Physico-chemical characterization of airborne particulate impurities deposited in snow around a copper smelter, Rouyn-Noranda, Quebec

C. Zdanowicz[1], D. Kliza[2], D. Paktunc[3], and G.F. Bonham-Carter[2]

Abstract: Microbeam analysis was used to characterize airborne particles deposited in snow around the Horne copper smelter in Rouyn-Noranda, Quebec. Over 85% of particles are composed of common rock-forming elements such as Ca, Si, and Mg. The approximately 15% remaining contain As, Cd, Cr, Cu, Fe, Ni, Pb, V, and/or Zn. Of the roughly 600 compositional types identified, only 20 account for more than 1% of all metal-bearing particles. The most common type is Fe-S-Cu, although other metal–sulphur associations (Zn-S, Fe-S, Cu-S) are also common. The relative abundance of many elements (e.g. As and Fe) differs considerably between reported bulk stack dust composition and snow particles, indicating that some unspecified mechanisms modify the composition of particulate metals between the time of their emission and their deposition in snow. Particulate loadings of the elements (mass deposited per unit area) are highest within 50 km of the smelter and decrease rapidly with distance. This is most evident for smelter-related elements (As, Cd, Cu, Ni, Pb, S, V, Zn) but is also apparent for common rock-forming elements (Al, Fe). However, no discernible spatial trend exists in the total frequency of metal-bearing particles in snow. Only particles containing Fe and/or Pb show a pattern of decreasing frequency away from the smelter. The volume size distribution of individual metal-bearing particles obeys a unimodal log-normal pattern with a modal diameter D_v between 1.8 and 2.8 µm, which is typical for aged mineral aerosols. There is no indication that D_v varies systematically with increasing distance from the smelter

Résumé : On a recouru à des analyses par microsonde à faisceau d'électrons pour identifier des particules atmosphériques qui ont été déposées dans la neige autour de la fonderie Horne, à Rouyn-Noranda (Québec). Plus de 85 % des particules se composent d'éléments lithogénétiques communs comme le calcium, le silicium et le magnésium, alors qu'environ 15 % d'entre elles contiennent de l'arsenic, du cadmium, du chrome, du cuivre, du fer, du nickel, du plomb, du vanadium ou du zinc. Parmi les quelque 600 compositions identifiées, seules 20 d'entre elles représentent plus de 1 % de toutes les particules métallifères. Le type le plus commun se compose de Fe-S-Cu, bien que d'autres associations de métaux et de soufre (Zn-S, Fe-S et Cu-S) soient également fréquentes. L'abondance relative d'un grand nombre d'éléments, comme l'arsenic et le fer, varie considérablement lorsque l'on compare la composition de l'ensemble des poussières de cheminée à celle des particules dans la neige, ce qui indique que certains processus inconnus modifient la composition des particules de métaux entre leur émission et leur dépôt dans la neige. Les charges en particules (masse surfacique) les plus élevées ont été relevées à moins de 50 km de la fonderie et elles diminuent rapidement en s'éloignant de cette dernière. C'est tout particulièrement le cas des éléments émis par la fonderie (As, Cd, Cu, Ni, Pb, S, V et Zn), mais également d'éléments lithogénétiques communs (Al et Fe). Cependant, aucune tendance spatiale n'est discernable quant à la fréquence totale des particules métallifères dans la neige. Les particules qui contiennent du fer ou du plomb ou les deux sont les seules dont les fréquences diminuent en s'éloignant de la fonderie. La granulométrie volumétrique de chaque particule métallifère est log-normale unimodale et comporte un diamètre modal

[1] Geological Survey of Canada, 562 Booth Street, Ottawa, Ontario, Canada K1A 0E4
[2] Geological Survey of Canada, 601 Booth Street, Ottawa, Ontario, Canada K1A 0E8
[3] Applied Mineralogy Laboratory, Canada Centre for Mineral and Energy Technology, 555 Booth Street, Ottawa, Ontario, Canada K1A 0E4

INTRODUCTION

The GSC MITE initiative

The Geological Survey of Canada (GSC) launched the Metals in the Environment (MITE) initiative in 1997 in order to provide a sound geological basis for investigations of the occurrence, speciation, mobility, and fate of metals in the surface environment. The GSC MITE initiative also aimed to develop criteria to differentiate between metals in the environment derived from natural (geogenic) and anthropogenic sources, and to validate various types of natural archives of metal deposition (e.g. surficial and lake sediments, snow, tree rings) in light of natural processes and variability. The Point Sources program of the GSC MITE initiative is concerned with the effects of major point sources on the natural biogeochemical cycling of metals. Much of the relevant research was carried out in the vicinity of the Horne copper smelter and refinery complex located in the town of Rouyn-Noranda, in western Quebec.

As part of the GSC MITE initiative, a regional-scale investigation of snow geochemistry in the Rouyn-Noranda area was initiated in March 1998. The objectives were to quantify atmospheric metal deposition in the snowpack and define the spatial dispersal pattern around the Horne smelter under current conditions. The 1998 survey was conducted by truck (road access) or helicopter along three 50 km long linear transects extending north, southwest, and southeast from the Horne smelter. Snow samples were analyzed for total water-soluble (<0.45 μm) and particulate (>0.45 μ) chemistry (57 elements) by inductively coupled plasma mass spectroscopy (ICP-MS) and inductively coupled plasma emission spectroscopy (ICP-ES). Results are discussed in Telmer et al. (2004). Numerical modelling of the metal distribution in snow revealed that concentrations at 50 km from the smelter were still above regional background levels (Kliza et al., 2005). Accordingly, a follow-up survey was planned to extend the spatial coverage farther away from the smelter in order to better define the total area affected by fallout. This paper presents results from a study that focuses on smelter-derived particulate metal pollution measured in the snowpack around Rouyn-Noranda.

The Noranda Horne smelter

The Horne smelter was established in 1927 by Noranda, Inc. to treat gold- and silver-bearing copper concentrates from the prolific Horne mine and other nearby deposits; it has been in continuous operation ever since. Between the 1930s and 1970s, the smelter was gradually transformed to accommodate continuous, custom smelting of various complex copper concentrates. After World War II, the company further expanded its activities to include the treatment of recycled materials and residues containing copper and precious metals. By 1976, all materials processed at the Horne smelter came from outside customers. On a daily basis, the individual feed to the smelter can include chalcopyrite-type or gold-bearing pyritic concentrates, silver- or copper-bearing smelting residues, and mixed metallic scrap that originates primarily from suppliers in North America and Asia and typically consists of a mixture of jewellery, automobile parts, and telephone, computer, and other electronic scrap containing precious metals in various quantities (Bédard et al., 1990). In 1989, an H_2SO_4 plant was added to the Horne smelter in order to treat the sulphur dioxide (SO_2) produced by the reactor; Noranda, Inc. became one of the leading producers and distributors of H_2SO_4 in North America.

The 'Noranda process' in use at the Horne smelter since 1973 is a pyrometallurgical smelting technique that allows for the continuous and simultaneous conversion of iron sulphide to iron-silicate slag and the reduction of copper sulphides to produce high-grade copper matte in a single reactor. The conversion can be described schematically by the following reaction:

$$Cu_2S\backslash FeS_2\backslash FeS + O_2 \rightarrow Cu_2S(Cu^0) + FeO + SO_2$$
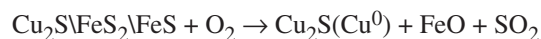
(Themelis et al., 1994)

A more detailed description of the Noranda process is given by Themelis et al. (1972). Only the main steps are summarized here. Inside a high-temperature primary smelting reactor (T about 1300°C), complex copper concentrates are melted to form a stratified bath in which iron silicate+oxide slag is segregated from denser, copper-enriched matte. Coal (refined coke) and silica flux are added to the bath. Turbulent agitation with oxygen-enriched air (typically 32–37% enrichment; El-Barnachawy et al., 1987) provides dynamic conditions that allow for the conversion of copper sulphides to metallic copper even as the bath still contains a substantial quantity of unoxidized iron sulphides. The exothermic oxidation of iron and sulphur provides most of the heat needed in the smelting process. The slag skimmed from the melt surface is cooled, milled, concentrated by flotation, and recycled through the reactor to recover copper and other precious metals. The enriched 'blister copper' matte (about 55–75% Cu) is tapped from the reactor sump and fed to the Noranda converter (continuous process) and a series of Peirce-Smith converters (batch process) where it is gradually refined by oxidation to produce 98% pure copper. The last steps of refining take place in anode furnaces where final oxidation of the sulphur and iron take place, resulting in 99% pure copper.

The pyrometallurgical processing of copper ores and concentrates produces large quantities of SO_2 gas, fumes, and dusts. In this context, dust is operationally defined as particulate material >1 μm (aerodynamic diameter), whereas fumes are within the 0.001 to 1 μm size range (Perry and Green, 1984). In a typical copper-smelting operation, the major source of dust emissions to the ambient environment is the converter (J.C. Taylor, unpub. rept., 1979). The amount of dust produced depends on such variables as fineness of the feed charge, the degree of agitation in charging and processing of the feed, and the specific gravity of the feed materials. Fumes consist of compounds that have volatilized or sublimed during smelting and then condensed from the gases on cooling. The main fume constituents in copper smelting are oxides, sulphates, and oxy-sulphates of lead, zinc, bismuth, and cadmium, together with water and H_2SO_4. The collecting equipment used to clean the smelter gases does not adequately

differentiate between dust and fume, and the resulting mixture is generally called 'flue dust' (R.W. Stanley, P.H. Jennings, and E.S. Stratigakos, unpub. rept., 1972).

Since the decommissioning of the reverberatory furnaces after 1990, flue gases and dusts at the Horne smelter are produced either in the smelting reactor itself or in the secondary Peirce-Smith converters and anode furnaces. Off-gases from the reactor are cooled to about 350°C in an evaporative cooler and then circulated through electrostatic precipitators that remove approximatelt 95% of particulates from the gas stream. Most of the remaining particulates are removed in the gas-cleaning section of the H_2SO_4 plant, where gases are cooled to approximately 80°C and cleaned using cyclonic separators, scrubbers, and electrostatic precipitators. These combined systems reportedly capture 99% of airborne particulates carried in the off-gases (Noranda, Inc., unpub. data, 1999). Flue dust from the Peirce-Smith converters and anode furnaces is collected in Cottrell-type precipitators and returned to the secondary smelting circuit. Beginning in 1980, tight-fitting waffle hoods were installed on the converters to reduce fugitive dust emissions. As of 1997, Noranda, Inc. was reporting a mean monthly dust emission rate out its stacks of about 1 kg/t of feed (Noranda, Inc., unpub. data, 1997). Given that the smelter currently processes over 800 000 t of feed annually, this should translate to dust emissions of about 800 t/a. For comparison, the reported total atmospheric emissions of As, Cd, Cu, Pb, Ni, and Zn from the Horne smelter in 1998 were 363 t. The balance of the dust mass is made up largely of Fe, Si, and O since oxides and silicates are major constituents in the flux and slag. However, little data are currently available on the composition of individual dust particles emitted from the Horne smelter stack.

