Heavy metals and Zn isotope ratios in the snow of the Karabash copper smelting area (Southern Urals, Russia)

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Abstract. This work presents the first results of winter fieldworks aimed at the assessment of heavy metal content and Zn isotope composition in the snow cover of a smelting area in South Ural. Twenty one snowpacks were sampled at the end of the winter 2018 in the vicinity (1.0-95 km) of the copper smelter of the Karabash town (South Ural, Russia). The snow samples were analyzed for major and trace element composition using ICP-MS and ICP-OES techniques. Zn isotope analysis was performed by MC-ICP-MS with preliminary chromatographic purification. pH and water hardness values were obtained as well. Zn, Cu, Pb, Cd and Sr enrichment factors were calculated. The contaminant particles in snow were established to have been derived from the technogenic source through the distances up to 95 km from the industrial smelting area.

1 Introduction

Recently, the number of studies on the chemical characteristics of the snow aimed at assessing the contribution of natural and anthropogenic pollution sources, that has rapidly increased [1-3]. Having the ability to accumulate the contaminants absorbed on the crystal surfaces during their crystallisation, snow cover comprises an indicator of air pollution [4, 5]. Therefore, the chemical composition of the snow cover can reflect the changes in the atmospheric emissions both of natural and anthropogenic origin. Apparently, the sources of trace metals and metalloids in atmospheric emissions are associated not only with natural processes, such as rock weathering, mineralization and dust storms, but also with industrial activity as well, presented by smelting (Zn, Cu, As, Pb, Cd). Large volumes of smelting activity result in significant spatial and temporal variability in heavy metal concentrations in the lower atmosphere [6]. In this regard, Zn isotopes may be used to fingerprint the sources and dispersion pathways of pollutants in the environment. However, the information about $\delta^{66}\text{Zn}$ values in liquid and solid forms of atmospheric deposition is insufficient [7, 8]. This particularly applies to the natural and anthropogenic landscapes of

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the Urals. Variations known of Zn isotopes in sulfide-rich ores from -0.43 to 0.23‰ in Alexandrinka ore deposit from South Ural [9]. Moreover, in the case of Urals, the snow has never been analyzed for Zn isotope composition, though its potential for isotope fingerprinting in environmental health studies appears to be obvious.

2 Methods

Sampling. In order to assess the total atmospheric contribution of heavy metals and metalloids of interest (i.e. Zn, Cu, Pb, Cd and As) during the 2017/2018 winter season, snowpack sampling was carried out at the end of February 2018. The locations under study are shown in Figure 1. These included South-West transect, East transect (at distances between 1.0 and 95 km from the smelter) and the nearby area of the emission source (Karabash town). The total depth of snow cover varied between 50 and 85 cm. Sampling was carried out via snow sampling polyethylene tube (1 m x 100 mm) except the cases of a thick 5-cm snow layer. Snow samples were collected in polyethylene bags and kept frozen.

Sample preparation. Sample processing prior to analysis was performed at the Institute of Mineralogy UB RAS, Miass. Snow samples were melted and vacuum filtered through 0.45 µm Millipore cellulose filters. As a result, snow dust and filtrate samples were obtained. Filtrates then were divided into two equal parts. One aliquot was acidified with HNO₃ and purified twice in quartz purification system in order to carry out the ICP-OES, Q-ICP-MS and Zn isotope analysis. The non-acidified aliquot was analyzed by potentiometry and titrimetry. The snow dust samples were carefully weighed, and the total dust content of the snow (dust load) was calculated for the entire snow accumulation period (mg/m²).

Fig. 1 Location map of studied area near the Karabash smelter. Sampling locations are depicted by black dots.

Each snow dust sample was autoclaved in HCl-HNO₃-HF suprapure acid mixture at 160–190 °C in PTFE screw cap vessels for subsequent microelement Q-ICP-MS and Zn isotope analysis. Procedural blanks for Zn isotopic measurements were below 1 ng total Zn.

Methods. Five methods were applied to analyze obtained samples. ICP-OES, titrimetry test and pH measurements were performed at the Institute of Mineralogy UB RAS, Miass.

