the air sample to put it into perspective.

Chris — We looked at a minimum of 30 nickel particles, and likely in excess of 10,000 particles generically in the area of study. Of those 30 nickel particles, only one Ni3S2 particle was noted. Cautioned that one would need several hundred particles to properly quantify and give a more confident answer.

Rusty	What is the matrix of the air filter?
Chris	Silica fiber.
Rusty	So essentially a glass fiber. If the Ni3S2 is so small, is it possible you have particles buried in the filters you can't see, or pass right through?
Chris	Certainly, they could be buried at depth. However, any other nickel species are likely going to overwhelm and swamp trace amounts of Ni3S2.
Rusty	Suggests that in an absolute counting, we don't know how many particles are really in that filter.
Chris	Exactly. We are not counting the whole filter in the first place, and we are only looking at the upper most surface of the filter.
Bruce	The thing that one does in this kind of analyses is, you are really looking at a field and that field represents an area … and you assume the area that the polished section goes through is representative of any particular slice through the filter. There are probably many Ni3S2 particles within the filter. That is not critical to the analysis, as long as you use the area of the field that you are examining in the polished section and ratio the occurrence of the one particle in that field. Then when you look at the volume, you will have the percentage of Ni3S2 particules within the volume as you see within this random section.
Chris	Exactly.
Glenn	Would it be possible to quantify the percentage of Ni3S2 present within the sample?
Chris	Based upon these results, we could go back and based upon the proportion of Ni species we could give a ratio of nickel sulphide as pentlandite to nickel sulfide as Ni3S2. Based upon the current results, it appears to be 10:1 ratio or higher. However, I would really need higher statistics than that through more SEM work to get a more accurate number.
Bruce	Chris, are you talking about 10:1 in terms of number of particles or the area in the field those particles represent?
Chris	In this case here, I am speaking of area.
Glenn	We would like to be able to get a percentage of Ni3S2 in the sample, or at least a range. Does the group think we can get that information from the current analyses?

Bruce Believes the question is what other options do we have? Either we say we don't know anything and so we won't do cancer analysis of inhalation of nickel or we give a reasonable upper bound of the amount of Ni3S2 in ambient air. We have to take, at this point in time, some number, give it context, recognize that this is the information that exists – nobody can fault you for this.

Evert Believes there is not much difference between the slope factors, not orders of magnitude. As such, believes this discussion may be academic. Also believes there are uncertainties present in the analyses.

Bruce Agrees that there are uncertainties present in the analyses and statistics used, but still a very useful bit of data for the HHRA.

Analysis by CLS

Unfortunately, Jeff Warner could not participate in the meeting due to technical difficulties.

Glenn Points out that the SGS data indicated that when wind direction is taken into account in the latest round of analyses that Ni3S2 was identified when the wind was blowing from the west / southwest, and not when blowing from the opposite direction. However, the CLS data did not appear to exactly align with these results, and bears closer examination.

Also, the CLS analyses of the samples on November 29th and September 30th showed a small peak which appeared to be sulfate and pyrrhotite. Any comment from the group as to what this indicated?

Bruce Pyrrhotite is iron-deficient iron sulfide, which is able to bring nickel into its crystal lattice. So you find pyrrhotite can have some nickel in it … not much, but some. Therefore, pyrrhotite can reveal nickel and sulphur in the CLS analyses. Pyrrhotite is present in Inco tailings, though there isn't much pyrrhotite left after smelting. Wind could pick up tailings, and the resuspended particles can contain some pyrrhotite. So its not unusual that an ambient air monitor would detect some pyrrhotite in Sudbury.

Glenn Opens up discussion on CLS report to get impressions of call participants.

Bruce When CLS says they see mainly sulfate and oxidic nickel, it is what everyone would expect to see in ambient air. However, if we assume arbitrarily that 75% is as sulfate and 23% is as oxidic. You add those two together, and you get 98%. So maybe 2% of the nickel is present as Ni3S2, and/or pentlandite, and/or pyrrhotite. The question becomes whether CLS can detect that on the shoulder of some other peak. So can

	CLS determine at what concentration they will be able to detect small concentrations of Ni3S2.
Glenn	So we almost need a method detection limit.
Bruce	Yes, and they probably, with some more work, can tell us what they think their detection limit is. And it would be compound-specific and matrix-specific.
Evert	On page 5 of the report, they make the point that they need to know the total amount of nickel and dust in the sample. If one takes the data from the HHRA report, we are looking at very tiny amounts.
Glenn	This information can be easily provided to CLS.
Glenn	Does anyone have any comments on the CLS dust results?
Evert	Seems to indicate it is more consistent with nickel sulfide rather than nickel subsulfide.
Glenn	This is consistent with what they reported in previous analyses.
Bruce	The amount of Ni3S2 is not essential information for the assessing of oral ingestion of dust by toddlers. So he didn't believe that much more attention should be paid to speciation in dust, given we have information on the bioaccessibility of the dust already.
Glenn	One issue we are exploring right now is resuspension of dust within the home.
Bruce	Well, then the question would be how did you sample the dust? You sampled it with a very aggressive sampling, which would suck up particles trapped within the cracks of floors and wedged within rugs, and so the amount of nickel you have there in the dust sample, only a small fraction of that is susceptible for resuspension. It becomes very difficult without a particle size fraction to determine what fraction could be easily resuspended.
Glenn	Agreed. We have the same difficulties with it within the SARA Group. A final decision hasn't been made yet as to whether it will be included in final assessment.
Evert	Concerned from an epidemiological point-of-view that a lot of effort is being put into something that can't really be measured. He feels that the approach taken in the previous draft is reasonable and protective.

Bruce	Can we go back to CLS and ask them for a level of detection?
Glenn	Yes, that is on my todo list.
Bruce	Without doing any further polished section work, can SGS' results be used to estimate a reasonable upper limit of Ni3S2 relative to all nickel?
Glenn	Or even nickel sulfide as a whole?
Chris	Would be comfortable providing a ratio of pentlandite to Ni3S2, on the caveat that these are only limited statistics. Based upon the first samples, by area it comes to 4.5% Ni3S2 of all sulfides.
Bruce	That doesn't take into account the oxides and the sulphates?
Chris	No, it doesn't. As a scoping analyses, given the constraints, can provide the relative percentages of each grouping. Though there may be difficulty discriminating the sulfates.
Glenn	This would be very useful in the HHRA, even with the caveats.
Evert	Recommended looking at the MOE (2004) report on the development of air standards, which contains a table which shows the various species.
Glenn	Rusty, do you think this is a reasonable approach to assessing the risk – through subdividing the various species?
Rusty	It's worth a shot.
Glenn	Anyone have any other issues to raise?
Bruce	Based upon his review of the two latest reports, he doesn't believe that these two analytical techniques are in disagreement. This may not be the impression we have conveyed previously to the TC and other stakeholders. But the recent work shows that they are each saying nearly the same thing, and that it only comes down to an issue of detection. So it is important to communicate this issue.
Evert	Concurs, that it is a difference in sensitivity, and the two techniques are somewhat complementary.
Glenn	Thank you to all those involved in the meeting.

Meeting adjourned.

EMAIL CORRESPONDANCE

From: Jeff Warner [Jeff.Warner@lightsource.ca]
Sent: Monday, May 22, 2006 8:42 PM
To: Glenn Ferguson
Subject: RE: SARA Report

Hi Glenn,
We have done a number of studies related to quantifying the amount of one species in mixtures with another closely related species to help us in understanding the quantification techniques (eg. silver, nickel and arsenic). I recently collected data here on 3 component mixtures of nickel at the Ni L-edge.

In the first report to Cantox [dated: November 23, 2005] we looked at mixtures of NiS and NiSO4 [Table 4, Figures 6 and 8]. Figure 8 in that report puts the detection limit in that matrix at 7%. This agrees well with most of our work of this type which generally puts the analysis detection limit between 5-10%. We have achieved, in cases where we have good supplementary information on the samples, accuracies of ~3%.

Just to go over your comments on the sample Anov2903. Our results indicate that 27% of the nickel species are in the form NiS (no Ni3S2 detected but 32% of the nickel occurs as the Ni sulfate). If we look at the sulfur measurements we see that that same sample has 71% of sulfur in the form of sulfate and 29% in the form of pyrrhotite, essentially an iron deficient sulfide. The results are consistent but without knowing the total amounts of nickel and sulfur cannot be cross-correlated. From that report, there is no detectable Ni3S2 in the aerosol samples.

I would place as a conservative upper bound the 7% value.

I hope this helps.

jeff

SGS

MEMO

To: Glen Fergusson, CANTOX Environmental

From: Chris Hamilton

Date: 24 May, 2006

Copies:

Re: Quantifying Ni-sub-sulphide.

After much thought, there are potentially two ways of arriving at an estimate of the Ni reporting as sub-sulphide, namely:

1. Direct mineralogy
2. Combination of mineralogy & other.

Direct Mineralogy

This method consists of performing a surface scan as we have produced in the past. The method detects a certain number of particles and a record is made of the two-dimensional area of the particle (length * breadth) and a tally made of area scanned per mineral species. Results of the analyses from the 2 dust samples recently analysed are given in Table 1. The area is calculated for this Ni-bearing particle population (first caution: Low statistics!) and a percentage area (column 3) determined. Using known SG's (column 4), this data is converted to relative mass units (col 5) and from there, relative mass % for the population. This ratio (column 5) is best to use as the contained metal (column 7) and relative Ni distribution assumes compositions that may not be accurate.

This is an estimate only due to limited statistics and the fact that this work is biased towards higher atomic number species. Lower atomic number Ni-species (e.g. hydrous Ni sulphates) will likely go undetected in this method so the sulphate percentage may be totally misreported. The reported particles are also based on a given area scanned, and this may vary between samples, hence the use of relative proportions.

To counter this effect and to be more accurate, a significantly more exhaustive and costly method would be to perform what is known as a mass- or general particle scan. In this method, all particles encountered are recorded, which then gives a far more accurate accounting of all species but can take many hours to perform. I'd estimate this would take an order of magnitude longer to do relative to the specific scan method we have done to data. The abbreviated method has to date been used simply to record the relative volumetric ratios of heazlewoodite/sub-sulphide to other high atomic number species (pentlandite, Ni-oxide etc.), or simply record/confirm the presence of heazlewoodite.

Table 1. Dust Analysis Summary.

	1	2	3	4	5	6	7	8
Dust 582-03-1307	**Particles N**	**Area (um2)**	**Area %**	**SG g/cm3**	**Relative Mass Units**	**Relative Mass %**	**Contained % Ni**	**Relative Ni ratios**
Pentlandite	8	392.2	23.3	5.1	118.83	24.8	34.2	8.5
Ni-Subsulphide	1	19.4	1.2	5.9	7.08	1.5	73.3	1.1
Ni-Oxide	4	697.7	41.4	6.8	281.52	58.8	78.6	46.2
Ni-Sulphate	4	573.4	34.1	2.1	71.61	14.9	22.3	3.3
			100.0		479.04			

Dust 602-05-1311	Particles N	Area (um2)	Area %	SG g/cm3	Relative Mass Units	Relative Mass %	Contained % Ni	Relative Ni ratios
Pentlandite	8	768	50.1	5.1	255.51	43.0	34.2	14.7
Ni-Subsulphide	1	20.3	1.3	5.9	7.67	1.3	73.3	0.9
Ni-Oxide	5	743.9	48.6	6.8	330.48	55.7	78.6	43.8
Ni-Sulphate	0	0	0.0	2.1	0	0.0	22.3	0.0
			100.0		593.66			

All of these assumptions and parameters would need to be cross-referenced against prior knowledge of the material. For example, we would ideally want to match mineral species with historic and other data from INCO etc., as the average Ni-content in Ni-oxides can be quite variable, and the exact type of sulphate may be critical. For the anhydrous oxides, they range from pure green-NiO (bunsenite), through to Ni-ferrite, for instance, and the finer grained one goes, the less accurate identification and characterization will be.

Combined Mineralogy/Other Methods

If the Synchrotron data can be satisfactorily be used to quantify relative ratios of pentlandite to oxide-Ni, and this data can be demonstrated to "converge" with the "abbreviated mineralogy" or a more detailed method as outlined above, that would be the "holy grail". I suspect, however, that the sensitivity of the synchrotron results is questionable. I would, therefore, recommend more detailed work and possibly even investigating the option of Transmission Electron Microscopy (TEM) as in the paper I previously sent you. Alternatively, a compromise between these methods may be to use a Field Emission Scanning Electron Microscope (The University of Waterloo has one) which has higher sensitivity and magnification which is better suited to identifying fine grained species.

Please call me if you need further clarification of the above.

Chris Hamilton
Consulting Mineralogist
SGS Minerals Technologies
Lakefield Site

Detailed Speciation Results from SGS (May 24, 2006)

Sudbury Soils Study

Residential Dust Sample Results

Dust 582-03-1307	**Particles N**	**Area (um2)**	**Area %**	**SG g/cm3**	**Relative Mass Units**	**Relative Mass %**	**Contained % Ni**	**Relative Ni ratios**	**Normalized Ni ratios**
Pentlandite	8	392.2	23.3	5.1	118.83	24.8	34.2	8.5	14.4
Ni-Subsulphide	1	19.4	1.2	5.9	7.08	1.5	73.3	1.1	1.8
Ni-Oxide	4	697.7	41.4	6.8	281.52	58.8	78.6	46.2	78.2
Ni-Sulphate	4	573.4	34.1	2.1	71.61	14.9	22.3	3.3	5.6
			100.0		479.04			59.1	100.0

Dust 602-05-1311	Particles N	Area (um2)	Area %	SG g/cm3	Relative Mass Units	Relative Mass %	Contained % Ni	Relative Ni ratios	**Normalized Ni ratios**
Pentlandite	8	768	50.1	5.1	255.51	43.0	34.2	14.7	24.8
Ni-Subsulphide	1	20.3	1.3	5.9	7.67	1.3	73.3	0.9	1.6
Ni-Oxide	5	743.9	48.6	6.8	330.48	55.7	78.6	43.8	73.6
Ni-Sulphate	0	0	0.0	2.1	0	0.0	22.3	0.0	0.0
			100.0		593.66			59.4	100.0

*Assumes noted chemistry of Ni in phase (Col. 7)

Travers Street Monitoring Station - Air Filter Sample Results

TRA NOV 29.03	Particles N	Area (um2)	Area %	SG g/cm3	Relative Mass Units	Relative Mass %	Contained % Ni	Relative Ni ratios	**Normalized Ni ratios**
Pentlandite	18	339	62.0	5.1	316.0694698	53.2	34.2	18.2	35.7
Ni-Subsulphide	2	44	8.0	5.9	47.45886654	8.0	73.3	5.9	11.5
Ni-Oxide	7	164	30.0	6.8	203.8756856	34.3	78.6	27.0	52.9
Ni-Sulphate		0	0.0	2.1	0	0.0	22.3	0.0	0.0
		547	100.0		567.4040219			51.1	100.0

TRA JAN 04.04	Particles N	Area (um2)	Area %	SG g/cm3	Relative Mass Units	Relative Mass %	Contained % Ni	Relative Ni ratios	**Normalized Ni ratios**
Pentlandite		0	0.0	5.1	0	0.0	34.2	0.0	0.0
Ni-Subsulphide		0	0.0	5.9	0	0.0	73.3	0.0	0.0
Ni-Oxide		0	0.0	6.8	0	0.0	78.6	0.0	0.0
Ni-Sulphate	30	178	100.0	2.1	210	35.4	22.3	7.9	100.0
		178	100.0		210			7.9	100.0

TRA MAR 10.04	Particles N	Area (um2)	Area %	SG g/cm3	Relative Mass Units	Relative Mass %	Contained % Ni	Relative Ni ratios	**Normalized Ni ratios**
Pentlandite	5	284	59.0	5.1	301.1226611	50.7	34.2	17.3	60.3
Ni-Subsulphide	3	15	3.1	5.9	18.3991684	3.1	73.3	2.3	7.9
Ni-Oxide	7	36	7.5	6.8	50.89397089	8.6	78.6	6.7	23.4
Ni-Sulphate	13	146	30.4	2.1	63.74220374	10.7	22.3	2.4	8.3
		481	100.0		434.1580042			28.8	100.0

TRA JUL 02.04	Particles N	Area (um2)	Area %	SG g/cm3	Relative Mass Units	Relative Mass %	Contained % Ni	Relative Ni ratios	**Normalized Ni ratios**
Pentlandite	11	122	48.0	5.1	244.9606299	41.3	34.2	14.1	61.2
Ni-Subsulphide		0	0.0	5.9	0	0.0	73.3	0.0	0.0
Ni-Oxide	4	15	5.9	6.8	40.15748031	6.8	78.6	5.3	23.1
Ni-Sulphate	13	117	46.1	2.1	96.73228346	16.3	22.3	3.6	15.8
		254	100.0		381.8503937			23.1	100.0

TRA SEP 30.04	Particles N	Area (um2)	Area %	SG g/cm3	Relative Mass Units	Relative Mass %	Contained % Ni	Relative Ni ratios	**Normalized Ni ratios**
Pentlandite	2	8	0.9	5.1	4.551641045	0.8	34.2	0.3	0.3
Ni-Subsulphide*	14**	118.38	13.2	5.9	77.91807046	13.1	73.3	9.6	11.0
Ni-Oxide	5	770	85.9	6.8	584.1272675	98.4	78.6	77.3	88.7
Ni-Sulphate	0	0	0.0	2.1	0	0.0	22.3	0.0	0.0
		896.38	100.0		666.596979			87.2	100.0

* Assumes the matte component is 33% Ni-Sub-sulphide (57 parts Ni3S2 + 186 parts Matte by area)

** One mono-mineralic Ni3S2 and 13 matte particles with essential Ni3S2***

*** Matte may in fact have substantially more Ni3S2 within; but 33% Ni3S2 is reasonable estimate:
Best to change this according to known matte mineralogy.

