

# Use of isotope ratios to assess sources of Pb and Zn dispersed in the environment during mining and ore processing within the Orlovka–Spokoinoe mining site (Russia)

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## Abstract

Element concentrations, element ratios and Pb and Zn isotope data are reported for different geologic samples (barren and ore-bearing granites and host rocks), technogenic products (ore concentrates and tailings) and biologic samples (lichens and birch leaves) from the Orlovka–Spokoinoe mining district, Eastern Transbaikalia, Russia, with the aim to trace the sources of Pb and Zn at a local level within the mining site. Lichens and birch leaves were used as receptors of contamination within the mining site. Pb/Zr and Zn/Zr values indicated Pb and Zn enrichment relative to host rocks. Zn isotope data of 15 geologic and 11 lichen samples showed different Zn isotopic signatures with the total range for the geologic suite of  $-0.4\text{‰}$  to  $+1.2\text{‰}$  and for lichens of  $+0.4\text{‰}$  to  $+1.4\text{‰}$  in  $\delta^{66}\text{Zn}$  relative to Lyon JMC Zn standard. The source of isotopically heavy Zn within the Orlovka–Spokoinoe mining site could be potentially associated with long-range atmospheric aerosols that also contributed Pb to the studied mining site. Our results demonstrated that Zn isotopes might be used as new tools for Zn source assessment.

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## 1. Introduction

Metals are transferred to the atmosphere, soils, vegetation, water reservoirs and sediments from local industries, mining and smelting, sewage sludge,

gasoline and coal combustion, and waste incineration. Fluxes of these metals due to anthropogenic activities exceed those linked to natural erosion, even in areas remote from cities and industries (Nriagu and Pacyna, 1988; Pacyna and Pacyna, 2001). The mining of metalliferous mineral deposits and associated metal processing activities have led to severe perturbations in the cycling of metals in the surface environment (Thornton, 1996). Where ore deposits

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are mined, local geochemical anomalies are created, which significantly intensify metal and potentially toxic element supply into the environment. Information about contamination can be gathered from analyses of metal concentrations alone, but a lot of uncertainties remain concerning their sources.

The use of Pb isotopes to identify and to distinguish between natural and anthropogenic sources of contamination have become a routine fingerprinting tool in the last few decades (Rosman et al., 1994, 1999; Chiaradia and Cupelin, 2000; Kober et al., 1999; Luck and Othman, 2002). Pb isotope ratios are variable in natural materials and environments due to the radioactive decay of U- and Th-nuclides. They are, however, not affected by industrial or biological processes (Ault et al., 1970) and do not fractionate during transport and deposition processes and therefore retain the isotopic composition of their sources with great potential as source tracers. The use of a multi-collector ICP-MS (MC-ICP-MS) allows collection of high-precision Pb isotope data and a large sample throughput at the same time. Although thermal ionisation mass spectrometry (TIMS) can also provide Pb isotope data of similar quality, its disadvantages are time-consuming analytical procedures and low sample throughput. The precise determination of isotope ratios including  $^{204}\text{Pb}$  allow a much improved identification of multiple natural and anthropogenic sources of Pb contamination within even a small area, as demonstrated for example in the vicinity of a Cu smelter (Urals, Russia) as reported by Spiro et al. (2004).

Although applications of Zn isotopes are at an early stage, the first studies showed significant Zn isotopic variability in a variety of geological (carbonates and sulphides) and biological (lobster liver, mussel tissue, phytoplankton and plants) samples (Maréchal et al., 1999; Maréchal et al., 2000; Maréchal and Albarède, 2002; Archer and Vance, 2002; Albarede, 2004; Weiss et al., 2005; Wilkinson et al., 2005; Mason et al., 2005). Zn is an essential element and its isotopes potentially offer a powerful tool for studying geosphere–biosphere interactions. Zn isotopes studied in higher plants indicated that several processes control the isotopic composition, with uptake favoring isotopically lighter Zn and adsorption favoring heavier Zn (Weiss et al., 2005). Two studies used Zn isotopes in rainwater, aerosols and loesses (Luck et al., 1999; Othman et al., 2001) to constrain atmospheric pollutants. Isotope variations in rainwater from two neighboring locations in Southern France showed Zn iso-

topes variations from  $-0.2\text{‰}$  to  $+0.2\text{‰}$  that tentatively were linked to two different sources of Zn: the source with heavier Zn isotopes corresponded to a Cu-enriched “chemical product” widely used in the catchment area, whilst the source of lighter Zn isotopes remained undetermined (Luck et al., 1999). Aerosols from Southern France and peri-Sahara regions exhibited different zinc isotopic signatures specific for each sampling area, whereas loesses sampled from Western USA, China and Europe displayed a rather uniform Zn isotope composition of  $0.2\text{--}0.3\text{‰}$  (Othman et al., 2001). Another study observed large mass-dependent variations in commercially available Zn metal reference materials compared to natural variability (Mason et al., 2004b). This was suggested to relate to the processes during metal purification and formed the basis of the initial idea that Zn isotopes could potentially provide a marker to distinguish between anthropogenic and natural Zn contaminants within the environment. Zn has five stable isotopes,  $^{64}\text{Zn}$ ,  $^{66}\text{Zn}$ ,  $^{67}\text{Zn}$ ,  $^{68}\text{Zn}$  and  $^{70}\text{Zn}$ , with average atomic abundances of 49.19%, 27.79%, 4.04%, 18.39% and 0.60%, respectively (Tanimizu et al., 2002).

While the impact of base metal mining on toxic element dispersal has been assessed in great detail before, much less is known about the effects of rare metal mining despite its importance in various parts of the world, such as Eastern Transbaikalia.

The aims of this study were thus twofold. Firstly, we wanted to investigate possible enrichment of toxic element during rare metal mining using Zn and Pb as proxies and secondly, we wanted to determine the potential of Zn and Pb isotopes to identify possible environmental pollution.

To achieve these two aims, we used the Orlovka–Spokoinoe mining site in Eastern Transbaikalia, Russia, as a case study. The site is situated far away from any obvious pollution sources and a source-receptor model was easy to constrain. The potential sources included geological (barren and ore bearing granites, host rocks) and technogenic (gasoline, ore concentrates, tailings) samples. Lichens and birch leaves sampled from around the mining site were used as receptors.

The main objectives of this study were: (i) to assess possible toxic element enrichment using Zn and Pb as proxies; (ii) to assess the isotopic variability of Pb and Zn isotope ratios and (iii) to distinguish among geological and anthropogenic sources within the mining environment using Pb and Zn isotopes.