Thus, the information about concentrations of major elements, as well as pH values and water hardness of snow samples were obtained. Q-ICP-MS and isotope analyses were conducted in the clean room facilities of the Zavaritsky Institute of Geology and Geochemistry UB RAS, Ekaterinburg, for both types of the samples in order to obtain microelement concentrations and Zn isotopic composition.

NexION 300S ICP mass-spectrometer instrumental parameters were as follows: RF power 1300 W, plasma gas flow rate 16 L/min, auxiliary gas flow rate 1.0 L/min and sample gas flow rate (Ar) 1 L/min. Instrumental detection system was configured to determine the following isotopes: ^{65}Cu , ^{66}Zn , ^{86}Sr , ^{111}Cd , ^{208}Pb with subsequent data processing for obtaining the concentrations of corresponding elements.

For isotope analysis, zinc was extracted from filtrates and snow dust solutions using modified chromatography technique, provided in [10]. Bio-Rad AG MP-1 resin (100–200 mesh) was loaded into pre-cleaned polypropylene column (Triskem®) fitted with two 35 μm PE frits with the following layer configuration: D=0.7 cm, h=4 cm, V=1.6 mL. The extraction protocol included 5 mL of 10 M HCl as a resin pre-condition followed by matrix elution sequentially in 11 mL of 10 M HCl, 5 mL of 1 M HCl and 2 mL of deionized water. After that, Zn was eluted in 2 mL of deionized water and yielded up to 100%. Two procedures were applied to zinc fractions before mass-spectrometry measurement. Considering the fact, that Zn concentrations of pure fractions were sufficient to assure the stability of ion beam and satisfactory precision of isotopic ratios, the elution of zinc was followed by adding the concentrated HNO_3 , purified twice in Savillex® DST acid purification system, in order to obtain the HNO_3 concentration in final solution equal to 3%.

Zinc isotope analysis was conducted using a MC-ICP-MS Neptune Plus. The measurement of samples was performed via standard-sample bracketing technique (SSB) using JMC-Lyon Zn isotopic reference solution to allow for the correction of instrument induced mass bias fractionation. Faraday collectors were configured to provide the simultaneous detection of the following ion beams: ^{64}Zn , ^{66}Zn , ^{67}Zn , ^{68}Zn . Each individual acquisition consisted of 60 ratios, collected at 8-second integrations, following a 30 second baseline measurement. Obtained $^{66}\text{Zn}/^{64}\text{Zn}$ ratios were expressed as $\delta^{66}\text{Zn}$:

$$\delta^{66}\text{Zn} = \left[\frac{\left(\frac{^{66}\text{Zn}}{^{64}\text{Zn}} \right)_{\text{sample}}}{\left(\frac{^{66}\text{Zn}}{^{64}\text{Zn}} \right)_{\text{JMC-Lyon}}} - 1 \right] \times 1000, \text{‰} \quad (1)$$

Precision and accuracy were controlled by repeated measurements of the certified reference material and triplicate measurements. Repeated analyses of our in-house Zn standards gave a mean value of $0.24 \pm 0.04\text{‰}$ (2SD, n=46) [11].

3 Results

The obtained concentrations of Cu, Zn, Pb, and Cd near the smelter comprise 3 770, 27 000, 651 and 66 $\mu\text{g/L}$ of melt water, respectively, and decrease dramatically to 1.1, 3.1, 1.25 and 0.012 $\mu\text{g/L}$ at the distance of 95 km (Tab. 1). The enrichment level of these elements in snow dust, relative to upper crustal abundances, decreases similarly from about 1000 to 10, forming an “enrichment gradient” stretched from proximal to distant sites. However, these results present a binary mix of smelter emissions and regional background contribution. For many elements, the slope of binary mixing line remains to be non-zero at a distance of 95 km, indicating that the impact of the smelter is still detectable and regional background levels have not been reached yet. The data, obtained at more distant sites, are used to estimate the regional background concentrations of 0.6, 1.0, and 0.24 $\mu\text{g/L}$ in melt water for Cu, Zn, and Pb, respectively.

Table 1. Chemical composition melt water from snow pack samles.