Additional Speciation Work at the Laboratory for Environmental and Geological Studies (LEGS)

In conjunction with a second round of bioaccessibility analyses, five outdoor soil samples and nine indoor dust samples were submitted for Electron Microprobe Analysis (EMPA) at the Laboratory for Environmental and Geological Studies (LEGS) at the University of Colorado, Boulder This analyses was conducted using an electron microprobe (*i.e.*, JEOL 8600) equipped with four wavelength spectrometers, energy dispersive spectrometer (EDS), BEI detector and the Geller, dQuant data processing system. It is important to note, that due to limitations on available quantities of materials, these were not the same soil and dust samples that were tested in previous rounds of speciation analyses.

This round of speciation analysis focused primarily on arsenic, lead and nickel elements present within the soil or dust samples, and provided a detailed percentage breakdown of the specific species in relation to the overall mass of COC. Table 1 and 2 provide a composition breakdown by COC form on the five outdoor soil samples and nine indoor dust samples, respectively. The pages following these tables provide the detailed analysis results used to generate the summaries presented in Tables 1 and 2.

Results of the EMPA speciation appear to indicate a similar pattern as that observed in the previous rounds of speciation analyses. However, one set of observations in the current analyses does provide potential information for future risk management decision making. As noted previously, the primary form of lead identified by SGS Lakefield was in the form of anglesite (*i.e.*, lead sulphate), which is known to be an emission from smelting/refining sources. However, SGS did indicate that a major proportion of lead present in their limited number of samples could not be accounted for mineralogically, and pointed to other potential forms such as lead carbonate (refer to their detailed report in Appendix I). SGS suggested that more sophisticated techniques or methods could be applied to attempt to better isolate the forms present. However, as this was not a requirement of the risk assessment, it was not undertaken at that time.

However, results of the EMPA speciation work indicated that a significant percentage of the lead present in some of the dust samples analyses was in the form of cerussite (*i.e.*, lead carbonate). This form of lead was detected in most of the dust samples analysed (but none of the soil samples), and typically ranged between approximately 20 and 85% of the total lead present in the sample. This is of some risk management significance because cerussite, or "white lead", is a key ingredient in lead-based paints.

Table 1 Species Percentage Results from EMPA Speciation of Residential Outdoor Soil Samples

Form	Soil 1			Soil 2			Soil 3			Soil 4			Soil 5		
	As	Pb	Ni	As	Pb	Ni	As	Pb	Ni	As	Pb	Ni	As	Pb	Ni
Anglesite															
Cerussite															
Chalcopyrite				0	0	0.25				0	0	0.14			
CrMO															
Cr-Ni metal	0	0	2.86												
CuMO															
FeCr metal															
FeOOH	89.47	63.49	3.01	90.83	90.43	5.45	95.04	62.91	4.49	97.43	88.37	6.06	87.31	2.47	4.34
FeS2	0	0.36	0.2	0	0.99	0.68	0	2.29	1.85	0	1.7	1.32	0	0.01	0.12
FeSiO2	8.28	29.6	4.27	0.72	3.6	0.66	2.67	8.91	1.94	0.22	1.01	0.21	8.49	1.21	6.48
FeSO4							0	0.51	0.43	0	2.51	2.01			
MnOOH	0.55	5.64	0.53	0.19	2.68	0.32									
Native Lead							0	24.97	0						
Ni metal													0	0	5.93
NiFeO	0.9	0.23	4.22	5.62	2.02	47.16	1.59	0.38	10.47				4.08	0.04	28.37
NiMClSO4															
NiMO	0.8	0.04	1.8	2.64	0.18	10.53	0.7	0.03	0	1.87	0.12	7.74	0.12	0	0.39
NiMS															
NiMSO4															
NiO	0	0	76.38	0	0	9.43				0	0	3.08	0	0	49.32
NiP															
NiS															
NiSO4				0	0.1	3.7				0	0.01	0.24			
Paint															
PbCrO4															
PbMO															
PbMSO4															
PbTiO2															
PbO															
PbSiO4													0	96.27	0
Pentlandite	0	0	5.08	0	0	21.83	0	0	80.82	0	0	79.19	0	0	5.04
Phosphate										0.48	6.29	0.01			
Plumbobarite															
Slag	0	0.63	1.66												
ZnMO															

Table 2 Species Percentage Results from EMPA Speciation of Residential Indoor Dust Samples (LEGS

Form	Dust 1			Dust 2			Dust 3			Dust 4			Dust 5			Dust 6			Dust 7			Dust 8			Dust 9		
	As	**Pb**	**Ni**	**As**	**Pb**	**Ni**	**As**	**Pb**	**Ni**	**As**	**Pb**	**Ni**	**As**	**Pb**	**Ni**	**As**	**Pb**	**Ni**	**As**	**Pb**	**Ni**	**As**	**Pb**	**Ni**	**As**	**Pb**	**Ni**
Anglesite	0	59.78	0																								
Cerussite	0	21.32	0	0	56.14	0				0	74.32	0	0	85.72	0	0	67.4	0	0	71.3	0	0	68.08	0			
Chalcopyrite																						0	0	0.02	0	0	0.01
CrMO																						0	0.63	2.06			
Cr-Ni metal	0	0	12.56																								
CuMO							0	0	6.81				0	0	7.36	0	0	1.97	0	0	1.2				0	0	0.71
FeCr metal																0	0.01	0.34	0	0.06	0.46						
FeOOH	41.3	11.53	5.2	4.47	1.15	2.25	6.19	6.13	2.54	64.07	16.94	3.67	17.47	4.33	2.88	71.62	0.55	0.59	13.01	6.36	0.83	91.98	17.15	0.93	95.23	7.02	3.75
FeS2	0	0.07	0.38	0	0.1	2.14	0	0.25	1.18	0	0.1	0.25	0	0.16	1.24	0	0.15	1.86	0	0.63	0.93	0	1.86	1.15	0	0.52	3.18
FeSiO2				0.58	0.75	4.46	0.02	0.09	0.12	0.43	0.57	0.38	0.48	0.6	1.21	1.99	0.08	0.25	0.54	1.33	0.53	2.38	2.23	0.37	2.07	0.77	1.25
FeSO4	0	0.05	0.28				0	0.08	0.37	0	0.3	0.77	0	0.2	1.53	0	0.01	0.12	0	0.05	0.07	0	0.33	0.21	0	0.21	1.29
MnOOH																											
Native Lead																											
Ni metal	0	0	6.21	0	0	5.97	0	0	10.89							0	0	8.61	0	0	7.99	0	0	56.11	0	0	18.78
NiFeO							0.03	0.01	1.96	0.62	0.06	4.96				11.18	0.03	12.79	0.35	0.06	3.13	2.05	0.14	2.91	1.55	0.04	8.52
NiMClSO4																9.41	0.04	2.53									
NiMO	1.35	0.03	11.3				0.68	0.05	18.63				0.89	0.02	9.72	5.8	0	3.16	0.22	0.01	0.94	2.5	0.03	1.69	1.15	0.01	3
NiMS																			0.7	1.63	2.93						
NiMSO4																						1.1	0.12	0.37			
NiO	0	0	4.77	0	0	25.77	0	0	30.48	0	0	11.64	0	0	10.6	0	0	33.06	0	0	25.68	0	0	15.18	0	0	29.48
NiP	0	0	10.27	0	0	7.52																					
NiS	0	0	13.76	0	0	33.04	0	0	16.51	0	0	68.3	0	0	17.47	0	0	11.92	0	0	40.75	0	0	3.98	0	0	7.42
NiSO4	0	0.08	21.45	0	0	1.23																					
Paint				0	0.88	0																					
PbCrO4				0	26.86	0																					
PbMO	57.35	7.14	0	94.31	10.86	0	92.17	40.73	0	34.14	4.03	0	81.16	8.98	0				85.19	18.58	0						
PbMSO4				0.65	1.4	0																					
PbTiO2				0	1.85	0																					
PbO																0	31.31	0							0	78.15	0
PbSiO4							0	39.75	0																0	12.06	0
Pentlandite	0	0	13.82	0	0	17.63	0	0	10.41	0	0	10.03	0	0	47.99	0	0	22.08	0	0	14.58	0	0	15	0	0	22.55
Phosphate							0.91	12.92	0.12	0.74	2.82	0.01							0	0	0						
Plumbobarite										0	0.86	0				0	0.41	0				0	9.42	0			
Slag																0	0.01	0.72							0	0	0.03
ZnMO																									0	1.21	0.01

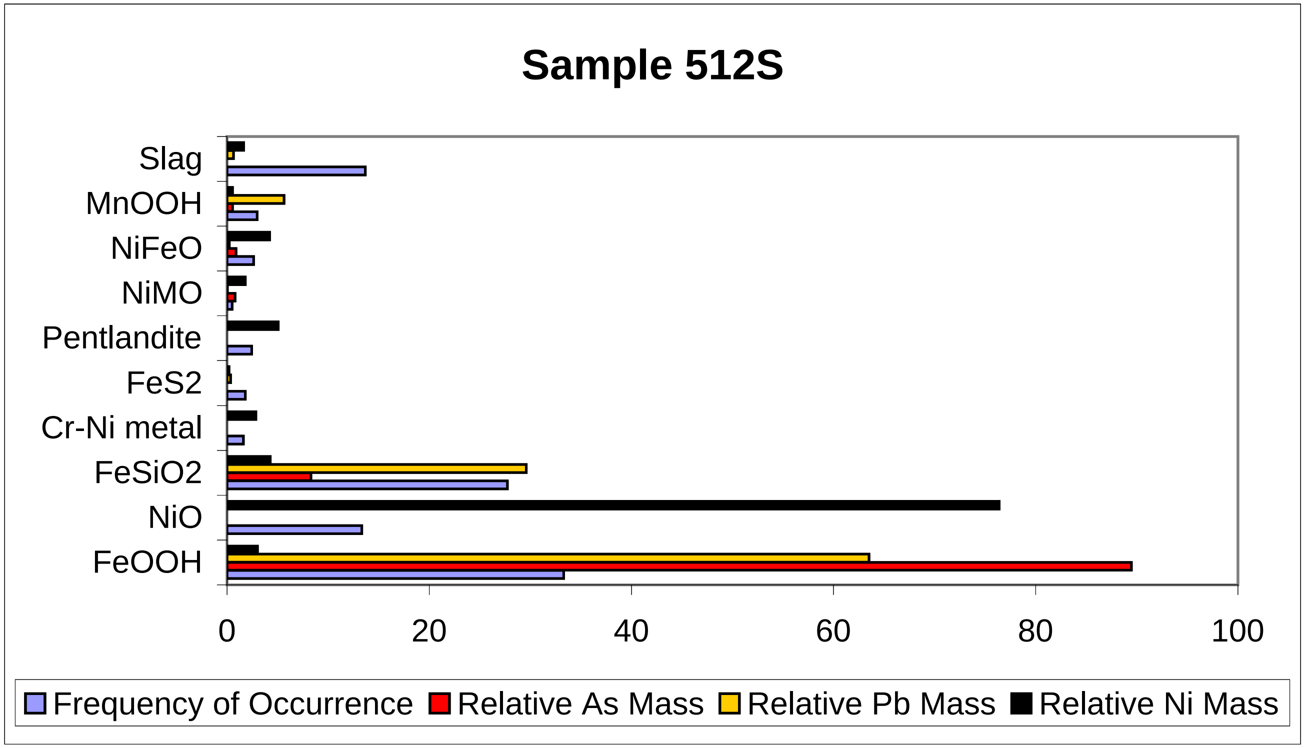
Detailed Speciation Results from LEGS (2007)
Sample 512s (Outdoor Soil)

Form	Association	Size
Fe	Liberated	32
Fe	Liberated	4
Fe	Liberated	22
nio	Liberated	16
Fe	Liberated	50
nio	Liberated	4
FeSi	Liberated	30
nio	Liberated	8
nio	Liberated	5
nio	Liberated	7
Fe	Liberated	7
Fe	Liberated	10
Fe	Liberated	11
Fe	Cemented	3
FeSi	Liberated	4
FeSi	Liberated	100
Fe	Liberated	7
crnio	Liberated	27
py	Liberated	23
nio	Liberated	6
FeSi	Liberated	5
nio	Liberated	4
Fe	Liberated	7
pent	Liberated	26
nio	Liberated	23
FeSi	Liberated	43
FeSi	Liberated	40
Fe	Liberated	30
Fe	Liberated	7
Fe	Liberated	50
Fe	Liberated	20
FeSi	Liberated	80
Fe	Liberated	13
Fe	Liberated	18
Fe	Liberated	4
Fe	Liberated	8
FeSi	Liberated	23
Fe	Liberated	4

Form	Number	Mean	Std-Dev	Range low	Range high
total	105	16.72	20.75	1	105
FeOOH	44	13.3	15.78	2	85
NiO	25	9.36	10.47	2	52
FeSiO2	15	32.47	28.43	4	100
Cr-Ni metal	2	27	ND	1	27
FeS2	2	16	9.9	9	23
Pentlandite	3	14.33	10.69	5	26
NiMO	1	9	ND	9	9
NiFeO	6	7.67	3.33	3	11
MnOOH	4	13	6.22	8	22
Slag	3	80	22.91	60	105

Form	(linear) freq	rm As	rm Pb	rm Ni	error-95%
%	%	%	%	%	
FeOOH	33.31	89.47	63.49	3.01	9.02
NiO	13.33	0	0	76.38	6.5
FeSiO2	27.73	8.28	29.6	4.27	8.56
Cr-Ni metal	1.6	0	0	2.86	2.35
FeS2	1.82	0	0.36	0.2	2.56
Pentlandite	2.45	0	0	5.08	2.96
NiMO	0.51	0.8	0.04	1.8	1.37
NiFeO	2.62	0.9	0.23	4.22	3.06
MnOOH	2.96	0.55	5.64	0.53	3.24
Slag	13.67	0	0.63	1.66	6.57

Fe	Liberated	9
Fe	Liberated	32
Fe	Cemented	5
nio	Liberated	9
nicuo	Liberated	9
Fe	Liberated	7
pent	Liberated	5
nio	Liberated	7
FeSi	Liberated	45
Fe	Liberated	8
nifeo	Liberated	4
nio	Liberated	5
nio	Rimming	8
nifeo	Liberated	9
FeSi	Liberated	19
nife	Rimming	3
nicr	Rimming	1
FeSi	Liberated	28
Fe	Liberated	7
nio	Liberated	9
pent	Liberated	12
nio	Liberated	52
Fe	Liberated	14
Fe	Liberated	6
nifeo	Liberated	9
nio	Cemented	3
nio	Liberated	22
Fe	Liberated	85
Fe	Liberated	5
Fe	Liberated	8
nio	Rimming	5
Fe	Liberated	7
nio	Liberated	4
Fe	Cemented	16
nio	Liberated	14
nio	Liberated	6
py	Inclusion	9
nio	Liberated	4
nio	Liberated	4
Fe	Liberated	7
Fe	Liberated	4
nio	Cemented	4
Mn	Cemented	22