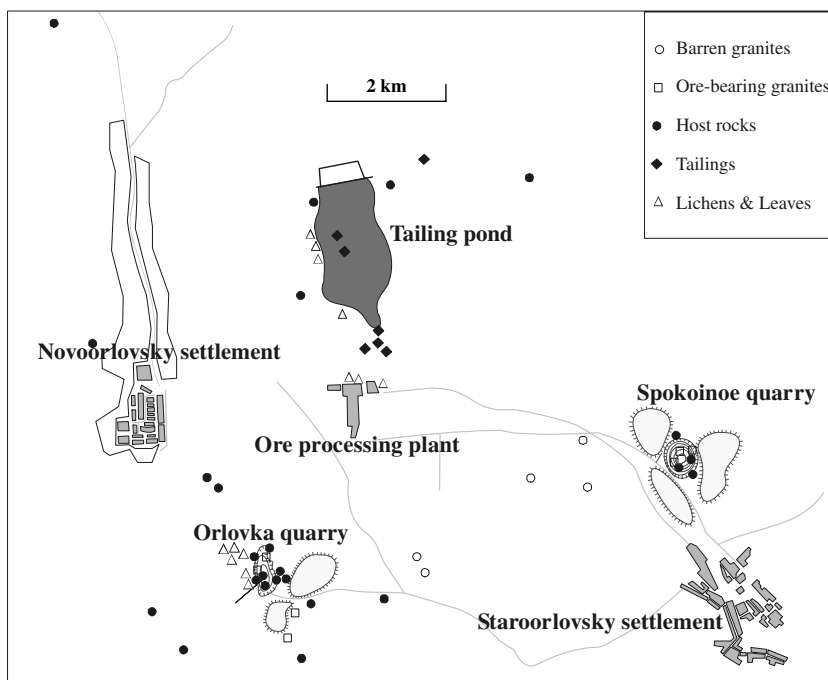


Fig. 2. Location of the sampling sites within the Orlovka–Spokoinoe mining site. Samples of geologic (granites, host rocks), biologic (lichens and leaves) and anthropogenic (tailings) origins were collected around main infrastructure units within the site. Ore concentrates were sampled from the ore processing plant.

magmatic intrusions into the host rocks (felsic volcanics, metasediments and hornfels) during the late Jurassic. Both deposits are hosted by satellite intrusions of the Khangilay granite pluton (Beskin et al., 1994; Kovalenko et al., 1999; Syritso et al., 2001). The Orlovka tantalum deposit is confined to the apical part of the Orlovka granite cupola. The tantalum minerals are represented by ferrocolumbite, ferrocolumbite–ferrotantalite, microlite and pyrochlore accumulated in the endocontact rocks of the granite cupolas. The Spokoinoe tungsten deposit is characterized by tungsten (tin-beryl) vein quartz-greisens and is composed of albite-muscovite granites. Major ore minerals are wolframite, russellite, cassiterite, and beryl.

### 2.2. Ore processing plant and tailing pond

The ore processing plant produces high-grade Ta–Nb and Sn–W concentrates from the ore-bearing granites of the Orlovka and Spokoinoe deposits through several low temperature physical and chemical separation stages. Firstly, the ore is crushed and milled to a particle size of 2 mm and then to a size down to 0.05 mm. The production of the raw concentrates consists of further gravity concentration,

magnetic separation and sulphide flotation (Dolgoplova et al., in press). The tailings from the ore processing are deposited next to the ore processing plant in and around a shallow pond.

## 3. Sampling and analytical techniques

### 3.1. Sampling of representative source and receptor material

Whole-rock samples were collected in the field and from the two quarries representing the granite intrusions of Orlovka and Spokoinoe, i.e., ore-bearing and barren granites, classified according to the mineralogy (see details in Zaisky et al., 1997; Dolgoplova et al., 2004a) and the host rocks represented by felsic volcanics, metasediments and hornfels. Samples from different technological stages of processing of the Orlovka ores, such as (1) crushing; (2) gravitation; (3) magnetic separation and (4) flotation were collected from the ore processing plant, and tailings were collected from shores of the tailing pond. Lichens (*Xanthoparmelia*) and birch leaves (*Betula pendula*) were sampled from trees growing around the quarries, the ore processing plant, the tailing pond and in the Novoor-

lovsky settlement. Gasoline samples were collected from the local petrol station.

In the laboratory, whole-rock samples, ore concentrates, tailings, lichens and leaves were placed into previously cleaned ceramic beakers and dried at 40 °C overnight. Lichens and leaves were ground in an agate mortar using liquid nitrogen. Whole rock samples, tailings and ore concentrates were prepared by milling in a Tema agate mill. Samples were sieved through a 100 µm stainless steel sieve, placed in ceramic beakers and dried overnight at 40 °C prior to analysis. Samples were homogenized and transferred into acid-cleaned plastic bottles for further use.

### 3.2. Chemical analysis

#### 3.2.1. Major and trace element analysis

Lichens and birch leaves were digested in HNO<sub>3</sub>/HF/H<sub>2</sub>O<sub>2</sub> acid mixture using a MARSX microwave oven system (Dolgoplova et al., 2004b). Three certified reference samples NIST 1515 (apple leaves), NIST 1547 (peach leaves) and CRM 482 #10 *Pseudovernia furfura* (lichens) were used to ensure quantitative recovery of Pb and Zn from lichens and birch leaves. The barren and ore bearing granites, host rocks, tailing pond sediments and ore concentrates were dissolved using hot plate digestion with a standard HNO<sub>3</sub>/HF acid mixture in closed Teflon beakers (Dolgoplova et al., 2004a). 0.2 ml of gasoline samples were at first evaporated until an oily dark brown drop was left. Then, a mixture of concentrated 2 ml HNO<sub>3</sub> and 0.2 ml HF was added to fume down the residue. Aliquots were used for measurements of element concentrations and isotope analyses. Pb and Zn concentrations in lichens, leaves and petrol were determined by Fison's Instruments ARL 3508B ICP-AES at Imperial College London. Precision and accuracy assessed using standard reference materials of lichens and leaves mentioned above were all within 10%.

Zirconium concentrations in lichens and leaves were determined by inductively coupled plasma mass spectroscopy (ICP-MS) using Perkin-Elmer Elan 6000 instrument at the Acme Analytical Laboratories Ltd. Vancouver, Canada. 0.5 g of samples were digested in HNO<sub>3</sub> followed by an Aqua Regia dissolution. The V6 standard comprised of dried twigs and needles of jack pine (*Pinus banksiana*) developed by the Geological Survey of Canada was used as the reference material to control analytical reproducibility and accuracy and they were within 12%.

Zinc concentrations in rocks, ore concentrates and tailings were determined by inductively coupled plasma optical emission spectroscopy (ICP-OES) using an OPTIMA 4300 (Perkin-Elmer) instrument at the laboratory of the All-Russia Geological Research Institute (VSEGEI) in St. Petersburg, Russia. 0.1 g of samples were digested in HNO<sub>3</sub>, HF and H<sub>2</sub>SO<sub>4</sub> acids, evaporated and redissolved in HCl media for further analysis. The basalt geo-standard BE-N (France) was used as the certified reference material for calibration. Precision and accuracy of measurements were within 10%.