Sample (R(Sn))/ distance to the smelter	West transect			Smelting area				East transect		
	915, 54 km	916, 95 km	917, 68 km	923, 5 km	924, 3 km	925, 0.3 km	926, 1 km	932, 60 km	933, 61 km	934, 52 km
pH	6.60	6.50	7.20	5.18	5.28	5.55	5.36	6.41	6.40	5.83
Eh, mV	266	276	260	345	335	328	330	290	288	328
γ, μSm/cm	26.5	18.3	65.8	24.0	35.4	99.0	31.9	26.0	20	19
HCO ₃ ⁻ , ppm	18.3	10.9	36.9	b.d.l.	b.d.l.	0.73	b.d.l.	3.66	3.97	3.17
Cl ⁻ , ppm	0.75	0.60	1.70	0.75	0.85	2.10	1.00	2.50	0.95	0.85
SO ₄ ²⁻ , ppm	6.05	3.70	7.05	6.24	8.22	68.5	15.1	5.65	4.75	4.65
NO ₂ ⁻ , ppb	7.4	5.1	3.6	5.5	3.6	6.5	6.5	7.2	5.8	6.2
NO ₃ ⁻ , ppm	0.39	0.39	0.52	0.53	0.52	0.61	0.49	0.74	0.63	0.69
NH ₄ ⁺ , ppm	0.35	0.31	0.24	0.39	0.34	0.52	0.58	0.59	0.64	0.55
Ca, ppm	2.63	2.13	2.04	1.43	1.73	3.20	1.70	2.50	2.67	2.10
Mg, ppm	3.45	1.83	8.20	0.20	0.39	0.74	0.31	0.44	0.47	0.42
K, ppm	0.59	0.54	0.83	0.27	0.14	0.44	0.47	0.23	0.21	0.50
Na, ppm	0.58	0.29	1.41	0.39	0.54	0.85	0.33	2.05	0.43	0.85
Li, ppb	0.085	0.048	0.162	0.072	0.0206	0.337	0.106	0.049	0.055	0.054
V, ppb	0.128	0.056	0.143	0.019	b.d.l.	b.d.l.	0.021	1.11	0.63	0.31
Cr, ppb	0.112	b.d.l.	0.114	0.056	b.d.l.	b.d.l.	0.197	0.20	0.62	0.083
Mn, ppb	14.3	8.74	11.1	19.3	3.38	44.0	23.7	23.7	22.2	16.6
Fe, ppb	2.00	2.00	1.00	83.0	27.0	1.00	34.0	3.00	8.00	3.00
Co, ppb	0.023	0.012	0.016	0.46	0.135	2.12	0.75	0.091	0.065	0.123
Ni, ppb	0.24	0.078	0.139	3.95	0.80	17.2	6.43	0.38	0.33	0.75
Cu, ppb	1.96	1.08	1.06	489	145	3770	1340	3.13	2.19	4.39
Zn, ppb	8.37	3.14	3.66	1341	516	27000	3230	16.5	28.8	25.2
As, ppb	1.17	0.92	0.47	5.27	5.23	108	47.9	0.60	0.69	0.75
Rb, ppb	0.94	0.37	1.34	0.23	0.046	0.96	0.34	0.34	0.37	0.43
Sr, ppb	2.18	1.53	2.88	2.67	0.53	4.61	3.11	3.32	3.81	3.56
Y, ppb	0.021	0.015	0.010	0.046	0.006	0.125	0.043	0.009	0.014	0.010
Mo, ppb	0.071	0.028	0.054	0.27	0.097	1.04	0.69	0.147	0.123	0.21
Cd, ppb	0.036	0.012	0.008	6.67	2.57	66.0	11.1	0.146	0.22	0.17
Sb, ppb	0.161	0.082	0.153	4.32	2.69	23.5	9.93	0.22	0.40	0.29
Cs, ppb	0.011	0.006	0.010	0.011	0.002	0.046	0.019	0.034	0.027	0.020
Ba, ppb	5.05	3.05	5.57	31.5	2.84	28.5	22.7	4.92	7.27	5.65
W, ppb	0.048	0.015	0.015	b.d.l.	b.d.l.	0.008	0.007	0.062	0.058	0.1
Tl, ppb	0.016	0.010	0.019	0.30	0.163	3.08	0.49	0.025	0.022	0.016
Pb, ppb	1.31	1.25	0.081	387	156	651	536	0.82	2.19	0.91