Mn	Cemented	12
Mn	Cemented	10
Mn	Cemented	8
FeSi	Liberated	6
Fe	Liberated	9
FeSi	Liberated	50
nifeo	Liberated	10
Fe	Liberated	5
Fe	Liberated	12
FeSi	Liberated	7
Fe	Liberated	3
Fe	Liberated	7
Fe	Cemented	2
Fe	Liberated	4
Fe	Rimming	3
nio	Rimming	3
nifeo	Liberated	11
Fe	Liberated	4
Fe	Liberated	9
FeSi	Cemented	7
nio	Cemented	2
Slag	Liberated	105
Slag	Liberated	60
Slag	Liberated	75

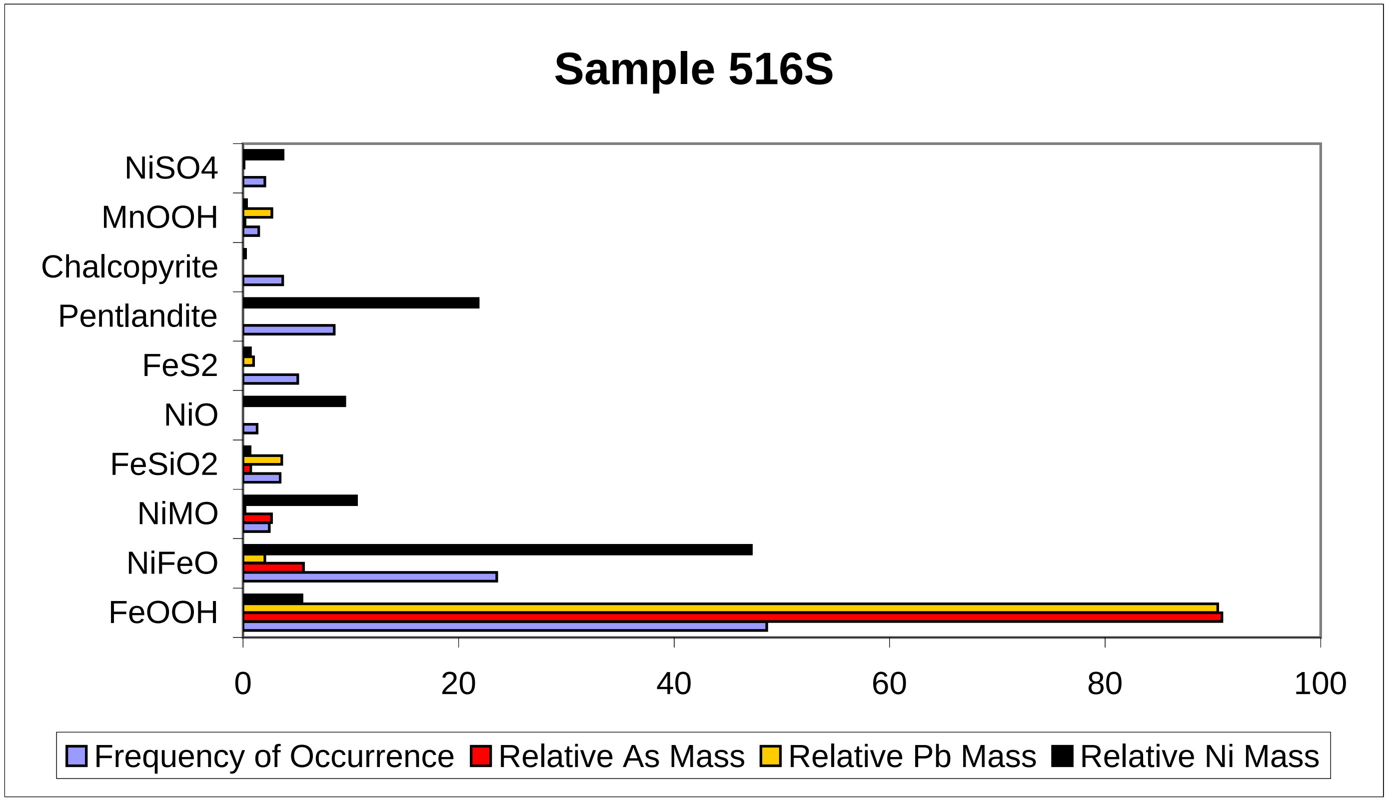
Detailed Speciation Results from LEGS (2007)
Sample 516s (Outdoor Soil)

Form	Association	Size
Fe	Liberated	9
Fe	Liberated	4
nifeo	Liberated	2
Fe	Liberated	4
Fe	Liberated	16
Fe	Liberated	45
nimo	Liberated	7
Fe	Liberated	3
Fe	Cemented	2
FeSi	Liberated	9
FeSi	Liberated	10
FeSi	Liberated	12
FeSi	Liberated	3
FeSi	Liberated	3
FeSi	Liberated	3
Fe	Liberated	2
Fe	Liberated	14
Fe	Liberated	6
Fe	Rimming	2
nio	Liberated	10
Fe	Liberated	3
Fe	Cemented	18
nifeo	Liberated	26
nio	Inclusion	11
nio	Inclusion	2
nimo	Liberated	27
nifeo	Liberated	14
Fe	Liberated	4
FeSi	Liberated	4
Fe	Liberated	28
Fe	Liberated	13
Fe	Liberated	4
Fe	Liberated	9
Fe	Liberated	11
Fe	Liberated	11
Fe	Cemented	32
Fe	Liberated	48

Form	Number	Mean	Std-Dev	Range low	Range high
total	101	17.2	24.11	2	135
FeOOH	48	17.58	22.35	2	98
NiFeO	9	45.44	53.56	2	135
NiMO	3	14	11.27	7	27
FeSiO2	8	7.5	4.99	3	16
NiO	3	7.67	4.93	2	11
FeS2	6	14.67	11.15	4	35
Pentlandite	14	10.5	6.44	3	26
Chalcopyrite	7	9.14	7.31	3	22
MnOOH	2	12.5	0.71	12	13
NiSO4	1	35	ND	35	35

Form	(linear) freq	rm As	rm Pb	rm Ni	error-95%
%	%	%	%	%	
FeOOH	48.59	90.83	90.43	5.45	9.75
NiFeO	23.55	5.62	2.02	47.16	8.27
NiMO	2.42	2.64	0.18	10.53	3
FeSiO2	3.45	0.72	3.6	0.66	3.56
NiO	1.32	0	0	9.43	2.23
FeS2	5.07	0	0.99	0.68	4.28
Pentlandite	8.46	0	0	21.83	5.43
Chalcopyrite	3.68	0	0	0.25	3.67
MnOOH	1.44	0.19	2.68	0.32	2.32
NiSO4	2.01	0	0.1	3.7	2.74

nifeo	Liberated	4
Fe	Liberated	6
Fe	Cemented	4
nimo	Liberated	8
nifeo	Rimming	7
Fe	Cemented	5
py	Inclusion	6
py	Inclusion	17
FeSi	Liberated	16
pent	Inclusion	8
pent	Inclusion	7
pent	Inclusion	3
pent	Inclusion	3
pent	Inclusion	3
Fe	Rimming	38
py	Cemented	15
py	Inclusion	4
cp	Inclusion	22
cp	Inclusion	15
cp	Inclusion	11
cp	Inclusion	7
Fe	Liberated	98
cp	Inclusion	3
cp	Inclusion	3
cp	Inclusion	3
py	Cemented	35
Fe	Rimming	30
Fe	Liberated	19
Fe	Liberated	3
Fe	Rimming	9
Fe	Liberated	6
Fe	Liberated	5
Fe	Liberated	3
Fe	Liberated	8
nifeo	Rimming	11
Fe	Liberated	2
Fe	Liberated	9
Fe	Liberated	15
Fe	Liberated	4
Mn	Rimming	12
Mn	Cemented	13
Fe	Liberated	52
Fe	Liberated	11



Fe	Liberated	7
pent	Cemented	14
pent	Liberated	10
pent	Liberated	26
pent	Cemented	12
pent	Cemented	12
pent	Cemented	12
pent	Cemented	15
pent	Cemented	5
Fe	Cemented	82
Fe	Liberated	25
nifeo	Rimming	115
nisio2	Liberated	35
Fe	Liberated	8
pent	Liberated	17
Fe	Liberated	85
py	Liberated	11
Fe	Liberated	9
Fe	Liberated	13
nifeo	Liberated	135
nifeo	Liberated	95

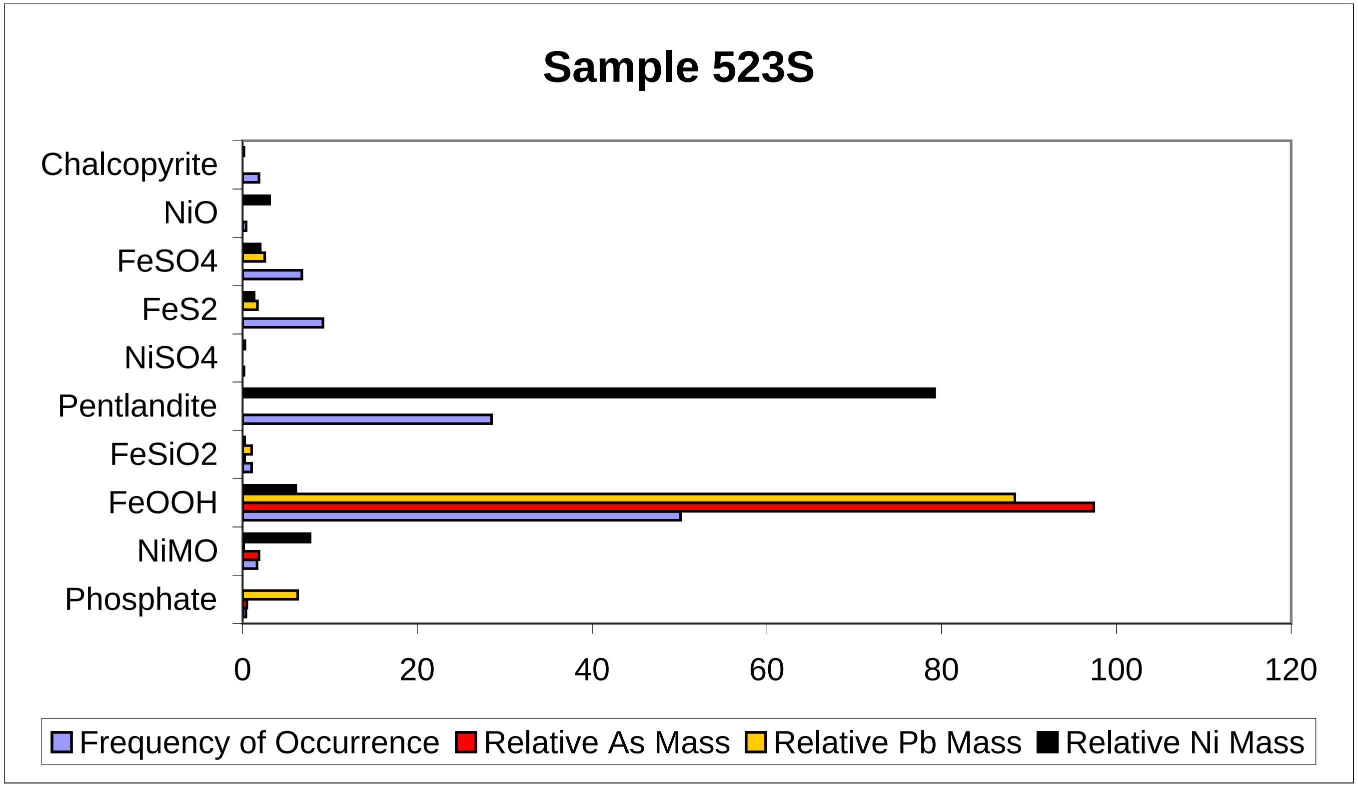
Detailed Speciation Results from LEGS (2007)
Sample 523s (Outdoor Soil)

Form	**Association**	**Size**
Phos	Liberated	2
nimo	Liberated	21
nimo	Liberated	16
Fe	Liberated	12
FeSi	Liberated	9
pent	Liberated	6
Fe	Rimming	7
pent	Liberated	7
pent	Liberated	35
Fe	Liberated	35
Fe	Liberated	6
Fe	Cemented	32
Phos	Liberated	6
nisio2	Rimming	3
py	Liberated	5
Fe	Liberated	11
py	Liberated	28
Fe	Liberated	22
Fe	Liberated	21
Fe	Liberated	12
Fe	Liberated	9
Fe	Liberated	36
Fe	Liberated	4
Fe	Liberated	40
Fe	Liberated	21
pent	Inclusion	2
pent	Inclusion	2
pent	Inclusion	4
pent	Liberated	16
Fe	Liberated	8
Fe	Liberated	14
Fe	Liberated	8
pent	Liberated	10
pent	Liberated	10
Fe	Liberated	60
Sulf	Liberated	29
pent	Liberated	80
Fe	Liberated	55

Form	Number	Mean	Std-Dev	Range low	Range high
total	115	19.5	18.15	1	88
Phosphate	2	4	2.83	2	6
NiMO	2	18.5	3.54	16	21
FeOOH	41	27.41	19.08	4	88
FeSiO2	2	11.5	3.54	9	14
Pentlandite	45	14.2	17.36	2	80
NiSO4	1	3	ND	3	3
FeS2	15	13.73	11.47	1	45
FeSO4	5	30.4	18.96	8	60
NiO	1	9	ND	9	9
Chalcopyrite	1	42	ND	42	42

Form	(linear) freq	rm As	rm Pb	rm Ni	error-95%
%	%	%	%	%	
Phosphate	0.36	0.48	6.29	0.01	1.09
NiMO	1.65	1.87	0.12	7.74	2.33
FeOOH	50.11	97.43	88.37	6.06	9.14
FeSiO2	1.03	0.22	1.01	0.21	1.84
Pentlandite	28.49	0	0	79.19	8.25
NiSO4	0.13	0	0.01	0.24	0.67
FeS2	9.18	0	1.7	1.32	5.28
FeSO4	6.78	0	2.51	2.01	4.59
NiO	0.4	0	0	3.08	1.16
Chalcopyrite	1.87	0	0	0.14	2.48

pent	Rimming	13
pent	Inclusion	2
pent	Inclusion	2
pent	Inclusion	2
Fe	Liberated	35
pent	Inclusion	16
Fe	Liberated	15
Fe	Liberated	38
pent	Liberated	21
pent	Liberated	3
pent	Liberated	3
Fe	Liberated	41
pent	Inclusion	20
pent	Inclusion	10
pent	Cemented	5
pent	Cemented	5
pent	Cemented	5
pent	Cemented	5
pent	Cemented	5
pent	Cemented	5
Fe	Liberated	52
py	Liberated	7
Fe	Liberated	28
Sulf	Liberated	60
Fe	Liberated	88
pent	Liberated	10
pent	Liberated	4
Fe	Liberated	19
py	Liberated	1
py	Liberated	17
Fe	Liberated	10
pent	Liberated	45
Sulf	Inclusion	8
Fe	Liberated	26
Fe	Liberated	48
pent	Liberated	4
pent	Liberated	47
Fe	Liberated	43
Fe	Liberated	43
pent	Inclusion	8
pent	Inclusion	7
pent	Inclusion	6
pent	Inclusion	3
py	Liberated	8



Fe	Liberated	22
py	Liberated	7
nio	Liberated	9
Fe	Liberated	7
FeSi	Liberated	14
Fe	Liberated	23
Fe	Liberated	32
py	Liberated	45
Fe	Liberated	60
pent	Liberated	10
Fe	Rimming	12
Sulf	Liberated	23
pent	Inclusion	10
pent	Inclusion	10
pent	Inclusion	10
pent	Inclusion	10
Fe	Liberated	7
Fe	Liberated	14
Sulf	Liberated	32
py	Rimming	10
pent	Liberated	9
violarite	Liberated	28
viol	Liberated	9
py	Liberated	28
py	Cemented	10
py	Cemented	10
py	Cemented	10
py	Cemented	10
py	Cemented	10
pent	Liberated	55
pent	Liberated	60
cp	Liberated	42
Fe	Liberated	48

