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The Black Rock Coatings in Rouyn-Noranda, Québec: Fingerprints of Historical Smelter Emissions and the Local Ore

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Abstract

Smelting of base-metal-sulfide rich ore in Rouyn-Noranda, Québec have resulted in the formation of black rock coatings on exposed rocks to a maximum distance of 6 km from the smelter centre. This study has shown that these coatings are excellent mineralogical and chemical fingerprints of smelter emissions, ore types, and elemental partitioning into mineral phases. The black coatings are composed of a silica-rich matrix that formed due to the intense chemical weathering of exposed silicate rocks interacting with acidic meteoric waters. They contain metal-sulfate rich layers along the atmosphere-coating interface (ACI) and rock-coating interface (RCI) formed by the *in situ* dissolution and precipitation of metal(loid)-bearing phases. Entombed within the silica matrix are spherical particulates and particles composed of Cu- and Zn- bearing Fe-oxides (e.g., spinels), Fe-oxides (e.g., hematite), Pb-silicates (e.g., alamosite), sulfates (anglesite (PbSO_4) and minerals of the jarosite group), amphiboles, pyroxenes, micas, Na-feldspar and clinocllore. Concentrations of elements are low in proximity to the smelter but drastically increase around 2 km from the stack, most likely the result of a shadow effect of the smelter. This shadow effect is more pronounced if an element is highly compatible with minerals of the jarosite and spinel groups, and is thus called the smelter-compatibility effect. Elements displaying a high smelter-compatibility effect are Ag, Cu, Se and As whereas elements such as Hg, incompatible with the jarosite and spinel structure, show a low smelter-compatibility effect. High $\delta^{34}\text{S}$ (5.5 ‰) values in proximity to the smelter and their decrease with distance is the result of mixing processes between primary and secondary sulfates in the atmosphere. The relative enrichments of metal(loid)s in coatings at Rouyn-Noranda and Sudbury, ON, when normalised to the MUd standard from Queensland, Australia (MUQ), reflect the composition of the smelter emissions, ore and lithologies. Coatings of the Rouyn-Noranda and Sudbury area are enriched for example in Pb and Fe,

45 respectively, reflecting higher abundances of galena and Fe-bearing minerals in the respective ore,
46 emissions and rocks in the region.

47

48 Keywords: *rock coatings; acidic precipitation; metals; compatibility effect; sulfur isotopes*

Draft

Introduction

Rock coatings form in a variety of geographical and geological environments. They can be found for example, in deserts and humid regions as rock varnish or silica glaze (Dorn and Oberlander 1982; Thiagarajan and Lee 2004; Liu and Broecker 2007; Dietzel et al. 2008; Krinsley et al. 2012), in urban regions as gypsum coatings on buildings and monuments (Buzek and Sramek 1985; Sánchez et al. 2009), and in smelter impacted regions as metal(loid)-rich black rock coatings (Mantha et al. 2012a; Mantha et al. 2012b; Schindler et al. 2012). Coatings in general, occur on exposed rocks on the nano- to micrometer scale at the interface between the lithosphere and atmosphere. Therefore, chemical and isotopic compositions of coatings can reflect the underlying lithology or particulate matter, past atmospheric compositions and changes in the environmental conditions over time (Dorn and Oberlander 1982; Thiagarajan and Lee 2004; Schindler et al. 2010; Mantha et al. 2012a; Mantha et al. 2012b; Schindler et al. 2012; Krinsley et al. 2012; Krinsley et al. 2013). The encapsulation of particulate matter into coatings results in the preservation of chemical and isotopic signatures of atmospheric components and can be used for deciphering historical atmospheric processes (Buzek and Sramek 1985; Thiagarajan and Lee 2004; Mantha et al. 2012a; Mantha et al. 2012b; Schindler et al. 2012).

Coatings as Environmental Indicators

The physical structure, as well as the chemical and mineralogical composition of rock coatings can be used as paleoenvironmental indicators. For example, the variations in the Ba and Mn-content of micro-laminations in rock varnish can provide information on paleoenvironmental conditions, specifically paleo-wetness and associated changes in pH (Zhou et al. 2000; Broecker and Liu 2001; Liu and Broecker. 2007; Dietzel et al. 2008; Dickerson 2011; Krinsley et al. 2012). For example, microlaminations enriched in MnO₂ and BaO formed during glacial periods characterized by high precipitation rates and less alkaline surface waters (Zhou et al. 2000; Broecker and Liu 2001; Liu and

Broecker. 2007; Dietzel et al. 2008; Dickerson 2011; Krinsley et al. 2012). On the contrary, microlaminations depleted in MnO₂ and BaO formed during dry climatic conditions characterized by surface waters of higher pH (Zhou et al. 2000; Broecker and Liu 2001; Liu and Broecker. 2007; Dietzel et al. 2008; Dickerson 2011; Krinsley et al. 2012). Hence, the Mn content in the coatings could be correlated with regional paleoclimatic records (e.g., the size of lake basins) to decipher past variations in wet- and dry- climatic conditions (i.e. larger basins reflect wetter conditions) from the Pleistocene to present day (Zhou et al. 2000; Broecker and Liu 2001; Liu and Broecker 2007; Krinsley et al. 2012).

Rock coatings often preserve the isotopic compositions of atmospheric components. For example, Hoar et al. (2010) demonstrated the ability of rock varnish to preserve ratios of Pu isotopes of radioactive fallout in the vicinity of nuclear test sites. Similarly, gypsum coatings formed in urban regions preserved the $\delta^{34}\text{S}$ values of sulfur-bearing particulates, SO₂ and dissolved sulfate, which were used to distinguish between natural and anthropogenic sources of sulfur (Buzek and Sramek 1985; Derda et al. 2006; Sánchez et al. 2009; Mašalaitė et al. 2012).

Black Rock Coatings in Smelter Impacted Areas and Objectives

Black rock coatings around the smelters of the Greater Sudbury Region contain evidence of historical atmospheric processes such as the emissions of smelter-derived particulate matter, atmospheric mixing and scavenging processes, depositional rates of sulfur-bearing aerosols and Ni-bearing particulate matter (Mantha et al. 2012a; Mantha et al. 2012b; Schindler et al. 2012). The coatings formed as a result of the intense chemical weathering of the underlying bedrock in a low pH environment (Mantha et al. 2012a; Mantha et al. 2012b; Schindler et al. 2012). The chemical weathering of silicates in the exposed bedrock allowed for the formation of a silica gel-type layer that was able to entrap detrital and particulate material (Mantha et al. 2012a; Mantha et al. 2012b; Schindler et al. 2012). This silica gel contained an interconnected system of pores that allowed for the exchange of pore fluids,

stimulating the *in situ* formation of sulfate minerals along the atmosphere-coating (ACI) and rock-coating interfaces (RCI) (Mantha et al. 2012a; Mantha et al. 2012b; Schindler et al. 2012). The dehydration and hardening of the silica gel resulted in the formation of nanometer scale environments in disequilibrium with each other and the current composition of meteoric water.

Black-rock coatings also occur in Rouyn-Noranda, Québec where the mining of metal-sulfide rich ore started in 1925. The construction and opening of the Horne smelter in 1927 released vast amounts of SO_{2(g)} and particulates, which provided the necessary ingredients to form the coatings of the region. The objectives of this study are to determine in detail, the mineralogical and chemical composition of the coatings in the Rouyn-Noranda region and their textural relationships with the substrate. The sulfur isotopic ($\delta^{34}\text{S}$) signatures of the coatings were used to determine whether mixing between primary and secondary sulfates or fractionation of S-isotopes occurred. The change in metal(loid) concentrations with distance from the Horne smelter will take into account the effect of element partitioning into mineral phases, and the effect of prevailing wind direction on elemental and coating distribution of the region. A comparison with the trace element composition of the coatings in Sudbury, Ontario will indicate whether rock coatings are chemical fingerprints of the smelted ore in their respective regions.

Methods

Background: Geographical Setting and Regional Geology

The city of Rouyn-Noranda is located in the northwestern region of Québec, approximately 550 km northwest of Montreal. The city is situated within the Noranda Volcanic Complex in the Blake River Group of the Abitibi Subprovince (Gibson et al. 2000). The Noranda Volcanic Complex consists of basaltic, andesitic and rhyolitic volcanic flows with minor pyroclastic rocks which have undergone lower greenschist facies metamorphism (Spence and De Rosen-Spence 1975; Gibson et al. 2000).

118 Rouyn-Noranda is part of a Volcanogenic Massive Sulfide (VMS) complex that hosts at least 19
119 VMS deposits, with the largest being the Horne deposit (Kerr and Gibson 1993). Mineralization in the
120 region consists of Au-Cu-Ag and Zn (Spence and De Rosen-Spence 1975; Kerr and Gibson 1993). Ore
121 minerals present within the deposits consist of pyrrhotite, pyrite, chalcopyrite, sphalerite, galena and
122 magnetite (Barrett et al. 1991; Kerr and Gibson 1993). Accessory minerals include native gold and silver
123 (Kerr and Gibson 1993).

