Silica- and sulfate-bearing rock coatings in smelter areas: Part II. Forensic tools for atmospheric metal(loid)- and sulfur-isotope compositions

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Abstract

Black silica- and sulfate-bearing rock coatings in the Greater Sudbury area, Canada provide a record of atmospheric processes and emitted particulate matter associated with historical smelting operations in this area. Coating samples collected over the Greater Sudbury region are characterized with scanning electron microscopy, electron microprobe analysis, laser ablation inductively coupled mass-spectrometry, S-stable isotope measurements and micro X-ray fluorescence. On the micrometer scale, Cu, Pb, As, Se and S occur in close association within metal–sulfate rich layers composed of Fe- and Cu-sulfates. The concentrations of these and other elements do not represent their chemical proportions in the smelter plumes due to dissolution–precipitation processes, element substitutions and the stability of various phases involved in the coating formation. On the regional scale, the atomic ratios of Pb:Ni, As:Ni and Se:Ni decrease in the coatings with increasing distance from the smelting centers. This observation is consistent with higher wet deposition rates of small diameter Pb, As and Se-bearing primary sulfate aerosols (<2.5 \( \mu \)m), compared to larger diameter (>2.5 \( \mu \)m) Ni-bearing particulate matter. The mixing of primary (higher \( \delta ^{34}S \) values) and secondary (lower \( \delta ^{34}S \) values) sulfates explains the \( \delta ^{34}S \) values of sulfates within the coatings close to smelting centers and the decrease in these values is attributed to the decrease in the ratio of primary to secondary sulfates with distance from the smelting centers. The information preserved in mineral surface-coatings together with an understanding of stoichiometry, geochemical processes and former environmental conditions provide a valuable record of atmospheric compositions, mixing, scavenging, deposition rates and oxidation processes, and the nature and source of anthropogenic releases to the atmosphere.

1. INTRODUCTION

Surface coatings on rocks and building stones are useful forensic tools for monitoring recent and past air pollutants and tracing their sources. Coatings formed in deserts, in proximity to smelters and in highly polluted urban environments may capture common pollutants such as metal-bearing particulate matter, sulfate aerosols and radionuclides during their formation (Nord et al., 1994; Hodge et al., 2005; Wayne et al., 2006; Smith and Prikryl, 2007; Hoar et al., 2010; Mantha et al., 2012). The forensic examination of rock coatings is also valuable in providing an understanding of past terrestrial or planetary environments (i.e. on Mars, McLenman, 2003; Milliken et al., 2008; Squyres et al., 2008), in which coatings may have preserved particles and mineral phases containing information about past climatic conditions, volcanic events and features related to biological activity.

An important fingerprinting tool for identifying sources of pollutants once present in the atmosphere is the identification of isotopic compositions of anthropogenic \( \text{SO}_x \). Studies have been undertaken to examine preserved traces

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of atmospheric pollutants in urban areas (e.g. Norman et al., 2006; Sinha et al., 2008), around coal-fired power plants (e.g. Forrest and Newman, 1977a) and smelters (Nriagu and Coker, 1978) as well as to interpret the related formation of weathering crusts on building stones (Buzek and Srámk, 1985). Complications may arise from applying this tool in environmental studies including the fractionation or absence of fractionation of S-bearing atmospheric species during different oxidation processes, the input from different S-sources, seasonal changes in oxidant concentrations as well as differences in deposition mechanisms.

The use of the chemical and sulfur-isotopic signatures of coatings as forensic tools for identifying environmental conditions can be tested quite effectively using silica coatings formed in the vicinity of smelters, such as those formed in Greater Sudbury, Canada (Fig. 1a). These coatings were formed in close proximity to a major point source of SO$_2$ and metals, active for over 70 years and for which historical records of local emissions and their chemical and isotopic composition are available. In this case, we can assume that the coating components originate predominantly from the local point source or sources whereas rock coatings formed in proximity to volcanoes (e.g. Schiffman et al., 2006), in deserts (e.g. Dorn, 1998; Perry et al., 2006; Schindler et al., 2010) and on Antarctica (Giorgetti and Baroni, 2007) have been affected by unknown inputs and processes that may range from local to global scales. Furthermore, an advantage with respect to coatings formed of encrusting sulfates such as gypsum-bearing coatings formed in urban areas (Nord et al., 1994; Smith and Prikryl, 2007), is their higher resistance to weathering and thus their ability to more effectively preserve isotopic and chemical signatures of embedded materials.

In this paper, we will compare the chemical, mineralogical and isotopic composition of silica coatings formed in the vicinity of base-metal smelters with historical data on metal emissions, metal speciation in smelter plumes and the isotopic composition of the smelted ore, sulfate aerosols and smelter-derived SO$_2$ gases. We will show that the chemical and isotopic signatures of the coatings provide records of the speciation of trace metals from the smelter plume as well as changes in the proportion of secondary and primary aerosols, and their sulfur isotope signature with distance from the smelters.

1.1. Environmental impact of smelters

Former and current smelting activities contribute to local and regional anomalies of atmospheric pollution in the form of metals, metalloids and sulfur dioxide. Metal (loid)-bearing particles emitted by smelter stacks influence the quality of soil and water systems and have an impact on human health through the inhalation of nanometer-size airborne particulate matter (Kalkstein and Greene, 1997). Sulfur dioxide emissions from smelters add to global sulfur concentrations in the atmosphere and contribute to acidic precipitation, climate forcing and global pollution (Brock et al., 1995; Hamill et al., 1997; Bao and Reheis, 2003).

Smelters are considered point sources of metal(loid) pollution where the concentration of emitted elements commonly decreases in surficial environments with distance from the source (Davies, 1983). The distribution pattern of elements emitted from point sources has been mapped in soils (e.g. Freedman and Hutchinson, 1980; Hogan and Wotton, 1984; Wren, 2012), peat (e.g. Zoltai, 1988), lake

![Fig. 1](https://example.com/fig1.png)

**Fig. 1.** (a) The black rock-coating of the Sudbury area, Ontario, Canada; (b) model for the formation of metal–sulfate-rich layers on the atmosphere-coating interface (ACI) and rock-coating-interface (RCI): (I) precipitations and fumigations of sulfuric acid and sulfur dioxide weathered exposed rock surfaces and formed a silica-gel type alteration layer, which promoted the incorporation of atmospheric metal(loid)-bearing particulates and aerosols; (II) dissolution of the latter components and the leaching of elements from the underlying rock resulted in the formation of a metal–sulfate-rich layer on the ACI; (III) corrosion of the underlying rock by metal–sulfate-rich solutions produces a metal–sulfate-rich layer on the RCI; (c) occurrence of metal–sulfate-rich layers on the ACI and RCI in a coating sampled around the Coniston smelter (Mantha et al., 2012).
1.2. Silica and metal–sulfate-rich coatings of the Sudbury area

The release of 11.2 million tons of SO$_2$ from 1890 to 1930 by roast yards (Laroche et al., 1979) and ca. 60 million tons of SO$_2$ between 1935 and 1975 by smelters (estimated on the basis of ca. 1.5 million tons per year; Wren, 2012) resulted in acidic fumigations and rain, which enhanced the chemical weathering rate of exposed rocks in the Sudbury area (Mantha et al., 2012, Fig. 1b). Non-stoichiometric dissolution of silicate minerals under these acidic conditions resulted in the formation of a silica-gel type coating (Schindler et al., 2009; Durocher and Schindler, 2011), which promoted the uptake and preservation of detrital grains from adjacent rocks and soils (feldspar, quartz, hematite, chlorite, montmorillonite) and smelter-derived nano- to micro-size particulate matter (metal–silicates, metal–oxides, C-spheres, Mantha et al., 2012). Dissolution of the underlying rock and metal-bearing particles by sulfuric acid resulted in the in situ formation of metal–sulfate-rich layers on the atmosphere-coating (ACI) and rock-coating interface (RCI) (Fig. 1b and c). These metal–sulfate-rich layers are composed of nanometer aggregates of Fe-sulfate-hydroxide and Fe–Cu–sulfate minerals (Mantha et al., 2012). Scanning electron microscopy (SEM) studies on selected samples showed that metal–sulfate-rich layers on the ACI are common, whereas layers on the RCI only occur on mafic rocks and coatings from roast yards.