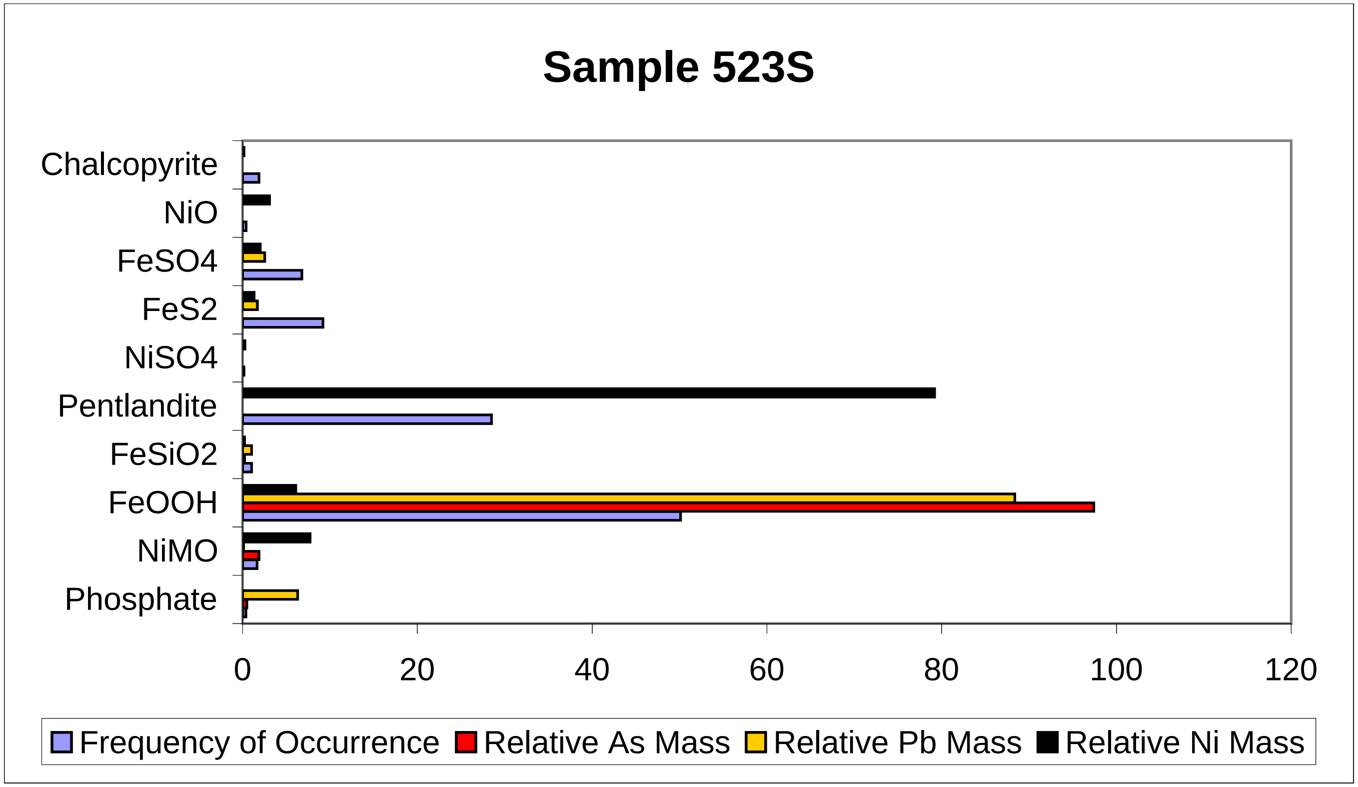
Detailed Speciation Results from LEGS (2007)
Sample 523s (Outdoor Soil)

Form	**Association**	**Size**
Phos	Liberated	2
nimo	Liberated	21
nimo	Liberated	16
Fe	Liberated	12
FeSi	Liberated	9
pent	Liberated	6
Fe	Rimming	7
pent	Liberated	7
pent	Liberated	35
Fe	Liberated	35
Fe	Liberated	6
Fe	Cemented	32
Phos	Liberated	6
nisio2	Rimming	3
py	Liberated	5
Fe	Liberated	11
py	Liberated	28
Fe	Liberated	22
Fe	Liberated	21
Fe	Liberated	12
Fe	Liberated	9
Fe	Liberated	36
Fe	Liberated	4
Fe	Liberated	40
Fe	Liberated	21
pent	Inclusion	2
pent	Inclusion	2
pent	Inclusion	4
pent	Liberated	16
Fe	Liberated	8
Fe	Liberated	14
Fe	Liberated	8
pent	Liberated	10
pent	Liberated	10
Fe	Liberated	60
Sulf	Liberated	29
pent	Liberated	80
Fe	Liberated	55

Form	Number	Mean	Std-Dev	Range low	Range high
total	115	19.5	18.15	1	88
Phosphate	2	4	2.83	2	6
NiMO	2	18.5	3.54	16	21
FeOOH	41	27.41	19.08	4	88
FeSiO2	2	11.5	3.54	9	14
Pentlandite	45	14.2	17.36	2	80
NiSO4	1	3	ND	3	3
FeS2	15	13.73	11.47	1	45
FeSO4	5	30.4	18.96	8	60
NiO	1	9	ND	9	9
Chalcopyrite	1	42	ND	42	42

Form	(linear) freq	rm As	rm Pb	rm Ni	error-95%
%	%	%	%	%	
Phosphate	0.36	0.48	6.29	0.01	1.09
NiMO	1.65	1.87	0.12	7.74	2.33
FeOOH	50.11	97.43	88.37	6.06	9.14
FeSiO2	1.03	0.22	1.01	0.21	1.84
Pentlandite	28.49	0	0	79.19	8.25
NiSO4	0.13	0	0.01	0.24	0.67
FeS2	9.18	0	1.7	1.32	5.28
FeSO4	6.78	0	2.51	2.01	4.59
NiO	0.4	0	0	3.08	1.16
Chalcopyrite	1.87	0	0	0.14	2.48

pent	Rimming	13
pent	Inclusion	2
pent	Inclusion	2
pent	Inclusion	2
Fe	Liberated	35
pent	Inclusion	16
Fe	Liberated	15
Fe	Liberated	38
pent	Liberated	21
pent	Liberated	3
pent	Liberated	3
Fe	Liberated	41
pent	Inclusion	20
pent	Inclusion	10
pent	Cemented	5
pent	Cemented	5
pent	Cemented	5
pent	Cemented	5
pent	Cemented	5
pent	Cemented	5
Fe	Liberated	52
py	Liberated	7
Fe	Liberated	28
Sulf	Liberated	60
Fe	Liberated	88
pent	Liberated	10
pent	Liberated	4
Fe	Liberated	19
py	Liberated	1
py	Liberated	17
Fe	Liberated	10
pent	Liberated	45
Sulf	Inclusion	8
Fe	Liberated	26
Fe	Liberated	48
pent	Liberated	4
pent	Liberated	47
Fe	Liberated	43
Fe	Liberated	43
pent	Inclusion	8
pent	Inclusion	7
pent	Inclusion	6
pent	Inclusion	3
py	Liberated	8



Fe	Liberated	22
py	Liberated	7
nio	Liberated	9
Fe	Liberated	7
FeSi	Liberated	14
Fe	Liberated	23
Fe	Liberated	32
py	Liberated	45
Fe	Liberated	60
pent	Liberated	10
Fe	Rimming	12
Sulf	Liberated	23
pent	Inclusion	10
pent	Inclusion	10
pent	Inclusion	10
pent	Inclusion	10
Fe	Liberated	7
Fe	Liberated	14
Sulf	Liberated	32
py	Rimming	10
pent	Liberated	9
violarite	Liberated	28
viol	Liberated	9
py	Liberated	28
py	Cemented	10
py	Cemented	10
py	Cemented	10
py	Cemented	10
py	Cemented	10
pent	Liberated	55
pent	Liberated	60
cp	Liberated	42
Fe	Liberated	48

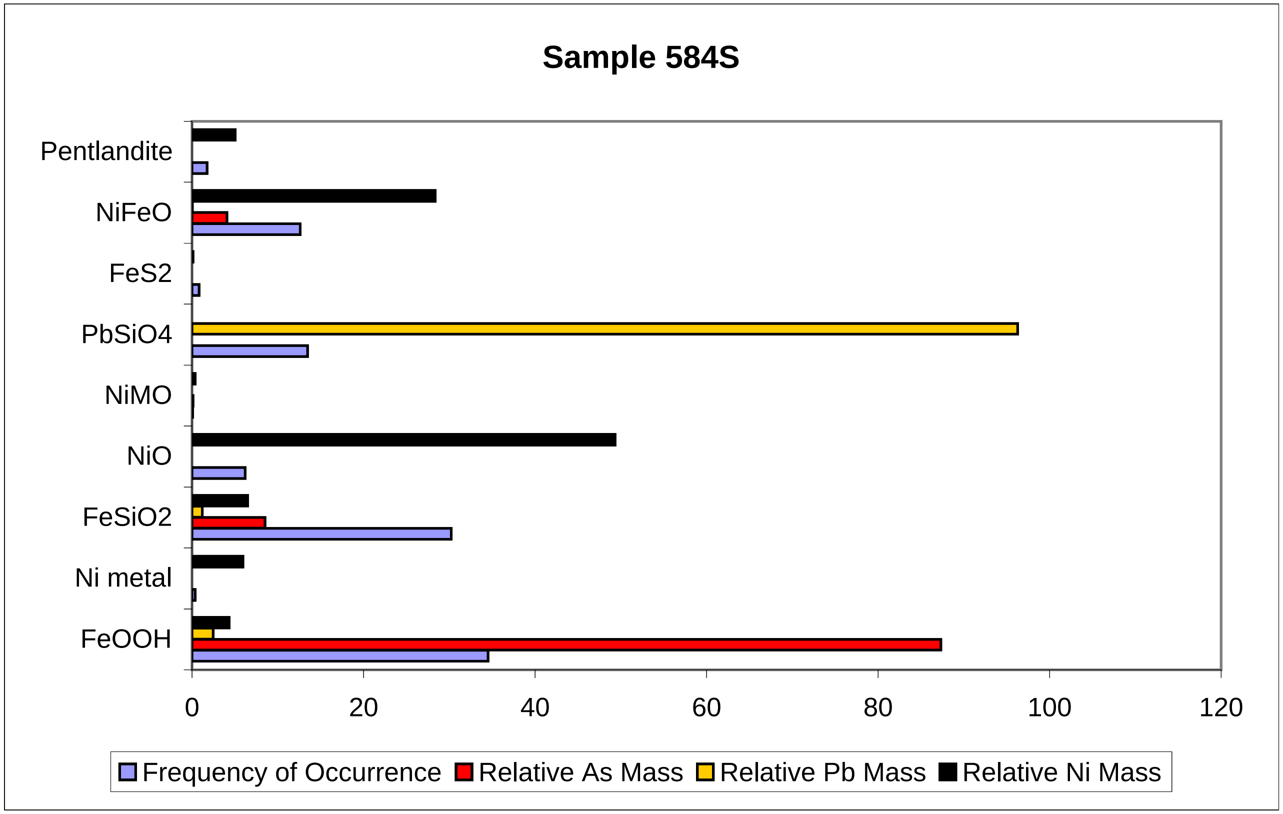
Detailed Speciation Results from LEGS (2007)
Sample 584s (Outdoor Soil)

Form	**Association**	**Size**
Fe	Liberated	12
ni	Liberated	3
Fe	Liberated	37
FeSi	Liberated	25
Fe	Liberated	10
nio	Liberated	4
FeSi	Liberated	80
nio	Liberated	5
FeSi	Liberated	32
Fe	Liberated	11
FeSi	Liberated	39
Fe	Liberated	11
nimo	Liberated	2
Fe	Liberated	5
FeSi	Liberated	5
Fe	Liberated	2
Fe	Liberated	10
Fe	Liberated	25
FeSi	Liberated	42
Fe	Liberated	9
PbSiO4	Rimming	40
PbSiO4	Rimming	40
PbSiO4	Rimming	40
PbSiO4	Rimming	40
PbSiO4	Rimming	20
PbSiO4	Rimming	20
PbSiO4	Rimming	20
PbSiO4	Rimming	20
PbSiO4	Rimming	20
PbSiO4	Rimming	20
PbSiO4	Rimming	25
PbSiO4	Rimming	35
FeSi	Liberated	13
nio	Liberated	12
nio	Liberated	18
Fe	Liberated	45
py	Liberated	10

Form	Number	Mean	Std-Dev	Range low	Range high
total	103	24.52	21.25	2	90
FeOOH	40	21.8	18.2	2	90
Ni metal	2	4.5	2.12	3	6
FeSiO2	20	38.15	25.37	4	85
NiO	17	9.18	6.7	3	29
NiMO	1	2	ND	2	2
PbSiO4	12	28.33	9.61	20	40
FeS2	2	10.5	0.71	10	11
NiFeO	6	53.17	28	2	80
Pentlandite	3	14.67	8.33	8	24

Form	(linear) freq	rm As	rm Pb	rm Ni	error-95%
%	%	%	%	%	
FeOOH	34.52	87.31	2.47	4.34	9.18
Ni metal	0.36	0	0	5.93	1.15
FeSiO2	30.21	8.49	1.21	6.48	8.87
NiO	6.18	0	0	49.32	4.65
NiMO	0.08	0.12	0	0.39	0.54
PbSiO4	13.46	0	96.27	0	6.59
FeS2	0.83	0	0.01	0.12	1.75
NiFeO	12.63	4.08	0.04	28.37	6.42
Pentlandite	1.74	0	0	5.04	2.53

nio	Liberated	8
Fe	Liberated	5
nio	Liberated	4
Fe	Liberated	15
FeSi	Liberated	50
FeSi	Liberated	14
nio	Liberated	8
nio	Liberated	4
Fe	Liberated	14
nio	Liberated	7
Fe	Liberated	8
Fe	Liberated	7
nio	Liberated	4
Fe	Liberated	50
Fe	Liberated	10
Fe	Liberated	3
FeSi	Liberated	65
Fe	Liberated	40
nio	Liberated	14
Fe	Liberated	38
Fe	Liberated	15
Fe	Liberated	4
nio	Rimming	4
Fe	Liberated	16
nio	Liberated	11
nio	Liberated	3
FeSi	Liberated	85
nifeo	Liberated	80
FeSi	Liberated	25
nifeo	Liberated	62
FeSi	Liberated	28
Fe	Liberated	9
Fe	Liberated	35
Fe	Liberated	13
FeSi	Liberated	4
Fe	Liberated	48
Fe	Liberated	18
nifeo	Liberated	48
FeSi	Liberated	52
nio	Liberated	29
Fe	Liberated	22
FeSi	Liberated	21



ni	Liberated	6
FeSi	Liberated	80
Fe	Liberated	13
Fe	Liberated	25
FeSi	Liberated	55
pent	Inclusion	24
Fe	Rimming	25
py	Liberated	11
pent	Inclusion	12
Fe	Liberated	45
nifeo	Liberated	75
FeSi	Liberated	8
Fe	Liberated	35
FeSi	Liberated	40
Fe	Liberated	8
nio	Liberated	13
nifeo	Liberated	2
Fe	Liberated	50
nifeo	Rimming	52
Fe	Liberated	90
nio	Liberated	8
pent	Inclusion	8
Fe	Rimming	18
Fe	Liberated	16