Lead concentrations in rocks, ore concentrates and tailings were determined by inductively coupled plasma mass spectrometry (ICP-MS) at the GFZ Potsdam. The procedure and instrumental parameters of the measurements are described in detail elsewhere (Dulski, 2001). Briefly, about 0.1 g of sample powder was dissolved using mixed acid digestion (HF/HClO<sub>4</sub>) under pressure. Prior to analysis, Ru, Re and Bi were added to aliquots of the solutions as internal standards for drift correction. Measurements were made using an ELAN 5000A quadrupole ICP-MS (Perkin-Elmer/SCIEX, Canada). Samples were measured in batches of five. Each batch was preceded by a 10 ng/ml calibration solution, two acid blanks and a procedure blank. To minimize the influence of drift effects on analytical precision relatively small batches of samples were analysed within one analytical run. Interference corrections were routinely applied to correct analyte isotopes for molecular and isobaric interferences (Dulski, 1994). Precision and accuracy were within 5–10%. The full list of geological standard reference materials used during the analytical work can be found in Dulski (2001).

#### 3.2.2. Pb isotopes analysis

A sample suite including 48 geologic samples represented by barren and ore-bearing granites and host rocks, 12 anthropogenic products, such as ore concentrates and tailings, two samples of local gasoline and 26 samples of lichens and birch leaves, was analyzed for Pb isotopes by thermal ionization-mass spectrometer (TIMS, University of Heidelberg) and GV Isoprobe multi-collector ICP-MS based at the Imperial College London – Natural History Museum Joint Analytical Facility (ICL/NHM JAF). Pb was purified through an ion chromatography Sr-resin from EiChrom in a hydrochloric acid medium (see details of procedure in Weiss et al., 2004). TIMS raw data were normalized to NBS

981 Pb with reference values of [Galer and Abouchami \(1998\)](#) (reproducibility on the 95% confidence level: 0.03% for ratios normalized to  $^{204}\text{Pb}$ ). MC-ICP-MS raw data were corrected for isobaric interferences on  $^{204}\text{Pb}$  using  $^{200}\text{Hg}$ . Mass discrimination correction was made using NBS 997 Tl as an internal standard. The Pb/Tl ratio was kept constant to 2:1 during the measurements. The  $^{205}\text{Tl}/^{203}\text{Tl}$  ratio was optimized for each measurement session based on repeated measurements of a spiked NBS 981 Pb international standard. The error on the isotope ratios was estimated using the long-term reproducibility of repeated NBS 981 measurements over the time of investigation and it was below 500 ppm for all ratios. Analytical blanks for the procedure estimated from intensity data were below 1 ng and always below 1% of the total Pb.

[Table 1](#) shows Pb, Zn and Zr element concentrations and Pb isotopes data for the Orlovka–Spokoinoe mining site.

### 3.2.3. Zn isotopes measurements

Fifteen geologic and 11 lichen samples from the same sample suite were also analyzed for Zn isotopes by multi-collector ICP-MS (ICL/NHM JAF) ([Table 2](#)). Zn was purified through ion chromatography AG MP-1 resin in hydrochloric medium. Isotopic measurements were made using 1 block of 25 integrations with an integration interval of 5 s. The sample-standard bracketing approach was used for Zn isotope measurements when an in-house Zn standard (IMP Zn) was measured before and after each sample. Every sample was measured four times. All data were on-peak baseline corrected using a 0.2% (v/v) ultra-pure  $\text{HNO}_3$  acid blank run directly prior to each analysis. A  $\delta^{66}\text{Zn}$  was calculated for each unknown sample relative to the bracketing standards, using equation

$$\delta^{66}\text{Zn} = \left( \frac{{}^{66}\text{Zn}/{}^{64}\text{Zn}_{\text{sample}}}{{}^{66}\text{Zn}/{}^{64}\text{Zn}_{\text{standard}}} - 1 \right) \times 1000 \text{ (‰)}.$$

The  $\delta^{66}\text{Zn}$  data reported in this paper are relative to the Zn standard from the Lyon group (Johnson Matthey metal, batch JMC # 3–0749 L, [Maréchal et al., 1999](#)). Repeated measurements ( $n = 10$ ) between the JMC # 3–0749 L and our in house IMP Zn standard (prepared from a Johnson Matthey Purotronic Zn metal, batch # NH 27040) showed a difference of  $-0.087 \pm 0.070\text{‰}$  for  $\delta^{66}\text{Zn}$  ([Mason et al., 2004b](#)). The full description of the analytical and data processing procedures including

the modified sample standard bracketing approach used for mass bias correction is given elsewhere ([Mason et al., 2004a,b](#)). The error on the  $\delta^{66}\text{Zn}$  was estimated from repeated measurements of individual samples and was  $\pm 0.06\text{‰}$  for  $\delta^{66}\text{Zn}$  and  $\pm 0.13\text{‰}$  for  $\delta^{68}\text{Zn}$ . This precision is similar to the one derived from repeated measurements of an internal plant standard, the rice standard IR34 ( $\delta^{66}\text{Zn} = 0.63 \pm 0.05\text{‰}$ ,  $n = 6$ ). To assess the accuracy, we made repeated measurements of the USGS terrestrial basalt BCR-1. Our value of  $0.29 \pm 0.12\text{‰}$  ( $n = 8$ ) ([Chapman et al., in press](#)) for  $\delta^{66}\text{Zn}$  agrees within error with the published value of  $0.20 \pm 0.09$  by [Archer and Vance \(2004\)](#).

## 4. Results

### 4.1. Pb and Zn concentrations

The ore-bearing granites of Spokoinoe and Orlovka contain the highest Pb concentrations (up to 282 ppm in Spokoinoe and up to 184 ppm in Orlovka) ([Table 1](#)). High Pb concentrations in geological samples from the Orlovka deposit can be explained by fractionation and metasomatic replacement processes in the ore-bearing granites as was previously discussed in [Dolgoplova et al. \(2004a\)](#). Pb enrichment here correlates with mineralogical observations on feldspar re-equilibration. Pb redistribution is associated with microclinization and further amazonite formation associated with  $\text{K} \leftrightarrow \text{Pb}$  isomorphic replacement ([Seltnann et al., 1999](#)). Galena (PbS) plays a subordinate role and is found only in hydrothermal veinlets and occasionally in the host rocks. Barren granites have up to 40 ppm of Pb and host rocks up to 27 ppm ([Table 2](#)). Tailing pond sediments have similar Pb concentrations (up to 25 ppm) to the average Pb content of the host rocks. Remarkable is the Pb enrichment during all stages of the ore processing reaching up to 0.35% of Pb in the concentrate after gravity concentration, 359 ppm after magnetic separation and up to 295 ppm after the sulphide flotation, final stage of the ore processing. Average Pb concentrations of lichens and leaves are lower than those of geological background represented by host rocks (17 versus 27 ppm).