Study rationale

Different types of natural archives can be used to document past and present atmospheric metal deposition. Such natural archives include lake sediments, peat bogs, epiphytic lichens, tree rings, or snow and ice cores. Of these, snow and ice cores are particularly useful because they can also provide information about the physical or chemical characteristics of atmospheric metal fallout. Snow and ice preserve atmospheric impurities in a simple matrix of frozen water, whereas lake sediments, for example, are made of a complex mixture of mineral phases and organic matter. The potential for postdepositional transformations of atmospheric fallout by inorganic or organic processes is therefore limited in snow and ice when compared to other natural archives. The extraction and analysis of impurities from snow or ice is also far simpler than from lake sediments or other media. Furthermore, the widespread extent of seasonal snow cover at middle to high latitudes makes snow a medium of choice for investigating spatial patterns of atmospheric deposition of, for example, acidic pollutants or trace metals (e.g. Barrie and Vet, 1984; Van Borm et al., 1987; Gorzelska, 1989; Äyräs et al., 1995).

The main objective of this study is to characterize the size distribution, chemical composition (elemental associations), and spatial dispersion pattern of individual smelter-derived particles found in the snowpack around Rouyn-Noranda, in order to better understand the origin(s) of these particles, their means of atmospheric transport and deposition, and their contribution to the total metal load measured in snow. In addition, this study aims to provide data on particulate metal deposition in snow that can be directly compared with in-plume and ground-level aerosol sampling conducted as part of a parallel investigation on stack emissions from the Horne smelter carried out by the Meteorological Service of Canada, Air Quality Research Branch (Downsview, Ontario). In order to ensure the compatibility of results, this investigation used the same analytical methodology that was developed for the aerosol study (Paktunc et al., 2001). The results will also be used to help validate numerical simulations of particle deposition from the smelter plume (Banic et al., 2000).

METHODS

Sampling methodology

The snow-sampling survey was conducted between February 19 and 23, 2001, roughly 3 months (99 days) after the first recorded autumn snowfall and before the onset of spring melt. A total of 57 sites were sampled, almost entirely by helicopter in order to achieve a more spatially uniform sampling pattern, not limited by road accessibility. The results of the winter 1998 survey indicated that the area located east-southeast of the Horne smelter was more affected by metal pollution. Accordingly, a larger number of sites were sampled in this quadrant. The distance between individual sampling sites and the Horne smelter ranged from 2 to 277 km (Fig. 1).

The physiography of the Rouyn-Noranda region is typical of the Canadian Shield, with gently undulating, low-relief uplands interspersed with numerous lakes, bogs, fens, streams, and a few broad, clay-filled valleys. A more complete description of the regional physiography and surficial geology can be found in Veillette et al. (2005). Most of the area is covered by dense boreal forest dominated by black spruce, birch, and muskeg. Agriculture is confined to the broader valleys. In addition to Rouyn-Noranda itself (pop. 30 000), the surveyed area included several towns with populations in the thousands (e.g. Val-d'Or, Malartic, and Cadillac; Fig. 1). The snow-sampling sites were distributed among suburban areas close to the Horne smelter, rural areas with a few farm houses or summer cottages, and remote forest lakes and marshes inaccessible by road.

The chemistry of the snowpack in a forested environment can be highly heterogeneous over short distances due to uneven snow accumulation and the combined effects of snow drifting around obstacles and sublimation (Pomeroy et al., 1999). In this study, almost all snow samples were collected from the frozen surface of lakes or ponds, under the assumption that both snowpack thickness and composition are more homogeneous at these sites. Moreover, sampling from open areas reduces the amount of particulate organic matter such as pine needles, bark chips, and leaf fragments that are deposited in the snowpack. It also minimizes the potential for postdepositional changes in snow composition that may result from chemical exchange at the soil–snow interface

3
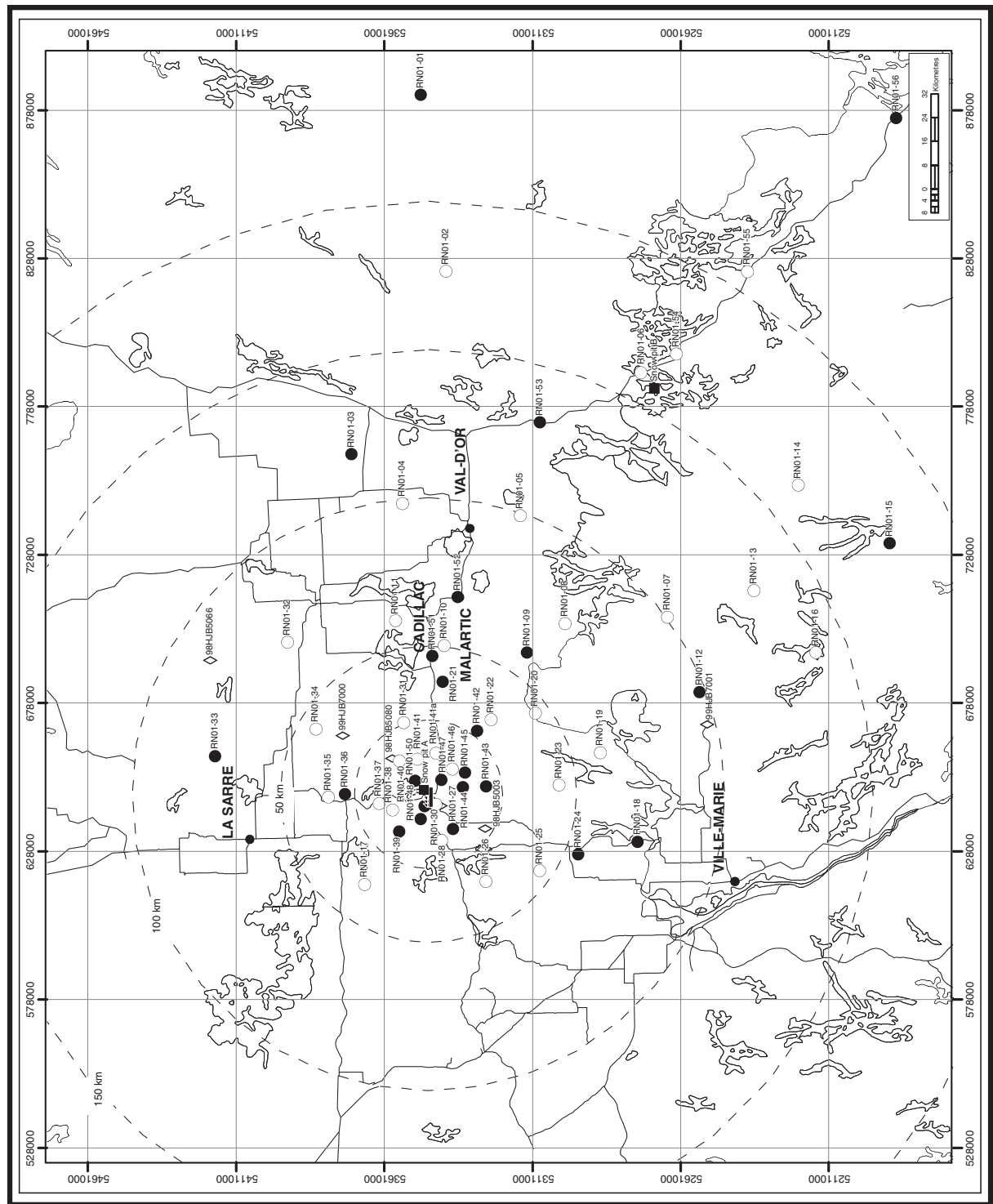
Figure 1. Location map of the winter 2001 snow-sampling sites around the town of Rouyn-Noranda, Quebec. The sampling sites (circles) are labelled RN01-01 to RN01-56. Full black circles identify sites from which individual particles were analyzed by VP-SEM. Also shown are the locations of two snow pits (A and B), as well as selected humus sampling sites from Knight and Henderson (2005).The concentric dashed circles indicate relative distance from the Horne smelter (centre).

(Leggett and Hogan, 1995). Finally, the numerous lakes that dot the study area are easily accessible by helicopter in the winter, which increased the spatial coverage of our study and the rapidity of sampling.

The Meteorological Service of Canada monitoring station in Val-d'Or recorded no extended intervals of above-zero temperature during winter 2001, prior to the sampling period. This was confirmed by examining the snow stratigraphy in two separate pits excavated at opposite ends of the sampling area (Fig. 1). The winter 2001 snowpack generally consisted of dry, loose to slightly compacted snow with a density ranging from 250 to 350 g/cm³. Snow crystals were subangular, platy, or dendritic. Neither of the snow pits showed any evidence of significant melting events, apart from a few thin (<1 cm) ice layers that probably formed at the snow surface during calm, sunny days. On the basis of these findings, we assume that no significant mass losses from the snowpack occurred over the course of the winter, apart from those brought about by wind scouring, drift, or sublimation.

The snowpack depth at the sampling sites varied from 19 to 96 cm, with an average of 70 cm (median value). Snow samples for bulk chemistry were collected and bagged using a polycarbonate tube, as described by Telmer et al. (2004). At approximately every second site (26 out of 57), a separate snow sample was also collected for analysis of individual particles. The samples were collected in acid-cleaned, Nalgene™, 1 L, high-density polyethylene (HDPE) bottles. Each sample represented a composite of the total snowpack thickness at the sampling site. The volume of snow obtained in each sample varied from 0.20 to 2.10 L, with an average of 0.82 L.

Analytical procedure

All snow samples were returned unmelted to Ottawa and stored in a freezer. The bagged samples were processed in a class 100 clean room at the GSC Ottawa Analytical Method Development laboratories, following the protocol described by Kliza et al. (2002). The samples were weighed, melted, and vacuum filtered through Millipore Duripore™ polycarbonate membranes with 0.1 µm pore diameter in order to retain most of the suspended particles. The membranes were then air dried and digested in an acid mixture. The filtered water and dissolved filtrate were analyzed separately in order to obtain a complete suite of major, minor, and trace elements, following standard analytical methods (Hall et al., 1996). Major and minor elements were determined by ICP-ES, whereas trace elements were analyzed by ICP-MS. In the following discussion, we use the operational terms 'dissolved' and 'particulate' to designate those elements measured in the filtered meltwater and in the filtered particulate matter, respectively. All concentrations are reported in parts per billion (ppb), corrected to the total weight of the snow samples. Detection limits and filter blank values are given in Kliza et al. (2002).

The bottled snow samples were processed separately in the GSC Ottawa Snow and Ice Core Laboratory. They were first melted overnight at room temperature (approximately 12 h);

the bottles were then immersed in an ultrasonic bath for 1 h in order to break up particle aggregates that may have formed by coagulation. After vigorous agitation, 10 mL aliquots from each sample were vacuum filtered through a Nuclepore™ polycarbonate membrane with 0.45 µm pore diameter. The volume of the filtered aliquots was chosen in order to optimize the dispersion of individual particles on the membrane surface for electron microscope analysis. The filter membranes were air dried and mounted on aluminium stubs overlaid by pure carbon disks. No coating was applied to the filter surfaces. All manipulations were performed under a laminar airflow hood.