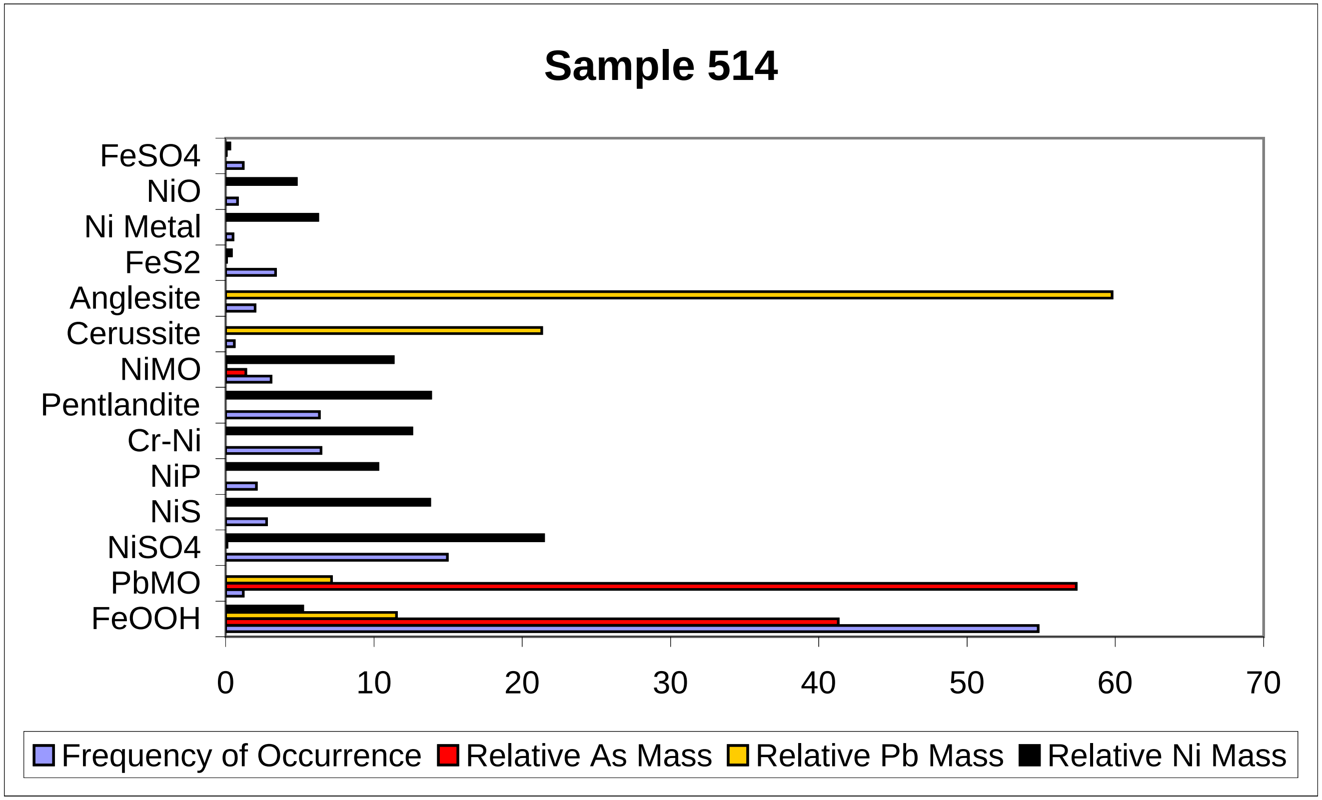
Detailed Speciation Results from LEGS (2007)
Sample 514 (Indoor Dust)

Form	**Association**	**Size**
Fe	Liberated	12
PbMO	Liberated	12
Fe	Liberated	7
niso4	Liberated	3
Fe	Liberated	15
Fe	Liberated	4
Fe	Liberated	7
Fe	Liberated	4
nis	Liberated	8
nip	Liberated	9
niso4	Liberated	10
Fe	Liberated	2
Fe	Liberated	13
niso4	Liberated	5
Fe	Liberated	3
niso4	Liberated	9
niso4	Liberated	4
nis	Liberated	3
Fe	Liberated	10
nis	Liberated	10
Fe	Liberated	3
Fe	Liberated	12
niso4	Liberated	9
crni	Liberated	13
nip	Liberated	3
Fe	Liberated	13
niso4	Liberated	8
niso4	Liberated	8
Fe	Liberated	36
Fe	Liberated	9
Fe	Liberated	11
niso4	Liberated	6
niso4	Liberated	8
pent	Liberated	10
crni	Liberated	12
Fe	Liberated	16
Fe	Liberated	5
Fe	Liberated	8
crni	Liberated	3

Form	Number	Mean	Std-Dev	Range low	Range high
total	100	10.11	7.75	2	45
FeOOH	47	11.79	9.34	2	45
PbMO	1	12	ND	12	12
NiSO4	17	8.88	7.26	3	35
NiS	4	7	2.94	3	10
NiP	3	7	3.46	3	9
Cr-Ni metal	9	7.22	4.87	2	15
Pentlandite	6	10.67	6.59	3	23
NiMO	3	10.33	5.51	5	16
Cerussite	1	6	ND	6	6
Anglesite	1	20	ND	20	20
FeS2	5	6.8	4.09	4	14
Ni Metal	1	5	ND	5	5
NiO	1	8	ND	8	8
FeSO4	1	12	ND	12	12

Form	(linear) freq	rm As	rm Pb	rm Ni	error-95%
%	%	%	%	%	
FeOOH	54.8	41.3	11.53	5.2	9.75
PbMO	1.19	57.35	7.14	0	2.12
NiSO4	14.94	0	0.08	21.45	6.99
NiS	2.77	0	0	13.76	3.22
NiP	2.08	0	0	10.27	2.8
Cr-Ni metal	6.43	0	0	12.56	4.81
Pentlandite	6.33	0	0	13.82	4.77
NiMO	3.07	1.35	0.03	11.3	3.38
Cerussite	0.59	0	21.32	0	1.51
Anglesite	1.98	0	59.78	0	2.73
FeS2	3.36	0	0.07	0.38	3.53
Ni Metal	0.49	0	0	6.21	1.37
NiO	0.79	0	0	4.77	1.74
FeSO4	1.19	0	0.05	0.28	2.12

crni	Liberated	5
crni	Liberated	3
nimo	Liberated	16
Cer	Liberated	6
Fe	Liberated	2
Fe	Liberated	7
Ang	Liberated	20
Fe	Liberated	13
Fe	Liberated	45
niso4	Liberated	5
Fe	Liberated	16
Fe	Liberated	13
Fe	Liberated	7
niso4	Liberated	35
niso4	Liberated	5
Fe	Liberated	17
crni	Rimming	7
nimo	Liberated	5
Fe	Liberated	10
Fe	Liberated	3
Fe	Liberated	3
Fe	Liberated	12
py	Liberated	14
crni	Liberated	15
Fe	Liberated	13
Fe	Liberated	28
niso4	Liberated	11
Fe	Liberated	7
niso4	Liberated	13
Fe	Liberated	13
niso4	Inclusion	4
pent	Liberated	9
Fe	Liberated	25
nimo	Liberated	10
Fe	Liberated	9
crni	Liberated	5
crni	Liberated	2
ni	Liberated	5
Fe	Liberated	12
pent	Liberated	23
nio	Liberated	8
nis	Liberated	7
pent	Liberated	9
Fe	Liberated	8



Fe	Liberated	13
nip	Liberated	9
pent	Liberated	10
pent	Liberated	3
Fe	Liberated	5
Sulf	Liberated	12
Fe	Liberated	7
Fe	Liberated	32
Fe	Liberated	30
Fe	Liberated	3
py	Liberated	4
py	Liberated	5
py	Inclusion	5
niso4	Liberated	8
Fe	Liberated	4
Fe	Liberated	7
py	Liberated	6

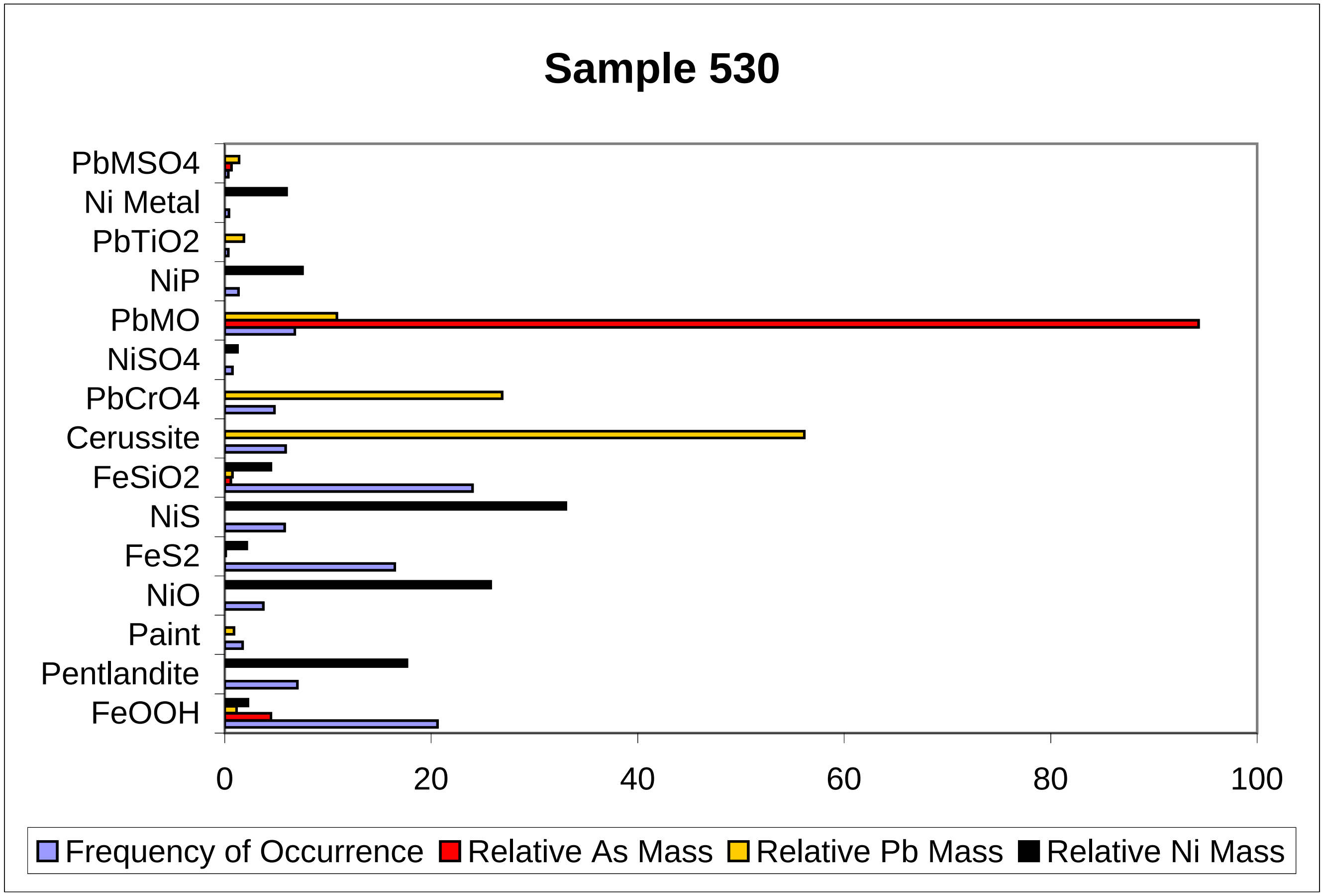
Detailed Speciation Results from LEGS (2007)
Sample 530 (Indoor Dust)

Form	**Association**	**Size**
Fe	Liberated	7
Fe	Liberated	13
Fe	Liberated	11
Fe	Liberated	13
Fe	Liberated	11
pent	Liberated	9
Fe	Liberated	4
Fe	Rimming	3
Fe	Liberated	6
Fe	Liberated	5
Paint	Liberated	14
nio	Liberated	8
Fe	Liberated	4
py	Liberated	32
pent	Liberated	2
nis	Liberated	24
py	Liberated	35
FeSi	Liberated	4
FeSi	Liberated	5
py	Liberated	3
FeSi	Liberated	7
FeSi	Liberated	15
Cer	Liberated	13
Fe	Liberated	13
FeSi	Liberated	6
nis	Liberated	10
nis	Liberated	9
Fe	Liberated	8
Paint	Liberated	7
FeSi	Liberated	16
FeSi	Liberated	45
nio	Liberated	7
Fe	Liberated	18
pent	Liberated	9
py	Rimming	40
pbcro4	Liberated	32
FeSi	Liberated	8
niso4	Liberated	9

Form	Number	Mean	Std-Dev	Range low	Range high
total	114	10.6	9.42	1	48
FeOOH	29	8.59	5.61	2	25
Pentlandite	10	8.5	4.74	2	18
Paint	2	10.5	4.95	7	14
NiO	6	7.5	7.53	2	22
FeS2	12	16.58	14.72	3	40
NiS	6	11.67	6.35	6	24
FeSiO2	19	15.26	10.66	3	45
Cerussite	14	5.07	4.45	1	14
PbCrO4	4	14.5	11.93	6	32
NiSO4	1	9	ND	9	9
PbMO	4	20.5	18.48	8	48
NiP	2	8	1.41	7	9
PbTiO2	3	1.33	0.58	1	2
Ni Metal	1	5	ND	5	5
PbMSO4	1	4	ND	4	4

form	(linear) freq	rm As	rm Pb	rm Ni	error-95%
%	%	%	%	%	
FeOOH	20.61	4.47	1.15	2.25	7.43
Pentlandite	7.04	0	0	17.63	4.7
Paint	1.74	0	0.88	0	2.4
NiO	3.73	0	0	25.77	3.48
FeS2	16.47	0	0.1	2.14	6.81
NiS	5.79	0	0	33.04	4.29
FeSiO2	24.01	0.58	0.75	4.46	7.84
Cerussite	5.88	0	56.14	0	4.32
PbCrO4	4.8	0	26.86	0	3.92
NiSO4	0.75	0	0	1.23	1.58
PbMO	6.79	94.31	10.86	0	4.62
NiP	1.32	0	0	7.52	2.1
PbTiO2	0.33	0	1.85	0	1.05
Ni Metal	0.41	0	0	5.97	1.18
PbMSO4	0.33	0.65	1.4	0	1.05

Fe	Liberated	2
FeSi	Liberated	14
Cer	Liberated	6
Fe	Liberated	12
pbcro4	Liberated	8
py	Liberated	7
Fe	Liberated	3
py	Liberated	14
py	Liberated	4
FeSi	Liberated	33
PbMO	Liberated	8
nip	Liberated	9
nio	Liberated	4
Fe	Liberated	15
Fe	Liberated	9
nis	Liberated	9
Fe	Liberated	8
FeSi	Liberated	11
nis	Liberated	12
FeSi	Liberated	15
FeSi	Liberated	12
Fe	Liberated	3
FeSi	Liberated	18
Cer	Liberated	3
Cer	Cemented	3
Cer	Cemented	2
Cer	Cemented	1
Cer	Cemented	1
Cer	Cemented	1
FeSi	Liberated	3
pent	Liberated	6
Cer	Liberated	9
Cer	Cemented	2
FeSi	Liberated	16
Fe	Liberated	2
pent	Liberated	7
nio	Liberated	22
Fe	Liberated	3
Fe	Liberated	5
py	Liberated	3
py	Liberated	17
pbcro4	Liberated	12
pbcro4	Liberated	6
py	Liberated	35



pent	Inclusion	18
Fe	Rimming	25
Fe	Cemented	4
FeSi	Liberated	16
nio	Liberated	2
pbtio2	Rimming	2
pbtio2	Liberated	1
pbtio2	Liberated	1
Cer	Liberated	9
nio	Liberated	2
Fe	Liberated	4
Fe	Liberated	16
pent	Liberated	6
nis	Liberated	6
PbMO	Liberated	13
PbMO	Liberated	13
pent	Liberated	5
py	Liberated	5
Cer	Liberated	4
py	Liberated	4
Fe	Liberated	12
ni	Liberated	5
FeSi	Liberated	16
Fe	Rimming	10
FeSi	Liberated	30
pent	Liberated	8
nip	Liberated	7
Cer	Liberated	14
Cer	Liberated	3
PbMO	Liberated	48
pent	Liberated	15
pbmso4	Liberated	4