TEM, SEM and XRD studies showed that the metal–sulfate-rich layers contain Fe-sulfate-hydroxide, Fe$^{3+}$SO$_4$ (OH)$_{10}$, meriterite, K$_3$Fe$^{2+}$/(SO$_4$)$_2$(H$_2$O)$_4$, goldichite, KFe$^{3+}$/SO$_4$ (OH)$_2$, butlerite, Fe$^{3+}$(SO$_4$)(OH)(H$_2$O)$_2$, guilde, CuFe$^{3+}$(SO$_4$)$_2$(OH)(H$_2$O)$_4$ and antlerite Cu$_3$(SO$_4$) (OH)$_{16}$, whereas smelter-derived particles are mainly composed of magnetite, Fe$_3$O$_4$, fayalite, Fe$_3$SiO$_4$ and unidentified Cu-oxides (Mantha et al., 2012).

Although the release of SO$_2$ and metal-bearing particles has been drastically reduced in the last 40 years, black micrometer-thick metal–sulfate-rich coatings still occur on exposed rocks in the Greater Sudbury area (Fig. 1a). X-ray photoelectron spectroscopy (XPS) indicated the occurrence of a metal-depleted silica-rich layer on the surface of the coatings and suggested the current leaching of metal(loid)s by meteoric water on a nanometer scale (Mantha et al., 2012).

1.3. Coatings on building stones formed through atmospheric pollution

Black coatings are also common features on building-stone surfaces in polluted, usually urban, environments (Nord et al., 1994; Smith and Prikryl, 2007). Similar to the black coatings found in the Sudbury area, the coatings form through interaction between minerals of the underlying building stone with S-bearing atmospheric components (SO$_2$, H$_2$SO$_4$, HSO$_4^-$). Here, dissolution of Ca-bearing minerals (mainly calcite and Ca-silicates) by sulfuric acid results in the formation of Ca–H$_2$SO$_4$-rich water films, which upon evaporation form gypsum-rich precipitates. Incorporated particulate matter commonly originates from anthropogenic sources and contains metal salts, nitrogen and sulfur-oxide compounds, radionuclides and carbon-bearing particles. Distribution and thickness of the gypsum coatings depends on the geographic location, air pollution level, rainfall infiltration and evaporation and the Ca-content of the underlying rock (e.g. Buzek and Sránek, 1985; Pye and Schiavon, 1989; Nord et al., 1994; Prikryl et al., 2004; McAlister et al., 2006; Smith and Prikryl, 2007 and references therein).

1.4. Environmental relevance of coatings in riverine, soils and tailings settings

The surface properties of minerals and amorphous phases change through their interaction with surface-, ground-, and pore waters. The properties and processes that occur at the mineral–water interface are critical for understanding the uptake and release of toxic elements in contaminated sediments, soils, rocks, aquifers and acid-mine drainage (AMD) systems. Abiotic and biotic leaching or dissolution–precipitation processes drive non-stoichiometric weathering of primary minerals forming secondary minerals (e.g. Fein et al., 1999). These processes promote the formation of clay-sized layers of silicate phases, as well as various Fe, Si, Al and Mn oxides and hydroxides, which form discontinuous thin layers that coat mineral surfaces (e.g. Chorover et al., 2007).

Hydrous oxides of Mn and Fe have long been recognized as important scavengers of metals in stream sediment, soil and in the ocean (e.g. Carpenter et al., 1975; Lion et al., 1982; Robinson, 1981, 1982; Deng et al., 2000). Studies have shown that films, cements and coatings of these oxides contain anomalously high concentrations of metals near oxidizing sulfide deposits (Filipek et al., 1981; Whitney, 1981). The “scavenging” of metals by Mn–Fe oxides has been widely investigated and is believed to include both co-precipitation and adsorption processes (Chao and Theobald, 1976). Robinson (1981) showed that adsorption may be more important than co-precipitation in producing anomalous levels of metals in these coatings. These coatings represent a complex multiphase system consisting of various Mn and Fe oxides and hydroxides (with different degrees of crystallinity) plus a mixture of organic components and silicates, such as clay minerals (Potter and Rossman, 1979; Filipek et al., 1981).

Iron-hydroxide and Fe-sulfate coatings are common in oxidized zones of sulfide mineral assemblages (e.g. McGregor et al., 1998; Durocher and Schindler, 2011) and may control the fate of metals and metalloids within many mine tailings facilities. The high specific surface area of the Fe-hydroxides allows them to act as powerful sorbents for dissolved species, particularly heavy metal contaminants, (PO$_4^{3-}$ and (AsO$_4^{3-}$ species (Cornell and Schwertmann, 1996). Iron-sulfate minerals of the jarosite group are able to accommodate significant proportions of cations of different valence and size within their structures (Dutrizac and Jambor, 2000).

Micrometer-thick hydrous silica-gel coatings have been found on exposed bedrock at tailings ponds located within sediments (e.g. Jackson, 1978), snow (Telmer et al., 2004) and in humus and till sediments (e.g. Henderson et al., 1998).
the Copper Cliff mine tailings disposal area in Sudbury, Ontario, Canada (Schindler et al., 2009; Durocher and Schindler, 2011). These silica-rich coatings were found to form a more or less continuous layer below Fe-hydroxide coatings with variable silica concentrations. Schindler et al. (2009) and Durocher and Schindler (2011) noted higher or similar trace-metal concentrations in the silica-rich to Fe-hydroxide coatings. Similar to the observations on the black rock-coatings of the Sudbury area (Mantha et al., 2012), metals in the silica-rich coatings occurred either finely distributed or were either found as discrete particles of oxy-hydroxide and K–Fe-sulfate particles (most likely jarosite).

1.5. Objectives

The black coatings of the Sudbury area formed during a period of high SO$_2$ emissions between 1888 and 1972, which correspond to the start of mining activities in the Sudbury area and the construction of a 381 m Super Stack respectively (a recent review on the mining history of Sudbury can be found in Mantha et al. (2012)). The latter stack is one of the tallest and largest point sources in North America, which initially emitted ca. 20% of all the SO$_2$ emitted annually in Canada (Nriagu and Coker, 1978). The corresponding smelter plume has been a desirable subject for chemical and isotopic studies by virtue of its high SO$_2$ concentration and its coherent form, at times extending to hundreds of kilometers (Lusis and Wiebe, 1976; Forrest and Newman, 1977b).

Chemical and isotopic studies were not carried out on smelter plumes emitted from the smaller stacks during the formation of the coatings. However ore smelted at the Copper Cliff centers did not change significantly over time (Wren, 2012) and therefore, emitted plumes may have had similar ratios between major-, minor and trace-elements as well as ratios between sulfur isotopes. In this way, chemical and isotopic composition of the black coatings are compared with those of the Copper Cliff Super Stack plume in order to derive a mixing model for the various S-bearing atmospheric species around the Copper Cliff smelter area. The objectives of this paper are in detail:

1. to describe the occurrence and speciation of metal(loid)s within the coating;
2. to illustrate their distribution and concentration in coatings over the Greater Sudbury area;
3. to depict the variation of the $\delta^{34}$S values in the coatings over the Greater Sudbury area;
4. to examine if these variations are related either to fractionation of sulfur isotopes during oxidation of SO$_2$ or to mixing of primary metal–sulfate aerosols with secondary sulfate species formed during oxidation of SO$_2$.

2. EXPERIMENTAL

2.1. Sampling and sample preparation

Coatings were sampled from 31 different locations within the Greater Sudbury area (Fig. 2). A sampling procedure was designed to procure samples in proximity to the three smelting centers (Copper Cliff, Falconbridge and Coniston) and the surrounding areas. Coatings are not prolific in the north-eastern area of Greater Sudbury because outcropping bedrock is rare due to dominant glacio-fluvial sediments. As a result, coated rock samples in the area of Falconbridge were collected mainly west of the Falconbridge smelter (Fig. 2). The collected samples were washed with distilled water and cross-sectioned samples with thick coatings (>10 $\mu$m) were polished in epoxy discs using silicon carbide.

2.2. Scanning electron microscopy (SEM)

Scanning electron microscopy (SEM) was conducted with a JEOL 6405 at 20 kV, equipped with both backscattered (BSE) and secondary (SE) electron detectors and an Energy Dispersive X-ray Spectrometer (EDS). The average composition of the coatings was determined via EDS analyses of selected areas in the distribution maps for Si and Fe.