Orlovka ore-bearing granites are enriched in Zn with concentrations up to 800 ppm, whereas Zn abundances in Spokoinoe ore-bearing granites are up to 30 ppm. There are two possible mechanisms that may lead to Zn accumulation in granites. The

Table 1

Pb, Zn and Zr concentration values ( $\mu\text{g/g}$ ) and Pb isotope ratios in geologic, anthropogenic and biologic samples from the Orlovka–Spokoinoe mining district, Eastern Transbaikalia, Russia

Sample ID	Sample description	Sampling location	Pb	Zn	Zr	$^{206}\text{Pb}/^{204}\text{Pb}$	$^{207}\text{Pb}/^{204}\text{Pb}$	$^{208}\text{Pb}/^{204}\text{Pb}$
<i>Barren granites</i>								
2050-T	Biotite/muscovite granite	Khangilay pluton	26	60	41	18.958	15.598	38.360
2079	Biotite granite	Khangilay pluton	38	60	175	18.896	15.446	38.209
2080	Biotite granite	Khangilay pluton	38	40	214	19.893	15.633	38.691
2084	Biotite/muscovite granite	Khangilay pluton	40	40	129	19.003	15.597	38.604
2096-T	Biotite granite	Khangilay pluton	44	60	198	19.070	15.599	38.789
2142-T	Biotite/muscovite granite	Orlovka stock	136	150	109	18.617	15.556	38.351
2149-T	Biotite granite	Orlovka stock	44	60	110	18.794	15.596	38.558
2151	Biotite/muscovite granite	Orlovka stock	34	60	107	18.796	15.581	38.481
<i>Ore-bearing granites</i>								
2143-T	Amazonite/muscovite granite	Orlovka stock	122	200	16	18.428	15.556	38.286
2144-T	Amazonite pegmatite	Orlovka stock	129	300	10	18.486	15.572	38.359
2147-T	Strongly weathered amz granite	Orlovka stock	71	150	45	18.460	15.559	38.326
2148	Intensely weathered amz granite	Orlovka stock	52	120	32	18.544	15.610	38.503
2162-T	Mineralized toz/amz/ab <sup>a</sup> granite	Orlovka quarry	167	60	6.9	18.407	15.565	38.332
2215-T	Mineralized toz/amz/ab granite	Orlovka quarry	108	120	10	19.320	15.596	38.599
2163-T	Mineralized toz/amz/ab granite	Orlovka quarry	19	120	35	19.589	15.631	38.817
2164-T	Mineralized toz/amz/ab granite	Orlovka quarry	20	300	50	18.502	15.571	38.360
2213-T	Mineralized toz/amz/ab granite	Orlovka quarry	184	800	26	18.407	15.562	38.328
2220-T	Greisenized granite	Spokoinoe quarry	35	30	17	19.202	15.608	38.445
2223	Mineralized greisen with wolframite	Spokoinoe quarry	282	30	5.4	18.504	15.567	38.328
2224	Mineralized greisen with wolframite	Spokoinoe quarry	71	30	5.8	18.531	15.581	38.363
2056-T	Mineralized greisen with wolframite	Spokoinoe quarry	32	30	20	18.976	15.598	38.410
<i>Host rocks</i>								
2068-T	Hornfels	Khangilay pluton	15	120	355	18.492	15.566	38.544
2166	Hornfels	Orlovka quarry	6.7	80	66	18.811	15.578	38.457
2169-T	Hornfels	Orlovka quarry	7.9	60	86	18.786	15.618	38.658
2173-T	Hornfels	Orlovka quarry	12	100	137	19.074	15.584	38.750
2174-T	Hornfels	Orlovka quarry	27	120	578	18.506	15.557	38.491
2177	Hornfels	Orlovka quarry	6.8	120	64	N/A <sup>b</sup>	N/A	N/A
2132	Hornfels	Spokoinoe quarry	11	60	197	N/A	N/A	N/A
2138	Hornfels	Spokoinoe quarry	90	120	224	18.264	15.581	38.046
2140	Hornfels	Spokoinoe quarry	16	120	155	N/A	N/A	N/A
2125	Hornfels	Spokoinoe quarry	59	150	240	18.060	15.505	38.304
2128	Hornfels	Spokoinoe quarry	155	60	217	N/A	N/A	N/A
2060	Hornfels	Spokoinoe quarry	18	60	151	18.542	15.588	38.267
2129	Hornfels	Onon group	12	80	161	18.948	15.599	38.803
2150	Rhyolite	Orlovka stock	44	20	143	18.071	15.501	38.376
2182	Rhyolite	Orlovka stock	9.4	15	201	18.869	15.594	39.345

(continued on next page)

Table 1 (continued)

Sample ID	Sample description	Sampling location	Pb	Zn	Zr	<sup>206</sup> Pb/ <sup>204</sup> Pb	<sup>207</sup> Pb/ <sup>204</sup> Pb	<sup>208</sup> Pb/ <sup>204</sup> Pb
2183	Rhyolite	Orlovka stock	4.4	30	167	N/A	N/A	N/A
2187	Andesitic dacite	Orlovka stock	6.3	60	106	N/A	N/A	N/A
2204	Andesitic dacite	Orlovka stock	10	100	190	18.515	15.578	38.550
2121	Dacitic lava	Orlovka stock	34	25	336	18.441	15.544	38.541
2101	Rhyodacitic lava	Orlovka stock	33	80	121	18.223	15.498	38.429
2010	Metasandstone	Orlovka stock	5.6	30	245	N/A	N/A	N/A
2011	Metasandstone	Orlovka stock	8.9	40	215	18.626	15.537	38.820
2028	Metasandstone	Orlovka stock	15	60	167	18.363	15.548	38.403
2029	Mica schist	Orlovka stock	25	120	226	18.267	15.518	38.371
2032	Chlorite/mica schist	Orlovka stock	22	60	170	18.587	15.861	39.010
SH2	Shale	Tailing pond	31.3	N/A	28.3	18.429	15.557	38.666
SH3	Shale	Tailing pond	32.8	N/A	31.9	18.265	15.536	38.400
<i>Tailings, ore concentrates and local gasoline</i>								
TP 3	Tailings	Tailing pond	25.4	59.6	35.6	N/A	N/A	N/A
TP 4	Tailings	Tailing pond	21.59	50.9	21.7	18.306	15.573	38.207
TP 5	Tailings	Tailing pond	17.85	113	24.5	19.182	15.612	38.563
TP 6	Tailings	Tailing pond	38.95	101	30.4	18.117	15.562	37.764
TP 7	Tailings	Tailing pond	20.83	37.8	19.8	19.032	15.611	38.487
SM1	Ore concentrate (after crushing)	Ore processing plant	60.23	83.5	24.7	18.802	15.618	38.551
SM2A	Ore concentrate (after crushing)	Ore processing plant	73.78	324	36.1	18.548	15.573	38.380
SM2B	Ore concentrate (after crushing)	Ore processing plant	60.39	259	26.4	18.564	15.578	38.383
SM3A	Ore concentrate (after flotation)	Ore processing plant	294.77	900	111	19.096	15.603	38.739
SM3B	Ore concentrate (after flotation)	Ore processing plant	74.2	416	20.2	18.962	15.679	38.816
SM4	Ore concentrate (after gravitation)	Ore processing plant	3514.08	3370	456	19.052	15.599	38.612
SM5	Ore concentrate (after magnetic separation)	Ore processing plant	359.16	851	122	19.101	15.598	38.762
G1	Gasoline	Orlovka settlement	N/A	N/A	N/A	18.650	15.665	38.307
G2	Gasoline	Orlovka settlement	N/A	N/A	N/A	18.653	15.655	38.306
<i>Lichens and birch leaves</i>								
LBL	Lichens	Lake Baikal	4.19	63.8	0.71	18.152	15.561	38.321
SEL 2	Lichens	Orlovka settlement	19.47	85.3	1.64	18.158	15.565	38.131
SEL 3	Lichens	Orlovka settlement	8.23	90.6	0.89	18.131	15.565	38.149
SEL 5	Lichens	Orlovka settlement	22.99	93.2	1.51	18.077	15.572	38.093
SEL 6	Lichens	Orlovka settlement	9.53	92.1	1.06	18.114	15.566	38.120
SEL 8	Lichens	Orlovka settlement	10.78	94.3	1.49	N/A	N/A	N/A
TPL 2	Lichens	Tailing pond	10.07	83.6	0.99	18.255	15.563	38.185
TPL 4	Lichens	Tailing pond	32.57	102.6	2.56	18.806	15.611	38.430
TPL1	Lichens	Tailing pond	10.5	N/A	N/A	18.300	15.567	38.180
TPL3	Lichens	Tailing pond	10.3	N/A	N/A	18.457	15.591	38.330
TPL4	Lichens	Tailing pond	30.56	N/A	N/A	18.892	15.606	38.410
ED								
QBL	Birch leaves	Orlovka quarry	0.79	395.8	0.02	17.949	15.540	37.899
BGEBL	Birch leaves	2km east of Orlovka settlement	0.16	27.8	0.01	18.319	15.546	38.177
L1 C	Lichens	Orlovka quarry	13.62	45.5	0.87	18.113	15.560	38.159
L1 ED	Lichens	Orlovka quarry	10.57	48.6	0.53	18.053	15.544	38.077
L2	Lichens	Orlovka quarry	21.68	41.7	1.37	18.100	15.555	38.113
OQL 2	Lichens	Orlovka quarry	13.37	49	1.11	18.127	15.564	38.170
OQL 3	Lichens	Orlovka quarry	17.88	50.3	1.29	18.089	15.562	38.139