124 **Background: Mining History**

125 Prospecting began in Noranda in 1911, with the official opening of the Horne mine in 1925
126 (Gibson et al. 2000; Kettles and Bonham-Carter 2002). Commercial production began in 1927, with the
127 Horne smelter consisting of two stacks, 161 and 127 m high (Gibson et al. 2000; Kettles and Bonham-
128 Carter 2002; Savard et al. 2004). Mining ceased in 1976, and the smelter started to process ore and
129 recycled metal-bearing electronics from diverse localities across the globe (Gibson et al. 2000; Telmer et
130 al. 2004; Mayer et al. 2007).

131 Before the implementation of control measures on smelters after the Clean Air Act (1970's), the
132 Horne smelter was one of North Americas largest emitters of SO_{2(g)} and particulates (Savard et al.
133 2004). For example, a total of 250 000 tonnes of particulate matter was released in 1928 alone (Kettles
134 and Bonham-Carter 2002), and a total of 52 810 tons of total metals (Pb, Zn, As, Cu and Cd) were
135 emitted between 1965 and 1976 (Savard et al. 2004). In 1965, particulate matter emissions peaked over
136 1.5 million metric tonnes per year, and subsequently decreased with the implementation of newer
137 techniques for capturing smelter emissions (Kettles and Bonham-Carter 2002). Since the 1980's, total
138 emissions have decreased by more than 80% (Savard et al. 2004).

139
140

Sampling

Thirty black-rock coating samples were collected up to a maximum of 6 km from the Horne smelter in late May of 2012 (Fig. 1). Coating samples were collected from exposed bedrock at topographic highs, at least 30 m from roads, buildings, and water bodies to minimize potential sources of contamination. Although prevailing wind directions are towards the ENE (Henderson and Knight 2005), samples were collected in a relatively isotropic manner around the smelter to record any chemical and mineralogical trends with varying distance and wind direction on coating composition and distribution (Fig. 1).

Sample Preparation and Reflected Light Microscopy

On the basis of coating thickness, rock composition, and distance from the smelter, cross-sections of five samples were chosen for detailed optical, SEM and XRD analyses. Cross sections of coatings and the underlying rock were prepared by mounting in epoxy pucks, grinding and polishing samples with silicon carbide.

Scanning Electron Microscopy and Powder X-Ray Diffraction

Scanning electron microscopy (SEM) was conducted at Laurentian University using a JEOL 6400 scanning electron microscope at 20 kV equipped with backscattering electron (BSE) and secondary electron detectors as well as with an Energy Dispersive Spectroscopy (EDS).

X-Ray Powder Diffraction patterns were recorded with a Philips PW 1729 X-Ray diffractometer using Co K α (1.79 Å) radiation at 40 kV and 30 mA. Data was collected over a range of 5 - 75° 2 θ using a 0.02° step size and a 4 second dwell time.

Mineralogical phases in the coatings were deciphered using a combination of reflected light microscopy, SEM, and Powder XRD.

Laser Ablation Inductively Couple Plasma Mass Spectrometry

Chemical analyses of major and trace element concentrations of thirty rock coating samples was conducted using a Thermo-Fisher X II Series inductively coupled plasma quadrupole mass spectrometer (ICP-MS) coupled to an ultra violet laser system (New Wave Nd:YAG 213 nm solid state laser). Samples containing the coating and underlying weathered rock were cut to appropriate size, cleaned using distilled water and mounted on a plastic thin section. The samples were ablated in a He atmosphere, with Ar being used as the carrier gas. Chemical analysis of coatings was carried out using depth profiling. Each sample was ablated along five depth profiles, using a 150 μm spot size. Each analysis was 30 s for each individual depth profile following 30 s of background acquisition. The ablation was conducted using a repetition rate of 5 Hz, with the energy density maintained at 11 J cm^{-2} . The standards NIST612 and MASS were analysed at the beginning and end of five analysed samples under the same operating conditions.

Two LA-ICP-MS maps were collected on the regions of interest in coatings on a felsic lapilli-tuff (sample RN11). Laser Ablation ICP-MS maps were recorded from selected areas in the cross section of sample RN11 as this cross section displayed characteristic textural relationships among the different components in the coatings (see below). The maps were recorded using a 5 μm spot size for 120 seconds per line scan. Line scans were set up to begin in the outer epoxy, and continued through the coating and into the underlying rock

All samples were quantified for their major and trace element concentrations using Igor Pro and Iolite 2.31 software. The breadth of an integration area in the LA-ICP-MS scan pattern was determined by monitoring the inflection points of the Fe and Si peaks, with the peaks for Cu, As and Pb being used to define the boundary between the coating and the underlying mineral(s). The count statistics for S, Se and Hg during ablation of the NIST612 standard did not allow quantification of these elements.

However, similar values for Cu quantified with MASS and NIST612 allowed the quantification of the S, Se, and Hg through calculation of their molar ratios relative to Cu using the MASS standard. Details on the quantification of elements in heterogeneous coatings can be found in Durocher and Schindler (2011). The calculation and normalisation procedure resulted in a semi-quantitative data set based on the uncertainty of the number of structurally bound H₂O groups per mol of Si, Fe or S ($\pm$ one H₂O group), with an estimated error of <9% for the concentration of trace elements in any individual measurement.

Sulfur Stable Isotope Analysis

The sulfur stable isotope compositions in the rock coating samples were analysed at the Queen's Facility of Isotope Research at Queen's University, Canada. The samples were washed with distilled water, dried and coatings were scraped off and placed into a glass vial. The absence of native S and sulfides in EDS distributions maps for S and O indicated that S occurs predominately as (SO₄)²⁻ in the coatings. Hence, approximately 15 mg of each sample was blended with V₂O₅ to allow the complete reduction of SO₄²⁻ to SO_{2(g)}. The samples were heated to 1000°C with O₂ in a tin capsule using a Carlo Erba CNS 2500 Elemental Analyser, thereby producing combustion temperatures in excess of 1400°C. Four standards were used for calibration analysis: 0.3-0.4 mg Sulfane, an in-house standard 0.5 mg MRC (pyrrhotite from Merensky Reef), an in-house standard 0.4 mg PRN 022 (alunite from the Pierena Au deposit, Peru), and approximately 0.5 mg NBS 127 (barium sulfate from seawater). Blanks were analyzed after every third sample, with duplicates being analyzed in every second set of samples to ensure accuracy and precision. Sulfur isotopic abundances were analysed using the above mentioned Elemental Analyser coupled in-line with a MAT 252 Stable Isotope Ratio Mass Spectrometer. The $\delta^{34}\text{S}$ values are recorded in units per mil (‰) relative to the Vienna Canyon Diablo Troilite (VCDT) standard, with sample values calculated by normalising $^{34}\text{S}/^{32}\text{S}$ ratios in coating samples to VCDT:

209 (1) $\delta^{34}\text{S} = \left(\frac{\left(\frac{^{34}\text{S}}{^{32}\text{S}} \right)_{\text{sample}}}{\left(\frac{^{34}\text{S}}{^{32}\text{S}} \right)_{\text{VCDT}}} - 1 \right) \times 10^3$

210 The error in the analysis based on duplicate analysis of the coating samples with the highest variance
211 was $\pm 1 \text{ ‰}$, but more typically was $\pm 0.3 \text{ ‰}$.

212 **Results**

213 The coatings in the Rouyn-Noranda area vary in colour from reddish-brown to black (Fig. 2a).
214 Coatings can be distributed in a uniform or non-uniform manner on outcrops and are observed up to a
215 maximum of 6 km from the Horne smelter. Pillow basalts (sample RN16) and felsic volcanoclastics
216 show non-uniform coating distribution due to their heterogeneous texture or composition. The ash
217 matrix of the latter rocks is coated by a thicker, darker coloured homogeneous coating with lower relief,
218 whereas coarser grained felsic angular clasts have greyish non-uniform thin coatings with a higher relief
219 (Fig. 2b). Fractures in outcrops generally have thicker, darker coatings relative to the entire outcrop (Fig.
220 2b). Coatings, visible to a maximum of approx. 6 km from the Horne Smelter, become very thin and
221 diverse on outcrops at greater distances.

222 The coatings often have a greyish to black coloured layer in reflected light microscopy (Fig. 2c),
223 with sharp visible contacts at the interface with the underlying rock. They have bright white embedded
224 particles which are anhedral angular-to-spherical in nature. Porous regions of the coatings contain
225 abundant particulate matter embedded in a greyish-white translucent silica matrix.

226 **Morphological and Chemical Features of Black Rock Coatings**

227 Collectively, mafic rocks are coated with thicker silica-rich layers than felsic rocks (Figs. 2d-i).
228 The mafic rocks sampled include basalts (sample RN16), gabbros (sample RN19) and meta-basalts
229 (sample RN20) that occur east, south, and south-southwest from the smelter, respectively (black dots in
230 Fig. 1).