The filters were analyzed at the Applied Mineralogy Laboratory of the Canada Centre for Mineral and Energy Technology (CANMET). The analyses were performed on a Hitachi S-3200N variable-pressure, automated scanning electron microscope (VP-SEM) equipped with a Link light-element window energy-dispersive spectrometer (EDS). The Si(Li) EDS detector has a resolution of 133 eV at 5.898 keV and 1000 cps. Analytical work was carried out at an accelerating voltage of 15 kV and a sample-chamber pressure of 40 Pa to compensate for charging on the surface of the particles. The filters were examined at 400X magnification and a working distance of 15 mm. Automated image analysis was carried out using a beam raster of 250 µm by 250 µm in the centre of each filter. Particles were differentiated from the substrate based on their backscattered-electron signals, and an average of 1035 particles were detected and analyzed on each filter. For each particle, the projected surface area was measured and an energy-dispersive X-ray spectrum was acquired for 5000 ms (livetime). The following 21 elements were measured using the X-ray lines specified in parentheses: C(K), O(K), Na(K), Mg(K), Al(K), Si(K), P(K), S(K), Pb(M), Cl(K), K(K), Ca(K), V(K), Cr(K), Fe(K), Ni(K), Cu(K), Zn(K), As(L), Se(L), and Cd(L). Blank filters were analyzed under identical conditions to determine the minimum detection limits in terms of X-ray counts for each element and/or line. These minimum detection limits were determined by averaging counts obtained for the characteristic X-ray lines of each element after three separate runs on a blank filter. After subtracting the carbon and oxygen counts, the average X-ray counts for the other elements were normalized to 100% (Table 1). Numerous standard samples were analyzed under identical conditions in order to determine the accuracy of the technique (Paktunc et al., 2002b). In addition, the samples were examined in manual mode to confirm the presence of the principal elements detected.

In the following sections, we restrict our discussion of results to the following 15 elements that were analyzed in individual particles (by VP-SEM) as well as in bulk snow samples (by ICP-MS/ES): Na, Mg, Al, S, K, Ca, V, Cr, Fe, Ni, Cu, Zn, As, Cd, and Pb. This suite of elements includes common rock- or soil-forming elements (Na, Mg, Al, S, K, Ca, Fe) as well as elements that may be found associated with non-ferrous smelting emissions (S, V, Cr, Fe, Ni, Cu, Zn, As, and Cd). The emphasis in the discussion is on the characteristics of individual particles; the bulk snow chemistry data are also used to evaluate the partitioning of specific elements between the dissolved (<1 µm) and particulate phases.

Table 1. Minimum detection limits (MDL) for the VP-SEM analyses performed on the snowpack particle samples (excluding elements C and O)

Element	MDL (X-ray counts)
Na	28
Mg	19
Al	40
Si	8
P	2
S	6
Pb	18
Cl	2
K	5.5
Ca	10
V	10
Cr	9
Fe	9
Ni	8
Cu	10
Zn	13
As	4
Se	4
Cd	6

RESULTS AND DISCUSSION

Particle types

A total of 27 000 individual particles were analyzed on the 26 filters prepared from the Rouyn-Noranda snow samples. The accurate quantitative X-ray microanalysis of individual small ($\leq 10\,\mu m$) atmospheric particles is difficult to achieve because of the size of the particles (which could be less than the electron beam interaction volume), their irregular surfaces (which could interfere with emitted X-rays), the occurrence of particle aggregates, and the lack of well characterized standards for comparison. Without appropriate correction algorithms and/or standards, microanalytical results can be regarded only as qualitative or, at best, semiquantitative (Newbury et al., 1995). In this study, the EDS data were processed using customized software so as to classify particles based on their chemical compositions (A.D. Paktunc, unpub. rept., 1999). Individual particles were assigned to compositional classes defined by those elements for which normalized X-ray counts exceeded the minimum detection limits defined in Table 1. This type of classification does not discriminate among particles composed of the same suite of elements but with different relative abundances (X-ray line intensities). Hence, results can be used only to define broad compositional categories or to assess the relative frequency of specific elemental associations in the samples. Furthermore, carbon and oxygen cannot be used as diagnostic elements because they are major constituents of the polycarbonate membrane substrate and of the carbon disk covering the aluminium sample holder. Consequently, organic particles composed primarily of these elements (e.g. pollen, vegetation fragments) cannot be identified. For the same reason, sulphates cannot be distinguished from sulphides, and the presence of oxides, hydroxides, and/or carbonates must be inferred indirectly.

Taking these limitations into account, particles detected in our snow samples can be classified into two broad compositional categories. Particles that are composed chiefly of a combination of common rock-forming (crustal) elements such as Si, Al, Fe, Mg, Ca, Na, K, and/or Cl are simply designated as 'crustal particles'. They are by far the most abundant particles in the snow samples. On average, they account for over 85% of all particles analyzed on each filter. Table 2 lists the most common elemental associations found in the 'crustal particles' category, along with plausible mineral identifications. These are mineral species commonly found in most soils and surficial sediments. However, we recognize that some unknown percentage of particles designated as 'crustal' may in fact originate from the smelter, since slag derived from the smelting of copper concentrates produced from rock ores will commonly contain these same common rock-forming elements that characterize soil dusts.

Most of the remaining non-crustal particles found in the snow samples contain one or more of the following metal species in detectable amounts: As, Cd, Cr, Cu, Fe, Ni, Pb, V, and/or Zn. For brevity, we designate all particles in this category simply as 'metal-bearing particles'. We consider such particles to be *most likely derived* from smelter stack emissions or from related sources (*see* next paragraph). Note that we exclude from this category iron-bearing particles that only contain commonly occurring crustal elements (e.g. Ca-Fe-Mg, Fe-Al, etc.), but we include particles in which iron occurs with any other of the aforementioned metal species. A total of 610 distinct metal-bearing particle types were identified in our snow samples, indicating a wide range of compositional variability. However, certain particle types may differ only by a few minor constituents (e.g. S-Fe and S-Fe-Se), whereas others may represent aggregates of compositionally distinct particles. Hence, there are probably fewer truly distinct particle types than were recognized in our analysis. Figure 2 shows some photomicrograph examples of metal-bearing particles,

Table 2. Commonly occurring crustal particle types identified in the Rouyn-Noranda snowpack samples.

Particle type	Abundance	Possible mineral species
Al-Si	35.5 %	Kaolinite, pyrophyllite
Si	21.1 %	Quartz
K-Al-Si	15.0 %	Muscovite, K-feldspar
Fe-Al-Si	7.6 %	Illite, biotite, chlorite
Fe	1.2 %	Iron oxide(s)/hydroxide(s)
Ca-Si	1.1 %	Garnet, calcite+quartz aggregate
Al	1.1 %	Aluminium oxide(s)/hydroxide(s)
Other crustal types	~ 3 %	*Undetermined*
Total	> 85 %	
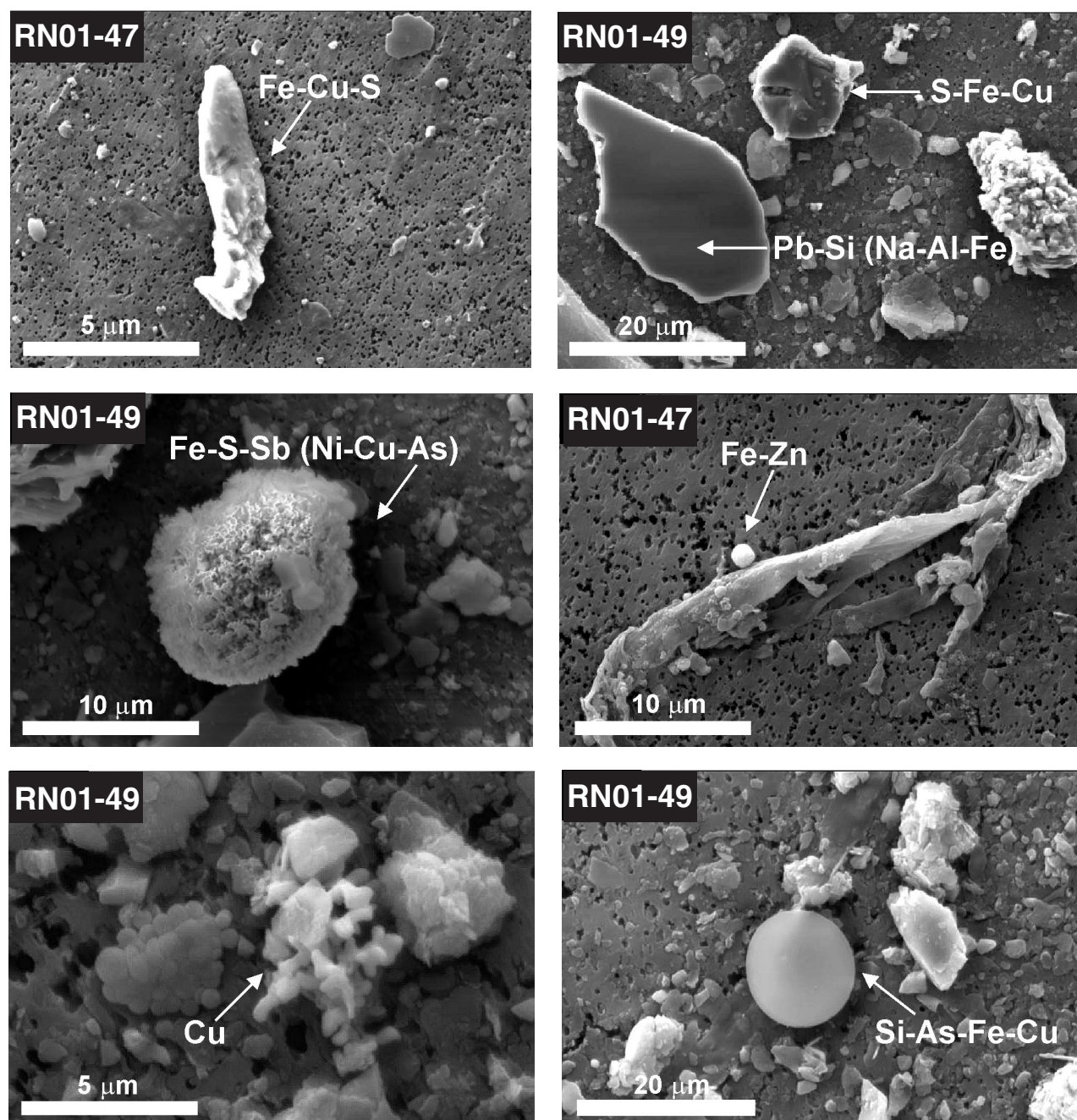
Figure 2. *Photomicrograph examples of individual metal-bearing particles observed in bulk particulate matter filtered from snow samples in the Rouyn-Noranda area. Major and minor constituents, as determined from EDS analyses, are indicated.* See *Figure 1 for sample site location.*

taken on bulk particulate filters from the snowpack samples. The morphological and compositional diversity of the particles illustrates how difficult the task of classifying them is.