Table 1 (continued)

Sample ID	Sample description	Sampling location	Pb	Zn	Zr	<sup>206</sup> Pb/ <sup>204</sup> Pb	<sup>207</sup> Pb/ <sup>204</sup> Pb	<sup>208</sup> Pb/ <sup>204</sup> Pb
OQL 4A	Lichens	Orlovka quarry	16.81	92.1	0.99	18.103	15.561	38.133
OQL 4C	Lichens	Orlovka quarry	11.57	43.4	0.89	18.114	15.555	38.148
OQL 5A	Lichens	Orlovka quarry	17.22	89.4	1.08	18.102	15.560	35.054
OQL 5B	Lichens	Orlovka quarry	14.59	50.3	0.9	18.128	15.548	38.134
SML 5	Lichens	Ore processing plant	17.7	107.5	1.66	18.216	15.560	38.194
SML 6	Lichens	Ore processing plant	32.52	83.7	2.57	18.212	15.567	38.118
SML 7	Lichens	Ore processing plant	19.73	87.9	1.67	18.140	15.574	38.139
SQL 4	Lichens	Spokoioe quarry	29.26	94	2.71	18.459	15.565	38.290

“T” next to the sample ID corresponds to samples that were measured by TIMS.

<sup>a</sup> Topaz–amazonite–albite.

<sup>b</sup> N/A, not analyzed.

first is related to country rock – granite magma interaction processes, when fragments of Zn-enriched wall rock sink into the magma. The second can refer to the hydrothermal alteration of granites

and in this case Zn may be incorporated as a diadochic element in potassium feldspar and micas. Sphalerite (ZnS) can be found in hydrothermal veinlets in the greisens and host rocks contributing to

Table 2

Zn isotopes data for lichens and geologic samples from the Orlovka-Spokoioe mining site

Sample ID	Sample description	Sampling location	$\delta^{66}\text{Zn}$	$\pm 2\sigma^a$	$\delta^{68}\text{Zn}$	$\pm 2\sigma$
LBL	Lichens	Lake Baikal	1.36	0.10	2.59	0.15
SEL3	Lichens	Settlement	0.42	0.02	0.77	0.03
SEL6	Lichens	Settlement	0.90	0.02	1.70	0.03
TPL4	Lichens	Tailing pond	0.97	0.04	1.86	0.08
TPL1C	Lichens	Tailing pond	1.38	0.03	2.61	0.03
OQL2	Lichens	Quarry	1.25	0.01	2.31	0.01
OQL3	Lichens	Quarry	0.87	0.02	1.64	0.06
OQL4C	Lichens	Quarry	0.84	0.02	1.72	0.05
L2	Lichens	Quarry	0.99	0.02	1.88	0.04
SML6	Lichens	Processing plant	0.97	0.04	1.82	0.07
SML7	Lichens	Processing plant	1.18	0.01	2.23	0.03
2142	Biotite/muscovite granite	Orlovka stock	0.35	0.06	0.58	0.07
2151	Biotite/muscovite granite	Orlovka stock	-0.24	0.12	-0.65	0.18
2163	Mineralized toz/amz/ab <sup>b</sup> granite	Orlovka stock	1.20	0.04	2.25	0.02
2164	Mineralized toz/amz/ab granite	Orlovka stock	0.83	0.01	1.59	0.02
2213	Mineralized toz/amz/ab granite	Orlovka stock	-0.04	0.06	-0.07	0.07
2215	Mineralized toz/amz/ab granite	Orlovka open pit	0.30	0.07	0.53	0.23
2144	Amazonite pegmatite	Orlovka stock	0.79	0.11	1.40	0.25
2148	Intensely weathered amz granite	Orlovka stock	-0.15	0.16	-0.56	0.63
2173	Hornfels	Orlovka stock	-0.39	0.02	-0.68	0.21
2068	Hornfels	Khangilay pluton	0.18	0.02	0.18	0.02
2166	Hornfels	Orlovka open pit	-0.34	0.13	-0.99	0.33
2174	Hornfels	Orlovka open pit	0.26	0.06	0.35	0.12
2220	Greisenized granite	Spokoioe open pit	-0.35	0.13	-0.86	0.30
2060	Biotite hornfels	Spokoioe open pit	-0.39	0.13	-1.01	0.14
2125	Mineralized hornfels	Spokoioe open pit	-0.27	0.13	-0.68	0.28

$\delta^{66}\text{Zn}$  values are given relative to Zn standard from the Lyon group (Johnson Matthey metal, batch JMC # 3-0749 L).

<sup>a</sup> Reproducibility estimated from four repeated measurements.

<sup>b</sup> Topaz–amazonite–albite.

elevated Zn values. In rocks other than ore-bearing granites, Zn concentrations are on average lowest in the barren granites (66 ppm), host rocks (76 ppm including one high value of 150 ppm), and tailings (72 ppm) but are higher in ore bearing granites (176 ppm, including one high value of 800 ppm). Ore concentrates contain on average 886 ppm of Zn with 84–324 ppm of this element found in the concentrate after the crushing stage, 3370 ppm after the gravitation stage, 851 ppm after magnetic separation and up to 900 ppm after flotation stage. Lichens and leaves have on average 91 ppm of Zn, which corresponds to the upper limit of an average Zn concentrations found in lichens and leaves (20–90 ppm, Bargagli, 1998).