2.3. Laser ablation inductively coupled mass-spectrometry (LA ICP-MS)

One coating sample from each location (except for the roast yards) was analyzed in situ with laser ablation inductively coupled mass-spectrometry (LA ICP-MS) using a Thermo-Fisher X II Series inductively coupled plasma quadrupole mass spectrometer with an ultra-violet laser beam (New Wave Nd:YAG 213 nm solid state laser). Ablation was carried out in a He atmosphere to which Ar was added for efficient transport of the ablated aerosol. The composition of the coating was probed via depth profiling, where material from each sample was ablated from the top of the coating down to the underlying rock. Five depth profiles were completed for each sample using beam diameters of 55, 40 and most commonly 30 $\mu$m. All analyses were carried out at a repetition rate of 5 Hz and the energy density maintained at 11 J cm$^{-2}$. Each spot was measured for 30–45 s following 30 s of background acquisition. The synthetic glass standard NIST612 which contains trace-element abundances of about 30–100 mg kg$^{-1}$ was used as the external standard. At the beginning of each analytical run and after each sample, the standard was ablated under the same conditions. All data were blank corrected and instrument drift was corrected using a linear interpolation between standard blocks (Ulrich et al., 2009).

2.3.1. Depth profiling versus line scans on coating surfaces and cross-sections

Depth profiling of all 30 samples was preferred to surface line-scans and surface rastering (e.g. Wayne et al., 2006), because the latter scans remove material from a certain depth (i.e. 30 $\mu$m) that can exceed the thickness of the coating (on average from <10 $\mu$m to >100 $\mu$m, Mantha et al., 2012). In such cases, material from the underlying rock would have ablated and their contributions would have resulted in erroneous count rates and thus in incorrect element concentrations for the coatings.

The depth profiling was also preferred to line scan analyses of cross-sectional samples because the former method
allows the use of larger laser spot-sizes without any loss in resolution (with respect to contributions of coating and rock). The use of large laser spot-sizes \(i.e.\) 50 \(\mu\)m has the advantage of ablating a larger volume of material, yielding better count statistics for elements of low concentration \(e.g.\) Cd, Se and Co).

2.3.2. Selection of integration areas in the LA-ICP-MS depth scans

Fig. 3a shows stacked depth-scan patterns for Fe and Si and selected elements through the black coating of sample LA-I (Fig. 2). These scan patterns depict a prominent peak for all elements once material is ablated from the coating’s surface. The peaks extend for ca. five seconds, which corresponds to a depth of ca. 25 \(\mu\)m. At greater depths, only the pattern for Si shows significant CPS, indicating the ablation of material from the underlying siliceous rock. Contrary to line scan traverses in cross sectional samples (Mantha et al., 2012), metal–sulfate- and silica-rich layers could not be resolved in the patterns of the depth profiles (Fig. 3a). Hence, the depth scan-pattern was quantified using two integration areas: one for the bulk coating and one for the underlying weathered rock. The integration area for the bulk coating was selected in the depth profile through inspection of the CPS of Pb, As, Cu and S (representing the metal–sulfate-rich part of the coating) as well as the CPS of Mg, Na, K, Ca, Al and Si (representing the underlying rock and most likely portions of the silica-rich layer of the coating). The integration area of the coatings was taken from the inflection point at the rising limb to the inflection point at the falling limb of the Pb, As, Cu and S-peaks (Fig. 3a). Hence, the selected integration boundary between a coating with a metal–sulfate-rich layer on the ACI and the underlying rock occurred within the silica-rich layer, whereas the integration boundary between a coating with a metal–sulfate-rich layer on the RCI and the underlying rock occurred most likely along the RCI. Consequently, the quantified LA-ICP-MS data of the coatings should represent the metal–sulfate-rich parts of the coatings rather than an average of the metal–sulfate and silica-rich layers. This can be verified when comparing concentrations obtained from LA-ICP-MS depth scans and electron microprobe (EMP). For example, EMP spot analyses on the ACI of sample \(F1\) (sampled around the Falconbridge smelter, Fig. 2) show that the average concentrations of Cu, As and Pb (major metal(loid)s) in the coatings are 0.5, 0.6 and 3.1 wt.% and that their concentrations in the metal–sulfate-rich layer vary in the range of 0.7–1.0, 0.8–1.4 and 3.9–8.2 wt.%, respectively (Mantha et al., 2012). The latter concentrations are more consistent with the corresponding LA-ICP-MS data of sample \(F1\) (Cu = 0.9–1.1, As = 1.3–2.0; Pb = 5.8–8.6 wt.%, Supplementary data A), in agreement with the argumentation above.

2.3.3. Quantification of the LA-ICP-MS data

An internal standard was required to quantify the LA-ICP-MS data because the ablation yield between the standard and the sample was not constant. SEM, EMP and
LA-ICP-MS indicated that Si is the most common element in the coating (Mantha et al., 2012) and therefore, the concentration of Si determined with an energy dispersive spectrometer (EDS) was used as an internal standard for the quantification of the LA-ICP-MS data. However, average concentrations of Si in the coatings could not be obtained for each sample because in most cases, coatings were too thin to be resolved adequately in the SEM images. Hence, a correlation between the concentrations of Si and the corresponding LA-ICP-MS data had to be identified.

Ratios between raw counts measured with LA ICP-MS can be used to identify associations between elements regardless of differences in ablation (Ulrich et al., 2009; Durocher and Schindler, 2011). Concentrations of Si were plotted versus the ratios of the Si:Fe raw counts from the corresponding LA ICP-MS data (Fig. 3b). A regression analysis \( R^2 = 0.94 \) showed a strong exponential relationship \( f(x) = 2.62\ln(x) + 27.8 \), which was used to calculate wt.% of Si for all other samples based on their respective Si:Fe raw counts. The resulting Si concentrations were then incorporated as an internal standard in addition to the external NIST 612 standard values in the Plasma Lab software to quantify the LA ICP-MS data of the coatings.

2.3.4. Error estimation and detection limits

The counts for S and K from the NIST standard were not above background and thus the measured concentrations of S and K were not considered in the data analysis. The ratios between the raw counts of Si and Fe for one sample (five depth profiles) varied on average in the range of \( \pm 0.05 \) (Fig. 3b) and resulted in an uncertainty of ca. \( \pm 1 \) wt.% for the corresponding Si-concentration. On the basis of this value, calculated concentrations for elements with \( >100 \) mg kg\(^{-1}\) varied in the range of \( \pm 10\% \) and concentrations of elements with \( <100 \) mg kg\(^{-1}\) in the range of \( \pm 7\% \).

Element-specific detection limits depend on the experimental setting of the laser scan (i.e. spot-size, repetition rate). Detection limits for elements measured in this study are provided in Supplementary data B.

2.4. Micro X-ray fluorescence using Synchrotron radiation

Polished samples embedded in epoxy were analyzed on the Very Sensitive Elemental and Structural Probe Employing Radiation (VESPER) Synchrotron beamline at the Canadian Light Source, Saskatchewan. Micro X-ray fluorescence (\( \mu \)-XRF) spectra were collected over raster areas to produce 2D element maps of two samples known to have multiple coating layers. Beam penetration is on the order of 100–250 \( \mu \)m, therefore only coating areas greater than 100 \( \mu \)m thick were selected to minimize the interference of fluorescence radiation emitted from mineral phases of the underlying rock. The samples were scanned using a beam size of 7 \( \mu \)m, a step size of 0.01 (dwell time 1.5 s) to 0.005 (dwell time 1 s) and analyzed for the elements Mn, Fe, Ni, Cu, Cr, Zn, As and Pb employing a Si solid state detector (Vortex-ME4).

2.5. Stable isotope measurements of sulfur

A total of 26 samples were prepared for sulfur isotope measurements by collecting scrapings of the coatings. The scrapings were dissolved in HNO\(_3\) and S was precipitated as BaSO\(_4\) under Ar atmosphere. The precipitates were
centrifuged, washed and subsequently treated with HNO₃ to remove any carbonates. Sulfur isotopes were analyzed using a MAT 252 Stable Isotope Ratio Mass Spectrometer coupled with a Carlo Erba NCS 2500 Elemental Analyzer at the Queen’s Facility for Isotope Research. The δ²⁸S values for the coating material were calculated by normalizing the ³⁴S:³²S ratios in the sample to the same ratio in the Vienna Canyon Diablo Troilite (VCDT) standard:

\[
\delta^{34}S = \left( \frac{³⁴S_{\text{sample}}}{³⁴S_{\text{VCDT}}} - 1 \right) \times 10^3
\]

and are expressed as δ values in units of permil. The uncertainty of the δ²⁸S values is ±0.1 and is based on measured variations of δ²⁸S values for the VCDT standard.