Metal-bearing particles can originate from several sources. They may represent direct atmospheric fallout from the Horne smelter stack emissions. They may also represent windblown concentrate dust and/or smelting residues that were not directly emitted from the smelter stacks. For example, slag and mine tailings were used for a long time as fill for road construction

in the study area. Hence, some metal-bearing particles observed in snow may represent such materials dispersed by winds or by road traffic. Other particles may represent atmospheric pollutants from sources such as vehicular or stationary fuel combustion. Some knowledge of the relative contribution from these sources may be gained by examining the various elemental associations detected among the metal-bearing particles. Table 3 lists the 20 most common associations, ranked by decreasing order of relative frequency. Together, these 20 particle types account for over 40% of

7

all metal-bearing particles in the snow samples. Each of the remaining 590 types accounts for less than 1% of all particles. The relative frequency of pairing between elements in the metal-bearing particles is listed in Table 4.

Not surprisingly, the most common elemental association is Fe-S-Cu, which may be tentatively identified with chalco-pyrite ($CuFeS_2$), the most abundant copper-bearing sulphide

Table 3. Most common elemental associations identified in the metal-bearing particles filtered from the snowpack.

Rank	Type	Frequency (%)
1	S-Fe-Cu	8.1
2	Si-V	2.8
3	Pb	2.8
4	S-Zn	2.8
5	S-Fe	2.6
6	Si-Pb	2.3
7	Si-Cu	2.0
8	Si-Zn	2.0
9	Al-Cu	1.8
10	S-Cu	1.7
11	Cr	1.7
12	Cu	1.6
13	Pb-Fe	1.5
14	Al-Si-V	1.4
15	V	1.3
16	Zn	1.2
17	Si-Fe-Cu	1.2
18	Si-S-Fe	1.0
19	Al-Zn	1.0
20	V-Fe	1.0

mineral of ore processed at the Horne smelter. Other common metal-sulphur associations include Zn-S (possibly sphalerite), Fe-S (pyrite), and Cu-S (chalcocite). Note that mineral identifications are only tentative; without knowledge of the exact stoichiometry of the particles, it is impossible to establish whether the elemental associations in Table 3 represent true mineral phases or are secondary products of smelting at the Horne smelter. Also common among the metal-bearing particles are individual metal species (e.g. Pb, Cu), which may represent native or oxidized forms of these metals. Again, such particles could originate from smelting of concentrates at the Horne smelter. This is more likely for copper-, zinc-, and lead-bearing particles, but may also apply to elements that commonly occur in association with these metals either in ore-derived concentrates (e.g. arsenic in sulphides) or in recycled materials (e.g. nickel or cadmium in electronic scrap). The association of silica with one or several of the transition metals (e.g. Si-V, Si-Zn, Si-Cu-Ni) is also common in the snowpack particles, as can be seen from Table 4, where Si is one of the most common elements associated with the metals As, Cd, Cr, Fe, Ni, Pb, Se, V, or Zn. Silica is a major constituent of slag produced during smelting of copper concentrates, where its concentration can sometimes exceed 25% by weight (Persson et al., 1986; Bérubé et al., 1987). It is therefore not surprising to find silica as a common constituent of flue dust. As mentioned earlier, most particulate metal emissions from the Horne smelter probably originate from the converting and fire-refining processes, because the smelting reactor itself is completely self contained and its off-gases are thoroughly treated prior to their processing in the H_2SO_4

Table 4. Relative frequency of element pairs identified in all particles analyzed by VP-SEM ($N = 27\,000$).

	Al	As	Ca	Cd	Cr	Cu	Fe	K	Mg	Na	Ni	Pb	S	Si	V	Zn
Al		3.9	14.6	3.4	6.1	6.2	25.8	35.5	6.2	3.9	5.7	5.9	5.7	73.4	8.8	5.6
As	0.0		0.7	1.3	2.6	0.6	0.3	0.1	0.0	0.7	1.0	2.4	0.5	0.0	0.7	0.9
Ca	1.4	11.6		8.2	8.8	6.1	3.3	1.7	10.9	10.9	9.2	7.7	4.2	3.7	6.6	8.7
Cd	0.0	2.0	0.7		2.8	0.6	0.3	0.6	1.0	1.0	1.6	1.0	1.0	0.1	1.5	1.4
Cr	0.2	12.6	2.6	9.5		3.8	1.0	1.3	4.1	4.2	5.5	4.4	3.2	0.5	2.4	3.9
Cu	0.4	6.8	4.6	5.4	9.6		6.5	1.9	5.2	8.5	8.5	9.1	21.9	0.9	6.5	7.8
Fe	6.7	12.6	9.0	10.2	9.4	23.5		2.8	8.6	7.7	10.7	16.2	26.5	10.3	12.0	10.5
K	5.6	2.9	2.7	11.6	7.4	4.1	1.7		4.5	5.9	6.3	6.9	3.4	6.5	5.9	5.9
Mg	0.3	0.0	4.7	4.7	6.1	3.0	1.4	1.2		15.8	5.5	5.1	3.1	1.1	4.8	4.7
Na	0.1	2.0	1.7	2.0	2.3	1.8	0.5	0.6	6.0		2.2	2.5	1.0	0.2	2.1	2.0
Ni	0.2	4.9	2.7	5.4	5.5	3.3	1.1	1.1	3.7	3.9		4.3	2.9	0.3	5.8	5.8
Pb	0.2	15.5	2.9	4.7	5.7	4.6	2.2	1.6	4.5	5.9	5.5		1.8	0.6	5.5	6.3
S	0.4	5.8	3.0	8.2	7.7	20.5	6.8	1.4	5.1	4.2	6.9	3.4		0.8	6.4	12.6
Si	83.9	7.8	43.6	10.2	16.9	13.8	45.5	47.2	30.9	16.5	14.4	17.8	13.1		24.7	18.1
V	0.4	4.9	2.7	7.5	3.3	3.5	1.8	1.5	4.5	5.3	8.1	5.9	3.7	0.8		5.8
Zn	0.3	6.8	3.9	7.5	5.9	4.6	1.7	1.6	4.9	5.6	8.9	7.4	8.1	0.7	6.4	
	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.1	100.1	100.1	100.1

plant. However, the common occurrence of vanadium in the metal-bearing particles found in snow suggests that some particles may be emitted from the H_2SO_4 plant itself, where V_2O_5 is used as a catalyst to oxidize SO_2 to SO_3 (Samuel et al., 1989).

A sample of bulk particulates captured in the copper smelter stack was analyzed (J. Skeaff, A.D. Paktunc, and J. McGeer, unpub. rept., 2001); the stack serves to vent gases and flue dusts from the converter aisle and anode furnace. The sample represents a composite mixture of dusts passing through the stack over a period of one month. However because the smelter feed composition varies considerably on a day-to-day basis, it is uncertain whether this sample can be considered representative of mean stack dust composition over a longer interval. The major constituents of the stack dusts were found to be S (17% by weight), Pb (13%), As (9%), Cu (8%), Na (8%), and Zn (3%). Other constituents such as Fe, Cd, Cr, Se, Ni, and the more volatile elements (Al, K, Ca, Mg) amounted to less than 1% each by weight. A VP-SEM analysis of individual dust particles revealed that they are commonly formed of a metallic copper or copper oxide core, surrounded by a rim containing Cu, Na, S, As, and O. Interestingly, the order of relative abundance for many elements in the stack dusts differs from that observed in the bulk chemical composition of our snow particles, where [Fe] > [S] > [Cu] > [Zn] > [Cr] > [Pb] > [Ni] > [As] > [V] > [Cd] (Kliza et al., 2005). It is noteworthy that iron, while one of the most common elements in metal-bearing particles deposited in snow, amounts to only 0.3% by weight in the stack dust analyses (J. Skeaff, A.D. Paktunc, and J. McGeer, unpub. rept., 2001). Conversely, arsenic is a major constituent in the bulk stack dust, yet is a rare and rather minor constituent in the snowpack particles, where it averages less than 0.5% by weight (based on bulk particulate chemistry). Arsenic is also rare in aerosols collected at ground level or in the smelter plume (Paktunc et al., 2002a). In general, the elimination of minor elements such as

As, Sb, and Bi from copper concentrates occurs primarily in smelting and secondarily during converting. At the Noranda Horne smelter, arsenic is separated from copper mostly by volatilization during the smelting process, when up to 75% of it passes into the flue dust (P.W. Godbehere, Horne Division, Noranda Minerals Inc., internal rept., 1990). On average, about 18% of the remaining arsenic is volatilized during converting. The VP-SEM analyses by J. Skeaff, A.D. Paktunc, and J. McGeer (unpub. rept., 2001) suggest that arsenic compounds emitted by the smelter may be readily soluble in water, which might explain the low frequency of arsenic as particulate constituent in the snowpack, but also in aerosols (Paktunc et al., 2001). On the other hand, some other major constituents in stack dusts such as copper, lead, and zinc also count among the most common and abundant ones in the snow particles, as well as in aerosols sampled at ground level and in the smelter plume (Paktunc et al., 2002a).

The differences between stack dusts and metal-bearing particles found in the snowpack suggest that some mechanisms contribute to modify the average composition of metal-bearing particulates between emission from the stack plume and deposition in snow. Some insights into the nature of these mechanisms may be gained by considering the spatial distribution of metal-bearing particles and specific metals in the snowpack.

Spatial distribution of particles and elements

Figure 3a shows the measured concentration of particulate matter in snow with distance from the smelter for all 57 sampling sites surveyed in 2001. Overall, there is no indication that particulate matter varies systematically with distance from the smelter. Although the highest particulate matter value (64 mg/L) was measured 12 km from the smelter, one
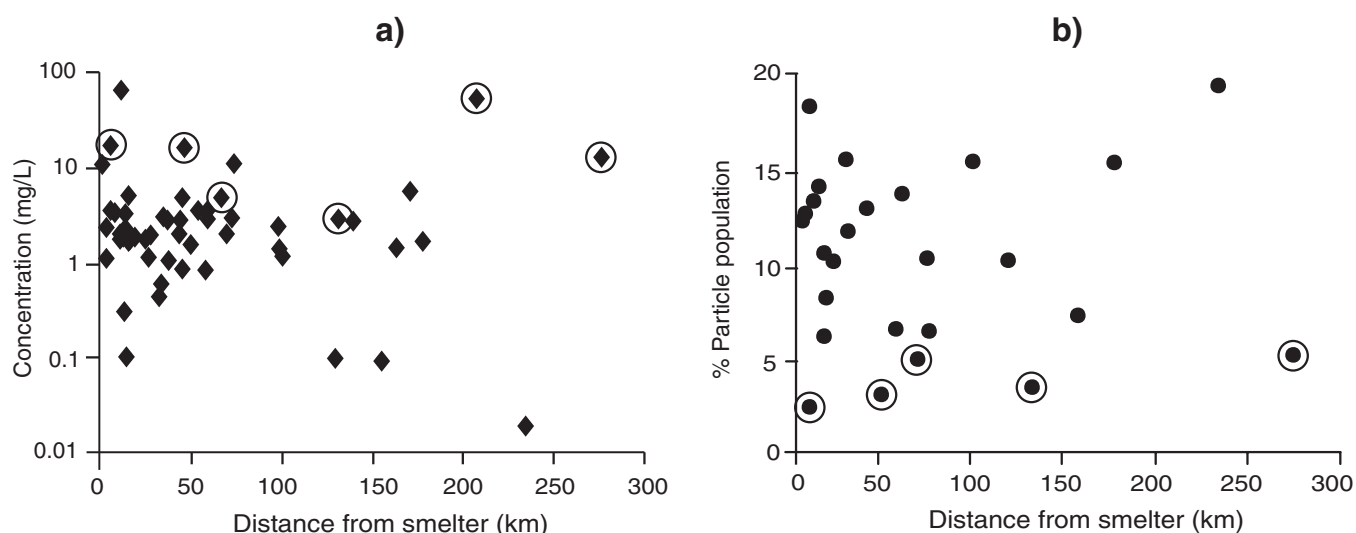
Figure 3. *Variations of **a)** total particulate matter concentration (D >0.1 µm; in mg/L) and **b)** relative frequency (%) of metal-bearing particles in snow samples as a function of distance from the Horne smelter. Number of samples (sites) plotted in a) = 57, in b) = 26. Data points that are circled correspond to sampling sites that may have been affected by road dusts.*