Coatings on mafic rocks are on average 30 μm thick, contain metal-sulfate rich layers along the rock-coating interface (RCI) (Fig. 2g) and atmosphere-coating interface (ACI) (Fig. 2h), and contain anhedral embedded spheres, particulates and detrital particles (Figs. 2d-h). Metal-sulfate rich layers located on the RCI are enriched in elements such as Fe, As, Sn, Pb, S, Cu, Zn, and occasionally in K relative to the silica-rich layer and underlying rock, and contain sulfate particles that are $<1\ \mu\text{m}$ in size.

Coatings on a felsic lapilli-tuff contain a metal-sulfate rich layer located along the ACI (Figs. 2i and 3) which ranges in thickness from 5 μm to 20 μm (Fig. 2i) and contain a large number of multi-sourced particulates (Fig. 2i). For example, spherical particulates up to 70 μm in diameter (approximately 10 times larger than the surrounding coating), are embedded within silica-rich layers in the coatings (Fig. 3f-h) on a felsic lapilli-tuff sampled at location RN11 (NNW of the Horne smelter, pink dot in Fig. 1).

Mineralogical Composition of Coatings

All coatings are composed of a silica-rich matrix that contains a large variety of embedded particles (Fig. 2e). Scanning electron microscopy and XRD analyses suggest the presence of detrital quartz, muscovite ($(\text{KAl}_2(\text{AlSi}_3\text{O}_{10})(\text{OH})_2)$), clinocllore ($(\text{Mg, Fe})_6(\text{Si, Al})_4\text{O}_{10}(\text{OH})_8$), Ca-Mg-Fe-Al amphiboles (Fig. 2i), and Na-rich feldspars. Sulfate minerals such as jarosite ($\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$), plumbojarosite ($\text{PbFe}_6(\text{SO}_4)_4(\text{OH})_{12}$), and minerals of the alunite group, presumably the Pb- sulfate end members hinsdalite – hidalgoite, $(\text{Pb}(\text{Fe}^{3+})_3(\text{SO}_4)_2(\text{OH})_6$, and $\text{Pb}(\text{Al})_3(\text{SO}_4)_2(\text{OH})_6$, are common in the metal-sulfate rich layer(s).

Spherical Fe - Cu and Fe - Zn particulate matter is also present in the coatings, with Cu : Fe and Zn : Fe ratios of 1 : 3 and 2 : 3, respectively. Spherical Pb-silicates with Pb : Si ratios of 1 : 1, point towards the presence of alamosite (PbSiO_3) (Fig. 2i) and angular Fe-rich particles with up to 11 wt% Cr suggest the presence of Fe-(hydr)oxides such as hematite or goethite.

Elemental Distributions and Sulfur Isotopes on the Local Scale

The examination of metal(loid)s on the local scale help to determine the anthropogenic impact of industrial sources in an area and the variations in sulfur isotope values can be used as a tool to define associated atmospheric processes (Nriagu and Glooschenko 1992; Knight and Henderson 2006; Mantha et al. 2012a; Schindler et al. 2012).

Inspection of the element distribution of selected elements in the Rouyn-Noranda area indicates that metal(loid)s such as Cu, As, and Hg have higher concentrations in the coatings towards the NNW and lower concentrations in the southern localities (Fig. 4). Highest concentrations exceed 1 wt%, 0.5 wt%, and 0.7 ppm for Cu, As and Hg, respectively (Fig. 4a-c). In contrast, higher concentrations of Zn occur in coatings of the northernmost regions of the study area (Fig. 4d) and can exceed 0.5 wt%. The $\delta^{34}\text{S}$ values show a similar trend as the aforementioned metal(loid)s with higher (+5.5 to +4.3 ‰) and lower (< 3.9 ‰) values being concentrated in the NNW and the south, respectively (Fig. 4e).

Discussion

The results highlighted above show that the textural relationships, chemical distribution of elements, and sulfur isotope compositions of black rock coatings in the Rouyn-Noranda area are strongly variable with lithology, and wind direction. Hence, the formation mechanism of the coatings will be discussed before addressing the origin of the particulate matter and the common association of elements in the coatings. The change in the sulfur isotope ratio with distance will be subsequently discussed in terms of the mixing or fractionation of S-components in the atmosphere.

Model for the Formation of Black Rock Coatings

Black rock coatings in the Rouyn-Noranda region share many similarities with black rock coatings in Sudbury, ON. For example, in both locations they contain silica-rich as well as metal-sulfate rich layers on felsic and mafic rocks located along the ACI. Basalts in Noranda and the Sudbury area have metal-sulfate rich layers along the RCI. Coatings in both regions contain embedded detrital

particles, spherical particulates and various metal-sulfates. They also contain Cu-bearing spinels, Fe-(hydr)oxides, metal-sulfate rich minerals, Pb-sulfates as well as detrital particles such as phyllosilicates, amphiboles, pyroxenes, and feldspars. Both studies show that the thickness of coatings is not only dependent on the distance from the point source, but also on the lithological composition of the rock. For example, basalts in the Rouyn-Noranda region at a distance of 3.9 km from the smelter have coatings thicker than those observed on monolithic felsic lapilli tuffs 1.2 km from the smelter (Mantha et al. 2012a; Mantha et al. 2012b; Schindler et al. 2012).

These observations suggest that the rock coatings of the Rouyn-Noranda area formed by a similar mechanism as the coatings in the Greater Sudbury area (Mantha et al. 2012a and b; Schindler et al. 2012). The vast amount of sulfur dioxide and sulfuric acid emissions from the Horne smelter created acidic fumigations associated with the onset of mining activities in the region (Savard et al. 2004; Alpay et al. 2006; Mayer et al. 2007). Interaction between acidic meteoric water and exposed bedrock in the region promoted the intense chemical weathering and the dissolution of silicate minerals resulting in the release of silicic and sulfuric acid (H_4SiO_4 , H_2SO_4), alkali and alkaline earth elements (Na, K, Ca, Mg), Fe and Al, and the formation of a silica gel-type layer (Fig. 2e). Mantha et al. (2012a) found that similar rock coatings in the Sudbury, ON region are composed mainly of a matrix of amorphous silica containing the silica modifications Opal-C, Opal-CT, and localised ordered cristobalite on the nanometer scale. The non-stoichiometric dissolution of the underlying rocks and formation of a silica gel-type layer explains the thicker coatings on mafic rocks as for example, minerals in basalts on average have a higher solubility than their counterparts in felsic rocks such as lapilli-tuffs (Mantha et al. 2012a; Schindler et al. 2012).

Particulate matter was likely the source for Cu, As, Zn, Pb and Fe as these elements occur mainly in and around spherical particulates in the coating (Fig. 2d-i and 3). The partial or complete dissolution

of these metal(loid) bearing phases (sulfates and oxides) results in metal(loid)-rich solutions and thus in the *in situ* formation of minerals of the jarosite group, concentrated in metal-sulfate rich layers along the ACI and/or RCI. Sources of sulfur in the coatings are mainly derived from sulfuric acid and SO₄-bearing particulates, as sulfide minerals are observed only in minute concentrations in the sampled rocks of the Rouyn-Noranda area (<3 modal percent) and therefore had little to no effect on the formation of metal-sulfate rich layers. The sharp boundaries observed between the silica-rich layers and underlying rock suggest that the coatings, similar to those in Sudbury, formed due to an evaporation-dissolution-precipitation process (Hellman et al. 2003; Mantha et al. 2012a; Schindler et al. 2012).

Dorn (2012) proposes a hierarchy for the formation of rock coatings. First order controls are explained by the exposure of barren rock due to natural geomorphic processes. Second order controls are the exposure of subsurface coatings due to erosional processes of the overlying material. Lithobionts acting as a catalyst for coating formation are the factor contributing to third order control and coating formation controlled by a positive mass balance of elements transported to accretion sites define fourth order processes. Fifth order controls are due to inhibition of elemental transport caused by physical, chemical and biological barriers which in turn cause the accretion of rock coatings on surfaces.

According to Dorn's Hierarchy scale, black rock coatings of the Rouyn-Noranda region appear to be first and fourth order controlled (Dorn 2012). First order controls are explained by the urbanization and industrialization of the region, following the regional logging after the opening of the Horne mine (Telmer et al. 2004; Savard et al. 2004; Dorn 2012). The combined smelting and forestry operations led to exposed bedrock in the region that created uncovered surfaces for acid fumigation-rock interactions. Fourth order processes include higher H₂SO₄ (in the form of aerosols emitted from the smelter, and the oxidation of SO_{2(g)} to SO₄²⁻ via gas-phase (homogenous) or aqueous phase (heterogeneous) oxidation processes, see Mantha et al. (2012b) and references therein) and particulate matter emissions causing a

positive mass balance of elements deposited in the environment. The lack of visible black rock coatings at distances greater than approx. 6 km from the smelter suggests that the amount of metal-bearing particulates and H₂SO₄ emissions deposited were insufficient for black coating formation at greater distances. The fact that elevated atmospheric sulfate concentrations have been detected beyond 6 km from the Horne smelter (Mayer et al. 2007) suggests that the deposition of metal-bearing particulate matter is the controlling factor in the formation of the black rock coatings. Colourless silica coatings formed during the interaction of acidic wetting events on exposed bedrock may have been formed at further distances but were not visible due to the lack of encapsulated particulate matter.