#### 4.2. Pb and Zn isotopes

##### 4.2.1. Pb isotopes

The following range of Pb isotopes characterizes the anthropogenic and biological samples:  $^{206}\text{Pb}/^{204}\text{Pb}$  from 18.55 to 19.10,  $^{207}\text{Pb}/^{204}\text{Pb}$  from 15.57 to 15.68 and  $^{208}\text{Pb}/^{204}\text{Pb}$  from 38.38 to 38.82 for ore concentrates;  $^{206}\text{Pb}/^{204}\text{Pb}$  from 18.12 to 19.18,  $^{207}\text{Pb}/^{204}\text{Pb}$  from 15.56 to 15.61 and  $^{208}\text{Pb}/^{204}\text{Pb}$  from 37.76 to 38.56 for tailings; and  $^{206}\text{Pb}/^{204}\text{Pb}$  from 17.95 to 18.89,  $^{207}\text{Pb}/^{204}\text{Pb}$  from 15.54 to 15.61 and  $^{208}\text{Pb}/^{204}\text{Pb}$  from 37.9 to 38.43 for lichens and birch leaves (Table 1, Fig. 3). Gran-

ites and ore concentrates exhibit the most radiogenic Pb isotope values of the analyzed sample suite while the majority of lichens and leaves exhibit the least radiogenic range of Pb isotopes and show a significantly different  $^{206}\text{Pb}/^{204}\text{Pb}$  composition than the rest of the groups. Host rocks and tailings show intermediate values of Pb isotopes between the two groups described above.

##### 4.2.2. Zn isotopes

The isotopic composition of Zn varies within the Orlovka–Spokoineo mining district with the total range for geologic samples of  $-0.4\text{‰}$  to  $+1.2\text{‰}$  and for lichens of  $+0.4\text{‰}$  to  $+1.4\text{‰}$  in  $\delta^{66}\text{Zn}$  (Fig. 4). These deviations are significant compared to the analytical uncertainties associated with individual analyses of  $0.06\text{‰}$ .

Mass-dependent fractionation of  $\delta^{66}\text{Zn}$  and  $\delta^{68}\text{Zn}$  is shown in Fig. 5. Geological samples from the Orlovka and Spokoineo deposits form a trend, where Orlovka ore-bearing granites are located at the isotopically heavier end ( $\delta^{66}\text{Zn}$  of up to  $+1.2\text{‰}$ ), and Orlovka barren granites, hornfels and Spokoineo ore-bearing granites at the end with the lightest Zn isotopes ( $\delta^{66}\text{Zn}$  reaching  $-0.4\text{‰}$ ). Hornfels and barren granites of Orlovka and ore-bearing (Sn–W) granite of Spokoineo show a rather narrow range of Zn isotopes ( $\delta^{66}\text{Zn}$  of  $-0.4\text{‰}$  to  $+0.4\text{‰}$ ) compared to the Orlovka ore-bearing

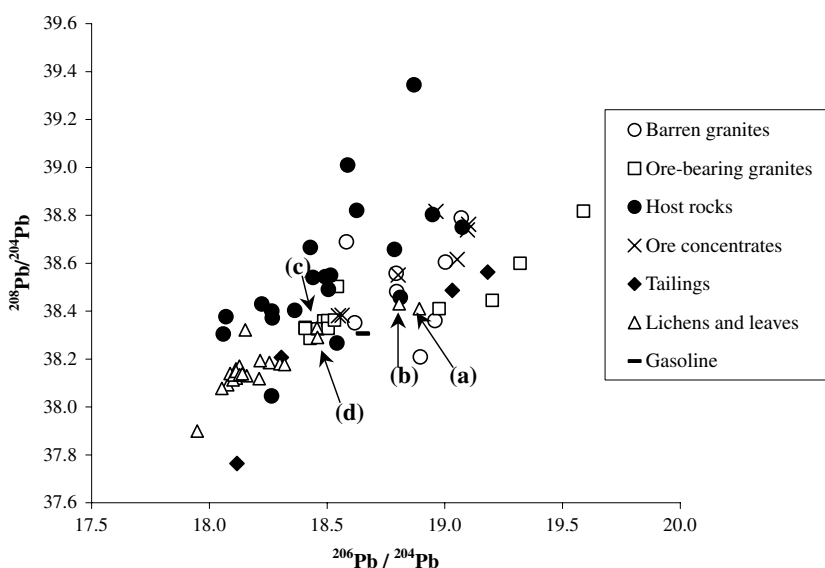


Fig. 3.  $^{206}\text{Pb}/^{204}\text{Pb}$  versus  $^{208}\text{Pb}/^{204}\text{Pb}$  for different potential sources (barren and ore-bearing granites, host rocks, ore concentrates, tailings and gasoline) and receptors (lichens and birch leaves) from the Orlovka–Spokoineo mining site. The error ( $2\sigma$ ) plots within the symbol size. (a) TPL4 ED; (b) TPL4; (c) TPL3 and (d) SQL4.

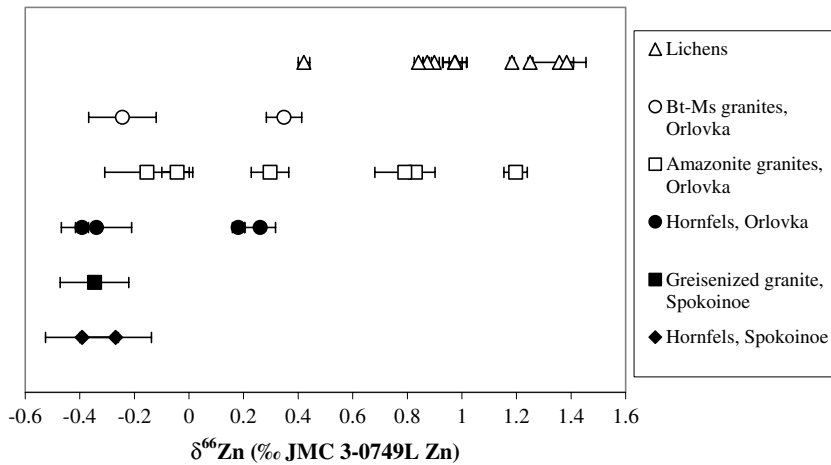


Fig. 4. Summary of  $\delta^{66}\text{Zn}$  data for geologic samples and lichens from the Orlovka–Spokoinoe mining site. All data are given relative to Zn standard from the Lyon group (Johnson Matthey metal, batch JMC # 3-0749 L). The number of replicates used for each samples is 4.