The scrapings of the coatings likely contained material from the underlying rock; however optical microscopy and SEM examination of the underlying rock did not indicate the presence of S-bearing minerals.

3. RESULTS

Black rock coatings are generally limited to exposed rocks within the Greater Sudbury area. Their distribution is consistent with the smelter impact zones in regards to atmospheric SO₂ pollution, metals in surface soils, low soil pH, and vegetation damage which were controlled by dominant SW → NE winds. The distribution of metals from a point source and subsequent environmental damage is consistently shown to be controlled in part by prevailing winds (Knight and Henderson, 2006).

3.1. Metal(loid)s in the coatings; distributions and associations on a micrometer, millimeter- and regional scale

In the following sections, the distribution and association of metal(loid)s in the coatings are discussed on a micro- and millimeter scale (i.e. within the coatings and the weathered surface of the rock) and on a regional scale (i.e. Greater Sudbury area). The results are presented in individual sections that discuss elements closely associated with each other (Pb and As), main elements of locally smelted ore (Cu and Ni) and elements that are toxic in small concentrations (>15 mg kg⁻¹ for Se). The occurrence and distribution of S will be addressed when discussing the variations of δ²⁸S values within the coatings of the Greater Sudbury area.

3.1.1. Lead and Arsenic

Fig. 4a and b show µ-XRF distribution maps for Pb and As in the cross section of sample RY-1. The large penetration depth of the beam (100–250 μm) and its inclination angle of 45° created three-dimensional distribution maps, in which not every feature can be related to those observed in an optical or SEM image. However, the location of the coating/weathered portion of the rock and the epoxy can

![Fig. 4. Micro X-ray fluorescence element distribution maps for (a) Pb and (b) As; (c) a plot between the CPS for Pb and As in the µ-XRF distribution map; (d) plot with the atomic percent (at.%) for Pb and As as determined by EMP analyses for the metal–sulfate- and silica-rich layers in the coatings of F1 and RY-1 (Mantha et al., 2012) the size of the symbol represents approximately the uncertainty of each data point; (e) plot with the concentration of Pb versus As (in mols per 100 g coating) for the 30 examined coating samples (a total of 152 LA-ICP-MS depth scan analyses); the uncertainty for the LA-ICP-MS data (±10%) is indicated for one data point; calculated linear regression lines and their equations are indicated in (d) and (e).](image-url)
be clearly distinguished and are labeled in both distribution maps. Fig. 4c shows a linear plot of the counts per seconds (cps) for Pb versus As from the distribution maps (Fig. 4a and b). Distribution maps and linear plot indicate the common occurrence of both elements and their strong association in the coatings and the weathered portion of the underlying rock.

The concentrations of all major elements in the metal–sulfate- and silica-rich layers of the samples F1 and RY-1 were characterized with 21 EMP spot analyses (Mantha et al., 2012). A correlation between the concentrations (at.%) of Pb versus As records their common occurrence in the metal–sulfate-rich layer and the corresponding linear regression curve depicts an average atomic As:Pb ratio 0.53(3) (Fig. 4d).

The chemical compositions from the 152 LA ICP-MS depth-scan analyses (Fig. 4e) indicate an average As:Pb ratio of 0.45(2), which is quite similar to the observed ratio in the metal–sulfate-rich layers of sample F1 and RY-1 (Fig. 4d). The apparent correlations indicate the close association of Pb and As in all examined coatings, independent of the geographic location or the type of underlying rock.

Coating samples were grouped by geographical location based on their proximity to former or current smelters (Copper Cliff, Coniston and Falconbridge) and their relative location in regards to the Greater City of Sudbury (Sudbury Center and Sudbury South, Fig. 2). The highest concentrations of Pb and As occur around the former and current smelters and decrease with distance from these point sources (Fig. 5a and b). They further show that the highest average concentrations of Pb are found in coatings near the Coniston smelter and that the highest average concentrations of As occur in the Copper Cliff and Coniston regions (Table 1 and Fig. 5a and b).

### 3.1.2. Copper and Nickel

Copper and Ni occur in different chemical environments within the black coatings. SEM, EMP and transmission electron microscopy (TEM) examinations of the coatings show that Cu is one of the major elements in the metal–sulfate-rich layer of sample F1 (Fig. 6a, Mantha et al., 2012). Nickel is typically found within spherical Fe-oxide smelter particles (Fig. 6b), which are embedded in the silica-rich matrix of the black coatings (Mantha et al., 2012). EMP spot analyses of multiple particles and regions within the coatings confirm these observations (Fig. 7a).

The different occurrences of Cu and Ni are also apparent in the μ-XRF distribution maps (Fig. 7b and c) and the plot of the cps of Ni versus Cu (Fig. 7d), wherein there are at least three different trends between Cu and Ni. Similarly, the concentrations of Ni and Cu do not correlate in all coatings of the Greater Sudbury area (Fig. 7e), which can be attributed to proportions of spherical particles and metal–sulfate-rich layers varying with the type of underlying rock and the geographic location of the coating (Mantha et al., 2012).

On the regional scale, higher concentrations of Ni and Cu occur at Copper Cliff, Falconbridge and Coniston. Concentrations of Ni are much higher at Copper Cliff than at Coniston and Falconbridge whereas the concentrations of Cu are similar at Copper Cliff and Coniston (Table 1 and Fig. 8a and b).

### 3.1.3. Selenium

The distribution of Se within the coatings was recorded with depth-profiles and LA-ICP-MS line scans, the latter of which traverse the coatings in cross-sectional samples (Mantha et al., 2012). Stacked LA-ICP-MS line scans of Si, S, Se and Cu through the metal–sulfate- and silica-rich layers...
layer in the coatings of sample F1 indicate that the peak/background ratio for the line scan of Se is much smaller than for the scans of Cu, S and Si. Similarities between the line-scan patterns of Se, Cu and S are apparent and suggest their common association in the coatings (Fig. 9b). The highest concentrations of Se occur in the coatings around Copper Cliff and decrease with distance from the Copper Cliff smelter (Fig. 9c and Table 1).
Table 1
Element concentrations (mg kg$^{-1}$ and weight %) for coatings from five different regions; n denotes the number of samples per region (Fig. 2), each sample was analyzed with five to six LA-ICP-MS depth scans.

<table>
<thead>
<tr>
<th>Region</th>
<th>Statistic</th>
<th>Se (mg kg$^{-1}$)</th>
<th>Ni (mg kg$^{-1}$)</th>
<th>Fe (wt.%)</th>
<th>Cu (wt.%)</th>
<th>As (wt.%)</th>
<th>Pb (wt.%)</th>
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<tr>
<td>Coniston</td>
<td>Min</td>
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<tr>
<td></td>
<td>Mean</td>
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<td>0.9</td>
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<tr>
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<td>0.1</td>
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<td>0.1</td>
<td>0.2</td>
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<td>0.4</td>
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<tr>
<td>Sudbury South</td>
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<td>632</td>
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<td>0.1</td>
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<td>0.2</td>
<td>0.2</td>
<td>0.8</td>
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</table>

Fig. 8. Maps of the Sudbury area with the average concentrations of (a) Ni and (b) Cu in the coatings from 30 locations within the Greater Sudbury area; the concentrations are expressed in ranges of weight % and indicated with solid spheres of different size and color. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
3.1.4. Sulfur and $\delta^{34}S$

Mantha et al. (2012) showed that the concentrations of S strongly correlate with those of Fe measured by EMP (WDS) in the coatings of F1 and RY-1. Similarly, the concentration of all major metal(loid)s in the metal–sulfate-rich layers of RY-1 and F1 (Pb, As and Cu) correlate with those of S. Correlations of high confidence ($R^2 > 0.70$) are rare between the concentrations of S and metal(loid)s for the 30 coatings examined using LA ICP-MS, most likely a result of the bulk analysis of the coatings and absence of metal–sulfate-rich layers in some coatings (Mantha et al., 2012). The correlation with the highest confidence ($R^2 = 0.71$) occurs between the cps of S and Pb (Fig. 10a), suggesting that S is more closely associated with Pb than with other metal(loid)s.