of the lowest values (0.1 mg/L) was measured comparably close (14 km) to it. And even when those sites located near highways (and therefore possibly affected by road dust) are excluded, the range of particulate matter values measured within 50 km of the smelter remains comparable to that measured at over 100 km from it. Figure 3b shows the percentage of metal-bearing particles detected by VP-SEM in filtered snow samples, plotted against distance from the Horne smelter. Again, no discernible trend in the distribution of metal-bearing particles is observed with respect to distance from the smelter. However, this may be partly due to insufficient sampling density, as samples for VP-SEM were collected from only 26 of the 57 sites visited. Remarkably, those sites identified as potentially affected by road dust also contain the lowest percentage of metal-bearing particles (<5%) of all sites where individual particles were analyzed. This would appear to suggest that the local road dust has a generally low particulate metal content, i.e. the particulate load in snow at these sites is dominated by non-metal-bearing, presumably crustal, particles.
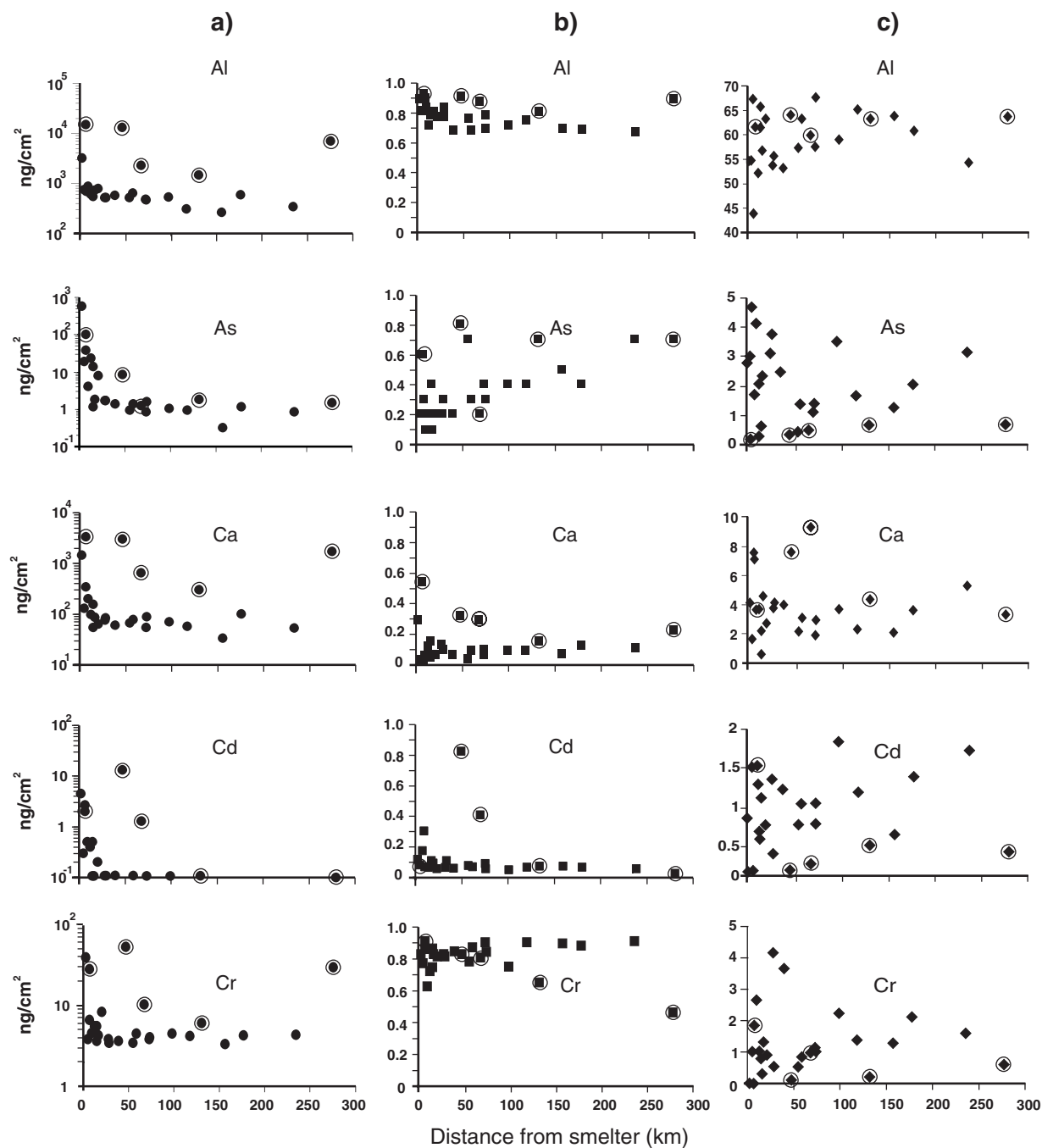
Figure 4 shows the spatial distribution of various chemical elements measured in the snowpack as a function of distance from the smelter. Figure 4a shows the particulate loading of each element in snow, i.e. the mass of this element, measured in the bulk >1 μm filtrate, that was deposited in the snowpack per unit surface area. Figure 4b shows the proportion of the total loading (dissolved + particulate) for this same element that occurs in particulate form. Figure 4c shows the percentage of individual particles analyzed by VP-SEM that was found to contain the element in detectable amounts. Note that the spatial distribution of Si (not shown on Fig. 4) is very similar to that of Al, undoubtedly because of the close association of Si and Al in silicate particles, whether these particles are primary minerals or secondary, smelter-derived phases. In terms of particulate loading, many elements show a similar pattern, with loading being highest within 50 km of the smelter and decreasing rapidly in concentration with increasing distance. This is most evident for elements that are related to smelter emissions (As, Cd, Cu, Ni, Pb, S, V, Zn) but is also apparent for more common rock-forming elements such as Al and Fe. These findings are in agreement with results from the 1998 snow survey (Telmer et al., 2004) and indicate that most metal-bearing particulates emitted from the smelter are probably deposited by gravitational settling within a relatively small radius of the stack(s). Figure 4b also shows that some elements, such as Cr, Fe, and V, are deposited mostly (>60%) in particulate form whereas others, such as Ca, Cd, and S, are deposited mostly as water-soluble phases or in very fine (<1 μm) particulate form. The proportion of metal-bearing particles containing Pb and Zn (and to a lesser extent Cu and Ni) decreases with increasing distance from the smelter. On the other hand, the proportion of arsenic-bearing particles apparently increases with distance from the smelter. A possible explanation would be that arsenic is initially emitted from the smelter as vapour or very fine aerosol and gradually condenses (in the case of vapour) or coagulates (in the case of aerosols) as it moves away from the stack. However, if this were the case, one should see particulate arsenic loading in snow increase with increasing distance from the smelter. In fact, both particulate and dissolved arsenic loadings decrease rapidly with increasing distance from the smelter (Fig. 4). The high loading of dissolved arsenic in snow near the smelter supports the idea that particulate arsenic compounds emitted by the smelter are readily water-soluble, as suggested by the work of J. Skeaff, A.D. Paktunc, and J. McGeer (unpub. rept., 2001). However, the rapidly decreasing concentration of particulate arsenic away from the smelter is at odds with the observed pattern of frequency for arsenic-bearing particles (Fig. 4b). Thus, the observed pattern could be due to uneven sampling density.

The sampling strategy of the 2001 snow survey was designed to quantify the atmospheric deposition of metals in snow around the Horne smelter. Unfortunately, this strategy made it difficult to evaluate spatial distribution patterns for total metal-bearing particles or individual particle types, because the sampling density was considerably higher close to the smelter (where most of the metal fallout occurs) than farther away. Although the majority of snow samples were collected west (downwind) of the smelter, a few were also taken to the east, north, and south. However, no clear relationship was observed between the frequency of metal-bearing particles in samples taken at comparable distances but in different directions relative to the smelter. Of all the particles identified by VP-SEM, only iron- and lead-bearing particles appear to show a clear pattern of decreasing frequency with increasing distance from the smelter (Fig. 4c). The roadside sampling sites (circled) show fairly high concentrations of such metals as Cu, Fe, Pb, V, and Zn in the bulk filtered particulate material (Fig. 4b). However, the individual particle counts obtained by VP-SEM do not reveal particularly high abundances of metal-bearing particles in these snow samples. Thus, the metal-bearing particle counts obtained by VP-SEM may not be quantitatively representative of the true abundance of metal-bearing particles in the snowpack, in part because many of the particles classified as 'metal-bearing' may only contain low concentrations of the elements As, Cd, Cr, Cu, Fe, Ni, Pb, V, and/or Zn. The VP-SEM particle classification used here is qualitative, not quantitative. In addition, some particles may contain more than one metal, i.e. a lead-bearing particle may also contain copper, and were therefore counted at least twice, in more than one category. Finally, although the snow samples used for VP-SEM analyses were composites of the total snowpack thickness, the distribution of particles in snow may be highly heterogeneous. Resources did not allow for a proper evaluation of the variability of particle distribution in snow. Consequently, we do not know whether the particle types and frequencies measured on any snow filter are representative of the particle population in the snowpack at this location. This sampling problem of spatial variability is central in studies of snowpack chemistry (e.g. Metcalf and Peck, 1990) and should be addressed in future surveys of this type.