The enrichment factor (EF) is often used for the evaluation of the pollution level of snow dust samples. The EF was determined using the following equation:

$$EF_{\text{metal}} = ([\text{metal}]/[\text{Sc}])_{\text{sample}}/([\text{metal}]/[\text{Sc}])_{\text{continental crust}},$$

(2)

where “metal” refers to the metal concentrations with continental crust values reported in the work of Taylor and McLennan [12]. Scandium is used as the reference element for normalization. As can be seen from Figure 2A, the enrichment factor ranges from 200 to 1000 near the emission source, depending on the element.

At the distances from the emission source between 20 and 40 km, the EF values fall into a stable range from 10 to 100. The comparison of the EF values of chalcophile elements with a typical lithophilic element (Sr) indicates the abnormal concentrations of Co, Zn, Pb and Cd. The δ⁶⁶Zn value in snow, i.e. melt water, varies from -2.45 to 0.42‰ (N = 5) and

from -4.2 to -0.6‰ (N = 6) near the smelter and in South-West transect, respectively. The $\delta^{66}\text{Zn}$ value in contaminants varies slightly from 0.17 to 0.34‰ in loess, shales and dust, reaching considerable variation (from 0.22 to 2.84‰) in carbonates and limestones (Fig. 2B).

The analysis of $\delta^{66}\text{Zn}$ distribution in the major contaminants (Ausmelt and converter fly ash) indicates the heavy Zn isotope composition (0.35-3.10‰, Fig. 2B), while the copper concentrates have the lighter Zn isotope composition ranging from -4.5 to -1.5‰. The melting water from the West transect is characterized by $\delta^{66}\text{Zn}$ from -4.05 to 0.72‰, while $\delta^{66}\text{Zn}$ values for the East transect are localized in a very narrow range from -0.75 to 0.0‰. Zn isotope composition of the snow dust demonstrates the behavior similar to snow melting water (Fig. 2B). The range of variations of Zn isotopy is really huge. It requires discussion to go beyond our small message. We suggest inserting the following sentence: All the same, the range of variations in Zn isotope ratios of natural and anthropogenic sources is from -1.0 to 2.0, as follows from a general review [13]. Our values far exceed this range.

Fig. 2. A - Log scaled plots of the enrichment factors for Cu, Zn, Pb, Cd and Sr in accordance with the distance from the smelter towards the South-West transect.
B - Zn isotope composition in snow samples of different types (solid and melted) and contaminant.

4 Conclusion

The snow from the Karabash copper smelting area (Southern Urals, Russia) was analyzed for heavy metal content and Zn isotope composition in order to trace the sources and dispersion pathways of pollutants. The concentrations of four chalcophile elements typomorphic for the Southern Urals’ ore-mining technogenesis – Cu, Zn, Pb and Cd – in the snow dust samples form an “enrichment gradient” stretched from proximal to distant sites representing a binary mix of smelter emissions and regional background contribution. The estimated regional background concentrations are 0.6, 1.0, and 0.24 µg/L in melt water for Cu, Zn and Pb, respectively. Heavy metal enrichment factors range from 200 to 1000 near the emission source, decreasing to 100-10 at the distances between 20-40 km from the emission source. Obtained $\delta^{66}\text{Zn}$ values in the melting water and snow dust are characterized by the lighter Zn isotope composition similar to the copper concentrates (-4.5 to -1.5‰), while the major contaminants (Ausmelt and converter fly ash) demonstrate heavy $\delta^{66}\text{Zn}$ (0.35-3.10‰). Thus, Zn isotope composition emphasises the connection

between the major raw materials for the copper pyrometallurgical processes (Cu concentrates) and the snow dust both from the West and East sampling transects.

Trace element analysis and Zn isotope analysis was carried out at the UB RAS “Geoanalitik” Center for Collective Use within the state assignment of FASO of Russia № 0393-2016-0025. Field work and snow samples preparation was carried at the State contracts IMin UB RAS and IGG UB RAS and support Scientific program UB RAS No. 18-5-5-43.

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