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*R. Rowe, J.B. Percival, and W.H. Hendershot*

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# Natural sources of trace metals from minerals in soils near smelters in the Rouyn-Noranda, Quebec, and Sudbury, Ontario, areas

R. Rowe, J.B. Percival, and W.H. Hendershot

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**Abstract:** This study forms part of a larger Metals in the Environment Research Network (MITE-RN) project to examine metal dynamics in soils in order to distinguish between and quantify contributions of metals from anthropogenic and natural sources. This study characterized the mineralogy of six soil samples from the Rouyn-Noranda and Sudbury areas in order to identify minerals that can be a source of trace metals and to determine suitable mineral fractions for future weathering experiments. The silt-sized, clay-sized, and heavy mineral fractions from B/C horizons were analyzed by X-ray diffraction and scanning electron microscopy. Mineralogy at all sites from both areas were comparable. The silt- and clay-sized fractions are dominated by quartz, plagioclase, and K-feldspar with minor chlorite, amphibole, and pyroxene. The heavy mineral fractions contain titanite, zircon, hematite, and magnetite. Due to insufficient amounts of fractionated material, the whole soil will be used in the weathering experiments with sequential extraction analyses of the fractions for comparison.

**Résumé :** La présente étude s'intègre dans un projet de plus grande envergure du Réseau de recherches sur les métaux dans l'environnement (MITE-RN) visant à examiner la dynamique des métaux dans le sol afin de distinguer et de quantifier les apports de métaux d'origine anthropique et naturelle. On a caractérisé la minéralogie de six échantillons de sol provenant des régions de Rouyn-Noranda et de Sudbury afin d'identifier les minéraux pouvant être source de métaux traces ainsi que pour déterminer les fractions minérales à soumettre à de futures expériences d'altération météorique. Les fractions de la taille des silts, de la taille des argiles et des minéraux lourds des horizons B/C ont été analysées par diffraction des rayons X et microscopie électronique à balayage. La minéralogie à tous les sites des deux régions était comparable. Les fractions de la taille des silts et de la taille des argiles renferment principalement du quartz, du plagioclase et du feldspath potassique avec des quantités mineures de chlorite, d'amphibole et de pyroxène. La fraction des minéraux lourds comporte de la titanite, du zircon, de l'hématite et de la magnétite. En raison des quantités insuffisantes de matériaux fractionnés, des échantillons de sol complet seront utilisés pour les expériences d'altération météorique. Des analyses des diverses fractions suivant un schéma d'extraction séquentielle seront effectuées à des fins de comparaison.

## INTRODUCTION

The distribution and fate of trace metals in boreal-forest ecosystems are poorly understood. Trace metals in forest soils can be derived from parent materials through atmospheric deposition or from litterfall (Starr et al., 2003). Their mobility is controlled by many factors including total concentration and form of metals, chemistry of the soil solution, and composition and texture of the parent material (Kabala and Singh, 2001; Henderson et al., 2002b). However, determining the relative contribution from internal (i.e. weathering) and external (i.e. atmospheric deposition) sources is difficult.

This study, part of a larger project examining processes that control metal movement in a boreal forest (Hale et al., 2001), was funded under the Metals in the Environment Research Network (MITE-RN) program ([www.mite-rn.org](http://www.mite-rn.org)). Part of the program is directed at distinguishing between anthropogenic and natural sources of metals in the environment through detailed studies near point sources (i.e. smelters) and in remote areas. This study is partnered with research underway at McGill University to understand the process that controls migration of metals such as Cd, Cu, Ni, Pb, and Zn in ecosystems affected by the mining and smelting industry (MacDonald et al., 2003). It focuses on identifying the minerals that can be a source of trace metals during weathering (Hendershot et al., 2003). Mineralogy is an important aspect of soil investigations and provides data to assist interpretation for other studies. In environmental studies, mineralogy is commonly overlooked, with emphasis being placed on geochemistry. However, as minerals can be the source of the trace metals of interest, mineralogy and geochemistry should be investigated in an integrated manner. Detailed mineral characterization may enable us to differentiate between smelter and weathering products and to determine the best fraction for further weathering experiments.

The objectives of this study are 1) to characterize the mineralogy of six soil samples from the Sudbury and Rouyn-Noranda areas, 2) to identify minerals that can be a source of trace metals in the weathering environment, and 3) to identify and prepare appropriate grain-size fractions or discrete minerals for weathering experiments. The mineralogical sample preparation and analyses were carried out at the Geological Survey of Canada and the soil chemical analyses were conducted at the Environmental Chemistry Laboratory at McGill University.

## STUDY SITES

Soils at six sites developed on glacial till or glaciofluvial deposits containing trace metals are under investigation. The sites are located at increasing distances from two smelters in Ontario and Quebec. Soils were sampled in 2000 in the Sudbury (Ontario) and Rouyn-Noranda (Quebec) areas. A brief description of each site is given below.

**Table 1.** Location of sampling sites in the Rouyn-Noranda and Sudbury areas.

Rouyn-Noranda	Distance/Location	Horizon	Depth (cm)
Site RN1	7 km, 48°17'4.4"N, 78°54'22.5"W	B/C	50–80
Site RN2	15 km, 48°16'46.8"N, 78°51'16"W	B/C	65–80
Site RN3	41 km, 48°32'18"N, 78°39'24"W	B/C	50–70
<b>Sudbury</b>			
Site Sud1	10 km, 46°35'47.9"N, 80°49'53.8"W	B/C	75–90
Site Sud2	25 km, 46°35'52.7"N, 80°37'21"W	C	65–80
Site Sud3	50km, 46°35'11.4"N, 80°49'34.14"W	B/C	65–80

### *Rouyn-Noranda sites*

The Horne smelter and refinery owned by Noranda Inc. has been releasing metal-rich, airborne particulates from copper and zinc smelting in the Rouyn-Noranda area since 1927 (Henderson et al., 2002a). Total emissions have decreased over the years because of improvements such as the addition of the Noranda reactor (1973), a sulphuric acid plant (1989) and the Noranda continuous converter (1997). Details can be found at: <http://my.noranda.com/Noranda/Corporate/Technology+and+Innovation/Industry+Firsts.htm>.

Three sampling sites were located along a downwind transect extending up to 41 km from the Horne smelter (Table 1). Each site was instrumented with bulk precipitation collectors, throughfall collectors, and lysimeters. The soils are developed on glacial till and are classified as Orthic Humo-Ferric Podzols with mixed mineralogy. The B/C horizons have a sandy loam texture and rapid drainage.