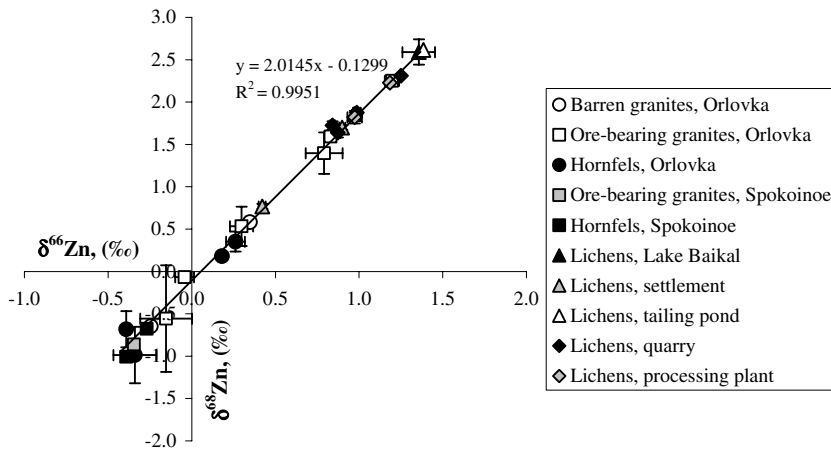


Fig. 5.  $\delta^{66}\text{Zn}$  versus  $\delta^{67}\text{Zn}$  for all samples discussed during the study. All  $\delta$ -values are given relative to the Lyon group JMC Zn (batch 3-0749 L). Gradient and intercept estimates for the regression line are consistent with mass-dependent isotopic variability of Zn, indicating spectral interferences were minimal during data collection for the majority of the samples analysed. Error bars represent the  $\pm 2$  combined internal precision associated with sample and standard analysed for each individual analysis.

(Ta–Nb) granites with larger variability and much heavier isotopic composition ( $\delta^{66}\text{Zn}$  of  $-0.2\text{‰}$  to  $+1.2\text{‰}$ ). Among ore-bearing Orlovka granites only one sample showed a heavy Zn isotopic composition of  $+1.2\text{‰}$ , whereas the most common isotopic composition of these granites is in the range between  $-0.4\text{‰}$  and  $+0.8\text{‰}$ .

Previously published  $\delta^{66}\text{Zn}$  data of terrestrial geologic materials, i.e., USGS terrestrial basalt BCR-1 showed small fractionations of  $\delta^{66}\text{Zn}$  of  $0.2 \pm 0.06\text{‰}$ , whereas black shales exhibited a positive fractionation of Zn isotopes with large variations in  $\delta^{66}\text{Zn}$  of  $+0.3\text{‰}$  to  $+1.1\text{‰}$  (Archer

and Vance, 2004). Both basalts and shales fall within the expanded range of Zn isotope variations typical for the Orlovka–Spokoinoe mining site. These variations are similar to the reported Zn isotope composition of sphalerite in carbonate-hosted Zn–Pb deposits of the Irish ore field ( $\delta^{66}\text{Zn}$  of  $-0.3\text{‰}$  to  $+1.2\text{‰}$ ) (Wilkinson et al., 2005).

Lichens show a positive and rather expanded range of Zn isotopes with  $\delta^{66}\text{Zn}$  of  $+0.4\text{‰}$  to  $+1.4\text{‰}$ . Compared to geologic samples, lichens have the heaviest values of Zn isotopes within the mining site.

## 5. Discussion

### 5.1. Pb and Zn enrichment

In this paper we calculated Pb and Zn enrichment relative to local geologic background using the following equation:

$$EF_X = (X/Zr)_{\text{sample}} / (X/Zr)_{\text{host rocks}},$$

where X is Pb or Zn,  $(X/Zr)_{\text{sample}}$  is the ratio of individual samples, and  $(X/Zr)_{\text{host rocks}}$  is the ratio of the host rocks representing the local background value. The used background values were:  $Pb/Zr = 0.207 \pm 0.288$  and  $Zn/Zr = 0.398 \pm 0.377$  ( $n = 27$ ). The  $Zn/Zr$  value of the local geological background is comparable with the upper crustal  $Zn/Zr$  value of 0.373, whereas the local  $Pb/Zr$  ratio is more than two times higher than the estimated upper crust value of 0.105 (Taylor and McLennan, 1995).

Fig. 6a shows the Pb enrichment ( $EF_{Pb}$ ) calculated for the barren granites (A), ore-bearing granites (B), tailings (C), ore concentrates (D) and lichens and birch leaves (E).

The  $Pb/Zr$  ratios are highest in the ore bearing granites (up to 52), lichens (up to 40) and ore concentrates (up to 8 after gravitation) but low (slightly below or above 1) in all host rocks, barren granites and tailings. Calculated Pb enrichment relative to host rock  $Pb/Zr$  shows significant Pb enrichment in lichens (35–96 times) and notable in the tailings (between 4 and 6 times).

$Zn/Zr$  values vary between different sample groups, reaching a maximum in lichens (61 on average) and a minimum in barren granites and host rocks (0.6 and 0.4, respectively).

$Zn/Zr$  for ore-bearing granites and ore concentrates are of higher values (9.3 and 9.5), compared to tailing pond sediments, where  $Zn/Zr$  is around 3.  $Zn$  concentrations in lichens and leaves do not

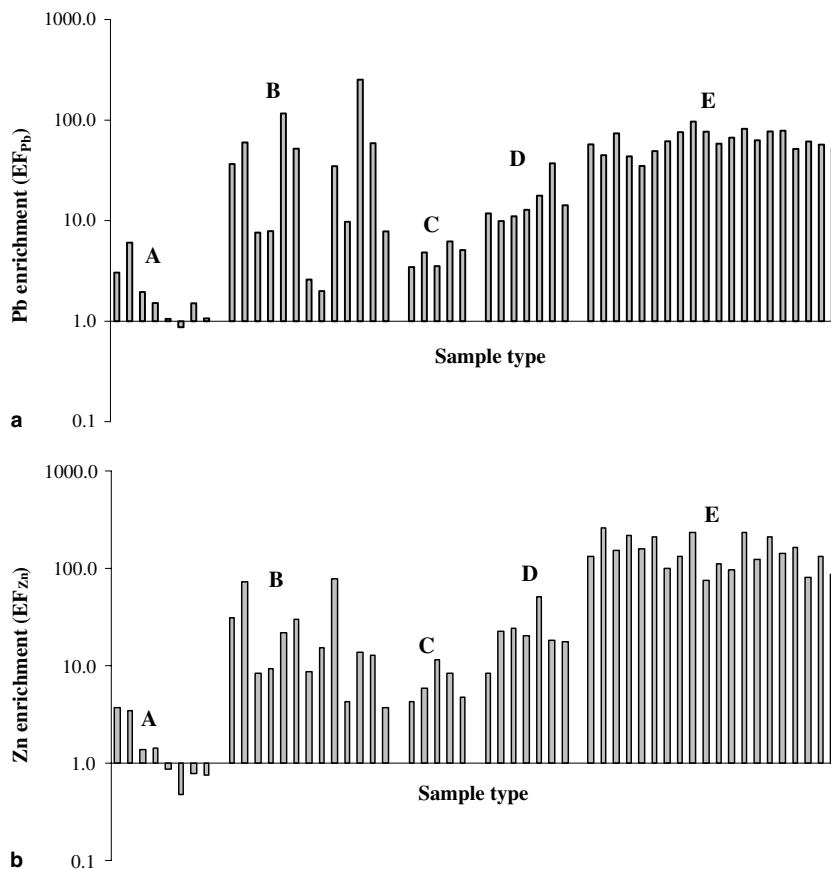


Fig. 6. Pb and Zn enrichment factor ( $EF_{Pb}$ ,  $EF_{Zn}$ ) of the different potential sources (A, barren granites; B, ore-bearing granites; C, tailings and D, ore concentrates) and receptors (E, lichens and birch leaves) relative to the  $Pb/Zr$  and  $Zn/Zr$  background values of the host rocks ( $0.207 \pm 0.288$  and  $0.398 \pm 0.377$ , respectively,  $n = 27$ ).

suggest any Zn pollution of the environment despite the high concentrations of potential sources, such as ore bearing granites. However, Zn enrichment relative to the average host rocks is noted for all sample suites with enrichment reaching up to 12 times in barren granites and tailings, 4–79 times in ore-bearing granites and ore concentrates and up to 152 times in lichens and birch leaves (Fig. 6b). This suggests significant Zn enrichment.