Size distribution of individual particles

The sizes of individual particles are determined on the basis of the projected area (number of pixels) of the particles as obtained by image analysis and scaled to micrometres squared (μm²). The area measurements are converted to describe the

Figure 4. *Spatial distribution of selected chemical elements in snowpack samples* (N = 26). *a) Total particulate loading of elements in snow (ng/cm²). **b)** Ratio of elements in bulk particulate fraction (>1 μm) to total concentration in snow (dissolved + particulate). **c)** Relative frequency (%) of individual particles containing the elements of interest. Data points that are circled correspond to sampling sites that may have been affected by road dusts.*
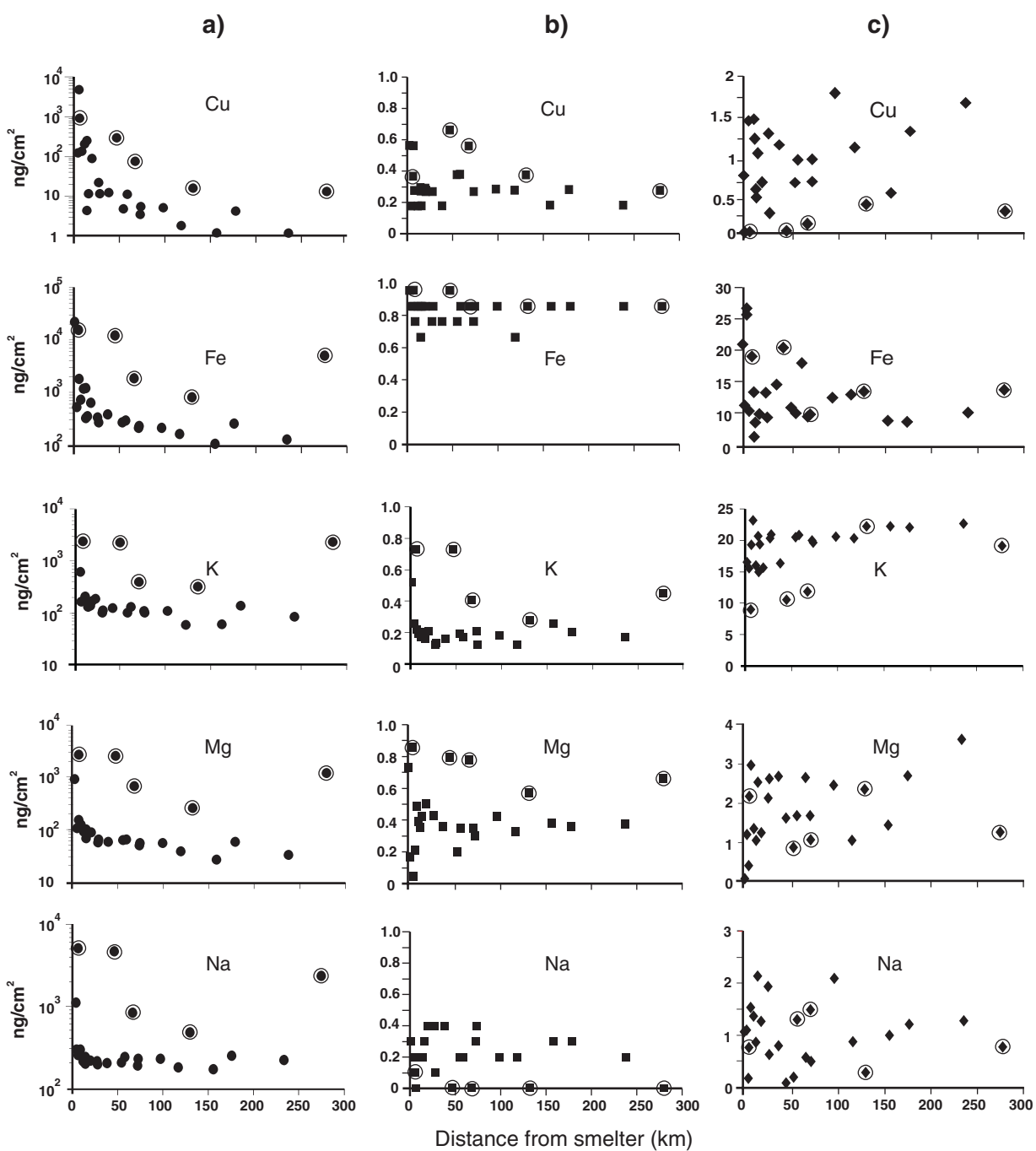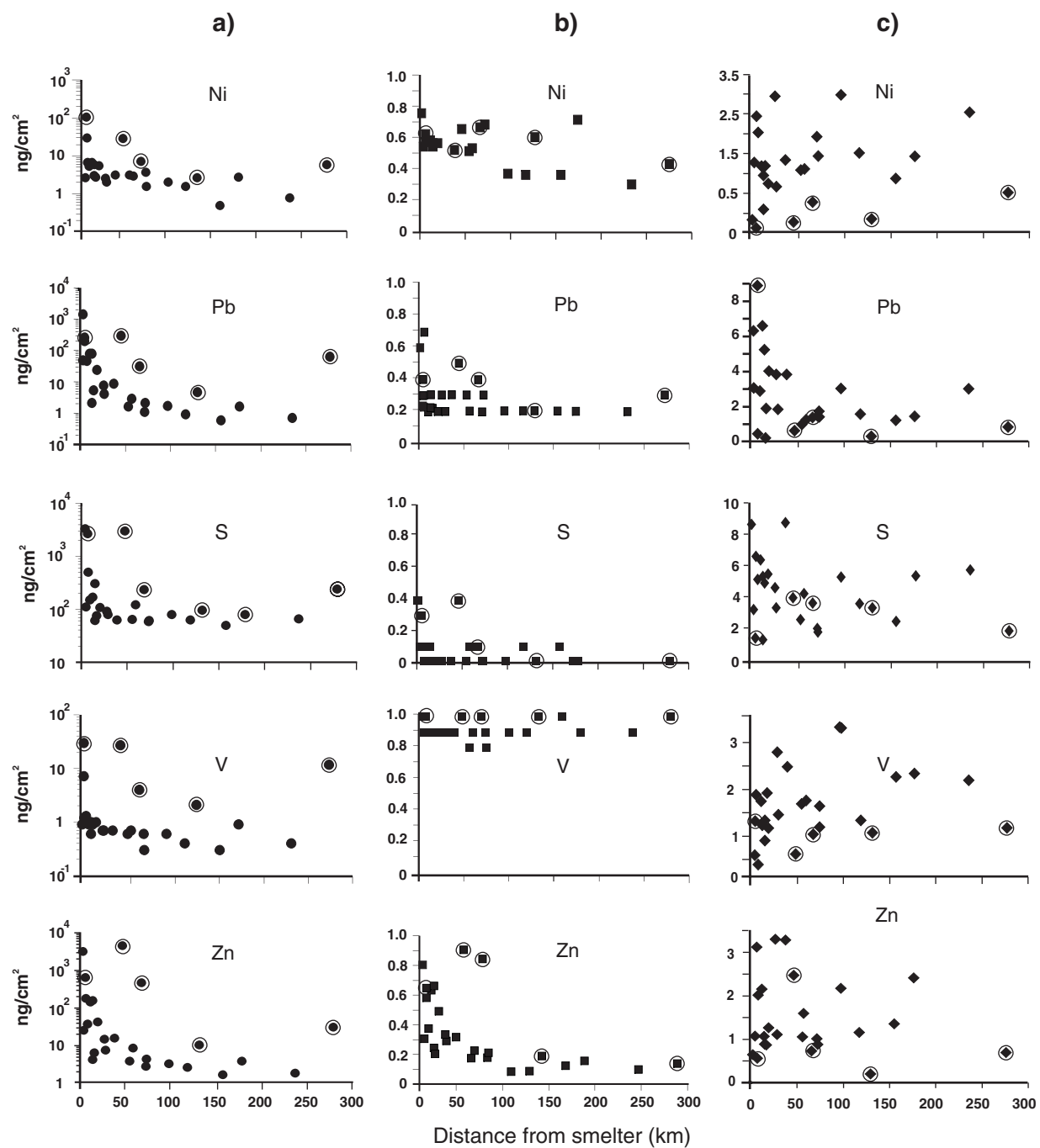
a)　　　　　　**b)**　　　　　　**c)**

Distance from smelter (km)

Figure 4. *(Cont.)*

***Figure 4.** (Cont.)*

particle populations in terms of the distribution of volume (V, in μm^3) as a function of the particle's equivalent spherical diameter (D, in μm). The parameter D is commonly used to characterize airborne particles in terms of their aerodynamic properties (Jaenicke, 1998). The parametrization necessarily assumes that particles are spherical, thereby introducing an unquantifiable error in the particle-size estimate. The minimum detectable particle size was approximately 0.1 μm^2, which corresponds to D ≈ 0.4 μm, slightly smaller than the pore diameter (0.45 μm) of the filter substrate. The measured size range for the entire particle population (N = 27 000) was 0.4 μm < D < 42.4 μm.

Figure 5 shows the (equivalent spherical) volume size distribution dV/dD of metal-bearing particles found in the snow-pack samples, plotted as a function of distance from the smelter. Data from multiple sampling sites were grouped to increase the robustness of the distribution curves. The histograms bins are arranged logarithmically following a progression on 2^a, with a ranging from -1 (D = 0.5 μm) to 5 (D = 32 μm) at increments of 0.25. The first and last bins also include outliers (D < 0.5 μm or D > 32 μm). The particle-size distributions can be approximated by a unimodal log-normal curve, as seen in Figure 5. The fit is generally good, as indicated by values of the chi-square test of $\chi^2/df \leq 0.1$ (where df = degrees of freedom). There is no indication that the modal diameter D_v of the volume size distribution varies systematically with increasing distance from the smelter. Altogether, D_v varies only over a narrow range of 1.8 to 2.8 μm (mean = 2.3 μm), with a standard deviation $\sigma_v \approx 2$ μm. These numbers are fairly typical for aged mineral aerosols (Schuetz, 1989).

Figure 6 presents the frequency distribution dN/dD (where N is the number of particles) of specific metal-bearing particle types as a function of distance from the smelter. Because there are fewer particles per category than in Figure 5, the number of size bins has been reduced by one half, with a log-step $a = 0.5$. Again, there is no clear indication of a systematic size variation with distance from the smelter for any of the particle types considered. All particle types fall in a very narrow range of approximately 1.3 to 2.3 μm. Nor is there any indication that the modal sizes D_N of different particle types (e.g. arsenic-bearing vs. lead-bearing) are significantly different. This is unexpected, given that such differences are known to exist in both urban and rural aerosols. Thus, Milford and Davidson (1985) report an average mass median diameter of 0.5 μm for airborne particulate Pb in non-urban continental regions, compared to 1.1 μm, 1.1 μm, and 1.3 μm for As, Cu, and Zn, respectively. However, one must remember that metal-bearing particles analyzed in this study have a widely varied elemental composition (*see* 'Particle types'), which may lead to double-counting in the classification scheme, thereby obscuring the characteristic size distribution of any single metal-bearing particle type.