The sulfur isotopic composition ($\delta^{34}S$) of the coatings varies between +2.6‰ and +5.7‰. The higher values are associated with samples in closer proximity to the smelting centers, notably Copper Cliff and Coniston (Fig. 10b). The $\delta^{34}S$ values in Copper Cliff showed the largest spread (+3.3‰ to +5.7‰) and included the single highest $\delta^{34}S$ value recorded (+5.7‰). The samples from Coniston and Falconbridge exhibit a smaller range of $\delta^{34}S$ values with +4.1‰ to +5.3‰ and +3.5‰ to +4.4‰, respectively. The samples from Falconbridge display the smallest $\delta^{34}S$ values of all samples collected around former and recent smelters. Sudbury Center and Sudbury South samples exhibit the lowest $\delta^{34}S$ values, +3.0‰ to +4.1‰ and +2.6‰ to +3.7‰, respectively.

A correlation between the $\delta^{34}S$ values of the coatings and their distance to the smelter centers can be established if one considers the prevailing SW → NE wind direction and the emission data from the various smelters. The smelters at the Copper Cliff area emitted more
sulfur dioxide and metals than the smelters at Coniston and Falconbridge. For example, the former smelters emitted 18-times more primary sulfates during the period 1973–1981 than the smelter at Falconbridge and eight-times more particular matter during the period 1930–1960 than the smelter at Coniston (Ozvacic, 1982; Wren, 2012). Emission data and prevailing wind direction suggest therefore that all coatings sampled west of Coniston and Falconbridge were predominantly affected by the emission of the Copper Cliff smelters and that only coatings sampled around Coniston and Falconbridge were significantly affected by the emissions of the stacks in these areas. In this way, distances between sample locations and the Copper Cliff smelter center (Table 2) were calculated for all areas west of Coniston and Falconbridge (labeled with stars, squares and crosses for the different areas indicated in Fig. 2 and listed in Table 1), whereas distances to the Coniston and Falconbridge stacks (Table 2) were only calculated for sampling locations in their vicinity (triangles and circles). Fig. 10c indicates a good correlation between the $\delta^{34}$S values of the coatings and their distance to the various smelters ($R^2 = 0.52$ and 0.62 for a linear and exponential regression, respectively).

4. DISCUSSION

The regional distribution of the black coatings indicates that its formation is primarily related to the occurrence of exposed bedrock and secondarily to the distance of the smelters. Anthropogenic exposures of bedrock surfaces as well as natural geomorphic processes provide a first-order control for the occurrence of the rock coatings according to Dorn’s hierarchal model of coating development (Dorn, 1998). In the Sudbury area, these first-order processes include extensive logging prior to and during early smelting activities (ore roasting in roast yards), and the occurrence of (sulfuric) acid rain and metal emissions, which both contributed to a barren landscape lacking soil and vegetative cover. The near-absence of black rock coatings in the northern and northeastern portion of Sudbury is related to a lack of exposed bedrock surfaces due to the presence of glacio-fluvial sediments, which were deposited during glacial events.

Transport and availability of raw ingredients for the formation of coatings, i.e. a positive mass balance at the rock-atmosphere interface is ranked as a fourth-order process in Dorn’s hierarchal model (Dorn, 1998). The absence of rock coatings in areas west of Sudbury is a product of such a fourth-order process, where the prevailing northeasterly
winds resulted in lower deposition rates of sulfuric acid, particular matter and metal–sulfate aerosols west of the city.

4.1. Emission data and metal(loid) concentrations in the coatings

The distribution of Pb, As, Cu, Ni, Se and S in the coatings on the micrometer, millimeter and regional scale showed that

1. Pb and As occur in close association in all coatings over the Greater Sudbury area.
2. Ni and Cu occur often in different areas on the micro- and millimeter scale and their concentrations in the coatings do not correlate on the regional scale.
3. Se and S are in closer association with Cu and Pb, respectively, than with other metal(loid)s in the coatings.

We will explain first the occurrences and associations of these metal(loid)s using the emission data by the smelters and the minerals present in the coatings. The regional distribution of the metal(loid)s in the coatings can be, however, only addressed when one considers their speciation in the plume and the deposition and mixing of the different S-bearing atmospheric species. The latter information can be gained by (a) comparing the $\delta^{34}$S values of the coatings with those of the smelter plume and precipitations and (b) by evaluating the possibility of S fractionation during oxidation of atmospheric SO$_2$.

4.1.1. Lead and Arsenic: emission data and potential hosts

On the basis of the historical data from Hutchinson and Whitby (1974), Ozvacic (1982) and Wren (2012), an estimated 200 tonnes year$^{-1}$ of Pb and 120 tonnes year$^{-1}$ of As were emitted by the Copper Cliff smelter complex between 1925 and 1975. In comparison, the smelters at Falconbridge and Coniston emitted together approximately one-fourth of the Pb and As emissions emitted by the Copper Cliff smelters during this time period (Ozvacic, 1982; Wren, 2012). On the basis of these emission data, the As:Pb atomic ratio within the smelter plume was approximately 1.5:1. This ratio differs from the average As:Pb atomic ratio

<table>
<thead>
<tr>
<th>Location</th>
<th>km</th>
<th>$\delta^{34}$S</th>
<th>As:Ni</th>
<th>Se:Ni</th>
<th>Pb:Ni</th>
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</tr>
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<td>1(5)</td>
</tr>
<tr>
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<td>1.5(2)</td>
<td>0.11(2)</td>
<td>13(2)</td>
</tr>
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Data for locations around the Falconbridge smelter

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<th>Pb:Ni</th>
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Data for locations around the Coniston smelter

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* The samples RY-1, TB and CC4 were not considered due to their locations within former Roast Yards and tailings disposal areas.
* Uncertainties are given in parentheses.
of 1:2 in the coatings of the Greater Sudbury area (Fig. 4d and e) and indicates that the incorporation of As and Pb was mainly controlled by the stoichiometry of the phases in the metal–sulfate-rich layers and not by the proportions of the elements in the smelter plume.

The common occurrence of K, Fe, S, Pb and As in the metal-rich layers and the correlation between Pb and S (Fig. 10a) suggests that Pb and As must be associated with the K–Fe sulfates mereiterite and goldichite. The potential substitution of K$^+$ by Pb$^{2+}$ in the interstitial complexes of mereiterite, and goldichite, is, however, only possible by means of a coupled substitution to maintain charge balance (Schindler et al., 2006).

The coupled substitution:

\[ \text{Pb}^{2+} + (\text{As}^{5+} \text{O}_4)^{3-} \leftrightarrow \text{K}^+ + (\text{SO}_4)^{2-} \]  

(R1)

is well documented for jarosite (Scott, 1987; Rattray et al., 1996; Rocea et al., 1999; Dutrizac and Jambor, 2000) and could occur in both goldichite, K$[\text{Fe}^{3+}(\text{SO}_4)_2(\text{H}_2\text{O})_4]$ and mereiterite, K$_2[\text{Fe}^{2+}(\text{SO}_4)_2(\text{H}_2\text{O})_4]$. The As: Pb ratio of 1:2 indicates that for every second Pb$^{2+}$ that substitutes for K$^+$ in the K–Fe-sulfates, one As$^{5+}$ substitutes for one S$^{6+}$. This requires an additional coupled substitution in order to balance the incorporation of each additional Pb$^{2+}$. There are two possibilities: (1) In the structure of the Fe$^{3+}$-sulfate goldichite, Fe$^{2+}$ can substitute for Fe$^{3+}$, maintaining the charge balance of the mineral structure:

\[ \text{KFe}^{3+}(\text{SO}_4)_2(\text{H}_2\text{O})_4 \leftrightarrow \text{Pb}_2[\text{Fe}^{3+}, \text{Fe}^{2+}(\text{SO}_4)_2(\text{AsO}_4)](\text{H}_2\text{O})_4 \]  

(R2)

(2) the deprotonation of H$_2$O groups, which would be required for mereiterite, K$_2[\text{Fe}^{2+}(\text{SO}_4)_3(\text{H}_2\text{O})_4]$, a mineral without significant amounts of Fe$^{3+}$. The deprotonation would involve (H$_2$O) groups of the Fe-octahedra, leaving behind underbonded Fe$^{3+}$-OH terminations along the [Fe(SO$_4$)$_2$(H$_2$O)$_3$] clusters (Giester and Rieck, 1995). This termination would most likely bond directly to Pb$^{2+}$ atoms, in order to minimize the number of underbonded O-atoms within the structure of the mineral:

\[ \text{K}_2[\text{Fe}^{3+}(\text{SO}_4)_3(\text{H}_2\text{O})_4] \leftrightarrow \text{Pb}_2[\text{Fe}^{3+}(\text{SO}_4)_2(\text{AsO}_4)] \times (\text{OH})(\text{H}_2\text{O})_3 \]  

(R3)

4.1.2. Copper and Nickel: emission data and hosts

Historical records of metal emissions from the Sudbury smelting facilities indicate that over 1000 tonnes of Cu and Ni were annually released between 1935 and 1975 (Hutchinson and Whitby, 1974; Ozvacic, 1982; Wren, 2012). The atomic ratios between these elements in the smelter plume varied annually and from stack to stack but were on average close to 1:1. Note that the smelters at Coniston and Falconbridge emitted only one fourth of the Cu and Ni-emasions by the Copper Cliff smelters (Wren, 2012).