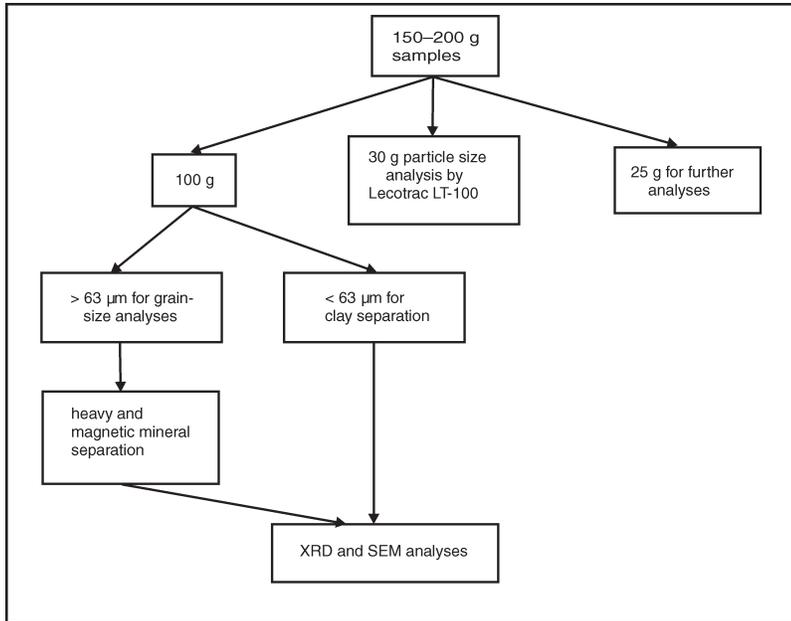
### *Sudbury sites*

Sudbury smelters process mainly nickel and copper, but cobalt and some platinum-group elements are also recovered. The total emission of airborne particulates has decreased over the last 20 years as a result of the addition of a sulphuric acid plant, safer extraction methods, and better filtration. Gundermann and Hutchinson (1995) noted that although the soil chemistry in areas up to 13 km from the smelters has improved since 1972 following the closing of the Coniston smelter, areas farther away (>20 km) have been affected by the Copper Cliff superstack.

Three sites were sampled along a downwind transect extending up to 50 km from the smelters (Table 1). Each site was instrumented with bulk precipitation collectors, throughfall collectors, and lysimeters. The soils are developed on glaciofluvial deposits and are classified as Orthic Humo-Ferric Podzols with mixed mineralogy. The B/C or C horizons have a sandy loam texture and rapid drainage.

## METHODS

A sample processing and analysis flowchart is shown in Figure 1. A stainless steel riffle splitter was used to split each sample (150–200 g) into a variety of subsamples for analysis.



**Figure 1.**

*Flow chart showing sample processing and analysis scheme.*

About 100 g of each sample were sieved to separate the  $>63\ \mu\text{m}$  and  $<63\ \mu\text{m}$  fractions. The  $>63\ \mu\text{m}$  fraction was then used for grain-size analysis by sieving whereas the  $<63\ \mu\text{m}$  fraction was used for separation of the clay-sized fraction. About 30 g were used for particle-size analysis with the Lecotrac LT-100 ASVR particle size analyzer.

Heavy mineral separation was based on the methylene iodide (density =  $3.3\ \text{g}/\text{cm}^3$ ) method using the 63 to  $500\ \mu\text{m}$  fraction; the magnetic fraction was separated using a hand magnet. Minerals with densities near the threshold may not be well differentiated in the fractionation process.

X-ray diffraction analyses were done on a Bruker D8 Advance powder diffractometer set at 40 kV and 30 mA using  $\text{Co K}\alpha$  radiation and a graphite monochromator. Digital X-ray patterns were reduced to provide semi-quantitative mineral analysis using JADE 3.1 (Materials Data, Inc.) software.

Scanning electron microscopy (SEM) of grain mounts was done on a Leica Cambridge SEM equipped with an Oxford/Link eXL-II energy-dispersion X-ray analyzer, Oxford/Link Pentafet Be window/light element detector, and an Oxford/Link Tetra backscattered-electron detector. The SEM is operated at an accelerating voltage of 20 kV. The different minerals were identified by their distinctive energy-dispersive X-ray spectrometer patterns (Rowe, 2003).

Major- and trace-element analyses were done on the  $<2\ \text{mm}$  fraction. Concentrations of amorphous aluminium, iron, and manganese oxides (weight per cent) are based on atomic absorption spectrometry (AAS) following ammonium oxalate extraction (Ross and Wang, 1993). Total trace-element concentrations (mg/kg or ppm) were determined by inductively coupled plasma atomic emission spectrometry (ICP-AES) or inductively coupled plasma mass spectrometry (ICP-MS) following microwave digestion with  $\text{HNO}_3/\text{HCl}$  (Environmental Protection Agency, 1998). Cation

exchange capacity, reported in  $\text{cmol}(+)/\text{kg}$ , was determined by the  $\text{BaCl}_2$  method (Hendershot et al., 1993a) and soil pH was measured in water (Hendershot et al., 1993b).

## RESULTS

### *Particle-size analysis*

Results from the particle-size analysis show that all samples are composed mainly of sand- and silt-sized material and can be classified as sandy loam. Only minor to trace amounts of clay-sized material were present in any of the samples. The soils from the Rouyn-Noranda area are poorly sorted as shown by their particle-size distribution (Fig. 2). The soils from the Sudbury area are well sorted as shown by the bell-shaped curves (Fig. 2), which suggests that they are texturally mature (Boggs, 1995). Sample Sud2 is finer grained than samples Sud1 and Sud3, with the bell curve skewed toward the fine sand size. Sample Sud3 is composed almost entirely of sand whereas sample Sud1 shows a bimodal distribution of fine sand and coarse silt. The variations in sorting reflect the glaciofluvial origin of the material.

Heavy and magnetic minerals account for a small proportion of the 63 to  $500\ \mu\text{m}$  fraction. They represent less than 2 per cent by weight of the total, but the ratio of magnetic to heavy minerals varies from 1:2 in sample Sud3 to 1:6 in sample RN2. In general, samples from Sudbury have a higher proportion of magnetic minerals.