Origin and Mineralogy of Particles in the Coatings

Smelter derived particulates consist mainly of Fe-oxides (Fig. 3f), Cu- and Zn-bearing Fe-oxides, and Pb-silicates. Spherical particulates are indicative of high temperature processes such as smelting operations (Henderson and Knight 2005; Lanteigne et al. 2012). The lack of alteration features on the surface of micrometer-sized particulates suggests minimum interaction between larger spherical particulates and pore solutions within the coatings. These observations are in agreement with studies by Mantha et al. (2012a) who showed the presence of preserved particulates in the coatings of the Sudbury area. The particulates can contain rims enriched in metal(loid)s such as Zn (Fig. 3h) that form due to the collision of dust particles and molten droplets at temperatures around 1000 °C (Connolly and Hewins 1995; Lanteigne et al. 2014). Henderson and Knight (2005), Knight and Henderson (2006) and Lanteigne et al. (2014) showed that high temperature smelter emitted particulates are composed of spinel minerals such as magnetite, cuprospinel, Cu-bearing spinels, trevorite, and other high temperature phases i.e. Fe-silicates such as olivine and pyroxenes and are found in acid soils and humus around the smelting sites of Sudbury, ON and Rouyn-Noranda, QC.

Lead occurs in the form of finer (2 μm diameter) spherical particulates, as well as spherical Pb-silicates such as alamosite (PbSiO_3) (Fig. 2i). The latter phase as well as minerals of the spinel group commonly forms in high temperature environments (660°C) (Smart and Glasser 1974) that occur in the smelter at Rouyn-Noranda when gases leave the reactors at 1260°C and subsequently cool to approximately 650°C in 0.5s (Safe and Jones 1998). Lead sulfates are present in black rock coatings in all studied lithologies, and appear to be compositionally similar to anglesite (PbSO_4). In this regard, Vítková et al. (2009) showed that anglesite forms under acidic conditions as a secondary product from the emissions of a Pb smelter in Příbram, Czech Republic. Lead-Al-sulfate end members of the alunite group, hidalgoite-hinsdalite ($\text{Pb}(\text{Fe},\text{Al})_3(\text{SO}_4)(\text{OH})_6$) are also observed in this study, in accord with their occurrence in acid mine tailings in Mexico (Méndez and Armienta 2003) and the acidic conditions required to form the black coating in the Rouyn Noranda region.

Minerals such as Ca-Mg-Fe-Al amphiboles, clinochlore, and Na-rich feldspars most likely originated from the chemical weathering of the underlying rock and adjacent soils containing a signature of the underlying lithologies or glacially deposited sediments.

Occurrence of Metal(loid)s within the Coatings

Correlations between the concentrations of Pb vs. As, Pb vs. Se, As vs. Ag, Pb vs. Ag, and Cu vs. As (Fig. 5a-f) can be attributed to their common occurrence in mineral phases in the coatings and are in accord with chemical distribution maps indicating the close association of these elements in the coatings (e.g., Fig. 3b and c). Correlations and close associations of for example Pb, As, Cu and Ag can be accredited to their common occurrence in minerals of the jarosite group ($\text{DM}_3(\text{TO}_4)_2(\text{OH},\text{H}_2\text{O})_6$).

Lead and Ag both substitute for cations on the *D* site in the jarosite structure, Cu can be incorporated at the *M* site and As substitutes for S on the *T* site in the jarosite structure (Dutrizac and Jambor 2000). Although minute concentrations of Hg^{2+} can substitute on the *D* site in jarosite group

minerals (Dutrizac and Chen 1981), the absence of correlations between Hg and Ag ($R^2 = 0.006$) and Hg and Pb ($R^2 = 0.020$) indicate that the former element occurs in distinct phases within the metal-sulfate rich layer.

Two different linear trends observed for Cu and Zn (Fig. 5c) suggest that these elements are incorporated in at least two different phases. This conclusion is in accord with the distribution maps that show that Cu and Zn generally occur in separate phases within the metal-sulfate rich layer (Figs. 3d, e, g and h). Copper appears more homogeneously distributed in the coatings relative to Zn (Fig. 3d), whereas the latter element appears to be concentrated within the particulates (Fig. 3e). Both elements are also concentrated in the particulates within the coating, but do not occur within the same grains: Zn occurs in the rim around smelter particulates (Fig. 3h), whereas Cu is concentrated within the coating surrounding the spherical particulates (Fig. 3g). These observations indicate that both elements can be associated with the same phases (minerals of the jarosite and spinel groups) but are not necessarily concentrated in the same particles.

The Smelter-compatibility Effect

A study by the Ontario Ministry of the Environment (2000) shows that the deposition of metals emitted from an industrial point source is lower on the leeward and higher in the windward side of the source, explaining the higher abundance of metal(loid)s in coatings on the windward side of the stack. The shadow effect of the smelter can be shown by grouping sampling sites with similar distances to the smelter, then averaging the concentrations of the elements in the coatings of each group, and associated distances from the Horne smelter. A plot of the mean distances versus the average concentrations of the assigned groups (Fig. 6) indicate lower average concentrations of the selected elements adjacent to the smelter, an increase in concentrations around 1.5 to 2 km and a subsequent decrease with distance from the stack (this trend is highlighted with the solid line in Fig. 6).

392 The initial low deposition of elements can be explained by the height of the smelter stack which
393 limits the deposition of particulates adjacent to the smelter. The increase in the absolute concentrations
394 of metal(loid)s around 2 km from the smelter is the result of precipitation events and the gravitational
395 settling of larger particulates (Fig. 6). However, the relative increase in metal(loid) concentrations in the
396 coatings around 2 km relative to areas adjacent to the smelter is controlled by the crystal chemical
397 compatibility of the corresponding metal(loid)s with the respective mineral phases in the coatings, i.e.
398 elements with a high compatibility towards the jarosite and spinel structure should show stronger
399 enrichments in the coatings relative to elements that can only be incorporated in trace concentrations.
400 Hence, the distribution and absolute concentration of an element should be affected by the smelter
401 shadow effect as well as by its compatibility towards the minerals formed or embedded in the coatings.
402 This smelter-compatibility effect may be calculated using the following formula:

403 (2) Smelter-compatibility Effect = $\left(\frac{\Delta_{\text{highest and lowest concentrations adjacent to the smelter}}}{\text{highest concentration}} \right) \times 100\%$

404 The highest smelter-compatibility effect is represented by Ag, Se, and Cu as a consequence of
405 their high compatibility with the jarosite and spinel structures (Fig. 6a-c) (Dutrizac and Jambor 2000).
406 Arsenic and Zn, Cd, Cr, Pb, Ti and S also show strong smelter-compatibility effects, whereas Sn and Fe
407 show moderate effects (see table A2 in supplementary data). Elements that show the lowest smelter-
408 compatibility effect are elements that occur naturally in relatively high abundances in the geosphere,
409 with the notable exception of Hg due to its low compatibility with the jarosite structure (Dutrizac and
410 Jambor 2000). The smelter compatibility effect for elements measured with LA-ICP-MS in this study
411 decreases in the sequence of Ag>Se=Cu>As>Zn>Cd>Cr>Pb>Ti>S>Sn>Fe>K>Al>Hg>Na>Si.

412 **Comparison to Coatings in other Smelter Impacted Areas and Ore Deposit Type**

413 The results in this study and of Mantha et al. (2012a) show that the coatings in the Rouyn-
414 Noranda and Sudbury areas are mineralogical fingerprints that allow the deduction of smelter processes

415 due to the occurrence of spherical high-T phases such as spinels. Hence the coatings of both areas
416 should show distinct features in their mineralogy and their major and trace element composition as they
417 are formed from the smelting of two distinct geological ore deposit types: the VMS complex in Rouyn-
418 Noranda, QC and the Sudbury Igneous Complex (SIC) in Sudbury ON. Mineralization in the Rouyn-
419 Noranda region is characterized by Au-Cu-Ag $\pm$ Zn rich ore hosted as chalcopyrite, pyrrhotite,
420 sphalerite, galena, native gold and silver (Kerr and Gibson 1993). The SIC is composed of Cu-Ni-PGE
421 mineralization, primarily chalcopyrite, pyrrhotite, pentlandite, pyrite, and millerite (Hawley and Stanton
422 1962; Lightfoot and Farrow 2002).