The coatings contain up to eight times more Cu than Ni (Table 1), which must be a result of their dominant occurrences in the metal–sulfate-rich layer and spherical particles, respectively. Concentrations of Ni in the metal–sulfate-rich layers are much lower relative to Cu (Fig. 7a). This observation may be explained by

1. The presence of Cu-sulfates and the absence of Ni-sulfates in the metal–sulfate-rich layers; most likely a result of the higher solubility of common acidic Ni-sulfates, Ni(SO$_4$)$_2$·n(H$_2$O) (n = 1–7) with respect to basic Cu-sulfates such as guildeite [Cu$^{2+}$Fe$^{3+}$(SO$_4$)$_2$(OH)$_2$·4(H$_2$O)] and antlerite [Cu$_3$(SO$_4$)$_2$(OH)$_6$] (Jambor et al., 2000).
2. The preferred incorporation of Cu in K–Fe-sulfates with respect to Ni (Dutrizac et al., 1996).
3. The higher affinity of Cu relative to Ni to sorb on silanol groups within the silica-matrix of the coatings (Dugger et al., 1964; Stumm, 1992).

4.1.3. Selenium: emission data and potential hosts

The Sudbury ore contains on average 40 mg kg$^{-1}$ Se and Sudbury smelters emitted ca. 50 tonnes year$^{-1}$ Se in the early 1980s (Nriagu and Wong, 1983).

High Se concentrations can be commonly found in Fe and Cu-sulfides, where the selenide ion replaces the sulfide ion (Hawley and Nichol, 1959). Similarly, the selenate ion replaces the sulfate ion in Fe- and Cu-sulfate minerals. For example, Dutrizac et al. (1981) successfully synthesized jarosite-group minerals in which (SeO$_4$)$_{2-}$ substituted for (SO$_4$)$_{2-}$ in mol ratios controlled by the composition of the mother solution.

The correlation between the concentrations of Se and Cu (Fig. 9b) suggests the presence of Se-rich Cu-sulfates in the coatings. A similar correlation does not exist for Se and Fe, which raises the question whether the correlation between Cu and Se is a result of the preferential incorporation of Se into Cu-sulfates, the occurrence of Se-rich Cu-sulfides in the Sudbury ore or the lower ratio between oxides (i.e. non-selenate bearing phases) and sulfates of Cu versus Fe.

Firstly, there are no crystal-chemical indications that (SeO$_4$)$_{2-}$ would preferentially replace (SO$_4$)$_{2-}$ in a Cu-sulfate rather than a Fe-sulfate. Selenium-rich Cu-sulfides are quite common in sulfide ore deposits in Canada. For example, Hawley and Nichol (1959) showed that Cu-sulfides in the magmatic ore deposit at Rouyn-Noranda, Quebec contain up to 1000 mg kg$^{-1}$ Se. Although the authors showed that Se is equally distributed between Fe-sulfides (pyrohotite) and Cu–Fe-sulfides (chalcopyrite) in the Sudbury ore, we cannot rule out that Se-rich Cu-sulfides were and are smelted at the Copper Cliff facilities. Finally, SEM and TEM studies showed that Fe-oxides are indeed more common in the coatings than Cu-oxides (Mantha et al., 2012), explaining the poorer correlation between the concentrations of Fe and Se relative to Cu and Se.

4.2. Sulfur isotope composition of the ore, smelter plume, precipitations, lakes and coatings in the surroundings of the Greater Sudbury area

The isotopic composition of sulfur-bearing aerosols is commonly used to trace their source and distribution in the atmosphere (e.g. Norman et al., 2006; Sinha et al., 2008). The isotopic signature of atmospheric sulfur may vary between $-5_{\text{os}}$ and $+25_{\text{os}}$ depending on the various contributing sources of sulfur (Krouse and Mayer, 2000). Sulfur of volcanic origin displays $\delta^{34}$S values of approximately $+5_{\text{os}}$.\
(Lein, 1991) whereas sulfur-bearing aerosols from salt spray range from +15‰ to +21‰ (Krouse and Mayer, 2000). It should be noted that there is no significant fractionation of sulfur during the transition from fluid (ocean) to vapor (atmospheric aerosol) (Mayer, 1998). Anthropogenic sulfur measured from precipitation (rain and snowfall) typically varies between −3‰ and +9‰ (Mayer, 1998).

Smelters in Sudbury have been documented to release both SO2 gas and sulfate (SO42−)-bearing particulate matter (Forrest and Newman, 1977b; Wren, 2012). Stable isotope studies of the main smelter plume (the Super Stack) showed that SO2 in the plume displayed low positive δ34S values of +0.9‰ to +1.2‰ (Nriagu and Coker, 1978), which is consistent with the isotopic composition of the majority of the smelted Ni–Cu ores (+0.2‰ to 3.5‰) in this region (Fig. 10d, Thode et al., 1962; Schwarzc, 1973).

Sulfates in the smelter plume mainly occur in the form of H2SO4 with minor amounts of metal–sulfate aerosols (see below). The proportion of these primary sulfates in the plume varies between 0.4% and 3% of the total SO2 emissions (Chan et al., 1982a,b, 1983) and their δ34S values are in the range of +4.2‰ to 7.6‰ (Fig. 10d, Luiss and Wiebe, 1976). Nriagu and Coker (1978) and Nriagu and Harvey (1978) examined in detail the sulfur-isotope composition of wet precipitation and lake water around Sudbury (up to 100 km from the Super Stack). They found seasonal variations of the δ34S values in wet precipitation with lower (+2.99‰ to 4.66‰) and higher (+5.64‰ to 6.19‰) values in the summer and winter, respectively. The δ34S values for lake water varied over a larger range with values between 2.66‰ and 8.43‰. In both studies, the authors noted that the average δ34S values in precipitation and lakes were similar to the values for the sulfate aerosols in the smelter plume (Fig. 10d) and that the individual values did not show any systematic variations with the distance to the smelter.

4.2.1. S- and O-fractionation during oxidation of SO2

The fractionation of S isotopes in the atmosphere can be mediated by a gas-phase or an aqueous-phase oxidation process. The gas-phase oxidation (also known as homogeneous oxidation) occurs via OH radicals in the troposphere and stratosphere and produces sulfuric acid (H2SO4) which condenses, forming aqueous (SO42−) and (SO3)2−-bearing aerosols (Saltzman et al., 1983; Tanaka et al., 1994):

\[
\begin{align*}
\text{SO}_2 + \text{OH} + \text{Metal} &\rightarrow \text{HSO}_3 + \text{Metal} & (R4) \\
\text{HSO}_3 + \text{O}_2 &\rightarrow \text{HO}_2 + \text{SO}_3 & (R5) \\
\text{SO}_3 + 2\text{H}_2\text{O} &\rightarrow \text{H}_2\text{SO}_4(aq) \text{H}_2\text{O} & (R6)
\end{align*}
\]

The measured fractionation factor ɛhom (Harris et al., 2012) for the equations (R4)–(R6) is

\[
\varepsilon = 1.0089 - 4 \times 10 - 57(°C) \tag{2}
\]