The lack of any significant changes in D_v or D_N with respect to distance from the smelter suggests that no significant size segregation of particles by gravitational settling (or other removal processes) occurs over the range of distance considered (≤300 km). However, this is at odds with findings
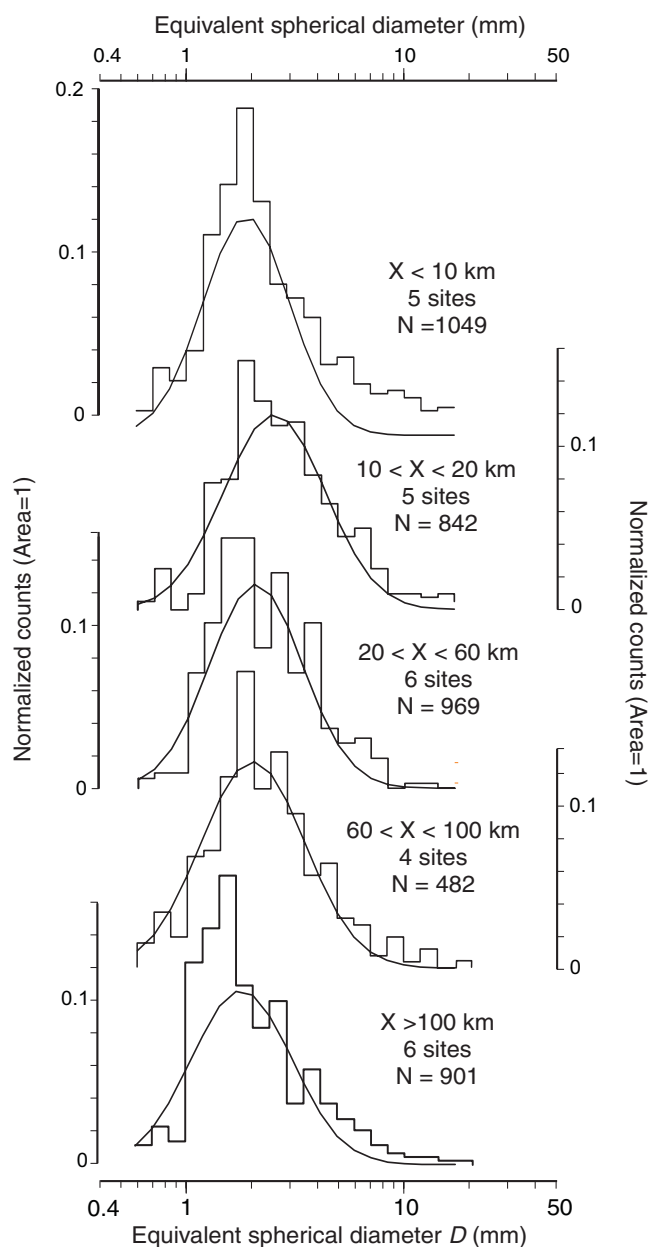

Figure 5. *Volume distribution (dV/dD) of metal-bearing particles in snow as a function of distance X from the Horne smelter. The histograms were fitted with a log-normal approximation. The area under each histogram (and curve) was normalized to facilitate comparisons. The number of sampling sites and the total number (N) of particles represented by each distribution is indicated.*

from studies of smelter dust fallout in humus around Rouyn-Noranda (Henderson et al., 1998; Knight and Henderson, 2005). Smelter dust particles observed in the mineral fraction of humus samples were examined individually by VP-SEM and their size (diameter), morphology, and textural characteristics were recorded. Figure 7 shows the size distribution of these particles (dN/dD), plotted as a function of distance between the smelter and the sampling sites (*see* Fig. 1 for sampling site locations). There is a clear indication that the modal particle size decreases with increasing distance from
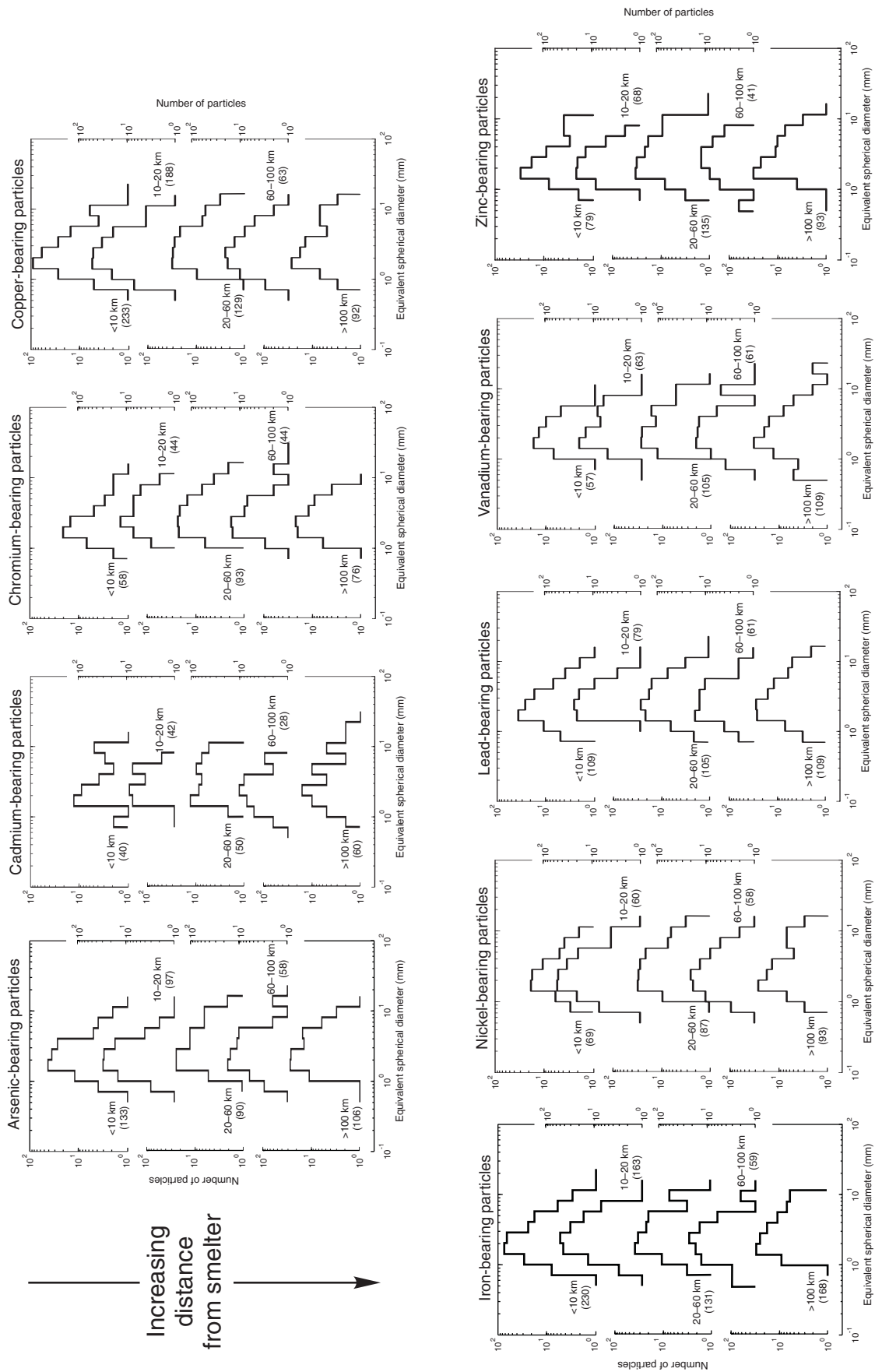
Figure 6. *Changes in the frequency distribution (dN/dD) of some specific metal-bearing particles types in the snowpack as a function of distance from the Horne smelter. Numbers in parentheses indicate the number of particles represented in each distribution.*

15
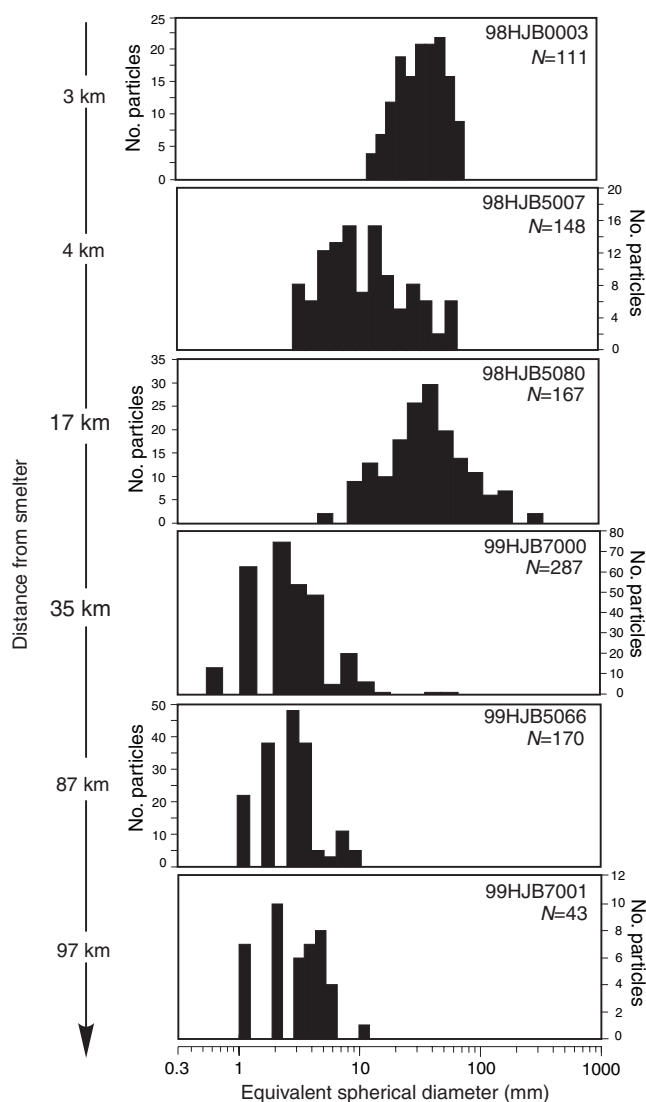
Figure 7. *Size distribution (frequency histograms) of smelter-derived dust particles observed in the mineral fraction from humus in the vicinity of Rouyn-Noranda. Data are from Knight and Henderson (2004). See Figure 1 for sampling site locations.*

the smelter, at least within a radius of 100 km. The first fundamental difference between the snow data and the results of Knight and Henderson (2005) is that our data were obtained by automatic (unsupervised) scanning and image analysis, whereas the smelter dust particles from the humus samples were identified and measured individually. Therefore, our data may actually encompass a large number of particles (or particle aggregates) that did not originate from smelter emissions. Secondly, the particles contained in humus accumulated from smelter fallout over a period of many years to decades, whereas the snow particles represent fallout from only one winter. Smelting processes and emission control technology at the Horne smelter have evolved considerably since 1927. Hence, the average composition of smelter-emitted particles that have accumulated in humus near Rouyn-Noranda is unlikely to be representative of present-day emissions. Furthermore, humus-bound metal-bearing particles have probably undergone considerable weathering and postdepositional alteration compared to particles recently deposited in snow. These considerations are examined in greater detail in Knight and Henderson (2005).

SUMMARY AND CONCLUSIONS

We used automated microbeam analyses to characterize 27 000 individual airborne particles deposited in snow at distances up to 300 km from the Horne copper smelter in the town of Rouyn-Noranda, Quebec. Over 85% of all particles are composed chiefly of common rock-forming elements such as Ca, Si, and Mg. The approximately 15% remaining contain As, Cd, Cr, Cu, Fe, Ni, Pb, V, and/or Zn. A total of 610 distinct compositional types of such metal-bearing particles were identified, but only 20 account for more than 1% of all metal-bearing particles. The most common compositional type is Fe-S-Cu, although other metal–sulphur associations (Zn-S, Fe-S, Cu-S) are also common. These metal- and sulphur-bearing particles probably represent residues of ore drying, roasting, or smelting from the Horne smelter, although some may also originate from secondary sources (e.g. mine tailings, road dust, etc.). Silica, a major constituent of the flux and slag, occurs commonly with Fe, Cu, Zn, etc. in the particles. Vanadium is also common, suggesting that some particles may be emitted from the smelter's acid plant, where V_2O_5 is used as an oxidation catalyst. The relative abundance of many elements (e.g. As and Fe) in reported bulk stack dust composition (J. Skeaff, A.D. Paktunc, and J. McGeer, unpub. rept., 2001) and in snow particles differs considerably, indicating that some unspecified mechanisms contribute to modify the average composition of particulate metals between the time they are emitted from the stack plume and deposited in snow.