423 If the ore type is considered to be a primary control on the character of the coatings, the
424 mineralogy and chemistry of the particulate matter should reflect the primary ore mineralogy and
425 chemistry, and thus the smelter emissions. For example, the presence and absence of Ni and Zn bearing
426 particulates in the Sudbury and Rouyn regions, respectively (indicated by Ni and Zn being below
427 detection limits in EDS), suggests that embedded particulate matter in coatings is a mineralogical
428 fingerprint for ore smelted in the region.

429 Furthermore, the Fe concentrations in the coatings of the Sudbury area are consistently higher
430 (>10 wt%) than in Rouyn-Noranda (<7 wt% Fe) and may be due to the higher abundances of Fe in the
431 rocks of the SIC relative to Noranda (Leshner et al. 1986; Lightfoot et al. 1997), and the quantity of
432 smelter emissions in the two areas. For example, the total quantity of particulates emitted within a 28
433 day period in Sudbury in 1971 was around 1218.6 tons, whereas for the entire year in Noranda total
434 metals emitted were only estimated at 5850 tons (Savard et al. 2004; Mantha et al. 2012a).

435 The enrichment and depletion of elements in the coatings in Rouyn Noranda relative to those in
436 Sudbury may be visualized in an elemental plot with the average concentrations of selected elements
437 normalised to MUd from Queensland, Australia (MUQ). MUQ is used as a proxy for the average

composition of the young continental crust derived from alluvial sediments from Queensland, Australia (Kamber et al. 2005). This plot indicates that the coatings in Sudbury are depleted in Cu and Pb relative to those in Rouyn-Noranda (Fig. 7). The depletion in Pb in the Sudbury coatings likely reflects lower proportions of galena in the SIC relative to a typical VMS deposit consisting of chalcopyrite, sphalerite and galena (Hawley and Stanton 1962; Lightfoot and Farrow 2002; Gibson and Kerr 1993). The enrichments of Pb relative to Cu and Zn in Noranda (Fig. 7) is the result of the higher emissions of Pb relative to the latter elements (Telmer et al. 2006) and suggests that the composition of the coatings is also controlled by the proportions of the emitted elements in the smelter plume .

Mixing Between Primary and Secondary Sulfates

Sulfur isotopes are excellent indicators of the presence of anthropogenic contaminants in the environment (Derda et al. 2006). The $\delta^{34}\text{S}$ values in the rock coatings in the Rouyn-Noranda region vary between +3.6 to +5.5 ‰, with an inverse relationship with distance (Fig. 8a) that can be assigned to the mixing between primary and secondary sulfates, similar to the coatings of the Sudbury, ON region.

Fractionation of Sulfur Isotopes during Oxidation

Variations in the $\delta^{34}\text{S}$ values either through fractionation or mixing can be understood if the presence of primary and secondary sulfates is considered. Primary sulfates are initially emitted from the stack during the smelting operations, whereas secondary sulfates form due to the oxidation of $\text{SO}_{2(g)}$. Previous studies showed that primary sulfate species emitted by the major smelter in the Sudbury area are characterized by higher $\delta^{34}\text{S}$ values (Lusis and Wiebe 1976) than emitted SO_2 with $\delta^{34}\text{S}$ values similar to the local ore (Nriagu and Coker 1978, for detail see Mantha et al. 2012b). The corresponding fractionation of S likely occurred during the partial oxidation of SO_2 to $(\text{SO}_4)^{2-}$ at high T during the smelting and refining processes of the local ore, but has not been explored in greater detail to our knowledge. Two types of oxidation processes of SO_2 occur in the atmosphere at lower T: the

homogeneous oxidation in the gas phases and the heterogeneous oxidation facilitated by water or particulate matter. Details on the fractionation factors and processes occurring during oxidation can be found in Eriksen (1971a), Eriksen (1971b), Tanaka et al. (1994), Harris et al. (2011), and Mantha et al. (2012b).

Estimates of the $\delta^{34}\text{S}$ values for the primary sulfates emitted by the Horne smelter are possible using $\delta^{34}\text{S}$ values in the coating most proximal to the smelter (sample number RN11). Mantha et al. (2012b) showed that the $\delta^{34}\text{S}$ values were similar for primary sulfates in the plume and the black rock coatings proximal to the smelter at Copper Cliff in Sudbury. By assuming a similar relationship for Rouyn, the sulfur isotopic composition of the primary sulfates in the Horne smelter plume is assumed to be identical to the $\delta^{34}\text{S} = 5\text{‰}$ measured for the coatings closest to the smelter (RN11). If there is no fractionation during oxidation, the secondary sulfates have the same $\delta^{34}\text{S}$ value as the emitted $\text{SO}_{2(\text{g})}$ from the smelter plume and of the local ore. Ryznar et al. (1967) measured the $\delta^{34}\text{S}$ isotopic values of the Quemont ore body to range between 0 and +1.8 ‰. The Horne deposit $\delta^{34}\text{S}$ values for massive ore is between -0.1 to +1.9 ‰, typical of Archean massive sulfides (Maclean and Hoy 1991). An average value of +0.95 ‰ for $\delta^{34}\text{S}$ for the Quemont ore body was calculated using data from Ryznar et al. (1967).

Fig. 8a and b display data from three separately conducted studies; the $\delta^{34}\text{S}$ values from black rock coatings (Fig. 8a and b), the moss, *Sphagnum* sp., from Rouyn-Noranda (Fig. 8b) and the $\delta^{34}\text{S}$ values from rock coatings in the Sudbury area (Fig. 8b). Mosses are extremely sensitive to sulfur oxide species (SO_x) and have been used to determine the effect of industrial sources on the surrounding environment (Nriagu and Glooschenko 1992). The $\delta^{34}\text{S}$ values in mosses in the Noranda region (collected from 20 to 33 km from the Horne smelter) range from +1.1 to +1.4 ‰ (Nriagu and Glooschenko 1992). Of significance, the $\delta^{34}\text{S}$ values in mosses, even though they may be affected by

reductive processes in the saturated wetlands, are similar in magnitude to the lowest $\delta^{34}\text{S}$ values measured in the black rock coatings in Rouyn-Noranda area. The combined sulfur-isotope plot indicates a reasonable agreement between the three studies, as they all fall along the same trajectory.

This agreement suggest that an increase in secondary sulfates ($\delta^{34}\text{S} = 0.95\text{ ‰}$) with increasing distance from the smelter, and decreasing abundance of primary sulfates having $\delta^{34}\text{S}$ values near 5 ‰ (Fig. 8a) could account for the net decrease in $\delta^{34}\text{S}$ values observed in the coatings and mosses in Rouyn-Noranda QC, and the Greater Sudbury areas (Mantha et al. 2012b; Schindler et al. 2012). It is our opinion that sulfur isotope fractionation in the smelter plumes of the Sudbury and Rouyn-Noranda area was minimal and that the mixing of primary and secondary metal-bearing sulfates aerosols are the dominant atmospheric processes occurring in proximity to $\text{SO}_2/\text{H}_2\text{SO}_4$ point source emitters.

Conclusion

The black rock coatings of the Rouyn-Noranda area are composed of silica rich layers, with or without the presence of metal-sulfate rich layers located along the atmosphere-coating interface and rock-coating interface (for mafic rocks). The sulfuric acid emissions from the Horne smelter caused the formation of a silica gel type layer allowing the entrapment of particulate matter and detrital particles from the underlying lithology and the local environment. The acidic environment and porosity of the gel promoted the dissolution-evaporation-reprecipitation of metal-sulfates within the coatings. The dehydration of the silica gel acts as a 'safe casing' for embedded and secondary particles, thus preserving them in the coating. These embedded particles can subsequently be used as fingerprints for pollutants emitted between 1927 and 1975.

The coatings preserved information on the speciation of elements in the plume (Cu- or Zn-bearing Fe spinels, Pb-silicates), products of interfacial crystallization processes (minerals from the jarosite group, Pb-Al sulfates of the alunite group (hinsdalite-hidalgoite), Pb-sulfates, Fe-(hydr)oxides

with or without the presence of Cr) and minerals from the surrounding lithologies (K-micas, Na-feldspars, and amphiboles). This study also concluded that the behaviour of Ag, As, Se, Cu and Zn in the plume and their resultant accumulation in the coatings is controlled by a smelter compatibility effect which is affected by 1) the height of the smelter stack, 2) the crystal chemical compatibility of elements with Fe-sulfate phases (such as jarosite group minerals) and spinel minerals and 3) depositional trends due to gravitational settling and wetting events causing the deposition of particulates. This study is in agreement with those conducted by Mantha et al. (2012a), Mantha et al. (2012b) and Schindler et al. (2012) with respect to coating morphology, chemical composition and the preservation of the mixing of primary- and secondary-sulfates in the smelter plume. Normalised elemental plots indicate that the coatings in Rouyn-Noranda and Sudbury can reflect the proportions of elements in the smelter plume as well as their general abundance in the ore and can be thus used as mineralogical and chemical fingerprint of both the local ore and smelter emissions.