### *Trends in mineralogy*

The clay-sized fraction for all samples is dominated by quartz, plagioclase, K-feldspar, and amphibole with minor illite and chlorite (Fig. 3a). Mineral proportions at each Rouyn-Noranda site are comparable (Fig. 3a). Sample Sud1

contains more felsic than mafic minerals compared to sample Sud2; both samples are more quartz-rich than the Rouyn-Noranda samples. Insufficient clay-sized material was available for analysis from sample Sud3.

The silt-sized fraction in Rouyn-Noranda and Sudbury samples is also dominated by quartz with subordinate plagioclase and K-feldspar (Fig. 3b). Quartz makes up between 50 and 85 per cent of the samples. Minor amounts (up to 10–12 per cent) of amphibole, pyroxene, and chlorite

are present. Mineral proportions are consistent among the Rouyn-Noranda samples and vary slightly among the Sudbury samples.

The nonmagnetic heavy mineral fraction of all samples contains epidote and pyroxenes with minor to trace amounts of amphiboles, titanite, zircon, hematite, and ilmenite (Fig. 3c). No metal-bearing minerals (e.g. sulphides) were detected in the samples.

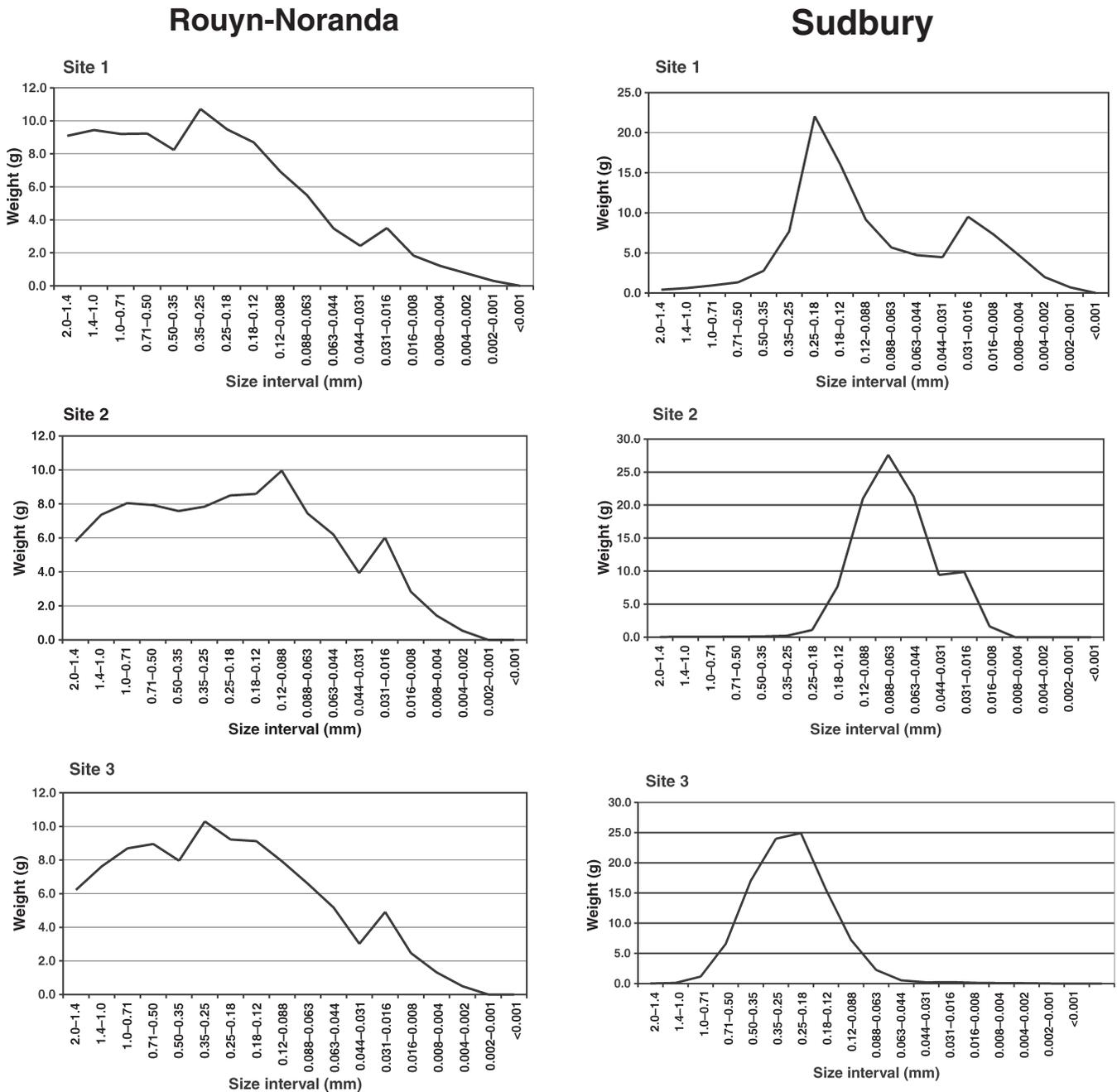
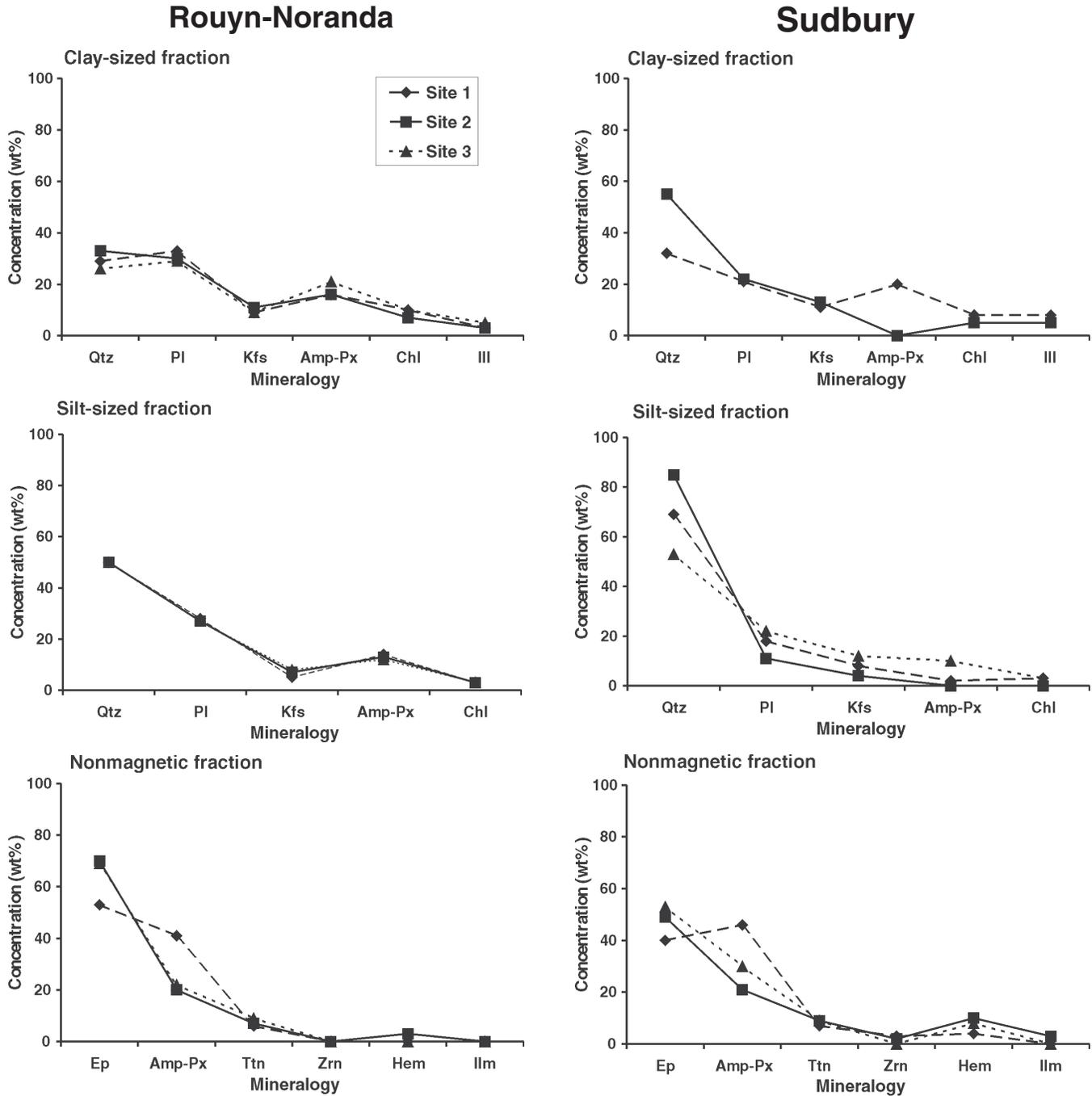