There is no indication that the concentration of particulate matter in snow varies systematically with distance from the smelter. Nor is there a discernible spatial trend in the relative abundance of metal-bearing particles in snow. Particulate loadings of the elements (mass deposited per unit area) are highest within 50 km of the smelter and decrease rapidly with distance. This is most evident for smelter-related elements (As, Cd, Cu, Ni, Pb, S, V, Zn) but is also apparent for common rock-forming elements (Al, Fe). These findings are in agreement with results from the 1998 snow survey and indicate that most metal-bearing particles emitted from the smelter are probably deposited by gravitational settling within a relatively small radius of the stack(s). Some elements such as Cr, Fe, and V are deposited predominantly in particulate form whereas others, such as Ca, Cd, and S, are deposited mostly as water-soluble phases or in very fine particulate form. Also, the particulate proportion of some smelter-related elements such as Pb and Zn decreases with increasing distance from the smelter. Of all the metal-bearing particles identified by VP-SEM, only those containing Fe and/or Pb show a clear pattern of decreasing frequency with increasing distance from the smelter. In general, it is difficult to evaluate spatial distribution patterns for individual particle types because the

sampling density for the 2001 survey was considerably higher close to the smelter (where most of the metal fallout occurs) than farther away. Furthermore, the heterogeneity of particle distribution in snow was not properly evaluated, thus making it difficult to determine to what extent the composition of particles from a single snowpack sampling site are representative of deposition over a larger area. These shortcomings should be addressed in designing future snow surveys of this type.

The volume size distribution dV/dD of individual metal-bearing particles obeys a unimodal log-normal pattern with a modal diameter D_v that varies over a narrow range of 1.8 to 2.8 μm, which is fairly typical for aged mineral aerosols. There is no indication that D_v varies systematically with increasing distance from the smelter. However, a study of smelter dust in the mineral fraction of humus in the vicinity of Rouyn-Noranda shows a trend toward decreasing particle size away from the smelter, at least within a radius of 100 km. The snowpack and humus particle data may not be directly comparable, as the metal-bearing particles in the snowpack represent recent (winter) fallout only, whereas the smelter dusts in humus may have accumulated over a period of many years and undergone postdepositional weathering.

ACKNOWLEDGMENTS

REFERENCES

Äyräs, M., de Caritat, P., Chekushin, V.A., Niskavaara, H., and Reimann, C.
1995: Eco-geochemical investigation, Kola Peninsula: sulphur and trace element content in snow; Water, Air, & Soil Pollution, v. 85, p. 749–754.

Banic, C.M., Leaitch, W.R., Strawbridge, K., Daggupaty, S., Shantz, N., Lu, J.Y., Bhyat, N., Tanabe, R., MacPherson, J.I., Wong, H.K.T., Nejedly, R., Campbell, J.L., Gariepy, C., Simonetti, A., Skeaff, J., Chatt, A., and Lamoureux, M.
2000: Aircraft study of the physical and chemical evolution of aerosols in smelter and power plant plumes; in Proceedings, 25th International Conference on Heavy Metals in the Environment, Ann Arbor, Michigan, August 6–10, 2000.

Barrie, L.A. and Vet, R.J.
1984: The concentration and deposition of acidity, major ions and trace metals in the snowpack of the eastern Canadian Shield during the winter of 1980–1981; Atmospheric Environment, v. 18, p. 1459–1469.

Bédard, M., Chapados, M., and Kachaniwsky, G.
1990: Advances in technology for complex custom feed material treatment at Noranda; in Materials Handling in Pyrometallurgy, (ed.) C. Twigge-Molecey and T. Price; Pergamon Press, New York, New York, p. 84–99.

Bérubé, M.A., Choquette, M., and Godbehere, P.W.
1987: Minéralogie des scories cuprifères produites par le réacteur Noranda; CIM Bulletin, February 1987, p. 83–90.

El-Barnachawy, S., Kachaniwsky, G., Persson, H., and Poggi, D.
1987: Oxygen use at Noranda's Horne smelter; in The Impact of Oxygen on the Productivity of Non-Ferrous Metallurgical Processes, (ed.) G. Kachaniwsky and C. Newman; Pergamon Press, New York, New York, p. 185–198.

Gorzelska, K.
1989: Locally generated atmospheric trace metal pollution in the Canadian Arctic as reflected by chemistry of snowpack samples from the Mackenzie Delta region; Atmospheric Environment, v. 23, p. 272–2737.

Hall, G.E.M., Vaive, J.E., and Pelchat, J.C.
1996: Performance of inductively coupled plasma mass spectrometric methods used in the determination of trace elements in surface waters in hydrogeochemical surveys; Journal of Analytical Atomic Spectrometry, v. 11, p. 779–786.

Henderson, P.J., McMartin, I., Hall, G.E., Percival, J.B., and Walker, D.A.
1998: The chemical and physical characteristics of heavy metals in humus and till in the vicinity of the base metal smelter at Flin Flon, Manitoba; Environmental Geology, v. 34, p. 39–58.

Jaenicke, R.
1998: Atmospheric aerosol size distribution; in Atmospheric Particles, (ed.) R.M. Harrison and R. Van Griecken; John Wiley & Sons, New York, New York, p. 2–28.

Kliza, D.A., Bonham-Carter, G.F., and Zdanowicz, C..
2005: Geochemistry of snow around the copper smelter at RouynNoranda, Quebec: comparison of 1998 and 2001 surveys; in Metals in the Environment Around Smelters at Rouyn-Noranda, Quebec, and Belledune, New Brunswick: Results and Conclusions of the GSC MITE Point Sources Project, (ed.) G.F. Bonham-Carter; Geological Survey of Canada, Bulletin 584.

Kliza, D.A., Telmer, K., Bonham-Carter, G.F., and Hall, G.E.M.
2000: Geochemistry of snow from the Rouyn-Noranda region of Western Quebec: an environmental database; Geological Survey of Canada, Open File 3869, 169 p.

Kliza, D.A., Zdanowicz, C.M., and Bonham-Carter, G.F.
2002: Geochemistry of snow from the Rouyn-Noranda region of Western Quebec: an environmental database, Part 2; Geological Survey of Canada, Open File 4205 (CD-ROM).

Knight, R.D. and Henderson, P.J.
2005: Characterization of smelter dust from the mineral fraction of humus collected around Rouyn-Noranda, Quebec; in Metals in the Environment Around Smelters at Rouyn-Noranda, Quebec, and Belledune, New Brunswick: Results and Conclusions of the GSC MITE Point Sources Project, (ed.) G.F. Bonham-Carter; Geological Survey of Canada, Bulletin 584.

Legget, D.C. and Hogan, A.W.
1995: A preliminary experiment to examine chemical exchange at the soil-snow interface; The Science of the Total Environment, v. 160/161, p. 403–408.

Metcalf, R.C. and Peck, D.V.
1990: Difficulties in deducing temporal changes in precipitation chemistry from snow cores and ice cores: the spatial variability problem; Nordic Hydrology, v. 21, p. 299–316.

Milford, J.B. and Davidson, C.I.
1985: The sizes of particulate trace elements in the atmosphere: a review; Journal of Air Pollution Control Association, v. 35, p. 1249–1260.

Newbury, D.E., Swyt, C.R., and Myklebust, R.L.
1995: "Standardless" quantitative electron probe microanalysis with energy-dispersive X-ray spectrometry: is it worth the risk?; Analytical Chemistry, v. 67, p. 1866–1871.

Paktunc, A.D., Kingston, D., and Skeaff, J.
2001: Characterization of individual particles emitted from a copper smelter and a coal-fired power plant — winter sampling; Proceedings, Sixth International Conference on the Biogeochemistry of Trace Elements, Guelph, Ontario, 29 July–2 August 2001, SP303, p. 532.
2002a: Composition of individual particles in aerosols emitted from a copper smelter; Geological Association of Canada–Mineralogical Association of Canada Annual Meeting, Saskatoon, May 27–29, 2002, Abstracts Volume, v. 27, p. 87.

Paktunc, A.D., Kingston, D., and Smith D.
2002b: Automated detection, microanalysis and characterization of particles by variable-pressure scanning electron microscope; Geological Association of Canada–Mineralogical Association of Canada Annual Meeting, Saskatoon, May 27–29, 2002, Abstracts Volume, v. 27, p. 87.

Perry, R.H. and Green, D.W. (ed.)
1984: Perry's Chemical Engineers' Handbook (6th edition); McGraw-Hill, New York, New York, 2137 p.

Persson, H., Iwanic, M., El-Barnachawy, S., and Mackey, P.J.
1986: The Noranda process and different matte grades; Journal of Metals, v. 38, no. 9, p. 34–37.

Pomeroy, J.W., Davies, T.D., Jones, H.G., Marsh, P., Peters, N.E., and Tranter, M.
1999: Transformations of snow chemistry in the boreal forest: accumulation and volatilization; Hydrological Processes, v. 13, p. 2257–2273.

Samuel, V., St-Armant, M., and Arcouette, J.
1989: Design of the gas cooling and cleaning section of the Horne acid plant; *in* Process Gas Handling and Cleaning, (ed.) C. Twigge-Molecey; Pergamon Press, New York, New York, p. 65–77.

Schuetz, L.
1989: Atmospheric mineral dust: properties and source markers; *in* Paleoclimatology and Paleometeorology: Modern and Past Patterns of Global Atmospheric Transport, (ed.) M. Leinen and M. Sarnthein; Kluwer, Dordrecht, The Netherlands, p. 359–383.

Telmer, K., Bonham-Carter, G.F., Kliza, D.A., and Hall, G.E.M.
2004: The atmospheric transport and deposition of smelter emissions: evidence from the multi-element geochemistry of snow, Quebec, Canada; Geochimica et Cosmochimica Acta, v. 68. no. 14, p. 2961–2980.

Themelis, N.J.
1994: Industrial insight: pyrometallurgy near the end of the 20th century; Journal of Metals, v. 46, no. 8, p. 51–57.

Themelis, N.J., McKerrow, G.C., Tarasoff, P., and Hallett, G.D.
1972: The Noranda process for the continuous smelting and converting of copper concentrates; Journal of Metals, v. 24, no. 4, p. 25–32.

Van Borm, W., Van Espen, P., Adams, F., and Demuynck, M.
1987: Source apportionment for the zinc-containing component of air particulate matter using automated electron probe micro-analysis of individual particles; International Journal of Analytical Chemistry, v. 31, p. 165–182.

Veillette, J.J., Paradis, S.A., and Buckle, J.L.
2005: Bedrock and surficial geology of the general area around Rouyn-Noranda, Quebec and Ontario; *in* Metals in the Environment Around Smelters at Rouyn-Noranda, Quebec, and Belledune, New Brunswick: Results and Conclusions of the GSC MITE Point Sources Project, (ed.) G.F. Bonham-Carter; Geological Survey of Canada, Bulletin 584.