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References

- Alpay, S., Veillette, J.J., Dixit, A.S., and Dixit, S.S. 2006. Regional and historical distributions of lake-water pH within a 100-km radius of the Horne smelter in Rouyn-Noranda, Québec, Canada. *Geochemistry: Exploration, Environment, Analysis*, **6**: 179-186.
- Barrett, T.J., MacLean, W.H., Cattalani, S., Hoy, L., and Riverin, G. 1991. Massive sulfide deposits of the Noranda area, Quebec. III. The Ansil mine. *Canadian Journal of Earth Science*, **28(11)**: 1699-1730.
- Buzek, F., and Sramek, J. 1985. Sulphur isotopes in the study of stone monument conservation. *Studies in Conservation*, **30(4)**: 171-176.
- Broecker, W.S., and Liu, T. 2001. Rock Varnish: Recorder of Desert Wetness?. *GSA Today*, **11(8)**: 4-10.
- Connolly Jr, H.C., and Hewins, R.H. 1995. Chondrules as products of dust collisions with totally molten droplets within a dust-rich nebular environment: an experimental investigation. *Geochimica et Cosmochimica Acta*, **59(15)**: 3231-3246.
- Derda, M., Chmielewski, A.G., Licki, J. 2006. Stable Isotopes of Sulphur in Investigating Pollution Sources. *Environment Protection Engineering*, **32(3)**: 63-68.
- Dickerson, R. 2011. Desert varnish - nature's smallest sedimentary formation. *Geology Today*, **27(6)**: 216-219.
- Dietzel, M., Kolmer, H., Pölt, P., and Simic, S. 2008. Desert varnish and petroglyphs on sandstone - Geochemical composition and climate changes from Pleistocene to Holocene (Libya). *Chemie der Erde*, **68**: 31-43.
- Dorn, R.I. 2012. Weathering and Soils Geomorphology: Rock Coatings. *In Treatise on Geomorphology. Edited by J, Shroder., Jr, G.A, Pope. Academic Press, San Diego, CA. pp. 70-97.*
- Dorn, R. I., and Oberlander, T. M. 1982. Rock Varnish. *Progress in Physical Geography* **6**: 317-36
- Durocher, J.L., and Schindler, M. 2011. Iron-hydroxide, Iron-sulfate and hydrous-silica coatings in acid-mine tailings facilities: A comparative study of their trace-element composition. *Applied Geochemistry*, **26**: 1337-1352.
- Dutrizac, J., and Chen, T.T. 1981. The synthesis of mercury jarosite and the mercury concentration in jarosite-family minerals. *Canadian Mineralogist*, **19**: 559-569.
- Dutrizac, J., and Jambor, J.L. 2000. Jarosites and Their Applications in Hydrometallurgy Reviews in Mineralogy and Geochemistry, **40(1)**: 405-452.
- Eriksen, T.E. 1927a. Sulfur isotope-effects I. Isotopic-exchange coefficient for sulfur isotopes ^{34}S - ^{32}S in the system $\text{SO}_{2\text{g}}$ - HSO_3^- aq at 25, 35 and 45 degrees C *Acta Chemica Scandinavica*, **26**: 573-580.

- 554 Eriksen, T.E. 1927b. Sulfur isotope-effects II. Isotopic-exchange coefficient for sulfur isotopes ^{34}S - ^{32}S in the system SO_2 -
555 aqueous solutions of SO_2 *Acta Chemica Scandinavica*, **26**: 573-580.
- 556 Gibson, H. L., Kerr, D. J., and Cattalani, S. 2000. The Horne Mine: Geology, History, Influence on Genetic Models, and a
557 Comparison to the Kidd Creek Mine. *Exploration Mining Geology*, **9(2)**: 91-111.
- 558 Hawley, J.E., and Stanton, R.L. 1962. The Facts: The Ores, Their Minerals, Metals and Distribution. *Canadian Mineralogist*,
559 **7(1)**: 30-145.
- 560 Henderson, P.J., and Knight, R.D. 2005. Regional distribution and mobility of copper and lead in soils near the Horne copper
561 smelter at Rouyn-Noranda, Quebec. *Geological Survey of Canada. Bulletin No.* **584**
- 562 Hellmann, R., Penisson, J.M., Hervig, R.L., Thomassin, J.H., and Abrioux, M.F. 2003. An EFTEM/HRTEM high-resolution
563 study of the near surface of labradolite feldspar altered at acid pH: evidence for interfacial dissolution-reprecipitation. *Physics*
564 *and Chemistry of Minerals*, **30**: 192-197.
- 565 Harris, E., Sinha, B., Hoppe, P., Crowley, J.N., Ono, S., and Foley, S. 2012. Sulphur isotope fractionation during oxidation of
566 sulphur dioxide: gas-phase oxidation by OH radicals and aqueous oxidation by H_2O_2 , O_3 and iron catalysis. *Atmospheric*
567 *Chemistry and Physics*, **12**: 407-424.
- 568 Hoar, K., Nowinski, P., Hodge, V., and Cizdziel, J. 2010. Rock Varnish: A Passive Forensic Tool for Monitoring Recent Air
569 Pollution and Source Identification. *Environmental Effects of Nuclear Technology*, **175**: 351-359.
- 570 Kamber, B.S., Greig, A., and Collerson, K.D. 2004. A new estimate for the composition of weathered young upper
571 continental crust from alluvial sediments, Queensland, Australia. *Geochimica et Cosmochimica Acta*, **69(4)**: 1041-1058.
- 572 Kerr, D. J., and Gibson, H. L. 1993. A Comparison of the Horne Volcanogenic Massive Sulfide Deposit and Intracauldron
573 Deposits of the Mine Sequence, Noranda, Quebec. *Economic Geology*, **88(6)**: 1419-1442.
- 574 Kettles, I.M., and Bonham-Carter, G.F., 2002. Modelling dispersal of metals from a copper smelter at Rouyn-Noranda
575 (Québec, Canada) using peatland data. *Geochemistry: Exploration, Environment, Analysis*, **2**: 99-110.
- 576 Krinsley, D., Ditto, J., Langworthy, K., Dorn, R.I., and Thompson, T., 2013. Varnish microlaminations: new insights from
577 focused ion beam preparation. *Physical Geography*, **34(3)**: 159-173.
- 578 Krinsley, D., Dorn, R.I., DiGregorio, B.E., Langworthy, K.A., and Ditto, J. 2012. Rock Varnish in New York: An accelerated
579 snapshot of accretionary processes. *Geomorphology*, **138**: 339-351.
- 580 Knight, R.D., and Henderson, P.J. 2006. Smelter dust in humus around Rouyn-Noranda, Québec *Geochemistry: Exploration*,
581 *Environment, Analysis*, **6**: 203-214.

- 582 Lanteigne, S., Schindler, M., McDonald, A. 2014. Distribution of Metals and Metalloids in Smelter-derived Particulate
 583 Matter in Soils and Mineralogical Insights to their Retention and Release in a Low T-environment. *The Canadian*
 584 *Mineralogist*, **52(3)**: 453-471.
- 585 Lanteigne, S., Schindler, M., McDonald, A., Skeries, K., Abdu, A., Mantha, N.M., Murayama, M., Hawthorne, F., Hochella,
 586 M.F Jr. 2012. Mineralogy and Weathering of Smelter-Derived Spherical Particles in Soils: Implications for the Mobility of
 587 Ni and Cu in the Surficial Environment. *Water, Air, Soil, Pollution*, **223(7)**: 3619-3641.
- 588 Leshner, C.M., Goodwin, A.M., Campbell, I.H., and Gorton, M.P. 1986. Trace-element geochemistry of ore-associated and
 589 barren, felsic metavolcanic rocks in the Superior Province, Canada. *Canadian Journal of Earth Science*, **23**: 222-237
- 590 Liu, T., and Broecker, W.S. 2007. Holocene rock varnish microstratigraphy and its chronometric application in the drylands
 591 of western USA *Geomorphology*, **84**: 1-21.
- 592 Lightfoot, P., and Farrow, C.E.G. 2002. Geology, Geochemistry, and Mineralogy of the Worthington Offset Dike: A Genetic
 593 Model for Offset Dike Mineralization in the Sudbury Igneous Complex. *Economic Geology*, **97**: 1419-1446.
- 594 Lightfoot, P.C., Keays, R.R., Morrison, G.G., Bite, A., and Farrell, K.P. 1997. Geochemical Relationships in the Sudbury
 595 Igneous Complex: Origin of the Main Mass and Offset Dykes. *Economic Geology*, **92**: 289-307.
- 596 Lusis, M.A. and Wiebe, H.A. 1976. The rate of oxidation of sulfur dioxide in the plume of a nickel smelter stack.
 597 *Atmospheric Environment*, **10**: 793-798.
- 598 Maclean, W.H., and Hoy, L.D. 1991. Geochemistry of Hydrothermally Altered Rocks at the Horne Mine, Noranda, Quebec.
 599 *Economic Geology*, **86**: 506-528.
- 600 Mantha, N. M., Schindler, M., Murayama, M., and Hochella Jr, M. F. 2012a. Silica- and sulphate-bearing rock coatings in
 601 smelter areas: Products of chemical weathering and atmospheric pollution I. Formation and mineralogical composition.
 602 *Geochimica et Cosmochimica Acta*, **85**: 254-274.
- 603 Mantha, N. M., Schindler, M., and Kyser, K. T. 2012b. Silica- and sulphate-bearing rock coatings in smelter areas: Part II.
 604 Forensic tools for atmospheric metal(loid)- and sulphur-isotope compositions. *Geochimica et Cosmochimica Acta*, **90**: 221-
 605 241.
- 606 Mašalaitė, A., Garbaras, A., and Remeikis, V. 2012. Stable Isotopes in Environmental Investigations. *Lithuanian Journal of*
 607 *Physics*, **52(3)**: 261-268
- 608 Mayer, B., Alpay, S., Gould, W.D., Lortie, L., and Rosa, F. 2007. The onset of anthropogenic activity recorded in lake
 609 sediments in the vicinity of the Horne smelter in Quebec, Canada: sulphur isotope evidence. *Applied Geochemistry*, **22**: 397-