The aqueous-phase oxidation (also known as heterogeneous oxidation) occurs in the aqueous component or on particle surfaces in the atmosphere. The major oxidants are H2O2, O3 and O2, the latter being catalyzed by Fe3+ and other transition metal ions (Hermann et al., 2000). Dissolution and oxidation of SO2 in the aqueous phase can be formulated as follows: (Eriksen, 1972a–c)

\[
\begin{align*}
\text{SO}_2(g) &\leftrightarrow \text{SO}_2(aq) \tag{R7} \\
\text{SO}_2(aq) + \text{H}_2\text{O} &\leftrightarrow \text{HSO}_3^- + \text{H}^+ \tag{R8} \\
\text{HSO}_3^- + (\text{H}_2\text{O}_2/\text{O}_3/\text{particulates}) &\leftrightarrow \text{SO}_4^{2−}(aq) + \text{H}^+ \tag{R9}
\end{align*}
\]

Measured fractionation factors are for the equilibrium reaction (R7) (Eriksen, 1972b):

\[
x = 1.0029 \text{ at } 10 °C \tag{3}
\]

for the equilibrium reactions (R7) and (R8) (Eriksen, 1972a).

\[
x = 1.01033 \text{ at } 25 °C \tag{4}
\]

for the equilibrium reactions (R7)–(R9) with O3 and H2O2 as oxidants (Harris et al., 2012):

\[
x = 1.0167 - 8.7 \times 10 - 57(°C) \tag{5}
\]

and for the equilibrium reactions (R7)–(R9) with Fe and O2 as oxidants (Harris et al., 2012):

\[
x = 0.9894(\text{at } 19 °C) \tag{6}
\]

The mechanism for SO2 oxidation can also be inferred from its O-isotopes. Holt et al. (1982), Holt and Kumar (1984) and Holt (1991) showed that δ18O in primary sulfates (sulfates formed before their release to the atmosphere) are isotopically heavier than secondary sulfates (formed through oxidation of SO2 in the atmosphere). For example, Norman et al. (2004a,b, 2006) used S- and O-isotope measurements to study the atmospheric sulfur budget for two urban environments with different degrees of humidity (Vancouver and Calgary). Their studies showed that primary and secondary sulfates emitted from different sources can be distinguished on the basis of their S and O isotope signature and that S fractionation did not occur during oxidation of SO2 in the atmosphere.

It should be noted here that δ18O measurements on the black coatings would have been possible with, for example, Secondary Ion Mass Spectroscopy (SIMS), but would have resulted in the measurement of δ18O values from embedded sulfates, smelter-particles, Fe-oxides and clays as well as from the surrounding silica matrix.

4.2.2. Rate of SO2 oxidation and proposed S fractionation in the Super Stack plume

Luiss and Wiebe (1976) and Forrest and Newman (1977b) showed that the oxidation rate of SO2 in the Super Stack plume is on average 1% per hour and suggested that heterogeneous oxidation is the predominant process in the conversion of SO2 into H2SO4. Forrest and Newman (1977b) argued further that the relatively low oxidation rate in the Sudbury plume (in comparison to plumes emitted by coal-fired power plants) was the result of a low particulate loading (i.e. low amounts of metal–surface catalysts) and a low pH value, which slowed down the conversion of SO2(aq) and HSO3− in the equilibrium reactions (R7)–(R9).

On the basis of these small oxidation rates, Nriagu and Coker (1978) explained the differences in the δ34S values between sulfates and SO2 in the smelter plume with the fractionation of S during the conversions of SO2(gas) into
SO$_2$aq and SO$_2$ag into HSO$_3^-$ (reactions (R7) and (R8)). They explained furthermore the seasonal variations of $\delta^{34}$S in precipitation around Sudbury with higher washout rates of (SO$_2$)aq in the summer (lower positive $\delta^{34}$S values) than during the winter months (higher positive $\delta^{34}$S values).

The interpretations by Nriagu and Coker (1978) did not account for the occurrence of primary sulfates in the smelter plume (0.4–3%), which occur in at least equal proportions to secondary sulfates (formed through the oxidation of SO$_2$) within the first or second hour the smelter plume is emitted (considering an oxidation rate of 1%). The studies on the smelter plume by Lusis and Wiebe (1976), Forrest and Newman (1977b) and Nriagu and Coker (1978) showed that the plume traveled on average 40 km h$^{-1}$. The sample locations of the black coatings were all within 40 km of the smelter centers, suggesting that their isotopic signature was significantly influenced by primary sulfates and their mixing with secondary sulfates.

4.2.3. Decrease of $\delta^{34}$S with the distance from the smelter, a result of $S$ fractionation?

The small variations of $\delta^{34}$S for SO$_2$ in the Super Stack plume (+0.9$\%_{\text{iso}}$ to +1.2$\%_{\text{iso}}$) suggest that SO$_2$ fumigations and plumes prior to the Super Stack had similar isotopic compositions. If this was indeed the case, the isotopic composition of secondary sulfates ($\delta^{34}$S$_{\text{H}_2\text{SO}_4}$) formed during Rayleigh distillation can be calculated using the following equation:

$$\delta^{34}\text{S}_{\text{H}_2\text{SO}_4} = 2(\delta^{34}\text{S}_{\text{SO}_2} + 10^f) - 10^f$$  \hspace{2cm} (7)

where $\delta^{34}\text{S}_{\text{SO}_2}$ is the initial $\delta^{34}$S value for SO$_2$ (average value of SO$_2$ in the plume = 1.11$\%_{\text{iso}}$ for $f$ = 1) and $f$ the fraction of SO$_2$(gas) remaining (Faure, 1998). For the equilibrium reactions (R7) and (R8), (R7)–(R9)$_{\text{H}_2\text{O}_2}$, and (R7)–(R9)$_{\text{Fe-surface}}$ at $T$ = 19 $^\circ$C, the fractionation factors $f$ would be 1.01033, 1.01505 and 0.9894, respectively.

If the remaining fraction of (SO$_2$) gas decreases in steps of 0.01 (corresponding to an oxidation rate of 1% h$^{-1}$), secondary sulfates would have either large positive or negative values depending whether the oxidation was catalyzed by O$_2$/H$_2$O$_2$ or metal–surface catalysts. For example two hours after emission of the plume with $f$ = 0.98, the $\delta^{34}$S$_{\text{H}_2\text{SO}_4}$ would be in the range of 11$\%_{\text{iso}}$, 16$\%_{\text{iso}}$ and $-9\%_{\text{iso}}$ for the equilibrium reactions (R7) and (R8), (R7)–(R9)$_{\text{H}_2\text{O}_2}$, and (R7)–(R9)$_{\text{Fe-surface}}$, respectively. These calculated $\delta^{34}$S$_{\text{H}_2\text{SO}_4}$ values for secondary sulfates formed within the greater Sudbury area (assuming plume velocities of 40 km h$^{-1}$) are not within the range of $\delta^{34}$S values observed in the black coatings. Even if one assumes higher oxidation rates of SO$_2$(gas) on the surface of exposed bedrocks (i.e. 3% h$^{-1}$), the corresponding $\delta^{34}$S$_{\text{H}_2\text{SO}_4}$ would be still much larger (+7.8$\%_{\text{iso}}$ to +9.5$\%_{\text{iso}}$) or smaller ($-6.5\%_{\text{iso}}$) than any observed value in the coatings (note that an oxidation rate of 3% h$^{-1}$ corresponds to the largest observed rate in a plume in North America; Newman, 1981). Hence, mixing of similar proportions of primary sulfates (+4.2$\%_{\text{iso}}$ to +7.6$\%_{\text{iso}}$) with secondary sulfates containing fractionated sulfur (with values higher than +7.8$\%_{\text{iso}}$ or less than $-6.5\%_{\text{iso}}$) would result in $\delta^{34}$S$_{\text{H}_2\text{SO}_4}$ values which are not consistent with those measured in the coatings (+2.6$\%_{\text{iso}}$ to +5.7$\%_{\text{iso}}$). As a result, $S$-fractionation during the equilibrium reactions (R7) and (R8) (R7)–(R9) did not result in the fractionation of $S$, as observed in the urban areas of Calgary and Vancouver (Norman et al., 2004a,b), the $\delta^{34}$S value for the secondary sulfates would have been similar to those for SO$_2$(gas) (average value = 1.11$\%_{\text{iso}}$) from which they formed. Hence, an increasing ratio between secondary and primary sulfates through scavenging of primary sulfates by wet precipitation (see below) and oxidation of SO$_2$(gas) would have yielded a decrease in the $\delta^{34}$S-value for atmospheric sulfates (and thus for the coatings) with increasing distance from the smelters. This mixing model can be verified through inspection of the regional distribution of trace metals in the coatings, which were found to be closely associated with primary sulfate aerosols in the smelter plume.