Figure 2. Grain-size distribution in the B/C horizons at each site in the Rouyn-Noranda and Sudbury areas, from sieving and particle-size analysis.

**Geochemistry**

Table 2 summarizes selected physical and chemical parameters of the samples. All soils are acidic with pH ranging from 4.9 to 5.6 for Sudbury and from 5.1 to 5.8 for Rouyn-Noranda. Aluminum, iron, and manganese contents from amorphous metal oxides range from 0.18 to 0.56 Al weight per cent, 0.08 to 0.34 Fe weight per cent, and 0.001 to 0.034 Mn

weight per cent, respectively, and are comparable for both study areas. Trace-metal concentrations of Cu, Ni, Pb, and Zn are less than 40 mg/kg for all samples with Cd less than 2 mg/kg. Total cation exchange capacity ranges from 0.2 to 0.4 cmol(+)/kg for samples from Sudbury and from 0.3 to 0.6 cmol(+)/kg for samples from Rouyn-Noranda; these values are low, reflecting the sandy texture of the subsurface horizons.



**Figure 3.** Semi-quantitative mineralogy of the a) clay-sized, b) silt-sized, and c) nonmagnetic heavy mineral fractions from the B/C horizons at each site in the Rouyn-Noranda and Sudbury areas. Amp-Px = amphibole-pyroxene; Chl = chlorite; Ep = epidote; Hem = hematite; Ill = illite; Kfs = K-feldspar; Pl = plagioclase; Qtz = quartz; Ttn = titanite; Zrn = zircon

**Table 2.** Selected physical and chemical parameters of the samples in this study (<2 mm fraction).

Site	Horizon	pH	Fe <sub>2</sub> O <sub>3</sub> (wt %)	Al <sub>2</sub> O <sub>3</sub> (wt %)	MnO (wt %)	Zn (mg/kg)	Cu (mg/kg)	Cd (mg/kg)	Ni (mg/kg)	Pb (mg/kg)	CEC (cmol(+)/kg)
RN1	B/C	5.77	0.23	0.33	0.001	24.3	23.4	nd	22.5	6.26	0.48
RN2	B/C	5.16	0.34	0.38	0.034	37.9	21.9	nd	28.9	nd	0.62
RN3	B/C	5.84	0.31	0.56	0.006	22.5	26.1	0.9	36.6	13.5	0.13
Sud1	B/C	4.83	0.14	0.18	0.004	15.3	16.2	0.9	28.8	nd	0.40
Sud2	C	4.90	0.08	0.21	0.001	11.6	8.05	1.79	11.0	5.37	0.24
Sud3	B/C	5.56	0.11	0.18	0.003	27.8	13.5	0.09	40.4	37.7	0.43

## DISCUSSION

### *Processes affecting cycles and distribution of trace metals*

Trace metals in soils around smelters can be the products of contamination by metal-rich airborne particulates or be derived from parent materials. McMartin et al. (2002) confirmed that in the vicinity of four point sources of metals in Canada, including the Rouyn-Noranda area, humus retained most of the trace metals derived from the smelting process. Contamination of the B horizon through leaching was significant in the Rouyn-Noranda area within 10 km of the smelter; however, the C-horizon trace-metal concentrations were controlled by natural sources (McMartin et al., 2002). Leaching of trace metals downward through the soil profile from the humus layer is controlled by many factors including total concentration of metals, mobility of metals in the organic layer, and composition and texture of the parent material (Kabala and Singh, 2001; Henderson et al., 2002b). These factors influence the pH and permeability of the soil. Therefore, in order to understand the bioavailability and toxicity of trace metals in soils, it is important to know how the metals are bound and what their concentration, solubility, and mobility are within the soil horizons (Hale et al., 2002).