- 610 414
- 611 Méndez, M., and Armienta, M.A. 2003. Arsenic phase distribution in Zimapan mine tailings, Mexico. *Geofísica*
- 612 *Internacional*, **42(1)**: 131-140.
- 613 Nriagu, J.O. and Coker, R.D. 1978. Isotopic composition of sulphur in atmospheric precipitation around Sudbury, Ontario.
- 614 *Nature*, **274**: 883-885.
- 615 Nriagu, J.O., and Glooschenko, W.A. 1992. Isotopic Composition of Sulphur in Mosses across Canada. *Environmental*
- 616 *Science and Technology*, **26**: 85-89.
- 617 Ryznar, G., Campbell, F.A., and Krouse, H.R. 1967. Sulfur isotopes and the origin of the Quemont ore body. *Economic*
- 618 *Geology*, **62**: 664-678.
- 619 Safe, P., and Jones, D.M. 1998. Process off-gas cooling design considerations for non-ferrous metallurgical processes.
- 620 Sulfide Smelting '98, TMS Annual Meeting, San Antonio Texas, February 16-19, 1998, pp. 401-415
- 621 Sánchez, S.J., Alves, C.A.S., Vidal Romani, J.R., Fernández Mosquera, D. 2009. Origin of Gypsum-rich Coatings on Historic
- 622 Buildings. *Water Air and Soil Pollution*, **204**: 53-68.
- 623 Savard, M. M., Bégin, C., Parent, M., Smirnov, A., and Marion, J. 2004. Effects of Smelter Sulphur Dioxide Emissions: A
- 624 Spatiotemporal Perspective Using Carbon Isotopes in Tree Rings. *Journal of Environmental Quality*, **33(1)**: 13-26.
- 625 Schindler, M., Fayek, M., and Hawthorne, F.C. 2010. Uranium-rich opal from the Nopal 1 uranium deposit, Peña Blanca,
- 626 Mexico: Evidence for the uptake and retardation of radionuclides. *Geochimica et Cosmochimica Acta*, **74(1)**: 187-202
- 627 Schindler, M., Mantha, N.M., Kyser, K.T., Murayama, M., and Hochella Jr. M.F. 2012. Shining Light on Black Rock
- 628 Coatings in Smelter-Impacted Areas. *Geoscience Canada*, **39(3)**: 148-157.
- 629 Smart, R.M., and Glasser, F.P. 1974. Compound Formation and Phase Equilibria in the System PbO-SiO₂. *Journal of the*
- 630 *American Ceramic Society*, **57(9)**: 378-382
- 631 Spence, C. D., and De Rosen-Spence, A. F. 1975. The Place of Sulfide Mineralization in the Volcanic Sequence at Noranda,
- 632 Quebec. *Economic Geology*, **70**: 90-101.
- 633 Tanaka, N., Rye, D.M., Xiao, Y., and Lasagna, A.C. 1994. Use of stable sulfur isotope systematics for evaluating oxidation
- 634 reaction pathways and in-cloud-scavenging of sulfur dioxide in the atmosphere. *Geophysical Research Letters*, **21(14)**: 1519-
- 635 1522.
- 636 Telmer, K., Bonham-Carter, G. F., Kliza, D. A., and Hall, G. E. 2004. The atmospheric transport and deposition of smelter
- 637 emissions: Evidence from the multi-element geochemistry of snow, Quebec, Canada. *Geochimica et Cosmochimica Acta*,

638 **68(14):** 2961-2980.

639 Telmer, K., Daneshfar, B., Sanborn, M.S,m Kliza-Petelle, D., and Rancourt, D.G. 2006. The role of smelter emissions and
640 element remobilization in the sediment chemistry of 99 lakes around the Horne smelter, Quebec. *Geochemistry: Exploration,*
641 *Environment, Analysis*, **6**: 187-202.

642 Thiagarajan, N. and Aeolus Lee, C-T. 2004. Trace-element evidence for the origin of desert varnish by direct aqueous
643 atmospheric deposition. *Earth and Planetary Science Letters*, **224**: 131-141.

644 Vítková, M., Ettler, V., Sebek, O., Mihaljevic, M., Grygar, T., and Rohovec, J. 2009. The pH-dependent leaching of
645 inorganic contaminants from a secondary lead smelter fly ash. *Journal of Hazardous Materials* **167(1-3)**: 427-433.

646 Zhou, B., Liu, T., and Zhang, Y. 2000. Rock varnish microlaminations from northern Tianshan, Xinjiang and their
647 paleoclimatic implications. *Chinese Science Bulletin*, **45(4)**: 369-372.

Draft

Figure Captions

Figure 1. Sampling locations in Rouyn-Noranda Québec and their location from the Horne smelting complex. Black and pink dots indicate mafic and felsic rocks, respectively. The average wind direction gathered from historical data between 1954 and 2001 (Henderson and Knight 2005) is indicated in the white box by the red arrow (upper right corner), and the location of Rouyn-Noranda, QC in Canada is shown in the lower left corner.

Figure 2. (a) Field image of black rock coatings on a felsic rock proximal to the Horne smelting complex (sample RN12); (b) a felsic tuff-breccia (Sample RN07) indicating thick coatings on the matrix and thin to no coatings on felsic clasts; (c) optical microscope image in reflected light of a gabbro (sample RN19) showing a thick coating and a sharp contact with the coating and underlying orange-brown weathered rock; (d) Back scattering electron (BSE) image of a basalt (sample RN16) indicating a thick silica layer without any metal-sulfate rich layers and embedded particulate matter; (e) EDS distribution map of Si of (d) indicating a thick silica-rich matrix; (f) BSE image indicating the presence of a metal-sulfate rich layer along the interface of an older silica-rich layer on the RCI of a basalt (sample RN16); (g) BSE image indicating the presence of a metal-sulfate rich layer on a basalt along the RCI; (h) BSE image of a metal-sulfate rich layer located along the ACI in a meta-basalt (sample RN20); (i) BSE image for a felsic lapilli-tuff (RN11) showing the presence of a metal-sulfate rich layer along the ACI, a spherical alamosite particle (labelled 1) and a large spherical Fe-spinel (labelled 2).

Figure 3. Felsic lapilli-tuff (sample RN11) (a) BSE image of the coating and underlying rock; LA-ICP-MS distribution maps of (b) Pb; (c) As; (d) Cu; (e) Zn; (f) BSE image of a Fe-oxide smelter particle embedded in a silica-rich matrix, and corresponding LA-ICP-MS distribution maps of (g) Cu; (h) Zn.

Figure 4. (a)-(d) The concentrations of metal(loid)s in Rouyn-Noranda at thirty different sampling locations; the maximum concentrations are indicated by the size of a solid sphere (a) Cu (in wt%); (b) As (in wt%); (c) Hg (in ppm); (d) Zn (in wt%); (e) Stable isotope values ($\delta^{34}\text{S}$ in ‰) at the thirty different sampling localities.

674 Figure 5. Element plots (ppm) for all collected coating samples: (a) Pb versus As; (b) As versus Ag; (c) two trends
675 for Zn versus Cu (labelled 1 and 2); (d) Pb versus Se; (e) Pb versus Ag; (f) Cu versus As.

676
677 Figure 6. Distance versus average concentration of an elements (in ppm) for defined ranges in distances to the stack
678 (see text for details) (a) Ag; (b) Se; (c) Cu; (d) As; (e) Zn; (f) Hg. The trend line was chosen by using a smoothing
679 function in SigmaPlot 11.0 software and drawn in manually. The smelter-compatibility effect of the stack on the
680 element distribution is given in percentages (see text for details) and solid lines emphasize the observed trend.

