



Stable isotope tracing of Ni and Cu pollution in North-East Norway: Potentials and drawbacks[☆]



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ABSTRACT

The use of Ni and Cu isotopes for tracing contamination sources in the environment remains a challenging task due to the limited information about the influence of various biogeochemical processes influencing stable isotope fractionation. This work focuses on a relatively simple system in north-east Norway with two possible endmembers (smelter-bedrock) and various environmental samples (snow, soil, lichens, PM₁₀). In general, the whole area is enriched in heavy Ni and Cu isotopes highlighting the impact of the smelting activity. However, the environmental samples exhibit a large range of $\delta^{60}\text{Ni}$ ($-0.01 \pm 0.03\text{‰}$ to $1.71 \pm 0.02\text{‰}$) and $\delta^{65}\text{Cu}$ ($-0.06 \pm 0.06\text{‰}$ to $-3.94 \pm 0.3\text{‰}$) values which exceeds the range of $\delta^{60}\text{Ni}$ and $\delta^{65}\text{Cu}$ values determined in the smelter, i.e. in feeding material and slag ($\delta^{60}\text{Ni}$ from $0.56 \pm 0.06\text{‰}$ to $1.00 \pm 0.06\text{‰}$ and $\delta^{65}\text{Cu}$ from $-1.67 \pm 0.04\text{‰}$ to $-1.68 \pm 0.15\text{‰}$). The shift toward heavier Ni and Cu δ values was the most significant in organic rich topsoil samples in the case of Ni ($\delta^{60}\text{Ni}$ up to $1.71 \pm 0.02\text{‰}$) and in lichens and snow in the case of Cu ($\delta^{65}\text{Cu}$ up to $-0.06 \pm 0.06\text{‰}$ and $-0.24 \pm 0.04\text{‰}$, respectively). These data suggest an important biological and biochemical fractionation (microorganisms and/or metal uptake by higher plants, organo-complexation etc.) of Ni and Cu isotopes, which should be quantified separately for each process and taken into account when using the stable isotopes for tracing contamination in the environment.

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1. Introduction

Mining and smelting activities are important sources of metals and metalloids in the environment and soils near smelters are highly polluted by a wide range of elements such as Pb, Zn, Cd, Cr, Cu, Hg, Ni, As, Sb, etc. (Ettler, 2016). Concentration, chemical speciation, and/or mineralogical composition analysis are the standard methods to study fate of the metal(loid)s in the environment (Gregurek et al., 1999; Gunawardana et al., 2012). Since

modern mass spectrometers are able to resolve slight variations in the stable isotope composition of elements, such as Cr, Ni, Cu, Zn, Se, Cd, Hg, isotope analysis has become a promising approach in the field of industrial contamination, especially in source tracing studies. In general, the identification of a source of metal contamination in the environment is based on comparison of the metal isotope composition in all potential sources (anthropogenic or natural) and in the environment (water, soil, air, or plants). Variation in stable isotope composition between the natural and anthropogenic sources is thus essential. Metals with relatively low boiling points such as Zn and Cd, were shown to evaporate during smelting, favoring escape of light isotopes in the exhaust (Cloquet et al., 2006; Chrastný et al., 2015). On the other hand, Ni and Cu are both known for high boiling temperatures (2913 °C and

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2562 °C, respectively), therefore no isotope fractionation is expected during the smelting process and the products of Ni and Cu smelting as well as Ni and Cu emissions to the atmosphere have similar isotope signatures as the processed ores (Ratié et al., 2015a; Bigalke et al., 2010). Whether the anthropogenic input can be distinguished from the natural background in the specific environment depends on the range of $\delta^{60}\text{Ni}$ and $\delta^{65}\text{Cu}$ in both the natural and the anthropogenic source (Wiederhold, 2015). Nickel isotope composition in various terrestrial samples (Fe-Mn crust, ultramafic (UM) rocks and soils, fresh water and seawater, river sediments or methanogens cultures and plants) have been recently determined. Published data suggests that the range of $\delta^{60}\text{Ni}$ is between approximately -1.5 and 2.5‰ (Gall et al., 2013; Ratié et al., 2015b; Cameron and Vance, 2014). Cameron et al. (2009) found that Ni assimilation during methanogenic growth produced substantial fractionation of Ni isotopes, up to $\Delta^{60}\text{Ni}_{\text{cells-medium}} -1.46\text{‰}$. Accumulation of Ni by plants resulted in isotope fractionation, $\Delta^{60}\text{Ni}_{\text{plant-solution}}$ from -0.63 to -0.90‰ (Deng et al., 2014). Ratié et al. (2015b) reported Ni isotope fractionation between bedrock (ultramafic rocks) and the upper soil horizon up to -0.47‰ suggesting an overall trend of heavier isotope depletion in the solid phase during weathering. Finally, Ratié et al. (2015a) reported the mass-dependent fractionation of Ni during Ni-laterite ore smelting and refining, $\delta^{60}\text{Ni}$ values from $0.01 \pm 0.05\text{‰}$ (fly ash) to $0.27 \pm 0.05\text{‰}$ (smelting slag). The dissolved Ni from the fly ash settling ponds appears to be enriched with heavy isotopes in comparison to pristine water. The authors thus highlighted the potential of Ni isotope analysis for distinguishing between anthropogenic Ni (heavier Ni isotope composition) and natural (lighter isotope composition) (Ratié et al., 2015a). In contrast to Ni, Cu isotope analysis has been applied in geochemical, biological, and environmental studies for over 15 years (Gale et al., 1999). The range of Cu stable isotope composition is much wider than in the case of Ni, with $\delta^{65}\text{Cu}$ of -16.5‰ to $+10\text{‰}$ in minerals and ores (Mathur et al., 2009). Large variations of $\delta^{65}\text{Cu}$ are found in sediments, biological material and secondary ore minerals, and mine tailings (Li et al., 2015; Weinstein et al., 2011; Rodriguez et al., 2013). Significant isotope fractionation was observed during interaction of Cu with Fe and Al oxy(hydr)oxides in solution, resulting in enrichment of heavy isotopes on the solid surface (Pokrovsky et al., 2008; Balistrieri et al., 2008). Cu adsorption from aqueous solutions onto bacteria and algae cause enrichment of the cell surface in the light isotope, especially at pH 1.8–3.5 (Pokrovsky et al., 2008).