The decomposition of plant litter is another source of trace metals involved in the cycle. Hale and Johnson (2002) looked at the contribution of foliage and fine roots as sources of Cu, Ni, Pb, and Zn at the Rouyn-Noranda and Sudbury sites in this study. They found that fine roots were the dominant source of Cu, Ni, and Pb and that Zn was introduced in equal proportions by both fine roots and foliage.

### *Role of trace metals in plants*

Some trace metals contained in soils are considered to be plant micronutrients, although they can be toxic at high concentration (Catlett et al., 2002). Voigt (2003) investigated the effects of Ca concentration and pH on the relative toxicity or bioavailability of metals. The relative toxicant strength of metals on plants was determined to be Cu > Ni > Pb > Cd > Zn. With decreasing pH (increase in H<sup>+</sup>), the rhizotoxicity of these metals decreases, but at high concentrations, H<sup>+</sup> itself becomes rhizotoxic. The presence of Ca decreases the rhizotoxicity of the metals at nearly neutral pH.

### *Trace metals in minerals*

Trace metals such as Zn tend to bind with oxides and clays (Catlett et al., 2002) but can also be present in trace amounts in many minerals. It is important to study the potential for minerals found in these soils to adsorb or host in their structure trace amounts of metals. Some minerals may adsorb some metals selectively and therefore a correlation may exist between the concentration of elements and the mineral. Metals and other elements released during weathering of primary minerals become part of the secondary environment and may be transported away from the weathering site by hydromorphic dispersion or mechanical process. The elements released can be immobilized and concentrated by a variety of processes (e.g. surface complex formation) and substrates (e.g. clay minerals). A brief description of the minerals found in these soil sites and their potential to host trace metals is presented below. The order of increasing susceptibility to weathering is oxides < silicates < carbonates = sulphides (Rose et al., 1979).

#### **Quartz**

Quartz is an extremely pure mineral; its structure is tightly bonded and restricts the entry of trace elements. Impurities in quartz are caused by atomic substitution and interstitial elemental occlusion, which give rise to the different quartz varieties. Impurities found in quartz include Al, Ti, Fe, Na, Li, K, Mg, Ca, and H (OH) (Drees et al., 1989). Trace metals are not commonly found in quartz.

#### **Potassium feldspar**

Potassium feldspar has an ideal composition of KAlSi<sub>3</sub>O<sub>8</sub>. Aluminium replaces one out of four silicon atoms in the tetrahedral framework, which induces a negative charge in the tetrahedron neutralized by a positively charged ion, K<sup>+</sup>. Potassium feldspar is rarely found with this ideal composition, as the K<sup>+</sup> site is extremely susceptible to substitution. This results in a solid solution with NaAlSi<sub>3</sub>O<sub>8</sub>. Other elements that can occupy the K positions are Ba, Ca, Cu, Cs, Ga, Pb, Rb, Sr, and Tl (Huang, 1989). Therefore, two metals of interest, Cu and Pb, can be common impurities in K-feldspars. The trace metals can be released into the environment as K-feldspar weathers; however, these minerals tend to be resistant to weathering.

## Plagioclase

Plagioclase has a chemical composition between that of albite ( $\text{NaAlSi}_3\text{O}_8$ ) and anorthite ( $\text{CaAl}_2\text{Si}_2\text{O}_8$ ). Both  $\text{Ca}^{2+}$  and  $\text{Na}^+$  have the same neutralizing role as  $\text{K}^+$  has in K-feldspars, so they are also susceptible to atomic substitution. The substitution of heavy metals such as Cu and Pb is more common in plagioclase than in K-feldspar, and these metals can be present in concentrations up to 20 mg/kg (Huang, 1989). On the basis of its abundance and higher weathering rate than K-feldspar, plagioclase has the potential to be an important natural supplier of these two trace metals.

## Amphibole and pyroxene groups

Amphibole- and pyroxene-group minerals have the ideal formulas  $\text{R}_{14}[(\text{OH})_4\text{Si}_{16}\text{O}_{44}]$  and  $\text{R}_2(\text{Si}_2\text{O}_6)$ , respectively, where R is Mg, Fe-II, or Ca, and less commonly Al, Fe-III, Ti, Mn-III, Na, K, or Li (Huang, 1989). Aluminium may substitute for silicon, but this occurs less commonly than in the feldspars. Trace-metal impurities (e.g. Ni, Pb, Zn) are not common but can be present in the amphibole and pyroxene structures. These minerals weather readily to form the secondary minerals chlorite or smectite (Rose et al., 1979).

## Epidote

Epidote minerals have an ideal formula of  $\text{X}_2\text{Y}_3\text{Z}_3(\text{O}, \text{OH}, \text{F})_{13}$ , where X = Ca, Ce, La, Y, Th, Fe-II, Mn-II, and Mn-III, Y = Al, Fe-III, Mn-III, Mn-II, Fe-II, and Ti, and Z = Si and Be. No trace metals are reported to occur in noticeable amounts in epidote-group minerals (Deer et al., 1986).

## Illite and mica

Illite and/or mica occur mainly in the clay-sized fraction. They have a high surface area and moderate cation exchange capacity and are efficient adsorbers. They can be precursors for expansible 2:1 minerals such as smectites and vermiculites as the nonexchangeable interlayer cation ( $\text{K}^+$ ) can be replaced by hydrated exchangeable cations during weathering. Trace metals such as Cd, Cu, Pb, and Zn are known to be incorporated in illite (Fanning et al., 1989).

## Chlorite

Chlorite is moderately abundant in these soils (10 per cent of clay-sized fraction). It has an empirical formula of  $(\text{R}^{2+}, \text{R}^{3+})_3(\text{Si}_{4-x}\text{Al}_x)\text{O}_{10}(\text{OH})_2 [(\text{R}^{2+}, \text{R}^{3+})_3(\text{OH})_6]$ , where Ni (and in some cases Cu) is common in the  $\text{R}^{2+}$  site. During weathering, chlorite is less stable than other clay minerals such as illite and kaolinite, and so may release some trace metals (Barnhisel and Bertsch, 1989).

## Titanite, ilmenite, and zircon

Titanite, ilmenite, and zircon are Ti- and Zr-bearing minerals that occur as resistant, residual minerals in soils. Their adsorption activities in soils are poorly understood, but they may have the potential for adsorbing Zn and Cu (Milnes and Fitzpatrick, 1989).