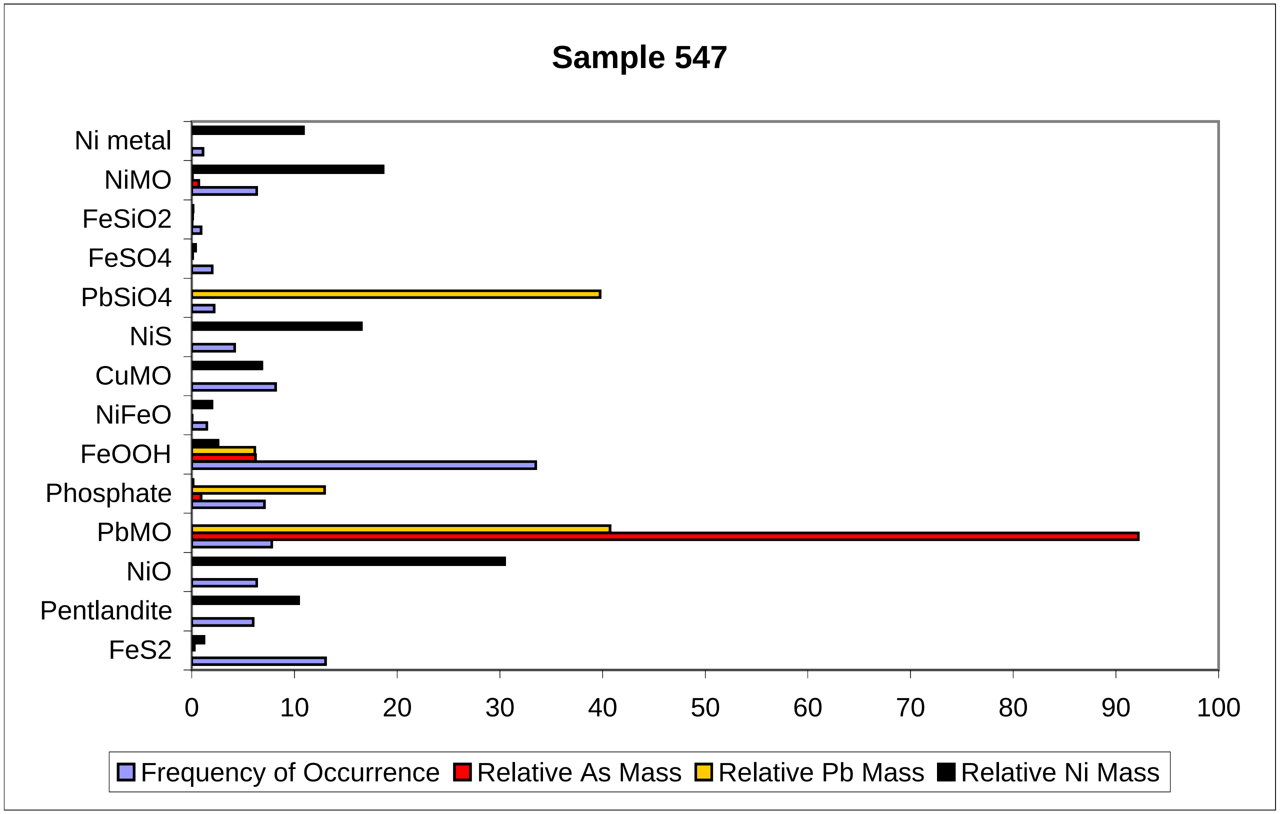
Detailed Speciation Results from LEGS (2007)
Sample 547 (Indoor Dust)

Form	**Association**	**Size**
py	Liberated	3
pent	Liberated	7
nio	Liberated	3
PbMO	Liberated	13
Phos	Liberated	8
Phos	Liberated	25
Fe	Liberated	7
PbMO	Liberated	2
nio	Liberated	8
PbMO	Cemented	2
Fe	Liberated	11
Fe	Liberated	8
nifeo	Liberated	8
py	Liberated	7
Fe	Liberated	3
pent	Liberated	10
cumo	Liberated	45
Fe	Liberated	21
Fe	Liberated	7
Fe	Liberated	11
py	Liberated	7
Fe	Liberated	8
Fe	Liberated	10
nis	Liberated	12
py	Liberated	6
PbMO	Liberated	12
nis	Liberated	11
py	Liberated	12
py	Liberated	5
PbMO	Liberated	10
Fe	Liberated	4
nio	Liberated	15
py	Liberated	8
Fe	Liberated	8
PbSiO4	Liberated	12
Sulf	Liberated	11

Form	Number	Mean	Std-Dev	Range low	Range high
total	58	9.52	8.15	1	45
FeS2	10	7.2	3.77	3	15
Pentlandite	3	11	4.58	7	16
NiO	5	7	5.15	2	15
PbMO	6	7.17	5.08	2	13
Phosphate	4	9.75	10.47	2	25
FeOOH	16	11.56	7.77	3	35
NiFeO	1	8	ND	8	8
CuMO	1	45	ND	45	45
NiS	2	11.5	0.71	11	12
PbSiO4	1	12	ND	12	12
FeSO4	1	11	ND	11	11
FeSiO2	1	5	ND	5	5
NiMO	2	17.5	13.44	8	27
Ni metal	5	1.2	0.45	1	2

form	(linear) freq	rm As	rm Pb	rm Ni	error-95%
%	%	%	%	%	
FeS2	13.04	0	0.25	1.18	8.67
Pentlandite	5.98	0	0	10.41	6.1
NiO	6.34	0	0	30.48	6.27
PbMO	7.79	92.17	40.73	0	6.9
Phosphate	7.07	0.91	12.92	0.12	6.59
FeOOH	33.51	6.19	6.13	2.54	12.15
NiFeO	1.45	0.03	0.01	1.96	3.08
CuMO	8.15	0	0	6.81	7.04
NiS	4.17	0	0	16.51	5.14
PbSiO4	2.17	0	39.75	0	3.75
FeSO4	1.99	0	0.08	0.37	3.6
FeSiO2	0.91	0.02	0.09	0.12	2.44
NiMO	6.34	0.68	0.05	18.63	6.27
Ni metal	1.09	0	0	10.89	2.67

Phos	Liberated	2
FeSi	Liberated	5
py	Liberated	3
Phos	Liberated	4
py	Liberated	6
nimo	Liberated	27
nimo	Liberated	8
Fe	Liberated	9
Fe	Liberated	18
Fe	Liberated	14
PbMO	Liberated	4
Fe	Liberated	11
py	Liberated	15
pent	Liberated	16
nio	Liberated	7
ni	Liberated	2
ni	Cemented	1
ni	Cemented	1
ni	Cemented	1
ni	Cemented	1
Fe	Liberated	35
nio	Rimming	2



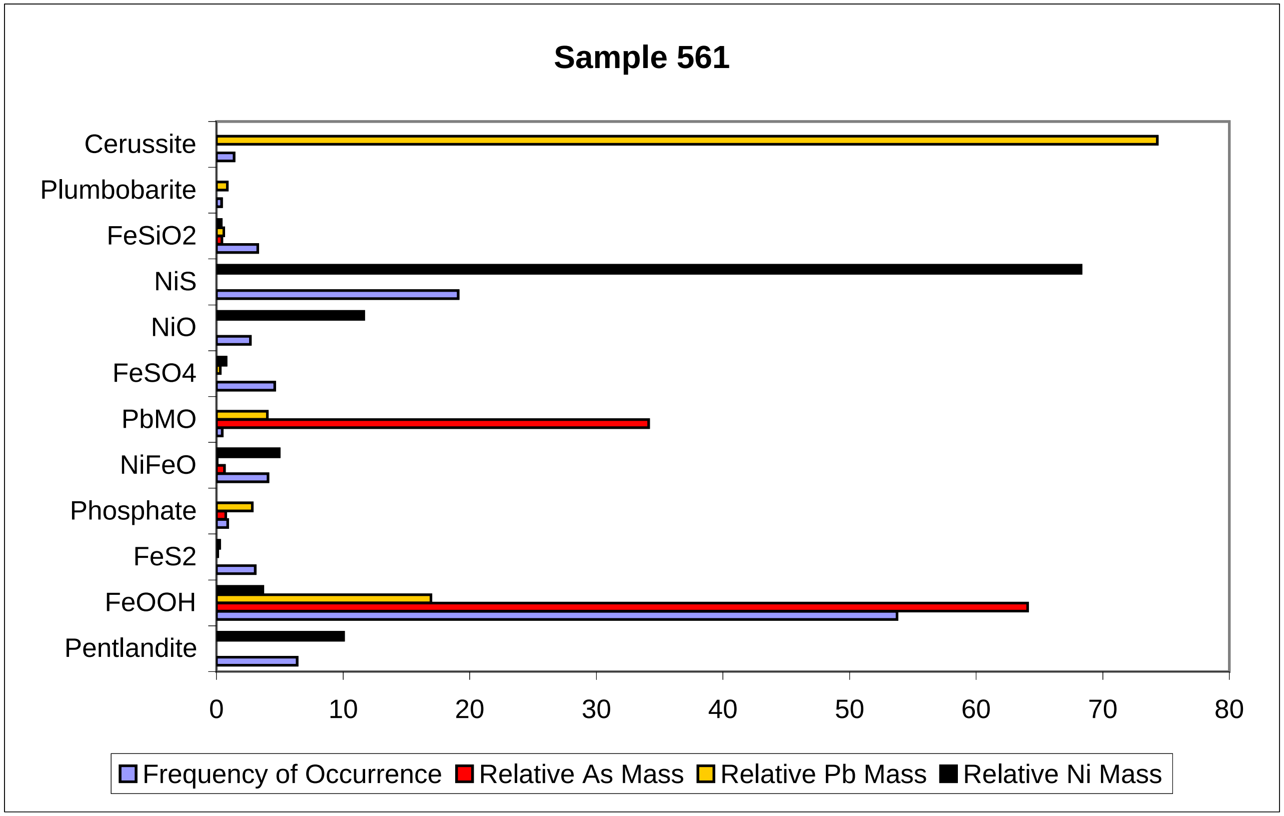
Detailed Speciation Results from LEGS (2007)
Sample 561 (Indoor Dust)

Form	Association	Size
pent	Liberated	34
Fe	Liberated	58
py	Cemented	7
Phos	Rimming	14
Fe	Liberated	15
Fe	Liberated	7
nifeo	Liberated	21
PbMO	Inclusion	2
PbMO	Inclusion	4
Fe	Liberated	7
Fe	Liberated	6
Fe	Liberated	80
Fe	Liberated	45
Fe	Liberated	38
Fe	Liberated	4
Fe	Liberated	28
Fe	Liberated	29
Fe	Liberated	23
Fe	Liberated	42
Fe	Liberated	33
Fe	Cemented	38
Sulf	Liberated	12
Fe	Liberated	9
Fe	Liberated	14
Fe	Liberated	11
Fe	Liberated	85
Sulf	Inclusion	2
Fe	Liberated	9
Fe	Liberated	5
Fe	Liberated	8
Fe	Liberated	3
Fe	Liberated	60
Fe	Liberated	7
Fe	Liberated	47
Fe	Liberated	9
Fe	Liberated	4
Fe	Liberated	8

Form	Number	Mean	Std-Dev	Range low	Range high
total	110	22.37	25.25	1	150
Pentlandite	11	14.27	13.76	5	48
FeOOH	48	27.56	28.84	3	150
FeS2	8	9.38	10.17	2	31
Phosphate	2	11	4.24	8	14
NiFeO	5	20	16.93	3	48
PbMO	6	1.83	1.17	1	4
FeSO4	4	28.25	24.88	2	50
NiO	6	11	12.38	3	35
NiS	15	31.33	28.74	10	105
FeSiO2	1	80	ND	80	80
Plumbobarite	1	10	ND	10	10
Cerussite	3	11.33	12.1	2	25

Form	(linear) freq	rm As	rm Pb	rm Ni	error-95%
%	%	%	%	%	
Pentlandite	6.38	0	0	10.03	4.57
FeOOH	53.76	64.07	16.94	3.67	9.32
FeS2	3.05	0	0.1	0.25	3.21
Phosphate	0.89	0.74	2.82	0.01	1.76
NiFeO	4.06	0.62	0.06	4.96	3.69
PbMO	0.45	34.14	4.03	0	1.25
FeSO4	4.59	0	0.3	0.77	3.91
NiO	2.68	0	0	11.64	3.02
NiS	19.1	0	0	68.3	7.35
FeSiO2	3.25	0.43	0.57	0.38	3.31
Plumbobarite	0.41	0	0.86	0	1.19
Cerussite	1.38	0	74.32	0	2.18

Fe	Liberated	3
Fe	Liberated	23
Fe	Liberated	8
nio	Liberated	3
nis	Rimming	20
nis	Cemented	35
]nis	Cemented	25
nis	Cemented	105
nis	Cemented	72
Fe	Rimming	150
nifeo	Liberated	3
PbMO	Liberated	2
PbMO	Liberated	1
PbMO	Liberated	1
PbMO	Liberated	1
Fe	Liberated	8
Fe	Liberated	10
Fe	Liberated	6
nio	Liberated	4
Fe	Cemented	4
FeSi	Liberated	80
Fe	Liberated	8
Sulf	Liberated	49
nis	Liberated	65
nis	Liberated	48
nis	Liberated	20
nis	Liberated	20
nis	Liberated	20
nis	Liberated	15
nis	Liberated	10
nis	Liberated	10
nis	Liberated	10
nis	Liberated	10
nis	Liberated	10
Fe	Liberated	4
Fe	Liberated	48
Fe	Liberated	50
Phos	Liberated	8
nio	Liberated	8
Fe	Liberated	60
py	Inclusion	17
Fe	Liberated	29
nifeo	Liberated	14



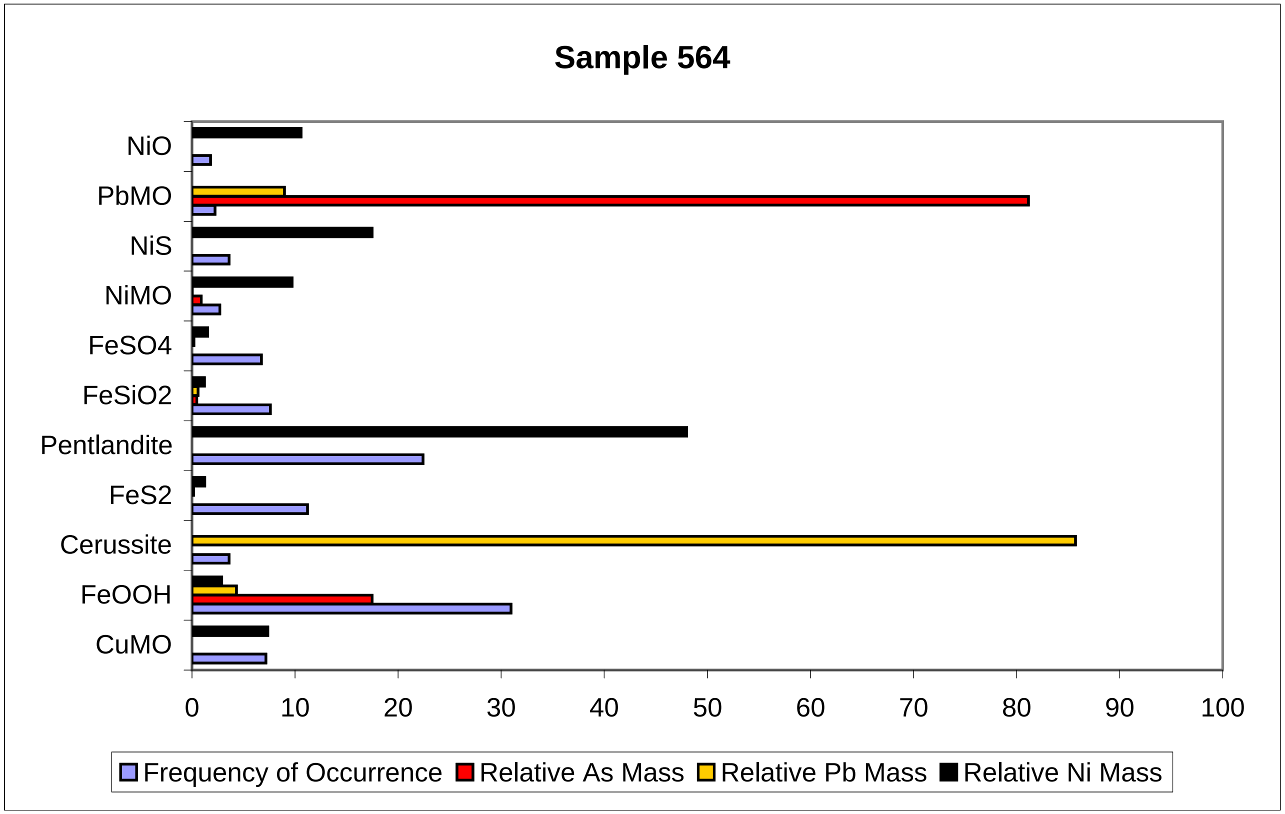
bar	Liberated	10
Fe	Liberated	26
pent	Inclusion	10
pent	Inclusion	10
pent	Inclusion	10
pent	Inclusion	10
pent	Inclusion	10
pent	Inclusion	10
pent	Cemented	48
pent	Inclusion	5
pent	Inclusion	5
pent	Inclusion	5
Fe	Rimming	75
nio	Liberated	3
nio	Liberated	35
nio	Liberated	13
py	Liberated	31
Fe	Liberated	9
nifeo	Liberated	48
nifeo	Liberated	14
py	Liberated	10
py	Liberated	4
py	Liberated	2
py	Liberated	2
py	Liberated	2
Cer	Liberated	25
Cer	Liberated	7
Cer	Liberated	2
Fe	Liberated	45
Sulf	Liberated	50