In this study we evaluate the suitability of Ni and Cu isotope analyses for tracing their potential sources in the environment around a Ni-ore processing smelter. Our approach is based on concentration, mineralogical, and isotope analysis in various environmental samples (soil, snow, moss, lichens). The objective is to verify the suitability of each method and sample type on a convenient and relatively simple system of a pure environment with only one anthropogenic source of Ni and Cu. The key question of this study is whether analysis of these two isotope systems can significantly contribute to identify the smelting facility as the source of pollution in the area.

2. Materials and methods

2.1. Study area and sources of contamination

The sampling network covers approximately 2000 km² in North-Eastern (N/E) Norway, near the Norwegian-Russian border. The region is known for the largest remaining area of primeval pine forest in Norway, an offshoot of the Siberian taiga. The annual average temperature is -1 °C, annual precipitation 400–500 mm/

year, and elevation between 80 and 280 m a.s.l. (NGU National report, 1995). The population density in the area is low (2.4 inhabitants per km²). The administrative center is town Kirkenes with approximately 3500 inhabitants. Human activities are mostly limited to fishery, reindeer-herding and forestry. Exception is the iron ore mine and mill at Kirkenes (Tvrdý et al., 2004). Over the past 70 years the Russian non-ferrous metal processing industry at the western part of Kola Peninsula has led to the development of industrial deserts and the local ore-processing plants are considered the world's largest point source emitters of SO₂ and metals (Gregurek et al., 1998a; Khokhar et al., 2008). There are two important facilities, the smelter near the town of Nikel (5 km from the border) and the concentrating and roasting plant near the town of Zapolyarny (15 km from the border). The Zapolyarny plant process disseminated Ni-Cu sulphide ore mined at Kola Peninsula, to produce Ni-Cu concentrate and subsequently Ni-Cu pellets. Recently the roasting technology was replaced by briquetting technology that prevents SO₂ emissions. The facility in Nikel consists of a roasting station and a smelter; the Ni-Cu pellets from Zapolyarny are processed here (Bellona report, 2010). In the mid-1990s the smelter processed Noril'sk ore, rich Pechanga ore, and lower-grade local ore (Boyd et al., 2009). The Pechanga district includes numerous massive and disseminated Ni-Cu sulphide ore deposits associated with mafic-ultramafic igneous rocks. These two plants combined with the farther complex in Monchegorsk, produced annually approximately 100 000 t of SO₂, 300 t of Ni and 180 t of Cu emissions (Reimann et al., 1997), and a wide range of elements: Ag, Al, As, Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Sb, Sr, Th, Tl, Zn and others (Kashulina et al., 2014; Reimann et al., 1996).

In total 17 sampling sites were chosen as a function of geography, geochemical background, prevailing wind direction, and distance from the smelters. Detailed geological description of the studied area is presented in the Supporting Information (Table S1). The sampling sites are divided into 3 transects. The transects run approximately 50 km to the south-west (S/W; sites 1, 2, 3, 4, 5), 90 km to the north-west (N/W; sites 6, 7, 8, 9, 13) and 40 km to the north-east (N/E; sites 10, 11, 12, 14, 15, 16, 17) from the smelter. The prevailing wind direction is north, north-east (N,N/E). Prevailing wind directions in the study area during summer and winter season 2015 are shown in Fig. S2. The study area, sampling sites, and the sources of Ni and Cu are shown in the Supporting Information (Fig. S1).

2.2. Sampling and sample treatment

Sampling was carried out in March 2015 (snow and lichens) and August 2015 (soil profiles, bedrock, moss). Snow, lichens, and mosses were collected at each site (1–17), and the soil profiles and bedrock only at selected sites of each transect (1, 4, 5, 6, 7, 8, 13, 15, 17). A PM₁₀ fraction from two monitoring stations were provided by the Norwegian Institute for Air Research and represents a month of atmospheric deposition from January and March 2015. The PM₁₀ samples come from the monitoring stations in Svanvik (near site 5, sampling 3 m above the ground) and in Karpdalen (near site 15, sampling 1.5 m above the ground). Finally, representative samples of the smelter slag (SS) and the feeding material (Ni-Cu concentrate from Zapolyarny) were obtained for analysis. Samples were homogenized and digested in a mixture of acids (HNO₃, HCl, HF) in order to obtain a liquid sample. Prior to digestion, the volume of the snow was reduced by evaporation on a hot plate to approximately 25 mL and the unfiltered samples were subsequently subjected to the acid digestion. Approximately 250 mg of lichen, moss and soil, and 100 mg of bedrock, smelter slag, and the feeding material was digested for each replicate. Particles of PM₁₀ on Teflon filter bases were digested according to the USEPA 3050B method (Method

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