## Iron oxides

Iron oxides with their high surface area have geochemical properties that give them a high adsorption potential; they can therefore act as a sink for trace-metal cations. Selective adsorption occurs in the following pattern in hematite:  $\text{Pb} > \text{Cu} > \text{Zn} > \text{Cd} > \text{Ni}$  (Schwertmann and Taylor, 1989). The major factor influencing the amount of adsorption by iron oxides is pH, with adsorption increasing with increasing pH. Iron oxides can adsorb cations on their surface or incorporate them into their structure. At a pH of 5, as in our samples, hematite will adsorb Pb and Cu in large amounts as shown in Figure 4, but Zn and Ni adsorption is proportionally insignificant. Trace-metal cations such as Ni, Cu, and Zn are commonly found replacing Fe in the structure, but Al substitution is more common. The atomic radii of Pb and Cd are too large for these metals to substitute for Fe.

The silt-rich samples are all dominated by quartz, which has the lowest potential to host trace metals. Although feldspars have the potential to host and eventually release trace metals, SEM analyses showed little weathering of their surfaces. Because of their natural high cation exchange capacities and surface areas, iron oxides and phyllosilicates are more likely to sorb trace metals from solution; however, they only occur in minor to trace amounts in these samples. In addition, as noted above, the Ti- and Zr-bearing minerals may have a role to play in sorbing and/or hosting trace metals. No (metal-bearing) sulphide minerals such as chalcopyrite or sphalerite were actually observed in these samples. The clay-sized fraction would be the most suitable material for future weathering experiments. However, the small proportion of clay-sized material in these samples prohibits their use. The nonmagnetic heavy mineral fractions containing the more reactive iron oxide minerals may be useful as sufficient material is available. Each of these fractions (silt, clay, and heavy minerals) needs to be tested for suitability. Sequential extraction experiments may provide a more cost-effective way to determine the preferred fraction.

## Trends in metal concentrations

The concentrations of trace metals of interest (i.e. Cd, Cu, Ni, Pb, and Zn) in these B/C horizon soil samples are all less than 40 mg/kg, reflecting the nature of the parent material. These parent materials are glacial in origin and do not contain highly anomalous concentrations of the metals as might be expected in a mining camp area. One area of concern is whether or not these concentrations are within acceptable guidelines for soils. The Canadian environmental quality guidelines for agricultural soils are 1.4, 63, 50, 70, and 200 mg/kg for Cd,

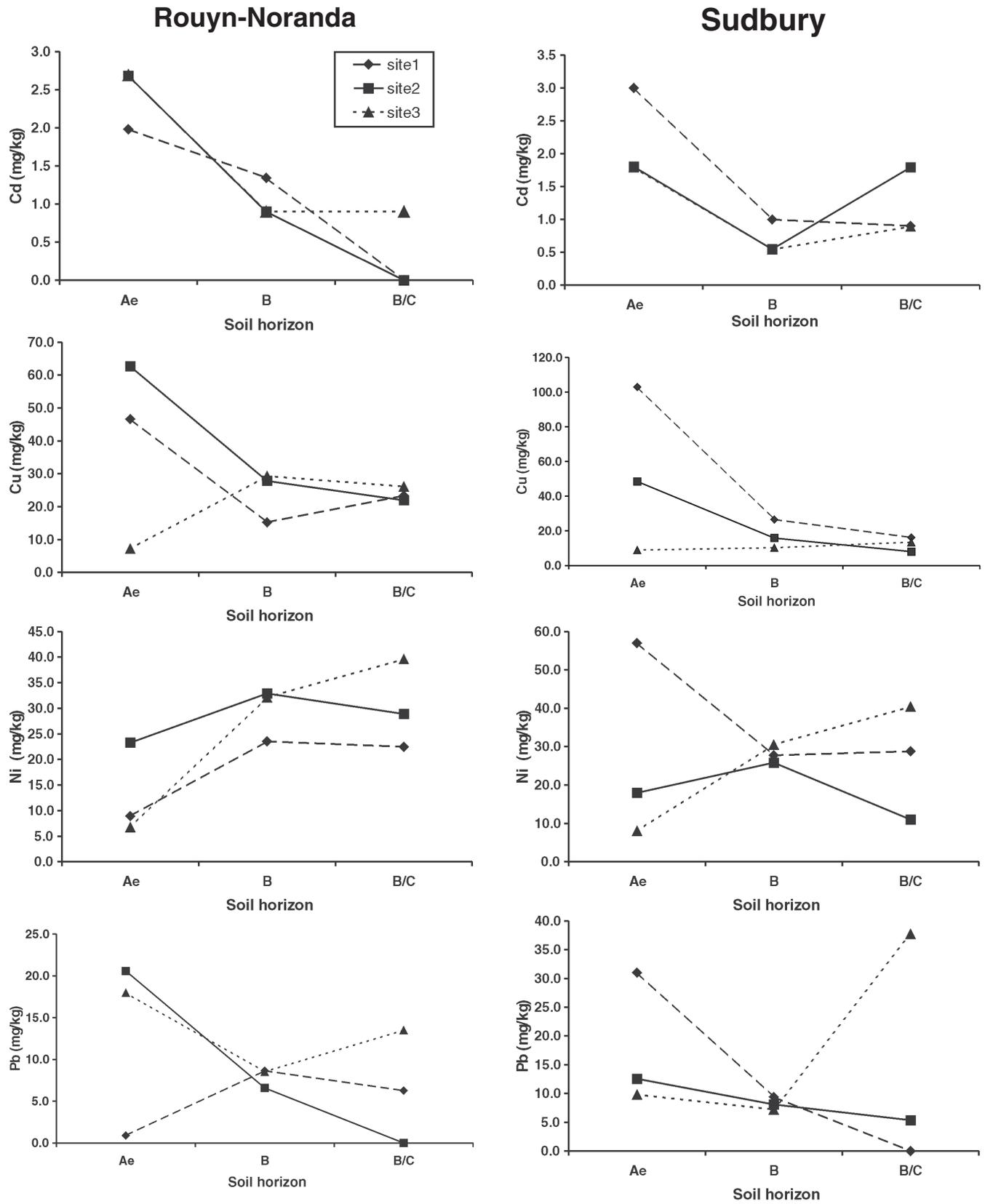


Figure 4. Concentrations (mg/kg) for Cd, Cu, Ni, Pb, and Zn in the Ae, B, and B/C horizons at each site in the Rouyn-Noranda and Sudbury areas.