Detailed Speciation Results from LEGS (2007)
Sample 564 (Indoor Dust)

Form	**Association**	**Size**
cumo	Cemented	3
cumo	Cemented	1
Fe	Liberated	2
Fe	Liberated	8
Cer	Liberated	8
cumo	Liberated	12
py	Liberated	6
pent	Liberated	7
FeSi	Liberated	8
pent	Inclusion	7
Sulf	Rimming	12
pent	Rimming	5
py	Liberated	5
nimo	Liberated	4
nis	Liberated	8
PbMO	Liberated	3
PbMO	Liberated	2
Fe	Liberated	12
Fe	Liberated	3
Fe	Liberated	3
Fe	Liberated	3
pent	Liberated	9
FeSi	Liberated	9
nimo	Liberated	2
Sulf	Liberated	3
Fe	Liberated	8
pent	Liberated	9
py	Liberated	11
Fe	Liberated	14
pent	Liberated	3
nio	Liberated	4
py	Liberated	3
pent	Liberated	10
Fe	Liberated	16

Form	Number	Mean	Std-Dev	Range low	Range high
total	34	6.56	3.92	1	16
CuMO	3	5.33	5.86	1	12
FeOOH	9	7.67	5.32	2	16
Cerussite	1	8	ND	8	8
FeS2	4	6.25	3.4	3	11
Pentlandite	7	7.14	2.48	3	10
FeSiO2	2	8.5	0.71	8	9
FeSO4	2	7.5	6.36	3	12
NiMO	2	3	1.41	2	4
NiS	1	8	ND	8	8
PbMO	2	2.5	0.71	2	3
NiO	1	4	ND	4	4

form	(linear) freq	rm As	rm Pb	rm Ni	error-95%
%	%	%	%	%	
CuMO	7.17	0	0	7.36	8.67
FeOOH	30.94	17.47	4.33	2.88	15.54
Cerussite	3.59	0	85.72	0	6.25
FeS2	11.21	0	0.16	1.24	10.61
Pentlandite	22.42	0	0	47.99	14.02
FeSiO2	7.62	0.48	0.6	1.21	8.92
FeSO4	6.73	0	0.2	1.53	8.42
NiMO	2.69	0.89	0.02	9.72	5.44
NiS	3.59	0	0	17.47	6.25
PbMO	2.24	81.16	8.98	0	4.98
NiO	1.79	0	0	10.6	4.46


Sample 564
NiO
PbMO
NiS
NiMO
FeSO4
FeSiO2
Pentlandite
FeS2
Cerussite
FeOOH
CuMO
0
10
20
30
40
50
60
70
80
90
100
Frequency of Occurrence
Relative As Mass
Relative Pb Mass
Relative Ni Mass

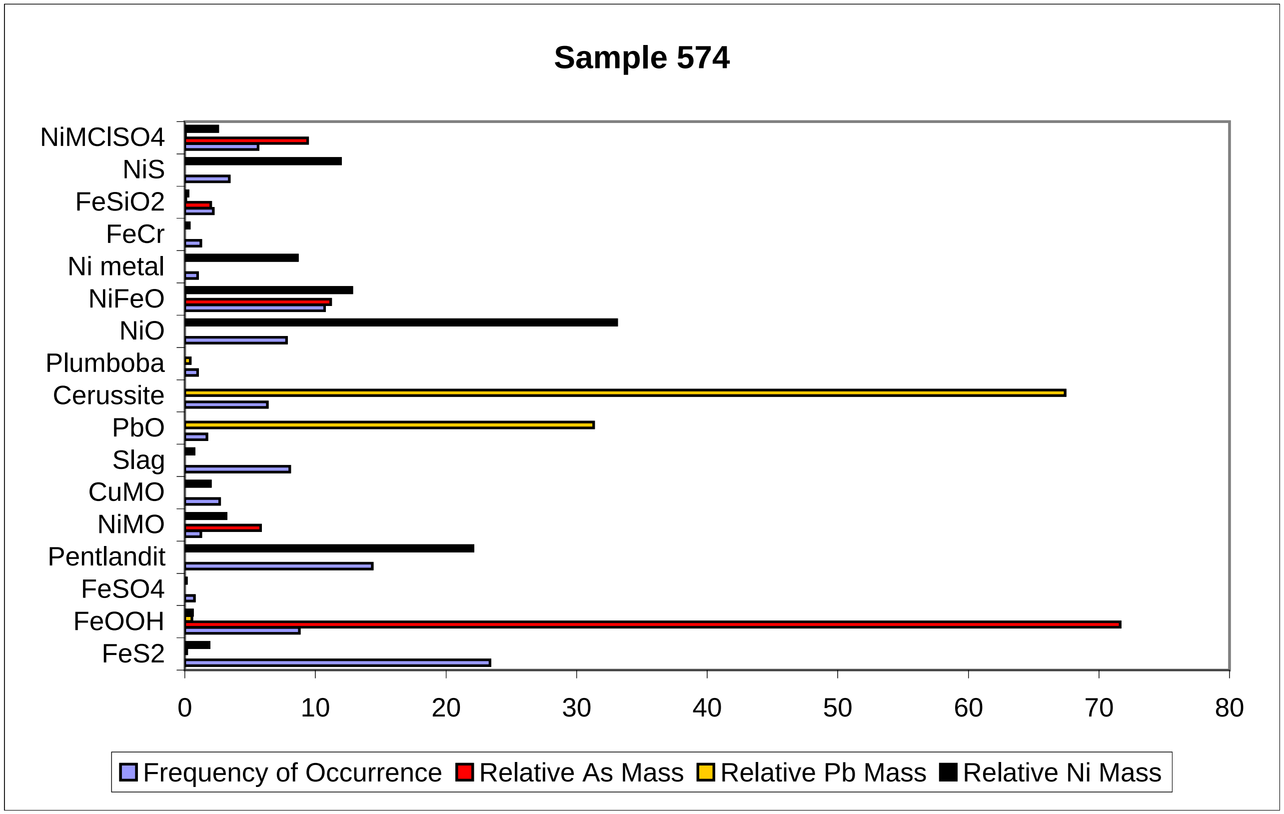
Detailed Speciation Results from LEGS (2007)
Sample 574 (Indoor Dust)

Form	**Association**	**Size**
py	Liberated	6
Fe	Liberated	4
Sulf	Liberated	3
pent	Liberated	6
py	Liberated	8
py	Liberated	9
nimo	Liberated	5
py	Liberated	7
cumo	Liberated	9
Slag	Liberated	33
PbO	Inclusion	7
Cer	Liberated	26
py	Liberated	14
Fe	Liberated	9
bar	Liberated	1
bar	Liberated	3
cumo	Liberated	2
nio	Liberated	13
nifeo	Liberated	35
py	Liberated	17
py	Liberated	7
nifeo	Liberated	9
ni	Liberated	2
py	Liberated	12
stainless	Liberated	5
FeSi	Liberated	9
nio	Liberated	12
ni	Liberated	2
nis	Liberated	9
nis	Liberated	3
Fe	Liberated	5
py	Liberated	7
Fe	Liberated	10
pent	Liberated	23
nis	Liberated	2
nio	Liberated	7
nimclso4	Liberated	23
pent	Liberated	6
pent	Liberated	8

Form	Number	Mean	Std-Dev	Range low	Range high
total	42	9.79	7.92	1	35
FeS2	10	9.6	3.6	6	17
FeOOH	5	7.2	2.59	4	10
FeSO4	1	3	ND	3	3
Pentlandite	5	11.8	7.5	6	23
NiMO	1	5	ND	5	5
CuMO	2	5.5	4.95	2	9
Slag	1	33	ND	33	33
PbO	1	7	ND	7	7
Cerussite	1	26	ND	26	26
Plumbobarite	2	2	1.41	1	3
NiO	3	10.67	3.21	7	13
NiFeO	2	22	18.38	9	35
Ni metal	2	2	0	2	2
FeCr metal	1	5	ND	5	5
FeSiO2	1	9	ND	9	9
NiS	3	4.67	3.79	2	9
NiMClSO4	1	23	ND	23	23

Form	(linear) freq	rm As	rm Pb	rm Ni	error-95%
%	%	%	%	%	
FeS2	23.36	0	0.15	1.86	12.8
FeOOH	8.76	71.62	0.55	0.59	8.55
FeSO4	0.73	0	0.01	0.12	2.57
Pentlandite	14.36	0	0	22.08	10.6
NiMO	1.22	5.8	0	3.16	3.32
CuMO	2.68	0	0	1.97	4.88
Slag	8.03	0	0.01	0.72	8.22
PbO	1.7	0	31.31	0	3.91
Cerussite	6.33	0	67.4	0	7.36
Plumbobarite	0.97	0	0.41	0	2.97
NiO	7.79	0	0	33.06	8.1
NiFeO	10.71	11.18	0.03	12.79	9.35
Ni metal	0.97	0	0	8.61	2.97
FeCr metal	1.22	0	0.01	0.34	3.32
FeSiO2	2.19	1.99	0.08	0.25	4.43
NiS	3.41	0	0	11.92	5.49
NiMClSO4	5.6	9.41	0.04	2.53	6.95

Fe	Liberated	8
py	Liberated	9
pent	Liberated	16



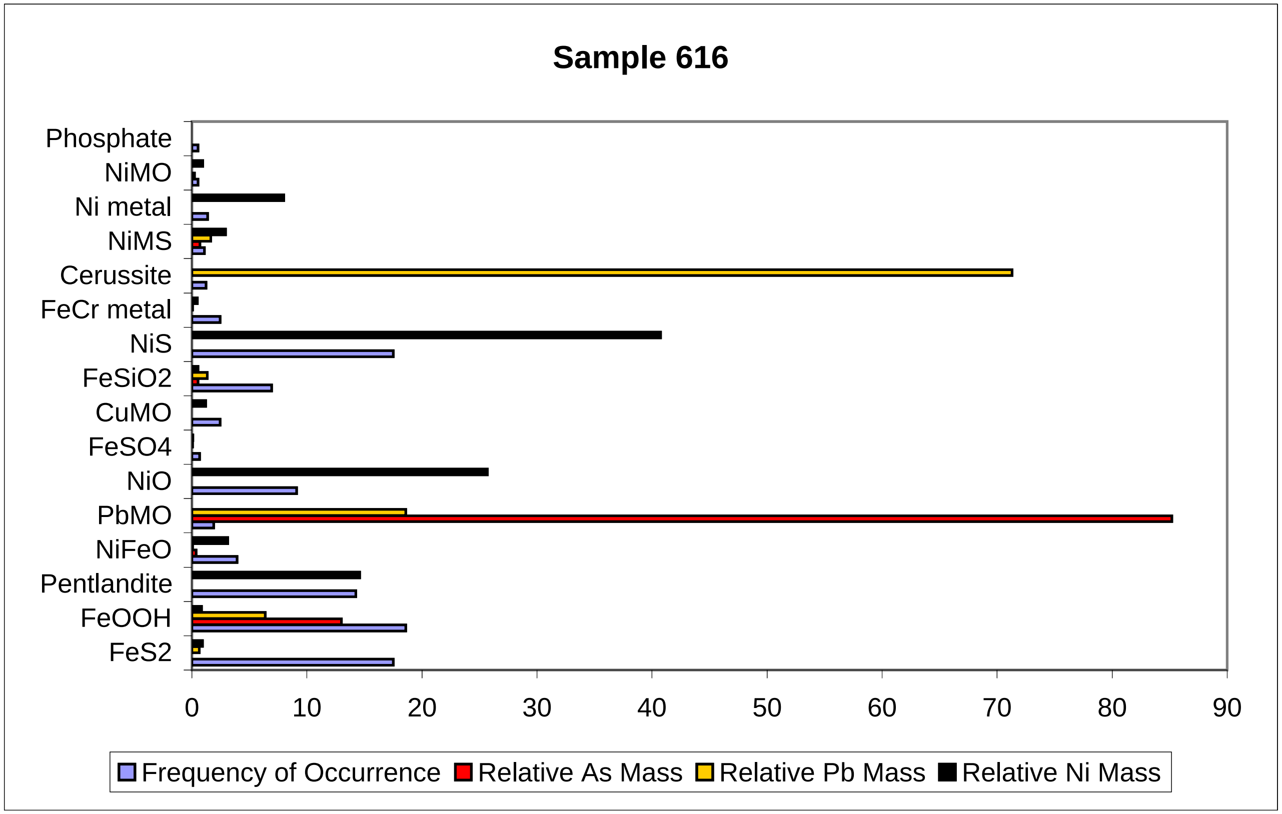
Detailed Speciation Results from LEGS (2007)
Sample 616 (Indoor Dust)

Form	**Association**	**Size**
py	Liberated	13
Fe	Liberated	2
pent	Liberated	9
nifeo	Liberated	5
PbMO	Liberated	10
nio	Liberated	6
py	Liberated	4
Sulf	Liberated	5
pent	Liberated	6
cumo	Liberated	4
FeSi	Liberated	13
Fe	Liberated	8
nio	Liberated	9
py	Liberated	7
nis	Liberated	8
nio	Liberated	8
Fe	Liberated	11
Fe	Liberated	13
nis	Liberated	8
Fe	Liberated	6
nis	Liberated	6
py	Liberated	8
fecr	Liberated	3
Cer	Liberated	1
py	Liberated	9
Fe	Liberated	3
py	Liberated	5
py	Cemented	4
fecr	Liberated	2
py	Liberated	5
nio	Liberated	2
pent	Liberated	3
nis	Liberated	12
nims	Liberated	8
pent	Liberated	5
nis	Liberated	2
Fe	Liberated	7
Fe	Liberated	9

Form	Number	Mean	Std-Dev	Range low	Range high
total	107	6.89	4.9	1	35
FeS2	17	7.59	3.76	2	16
FeOOH	16	8.56	5.24	2	23
Pentlandite	16	6.56	3.74	1	16
NiFeO	3	9.67	6.43	5	17
PbMO	2	7	4.24	4	10
NiO	11	6.09	2.91	2	10
FeSO4	1	5	ND	5	5
CuMO	4	4.5	2.38	3	8
FeSiO2	5	10.2	4.6	3	15
NiS	15	8.6	8.03	1	35
FeCr metal	6	3	1.55	2	6
Cerussite	4	2.25	1.5	1	4
NiMS	1	8	ND	8	8
Ni metal	4	2.5	1	2	4
NiMO	1	4	ND	4	4
Phosphate	1	4	ND	4	4