4.2.4. Decrease of $\delta^{34}$S with distance from the smelter, a result of mixing?

Studies by Chan et al. (1982c–e) and Chan and Lusis (1985) showed that sulfates and trace metals from the plume are efficiently scavenged during wet precipitation events. For example, typical scavenging coefficients for sulfates were found to be about 30–40% h$^{-1}$ and for trace metals such as Pb, Cu, Se and As in the 60–80% h$^{-1}$ range (see below). The same studies also showed that the scavenging coefficient for SO$_2$(gas) was insignificantly small relative to those of sulfates, indicating that mainly primary and secondary sulfates scavenged via wet precipitation likely interacted with exposed rocks in the Sudbury area.

The amount of primary sulfates in the plume was measured to be between 0.4% and 3%. Hence, an oxidation rate of 1% h$^{-1}$ for SO$_2$(gas) would have resulted in approximately equal amounts of primary and secondary sulfates within the first two hours after emission of the plume. The average $\delta^{34}$S value for the primary sulfates (5.4$\%_{\text{iso}}$) is similar to the $\delta^{34}$S values observed in the coatings proximal to the smelters (Fig. 10c). If the equilibrium oxidation reactions (R7)–(R9) did not result in the fractionation of $S$, as observed in the urban areas of Calgary and Vancouver (Norman et al., 2004a,b), the $\delta^{34}$S value for the secondary sulfates would have been similar to those for SO$_2$(gas) (average value = 1.11$\%_{\text{iso}}$) from which they formed. Hence, an increasing ratio between secondary and primary sulfates through scavenging of primary sulfates by wet precipitation (see below) and oxidation of SO$_2$(gas) would have yielded a decrease in the $\delta^{34}$S-value for atmospheric sulfates (and thus for the coatings) with increasing distance from the smelters. This mixing model can be verified through inspection of the regional distribution of trace metals in the coatings, which were found to be closely associated with primary sulfate aerosols in the smelter plume.

4.2.5. Deposition rates of sulfate aerosols and larger particular matter

Studies of airborne particulate matter in the Copper Cliff Super Stack smelter plume found that Pb, As and Se occurred in smaller particles with average diameters <2.5 $\mu$m, compared to Cu and Ni which were found mainly in larger particles (>2.5 $\mu$m; Chan et al., 1982a,b). The first observation is in agreement with studies of other smelter plumes, which in addition, showed that Pb commonly occurred as metallic Pb or Pb-sulfates in plumes (Sobanska et al., 1999; Chööl et al., 2006). The close association of Pb with sulfate aerosols in the Sudbury plumes may be exemplified by the correlation between the raw counts for Pb and S from the LA-ICP-MS study (Fig. 10a), which indicates that almost all Pb in the coatings is associated with S-bearing minerals.

Studies on the wet and dry deposition rate of metals from the Super Stack plume showed that deposition rates for the larger Fe–Ni particulate matter were similar during
Fig. 11. Correlations between the distance of the coatings to the Copper Cliff smelter facility and their concentration ratios for (a) Pb:Ni, (b) As:Ni and (c) Se:Ni; the uncertainty of a data point is given in Table 2; data from coatings in the Falconbridge and Coniston area were not considered because different ores and smelter and sintering techniques in comparison to the Copper Cliff smelters resulted in different emission data, especially with respect to the ratios Pb:Ni, As:Ni and Se:Ni (Wren, 2012); data from coatings in former and present Roast yards and tailings disposal areas were also not considered because their composition was affected by particles emitted from the roast piles and mine tailings; it is also important to note that these metal(loid):metal ratios are not affected by wind directions, because variations in wind directions do not cause any changes in the ratios between the concentrations of Pb and Ni, As and Se. Indeed, higher deposition rates of primary metal–sulfates occurred closer to the smelter. They also suggest that the ratio between primary Pb–As–Se bearing sulfates and secondary sulfates decreased with distance to the smelter, in agreement with our interpretation on the decrease in $\delta^{34}$S with the distance to the smelter (see above).

4.2.6. Comparison with the study by Nriagu and Coker (1978)

Nriagu and Coker (1978) collected rain samples from five to eight locations over ten different time intervals between January 1975 and October 1976 and found no variations in the $\delta^{34}$S values with the distance to the Copper Cliff smelter. On the contrary, the $\delta^{34}$S values of the coatings represent the isotopic composition of almost 70 years of wet and dry deposition events. The apparent statistical mismatch between both studies and their different results indicate that any systematic change in the ratio between atmospheric primary and secondary sulfates with distance can be only detected when monitoring the isotopic composition of dry and wet depositions over a longer period of time.

4.2.7. Comparison with S-isotope studies on gypsum coatings of building stones

The atmospheric origin of S in gypsum coatings on building stones was verified by many sulfur-isotope studies (e.g. Pye and Schiavon, 1989; Prikryl et al., 2004). The observed decrease in $\delta^{34}$S between gypsum coatings in the city center of Prague (4.3$_{\text{p}}$) and its surroundings (2.5$_{\text{p}}$) were explained with fractionation during the isotopic exchange reactions (R7) and (R8) and a decrease in particulates catalyzing the heterogeneous oxidation reaction (R9) (Buzek and Srámk, 1985). Considering the $\delta^{34}$S values for SO$_2$(gas) (2.3$_{\text{p}}$), aerosols (3.7$_{\text{p}}$) and sulfates scavenged in wet precipitation (5.7$_{\text{p}}$) for the city of Prague, the observed decrease of $\delta^{34}$S in the gypsum coatings could be also explained with a decrease in the ratio between primary and secondary atmospheric sulfate species.

4.3. Conclusions and outlook on the use of silica coatings as forensic tools for compositional atmospheric studies

The black coatings of the Sudbury area preserved trace metals from atmospheric constituents in the form of smelter particles (mainly Ni and minor Cu) and precipitated sulfates (S, Pb, As, Se and Cu). Good to excellent correlations between concentrations for Cu versus Se, Pb versus As and Pb versus S on the micrometer, millimeter and on the regional scale indicate the common occurrence of these elements in minerals within coatings as well as their common occurrence in atmospheric particulate matter and aerosols. On the regional scale, the coatings preserved in addition:

(a) A decrease in metal concentrations with the distance from the smelter point sources; an expected result that has been, however, never before described for rock coatings.
(b) The sulfur isotope composition of primary and secondary atmospheric sulfates incorporated into coatings, and an increasing ratio between secondary and primary sulfates with the distance to the smelter.

c) Higher scavenging and thus higher deposition rates of primary sulfates containing Pb, As and Se by wet precipitations.

d) Similar deposition rates of larger Ni-bearing particles under wet and dry conditions.

e) A decreasing ratio between primary metal–sulfate aerosols and larger Ni-bearing particulate matter with the distance to the smelter.

Although the latter observations may have been expected from the monitoring of wet and dry deposition rates of aerosols and particular matter, they have not been observed for soils, lakes and coatings in the vicinity of smelters prior to this study.

The comparison between emission data and atomic ratios for Pb and As and Cu and Ni in the coatings as well as the inverse correlations between the ratios for Pb:Ni, As:Se and Ni:Se and the distance to the Copper Cliff smelter showed that the coatings did not preserve the atomic ratios of elements in the smelter plume. This study as well as the study by Mantha et al. (2012) showed that the atomic ratios of elements in the coatings is mainly controlled by the occurrence of minerals in the sulfate-rich layers as well as their ability to incorporate trace metals with respect to their size, coordination and charge.

Similar to the black coatings of the Greater Sudbury area, silica-rich coatings on Mars are believed to be products of the weathering of the underlying rock and contain sulfates and amorphous silica as their main constituents (Tosca et al., 2005; Hurowitz et al., 2006; Tosca and McLennan, 2006). This study showed that silica and Fe-sulfate coatings preserve the isotopic signature of sulfur involved in their formation as well as deposition rates for atmospheric sulfate species. In this way, silica coatings on Mars may contain similar information with respect to atmospheric sources and processes.

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APPENDIX A. SUPPLEMENTARY DATA

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