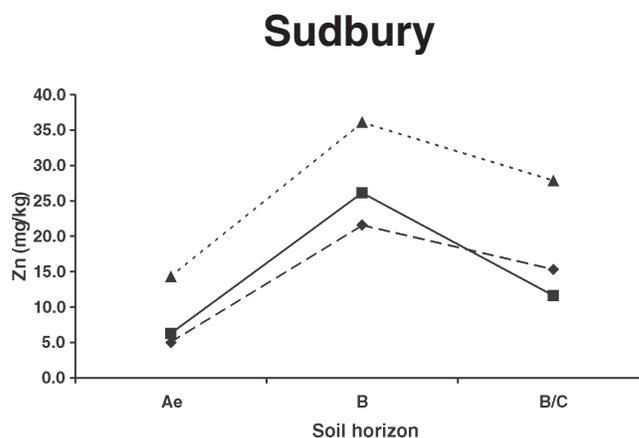
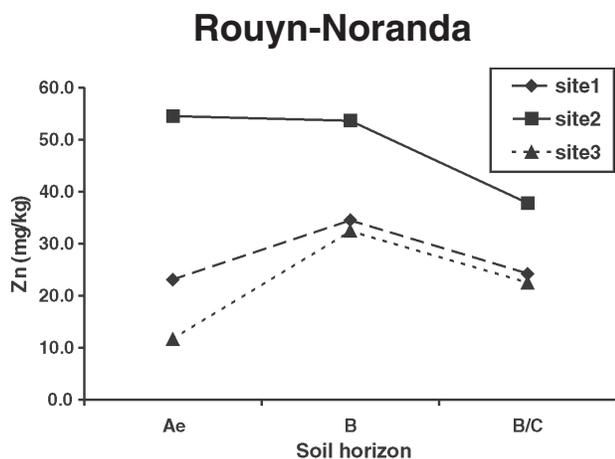


Figure 4 (cont.)

Cu, Ni, Pb, and Zn, respectively (Canadian Council of Ministers of the Environment, 2002). The concentrations in the B/C soil samples are well below these limits except for Cd in sample Sud2 (1.79 mg/kg).

The total metal concentrations for each soil horizon by site and area are shown in Table 2 and their trends are plotted in Figure 4. In general, trace metals occur at higher concentrations in the Ae horizon than in the B/C horizon at sites 1 and 2 in both areas, with a few exceptions (e.g. Ni at Rouyn-Noranda, Zn at Sudbury). These higher concentrations may reflect additions to the soil through smelter emissions, especially at the nearest site 1, as one would normally expect soluble trace elements to be leached from the Ae horizon in podzolic soils. Alternatively, weathering of the parent material with some translocation of metals in soil solution may have concentrated the metals in the organic-rich layer. Further discussions and analysis of lysimeter data will aid in interpreting these metal trends.

## SUMMARY AND CONCLUSIONS

The soils from Rouyn-Noranda developed on glacial till and the soils from Sudbury, on glaciofluvial deposits. All are classified as Orthic Humo-Ferric Podzols with mixed mineralogy. Samples from the B/C horizon are typical sandy loams. Samples from the Sudbury area are generally well sorted compared to those from the Rouyn-Noranda area. The heavy mineral and clay-sized fractions represent less than 5 weight per cent of the soils, which are characterized by an acidic pH (4.9–5.8) and a low cation exchange capacity that influences the adsorption properties of minerals.

In samples from the Sudbury area, epidote predominates in the heavy mineral fraction whereas pyroxene-group minerals predominate in the nonmagnetic heavy mineral fraction, which also has minor to trace amounts of amphibole-group minerals, titanite, zircon, hematite, and ilmenite. The clay-sized fraction is composed of quartz, plagioclase, K-feldspar, and amphibole-group minerals with minor amounts of

biotite, chlorite, ilmenite, and illite. Quartz, plagioclase, and K-feldspar predominate in the silt-sized fraction, which also has minor amounts of amphiboles, pyroxenes, and chlorite.

Rouyn-Noranda soil mineralogy is similar to that of Sudbury except for the absence of ilmenite and biotite in the clay-sized fraction. In general, mineral proportions are more constant in samples from Rouyn-Noranda than in those from Sudbury. Iron oxides, phyllosilicates, feldspars, and Ti- and Zr-bearing minerals may contain trace metals that can be released in the weathering environment. Iron oxides and phyllosilicates are potential sources of Cu, Cd, Ni, Pb, and Zn, feldspars, of Cu and Pb, and Ti- and Zr-bearing minerals, of Cu and Zn. Quartz, epidote, and amphibole- and pyroxene-group minerals are unlikely to contain trace metals.

Trace-metal concentrations of Cu, Ni, Pb, and Zn are all well below 40 mg/kg in the B/C horizon samples and those of Cd are less than 2 mg/kg. However, the concentrations of Cd, Cu, and Pb are slightly elevated at some sites in the Ae-horizon samples and probably reflect smelter additions to the soil column.

The rates of trace-metal release due to mineral weathering are the subject of another Sources Domain project. The data acquired will be used to calibrate a mineral-weathering model to predict the release rate of trace metals as a function of mineralogy and environmental conditions. Because insufficient amounts of fractionated material (i.e. clay-sized material or nonmagnetic heavy mineral) are available, the whole soil will be used initially in the weathering experiments. For comparison, the different fractions obtained from two selected sites will be analyzed using a sequential extraction scheme to determine the partitioning of the trace metals.