Form	(linear) freq	rm As	rm Pb	rm Ni	error-95%
%	%	%	%	%	
FeS2	17.5	0	0.63	0.93	7.2
FeOOH	18.59	13.01	6.36	0.83	7.37
Pentlandite	14.25	0	0	14.58	6.62
NiFeO	3.93	0.35	0.06	3.13	3.68
PbMO	1.9	85.19	18.58	0	2.59
NiO	9.09	0	0	25.68	5.45
FeSO4	0.68	0	0.05	0.07	1.56
CuMO	2.44	0	0	1.2	2.92
FeSiO2	6.92	0.54	1.33	0.53	4.81
NiS	17.5	0	0	40.75	7.2
FeCr metal	2.44	0	0.06	0.46	2.92
Cerussite	1.22	0	71.3	0	2.08
NiMS	1.09	0.7	1.63	2.93	1.96
Ni metal	1.36	0	0	7.99	2.19
NiMO	0.54	0.22	0.01	0.94	1.39
Phosphate	0.54	0	0	0	1.39

nio	Liberated	10
Fe	Liberated	2
pent	Liberated	1
cumo	Liberated	8
nis	Liberated	11
pent	Liberated	6
FeSi	Cemented	3
pent	Liberated	6
pent	Liberated	5
ni	Liberated	4
ni	Liberated	2
py	Liberated	16
pent	Liberated	4
nifeo	Liberated	17
nio	Liberated	6
Cer	Liberated	1
Cer	Liberated	3
py	Liberated	2
py	Liberated	2
nis	Liberated	7
pent	Liberated	10
cumso4	Liberated	3
fecr	Liberated	2
cumo	Liberated	3
fecr	Liberated	2
fecr	Liberated	6
FeSi	Liberated	11
Fe	Liberated	8
pent	Liberated	5
pent	Liberated	12
Fe	Liberated	4
py	Liberated	10
py	Liberated	9
pent	Liberated	3
Fe	Liberated	9
nis	Rimming	2
nis	Rimming	1
FeSi	Liberated	15
py	Liberated	8
Fe	Liberated	9
nimo	Liberated	4
nio	Liberated	8
pent	Liberated	16
Cer	Liberated	4



py	Liberated	11
nio	Liberated	2
pent	Liberated	6
fecr	Liberated	3
nis	Liberated	3
PbMO	Liberated	4
py	Liberated	9
py	Liberated	7
FeSi	Liberated	9
Fe	Liberated	14
nio	Liberated	2
Phos	Liberated	4
ni	Liberated	2
nio	Liberated	6
Fe	Liberated	9
nis	Liberated	8
Fe	Liberated	23
ni	Liberated	2
fenio	Liberated	7
pent	Liberated	8
nis	Liberated	35
nis	Liberated	10
nis	Liberated	8
nio	Liberated	8
nis	Liberated	8

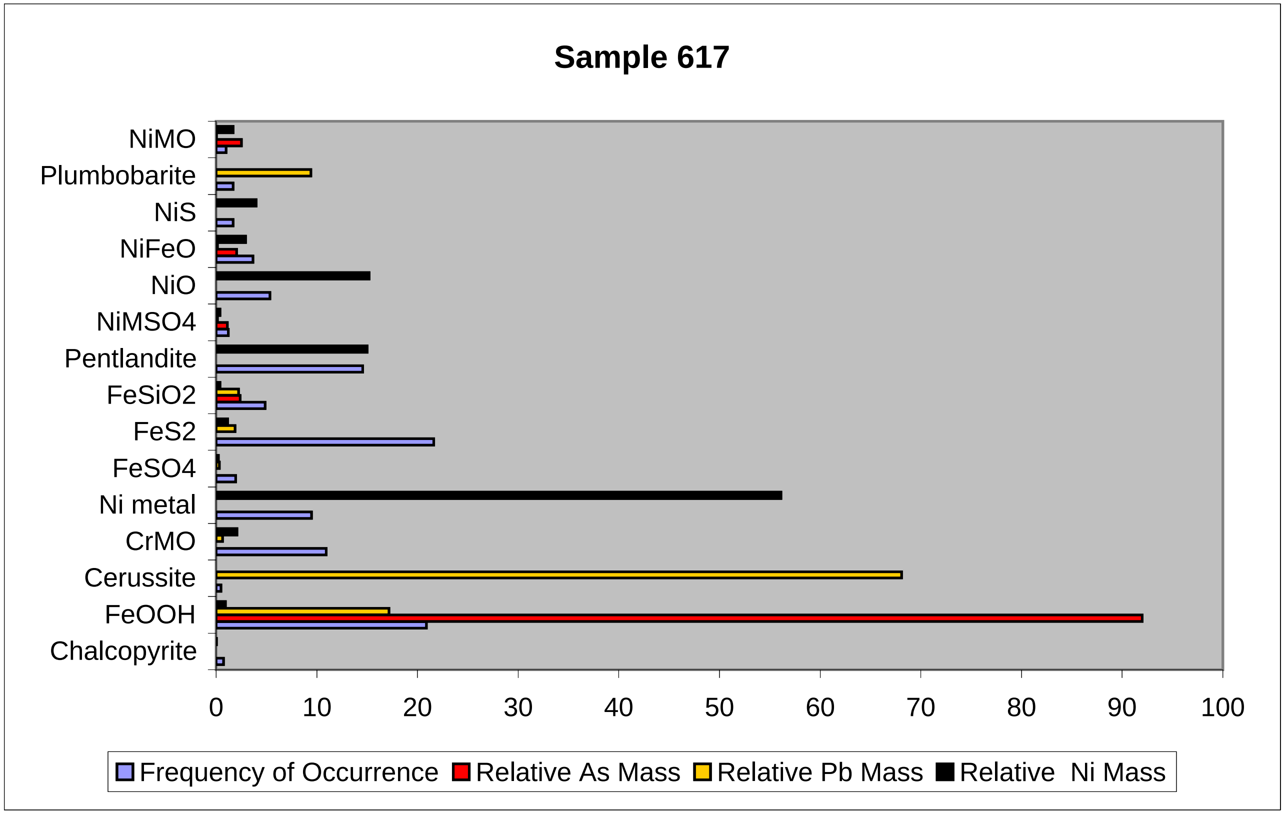
Detailed Speciation Results from LEGS (2007)
Sample 617 (Indoor Dust)

Form	Association	Size
cp	Liberated	3
Fe	Liberated	3
Fe	Liberated	4
Cer	Liberated	2
crmo	Liberated	32
Fe	Liberated	6
ni	Liberated	29
Sulf	Liberated	8
py	Liberated	25
Fe	Liberated	13
FeSi	Liberated	5
pent	Liberated	7
py	Liberated	5
pent	Liberated	5
pent	Liberated	4
nimso4	Liberated	5
py	Liberated	9
Fe	Liberated	4
pent	Liberated	9
pent	Liberated	6
pent	Liberated	12
nio	Liberated	5
crmo	Liberated	2
ni	Liberated	3
pent	Liberated	10
pent	Liberated	3
py	Liberated	14
py	Liberated	21
pent	Liberated	4
Fe	Liberated	10
nio	Liberated	9
crmo	Liberated	2
nifeo	Liberated	5
nio	Liberated	3
nio	Liberated	3
Fe	Liberated	8
nifeo	Liberated	10

Form	Number	Mean	Std-Dev	Range low	Range high
total	51	8.08	6.94	2	32
Chalcopyrite	1	3	ND	3	3
FeOOH	11	7.82	6.23	3	24
Cerussite	1	2	ND	2	2
CrMO	4	11.25	14.22	2	32
Ni metal	4	9.75	12.84	3	29
FeSO4	1	8	ND	8	8
FeS2	7	12.71	7.76	5	25
FeSiO2	2	10	7.07	5	15
Pentlandite	9	6.67	3.08	3	12
NiMSO4	1	5	ND	5	5
NiO	5	4.4	2.79	2	9
NiFeO	2	7.5	3.54	5	10
NiS	1	7	ND	7	7
Plumbobarite	1	7	ND	7	7
NiMO	1	4	ND	4	4

Form	(linear) freq	rm As	rm Pb	rm Ni	error-95%
%	%	%	%	%	
Chalcopyrite	0.73	0	0	0.02	2.33
FeOOH	20.87	91.98	17.15	0.93	11.15
Cerussite	0.49	0	68.08	0	1.91
CrMO	10.92	0	0.63	2.06	8.56
Ni metal	9.47	0	0	56.11	8.03
FeSO4	1.94	0	0.33	0.21	3.79
FeS2	21.6	0	1.86	1.15	11.29
FeSiO2	4.85	2.38	2.23	0.37	5.9
Pentlandite	14.56	0	0	15	9.68
NiMSO4	1.21	1.1	0.12	0.37	3.01
NiO	5.34	0	0	15.18	6.17
NiFeO	3.64	2.05	0.14	2.91	5.14
NiS	1.7	0	0	3.98	3.55
Plumbobarite	1.7	0	9.42	0	3.55
NiMO	0.97	2.5	0.03	1.69	2.69

Fe	Liberated	7
crmo	Liberated	9
py	Liberated	10
nis	Liberated	7
ni	Liberated	4
Fe	Liberated	24
Fe	Liberated	4
bar	Liberated	7
FeSi	Liberated	15
nio	Liberated	2
py	Liberated	5
nimo	Liberated	4
fepbo	Rimming	3
ni	Liberated	3



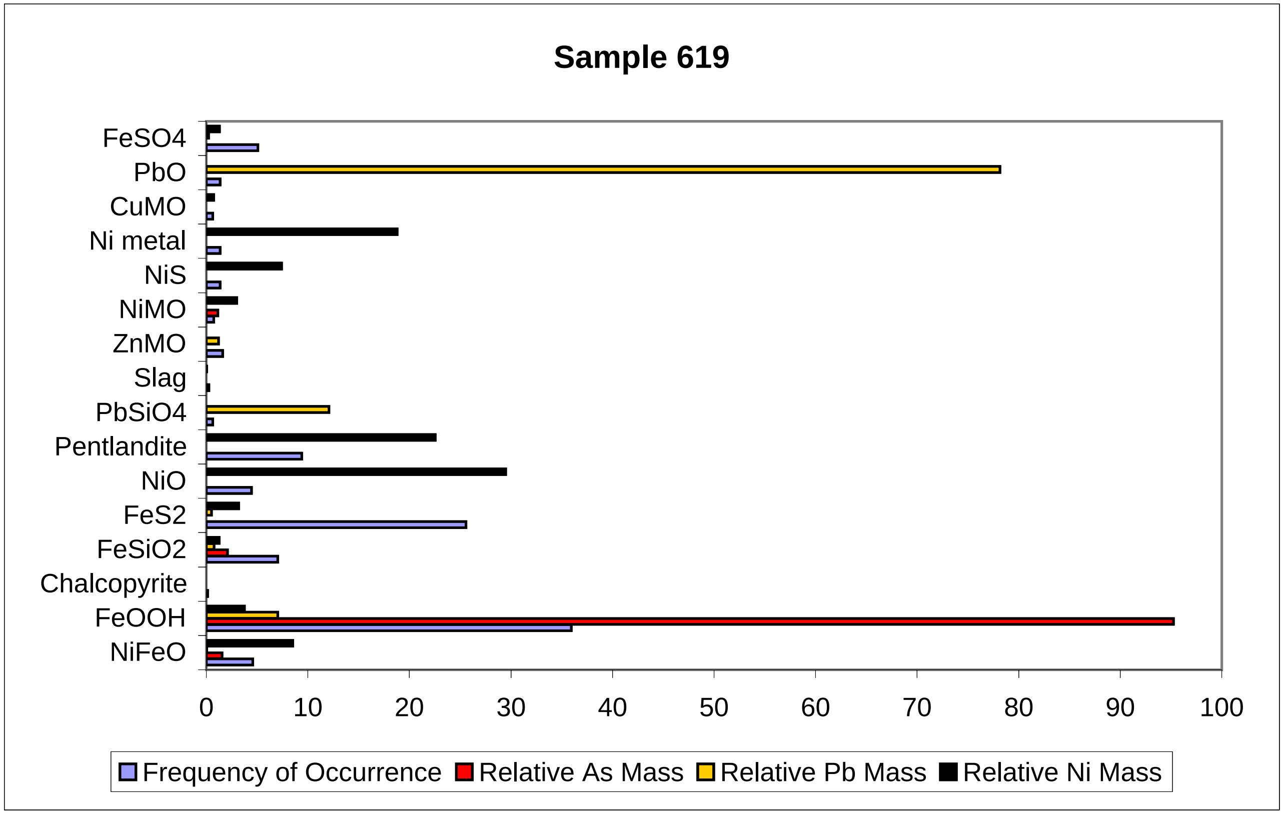
Detailed Speciation Results from LEGS (2007)
Sample 619 (Indoor Dust)

Form	Association	Size
nifeo	Liberated	9
Fe	Liberated	6
Fe	Liberated	2
cp	Liberated	1
FeSi	Liberated	3
py	Liberated	10
py	Liberated	4
py	Liberated	11
nio	Liberated	3
py	Liberated	3
FeSi	Liberated	2
py	Liberated	13
FeSi	Liberated	6
Fe	Liberated	10
nifeo	Liberated	3
py	Liberated	5
nifeo	Liberated	3
Fe	Liberated	3
py	Liberated	15
Fe	Liberated	8
pent	Liberated	8
py	Liberated	7
Fe	Liberated	14
PbSiO4	Liberated	5
Fe	Liberated	8
Slag	Liberated	2
Fe	Liberated	5
Fe	Liberated	7
FeSi	Liberated	4
znmo	Liberated	10
znmo	Liberated	3
nifeo	Liberated	7
nimo	Liberated	3
Fe	Liberated	26
nio	Liberated	4
py	Liberated	3
nis	Liberated	5
Fe	Liberated	4

Form	Number	Mean	Std-Dev	Range low	Range high
total	100	8.1	6.62	1	45
NiFeO	5	7.4	4.98	3	15
FeOOH	30	9.7	8.18	2	45
Chalcopyrite	1	1	ND	1	1
FeSiO2	7	8.14	6.91	2	21
FeS2	22	9.41	7.4	3	32
NiO	10	3.6	1.17	2	5
Pentlandite	8	9.5	5.5	3	20
PbSiO4	1	5	ND	5	5
Slag	1	2	ND	2	2
ZnMO	2	6.5	4.95	3	10
NiMO	2	3	0	3	3
NiS	2	5.5	0.71	5	6
Ni metal	1	11	ND	11	11
CuMO	1	5	ND	5	5
PbO	1	11	ND	11	11
FeSO4	6	6.83	3.66	4	14

Form	(linear) freq	rm As	rm Pb	rm Ni	error-95%
%	%	%	%	%	
NiFeO	4.57	1.55	0.04	8.52	4.09
FeOOH	35.93	95.23	7.02	3.75	9.4
Chalcopyrite	0.12	0	0	0.01	0.69
FeSiO2	7.04	2.07	0.77	1.25	5.01
FeS2	25.56	0	0.52	3.18	8.55
NiO	4.44	0	0	29.48	4.04
Pentlandite	9.38	0	0	22.55	5.72
PbSiO4	0.62	0	12.06	0	1.54
Slag	0.25	0	0	0.03	0.97
ZnMO	1.6	0	1.21	0.01	2.46
NiMO	0.74	1.15	0.01	3	1.68
NiS	1.36	0	0	7.42	2.27
Ni metal	1.36	0	0	18.78	2.27
CuMO	0.62	0	0	0.71	1.54
PbO	1.36	0	78.15	0	2.27
FeSO4	5.06	0	0.21	1.29	4.3

Fe	Liberated	4
py	Liberated	6
FeSi	Liberated	7
pent	Liberated	3
nio	Liberated	5
pent	Liberated	9
Fe	Liberated	8
Fe	Liberated	4
Fe	Liberated	7
py	Liberated	4
Fe	Liberated	12
nio	Liberated	4
ni	Liberated	11
Fe	Liberated	10
nifeo	Liberated	15
Fe	Liberated	8
Fe	Liberated	9
py	Liberated	3
Fe	Liberated	10
py	Liberated	3
nio	Liberated	3
cumo	Liberated	5
py	Liberated	14
py	Liberated	32
Fe	Liberated	8
py	Liberated	14
nio	Liberated	2
Fe	Liberated	13
pent	Liberated	15
Fe	Liberated	16
Fe	Liberated	7
pent	Liberated	20
py	Liberated	25
FeSi	Liberated	14
Fe	Liberated	45
FeSi	Liberated	21
PbO	Liberated	11
nio	Liberated	5
py	Liberated	8
pent	Liberated	5
py	Liberated	6
nio	Liberated	3
Fe	Liberated	9
nimo	Liberated	3



py	Liberated	10
Fe	Liberated	13
py	Liberated	4
Fe	Liberated	6
Sulf	Liberated	7
Fe	Liberated	5
nio	Liberated	5
Fe	Liberated	4
Sulf	Liberated	6
Sulf	Liberated	5
Sulf	Liberated	14
Sulf	Liberated	5
pent	Liberated	9
nio	Liberated	2
Sulf	Liberated	4
pent	Liberated	7
py	Liberated	7
nis	Liberated	6