681
682 Figure 7. Spider diagram of elements normalised to MUQ for both Sudbury (dashed) and Rouyn-Noranda (solid);
683 MUQ stands for MUd from Queensland (Kamber et al. 2004) and can be used as a representative for the average
684 composition of the upper continental crust.

685
686 Figure 8. $\delta^{34}\text{S}$ values versus distance for (a) the black rock coatings in Rouyn-Noranda; (b) the black rock coatings
687 of the Sudbury and Rouyn-Noranda region as well as for *Sphagnum* sp. (see text for details).

688 Table A1. $\delta^{34}\text{S}$ values for all rock coating samples collected in the region.

Sample Number	Distance from Horne (m)	$\delta^{34}\text{S}$ (‰)	Sample Number	Distance from Horne (m)	$\delta^{34}\text{S}$ (‰)
RN01	3809	3.7	RN16	3974	4.3
RN02	1662	4.1	RN17	3055	4
RN03	5143	3.8	RN18	4540	3.8
RN04	3640	3.8	RN19	5469	3.7
RN05	4848	3.6	RN20	1839	4.3
RN06	3345	3.9	RN21	2078	4.1
RN07	1950	5.5	RN22	2057	4.6
RN08	2027	4.3	RN23	2084	4.5
RN09	2117	4	RN24	1295	4.3
RN10	3032	4.3	RN25	1244	4.4
RN11	1213	5	RN26	2239	4
RN12	1638	4.3	RN27	2585	3.9
RN13	2374	3.8	RN28	1754	4.1
RN14	3056	4	RN29	1844	4.1
RN15	3842	4.4	RN30	2439	4

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690 Table A2. Percentage of the smelter compatibility effect in the coatings
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element	smelter effect (%)	Element	smelter effect (%)
Ag	90.2	S	68.8
Se	82.6	Sn	63.2
Cu	82.6	Fe	54.5
As	79.5	K	46.5
Zn	78.9	Al	40.5
Cd	75.4	Hg	38.6
Cr	74.7	Na	19.9
Pb	73.7	Si	18.7
Ti	73.5		

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693 Table A3. Bulk geochemistry of the black rock coatings in the Rouyn-Noranda area (LA-ICP-MS depth profiles).

Sample Number	Distance from Smelter	Na (wt%)	Mg (wt%)	Al (wt%)	Si (wt%)	S (wt%)	K (wt%)	Ca (wt%)	Ti (wt%)	Cr (wt%)	Fe (wt%)	Zn (wt%)	Cu (wt%)	As (wt%)	Se (ppm)	Ag (ppm)	Cd (ppm)	Sn (wt%)	Hg (ppm)	Pb (wt%)
RN01	3900	1.280	0.525	7.021	23.109	1.679	0.869	1.053	0.174	0.012	3.227	0.283	0.209	0.202	57.548	29.380	37.483	0.211	0.182	2.723
RN02	1798	1.600	0.652	5.222	27.929	1.163	0.956	0.786	0.228	0.008	3.063	0.157	0.261	0.158	36.856	44.959	36.590	0.148	0.155	3.030
RN03	5280	0.396	0.381	2.575	26.731	2.135	0.528	0.249	0.145	0.005	1.267	0.264	0.477	0.142	42.591	36.158	49.157	0.319	0.271	6.618
RN04	3799	0.833	1.276	3.652	26.073	1.322	0.814	1.753	0.175	0.008	1.794	0.255	0.183	0.150	37.385	138.886	64.339	0.220	0.098	3.825
RN05	5032	0.451	1.512	3.933	26.538	1.182	0.913	0.726	0.263	0.013	2.633	0.179	0.256	0.119	42.084	23.446	36.725	0.167	0.095	2.611
RN06	3537	0.573	0.937	6.221	26.407	0.538	0.625	1.144	0.346	0.010	2.514	0.135	0.132	0.096	25.780	23.207	23.337	0.159	0.607	0.921
RN07	2060	0.378	0.907	3.701	22.483	2.332	1.006	0.507	0.519	0.011	5.182	0.353	0.780	0.426	106.607	40.382	87.768	0.616	0.255	5.374
RN08	2149	0.435	0.896	4.387	23.976	1.508	0.654	0.822	0.342	0.009	3.464	0.344	0.696	0.230	60.577	118.166	103.349	0.348	0.212	5.897
RN09	2276	1.195	0.772	3.121	21.100	2.227	0.955	0.487	0.479	0.009	7.216	0.318	0.565	0.375	108.988	138.734	63.913	0.603	0.368	7.215
RN10	3069	0.751	1.144	4.458	21.841	1.936	0.786	0.899	0.318	0.007	5.643	0.424	0.430	0.386	97.672	202.132	103.250	0.412	0.249	5.711
RN11	1089	0.321	0.705	3.449	29.655	0.602	0.405	0.424	0.148	0.005	1.687	0.149	0.075	0.063	19.478	18.555	31.258	0.123	0.269	1.596
RN12	1571	0.507	0.347	3.414	16.980	4.321	1.714	0.337	0.151	0.053	8.138	0.496	1.320	0.828	310.666	326.900	90.692	0.816	0.518	9.076
RN13	2232	0.902	0.521	2.753	20.266	2.495	0.827	0.545	0.225	0.013	6.004	0.674	0.896	1.004	214.945	294.697	107.711	1.093	0.769	9.732
RN14	2864	0.914	0.648	3.641	20.700	3.123	0.660	0.776	0.192	0.017	9.133	0.467	0.415	0.298	52.811	107.305	28.599	0.174	0.501	3.199
RN15	3748	0.307	0.142	1.428	4.084	8.972	3.287	0.200	0.161	0.005	26.546	0.349	0.334	0.384	131.366	38.122	40.746	0.300	0.364	7.805
RN16	3982	0.437	0.756	4.339	21.391	1.869	0.676	1.666	0.384	0.008	7.032	0.331	0.740	0.385	100.964	23.691	69.295	0.234	0.310	5.348
RN17	3191	0.378	1.048	3.264	28.911	1.078	0.446	0.507	0.217	0.007	1.951	0.185	0.215	0.068	22.971	48.430	63.390	0.114	0.156	1.024
RN18	4883	0.563	0.616	4.271	22.621	3.062	1.336	0.728	0.305	0.008	6.024	0.255	0.672	0.279	88.310	21.356	58.006	0.175	0.210	5.240
RN19	5742	1.004	1.105	4.117	22.368	0.811	1.263	0.635	0.212	0.009	11.578	0.126	0.290	0.276	90.011	107.820	18.187	0.059	2.507	0.625
RN20	2058	0.561	1.289	3.418	15.867	3.891	0.807	1.203	0.455	0.015	10.006	0.759	1.476	0.576	155.395	68.337	171.718	0.592	0.365	8.311
RN21	2181	0.515	1.034	4.846	26.185	0.859	0.725	1.848	0.440	0.013	2.582	0.170	0.184	0.078	30.395	10.020	36.685	0.205	0.255	1.905
RN22	2206	1.324	0.515	4.588	25.557	1.290	0.649	0.556	0.172	0.014	1.526	0.437	0.378	0.264	56.112	92.505	99.620	0.586	0.225	4.838
RN23	2132	0.501	0.271	2.986	28.090	1.273	0.554	0.543	0.113	0.004	1.106	0.220	0.331	0.183	31.789	54.957	64.463	0.280	0.084	4.919
RN24	1221	1.336	4.337	9.363	17.266	0.606	1.020	7.814	0.576	0.037	4.208	0.047	0.089	0.013	7.302	12.495	3.180	0.018	0.409	0.174
RN25	1102	0.873	0.521	4.353	24.729	2.141	0.586	0.564	0.369	0.010	2.639	0.375	0.411	0.249	76.598	32.545	52.054	0.504	0.889	3.910
RN26	2045	0.754	0.913	4.662	18.265	4.299	1.224	0.444	0.343	0.008	6.436	0.437	1.059	0.523	179.839	140.734	91.620	0.462	0.445	6.029
RN27	3574	0.774	0.552	4.842	24.604	1.576	0.733	0.544	0.212	0.010	2.870	0.470	0.324	0.247	48.065	92.052	72.197	0.786	0.186	4.207
RN28	1613	0.900	0.776	4.733	21.865	2.830	0.791	0.545	0.269	0.008	4.373	0.468	0.580	0.228	85.955	50.524	61.832	0.350	1.184	5.298
RN29	1663	0.281	0.291	4.508	17.096	3.980	1.377	0.340	0.334	0.012	6.477	0.582	1.405	0.655	175.441	388.672	116.241	1.005	0.253	10.151
RN30	2203	0.476	0.373	2.910	25.114	1.917	0.698	0.288	0.200	0.007	3.332	0.488	0.397	0.162	47.356	75.916	78.632	0.459	0.453	6.633

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70µm

Rouyn-Noranda vs. Sudbury

Distance (km) vs. $\delta^{34}\text{S}$ in Coatings**Rouyn Noranda QC** **Distance (km) vs. $\delta^{34}\text{S}$** **Coatings and Mosses**