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## REFERENCES

- Boggs, S., Jr.**  
1995: Principles of Sedimentology and Stratigraphy (second edition); Prentice Hall, New Jersey, 774 p.
- Barnhisel, R.I. and Berstch, P.M.**  
1989: Chlorites and hydroxy-interlayered vermiculite and smectite; *in* Minerals in Soil Environments, (ed.) J.B. Dixon and S.B. Weed; Soil Science Society of America, Madison, Wisconsin, p. 729–788.
- Canadian Council of Ministers of the Environment**  
2002: Canadian soil quality guidelines for the protection of environmental and human health: summary tables, updated; *in* Canadian Environmental Quality Guidelines, 1999, Canadian Council of Ministers of the Environment, Winnipeg, Manitoba.
- Catlett, K.M., Heil, D.M., Lindsay, L.W., and Ebinger, H.**  
2002: Soil chemical properties controlling zinc<sup>2+</sup> activity in 18 Colorado soils; Soil Science Society of America, Journal, v. 66, p. 1182–1189.
- Deer, W.A., Howie, R.A., and Zussman, J.**  
1986: Rock Forming Minerals: Disilicates and Ring Silicates (second edition); John Wiley and Sons Inc., New York, New York, 629 p.
- Drees, L.R., Senkayi, A.L., Smeck, N.E., and Wilding, L.P.**  
1989: Silica in soils: quartz and disordered silica polymorph; *in* Minerals in Soil Environments, (ed.) J.B. Dixon and S.B. Weed; Soil Science Society of America, Madison, Wisconsin, p. 913–974.
- Environmental Protection Agency**  
1998: Method 3051A: microwave assisted acid digestion of sediments, sludges, soils and oils; *in* Draft Update IVA of SW-846 on-line; United States Environmental Protection Agency, Washington D.C. (<http://www.epa.gov/epaoswer/hazwaste/test/up4a.htm>)
- Fanning, D.S., Keramidis, V.Z., and El-Desoky, M.A.**  
1989: Micas; *in* Minerals in Soil Environments, (ed.) J.B. Dixon and S.B. Weed; Soil Science Society of America, Madison, Wisconsin, p. 561–634.
- Gundermann, D.G. and Hutchinson, T.C.**  
1995: Changes in soil chemistry 20 years after the closure of a nickel-copper smelter near Sudbury, Ontario; Canada; Journal of Geochemical Exploration, v. 52, p. 231–236.
- Hale, B. and Johnson, D.**  
2002: Relative flux of metals from foliage and fine roots to soils; *in* Metals in the Environment-Research Network, Annual Research Symposium, February 27–28, 2002, Ottawa, Ontario (abstract).
- Hale, B., Hendershot, W., Johnson, D., Ge, Y., and Macdonald, D.**  
2002: Post depositional mobility of trace elements in northern forest ecosystem; *in* Metals in the Environment-Research Network, Annual Research Symposium, February 27–28, 2002, Ottawa, Ontario (abstract).
- Hale, B., Hendershot, W., Macdonald, D. and Johnson, D.**  
2001: Metals in a northern ecosystem; MITE-RN News, Winter 2001, p. 3. (online at [http://www.mite-rn.org/publicat/mite\\_news\\_w2001\\_web.pdf](http://www.mite-rn.org/publicat/mite_news_w2001_web.pdf), accessed January 12, 2004).
- Hendershot, W., Lalande, H., and Duquette, M.**  
1993a: Ion exchange and exchangeable cations; *in* Soil Sampling and Methods of Analysis, (ed.) M.R. Carter; Lewis Publishers, Boca Raton, Florida, p. 167–176.
- Hendershot, W., Lalande, H., and Duquette, M. (cont.)**  
1993b: Soil reaction and exchangeable acidity; *in* Soil Sampling and Methods of Analysis, (ed.) M.R. Carter; Lewis Publishers, Boca Raton, Florida, p. 141–145.
- Hendershot, W.H., Percival, J.B., and Rowe, R.**  
2003: Is mineral weathering a significant source of trace metals in soils?; Metals in the Environment Annual Research Symposium, February 2003, Ottawa, Ontario (abstract).
- Henderson, P.J., Knight, R.D., and McMartin, I.**  
2002a: Geochemistry of soils within a 100 km radius of the Horne Cu smelter, Rouyn-Noranda, Quebec; Geological Survey of Canada, Open File 4169 (CD-ROM).  
2002b: Regional distribution of trace metals in soils surrounding a Cu smelter in Boreal Shield ecozone, northern Quebec, Canada; *in* Metals in the Environment-Research Network, Annual Research Symposium, February 27–28, 2002, Ottawa Ontario (abstract).
- Huang, P.M.**  
1989: Feldspars, olivines, pyroxenes and amphiboles; *in* Minerals in Soil Environments, (ed.) J.B. Dixon and S.B. Weed; Soil Science Society of America, Madison, Wisconsin, p. 975–1050.
- Kabala, C. and Singh, B.R.**  
2001: Fractionation and mobility of copper, lead and zinc in soil profiles in the vicinity of a copper smelter; Journal of Environmental Quality, v. 10, p. 485–491.
- MacDonald, D., Tailon, K., Johnson, D., Hale B., and Hendershot, W.**  
2003: Modeling the effect of trace metal emissions on boreal forest soils; Journal of Human Ecological Risk Assessment, v. 9, p. 723–747.
- McMartin, I., Henderson, P., Knight, R., and Plouffe, A.**  
2002: Comparison of Cu-Hg-Ni-Pb concentration in soils adjacent to four Canadian anthropogenic point sources; *in* Metals in the Environment-Research Network, Annual Research Symposium, February 27–28, 2002, Ottawa, Ontario (abstract).
- Milnes, A.R. and Fitzpatrick, R.W.**  
1989: Titanium and zirconium minerals; *in* Minerals in Soil Environments, (ed.) J.B. Dixon and S.B. Weed; Soil Science Society of America, Madison, Wisconsin, p. 1131–1206.
- Rose, A.W., Hawkes, H.E., and Webb, J.S.**  
1979: Geochemistry in Mineral Exploration (second edition); Academic Press, London, United Kingdom, 657 p.
- Ross, G.J. and Wang, C.**  
1993: Extractable Al, Fe, Mn, and Si; *in* Soil Sampling and Methods of Analysis, (ed.) M.R. Carter; Lewis Publishers, Boca Raton, Florida, p. 239–246.
- Rowe, R.**  
2003: Mineralogy of soils in the vicinity of smelters in Rouyn-Noranda and Sudbury areas; B.Sc. Thesis, Department of Earth Sciences, University of Ottawa, Ottawa, Ontario, 61 p.
- Schwertmann, U. and Taylor, R.M.**  
1989: Iron oxides; *in* Minerals in Soil Environments, (ed.) J.B. Dixon and S.B. Weed; Soil Science Society of America, Madison, Wisconsin, p. 379–438.
- Starr, M., Lindroos, A.-J., Ukonmaanaho, L., Tarvainen, T., and Tanskanen, H.**  
2003: Weathering release of heavy metals from soil in comparison to deposition, litterfall and leaching fluxes in a remote boreal coniferous forest; Applied Geochemistry, v. 18, p. 607–613.
- Voigt, A.**  
2003: Bioavailability of trace metals to plants; Ph.D. thesis, McGill University, Montréal, Quebec, 190 p.

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