### 5.2. Pb isotopes systematics

Geologic samples and anthropogenic products form a heterogeneous pattern distinct from those of lichens and leaves (Fig. 7). There is no clear relation of the isotope composition of most lichens and leaves to the patterns of the mining district (e.g., to the radiogenicity of the ore concentrates and ore bearing granites, to the overall pattern of the host rocks, to the barren granites and their higher radiogenicity, and to the tailing pond data, which are either oriented towards ore concentrates or low-radiogenic host rocks). Lichens and leaves from the Orlovka–Spokoinoe mining district form two groups. One, represented by four lichen samples (i.e., TPL4 ED, TPL4, TPL3 and SQL4), fits the pattern of the local mining district and is significantly more radiogenic than the other group of lichens and leaves (Fig. 3). The range of Pb isotopes for this group is comparable with the field of heterogeneous data of ore concentrates and tailing pond sediments. It is evident that lichens in the vicinity of the tailing pond are dominated by the influence of a

local component mobilized by mining and ore processing activities. The second (main) group of lichens and leaves (22 samples) is rather homogeneous but has a distinct high  $^{207}\text{Pb}/^{206}\text{Pb}$ . This group requires Pb deposition from yet unidentified source. Lichens are effective as tracers of atmospheric pollution on a regional scale as several studies indicated (Keinonen, 1992; Carignan and Gariépy, 1995; Getty et al., 1999; Simonetti et al., 2003; Zschau et al., 2003). The group of lichens and leaves plot closest to the combined group of Pb aerosols from Eastern Europe, Russia and Mongolia (the reference Pb aerosols values were taken from Bollhoefer and Rosman, 2001, 2002) (Fig. 8). Two tailing samples (e.g., TP4 and TP6) also show a contribution from such external source, where one sample plots within the lichens and leaves group and the second one between the remote component and ore concentrate data. Therefore, these two data points should be considered exceptional rather than representative of the local mining trend (Fig. 3). Interestingly, Pb isotope data of lichens sampled from the Lake Baikal area located ca. 500 km away from the mining site, fits the average isotope composition of the main biological material data group. This suggests the importance of atmospheric Pb transfer from distant sources to the lichens.

### 5.3. Zn isotopes systematics

We find an apparent spatial control of the isotopic Zn composition within the ore district. Heavier Zn is found in the Orlovka deposit ( $\delta^{66}\text{Zn}$  ranging

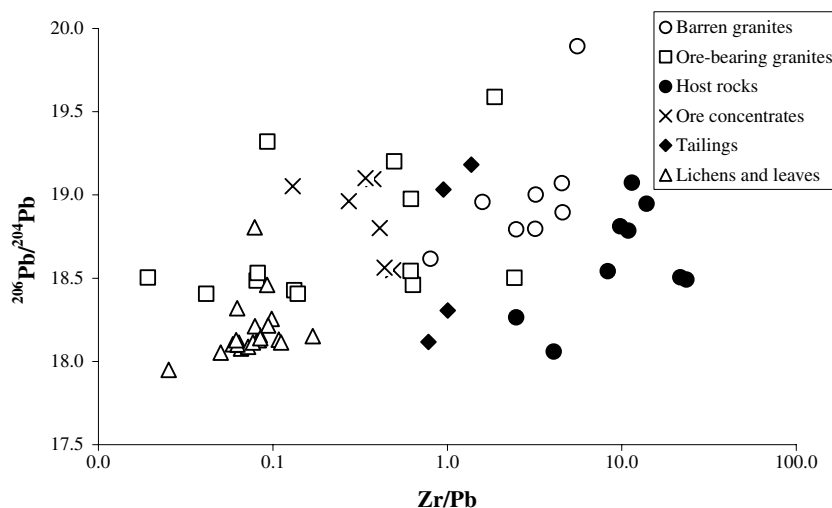


Fig. 7.  $^{206}\text{Pb}/^{204}\text{Pb}$  versus  $\text{Zr}/\text{Pb}$  diagram for different potential sources (barren and ore-bearing granites, host rocks, ore concentrates and tailings) and receptors (lichens and birch leaves) from the Orlovka–Spokoinoe mining site.

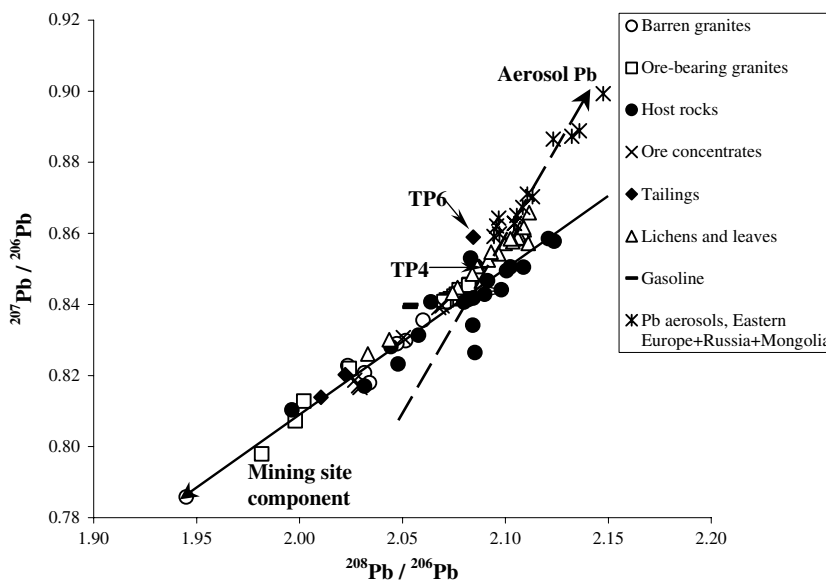


Fig. 8.  $^{208}\text{Pb}/^{206}\text{Pb}$  versus  $^{207}\text{Pb}/^{206}\text{Pb}$  plot for different potential sources (barren and ore-bearing granites, host rocks, ore concentrates, tailings, gasoline and Pb aerosols) and receptors (lichens and birch leaves) from the Orlovka–Spokoinoe mining site. Pb isotopes suggest two sources: atmospheric deposition of aerosol lead and non-atmospheric Pb derived from local mining activities. The error ( $2\sigma$ ) plots within the symbol size.

between  $-0.39$  and  $+1.20$ ) and lighter Zn ( $\delta^{66}\text{Zn}$  between  $-0.39$  and  $-0.27$ ) in the Spokoinoe deposit. This is in line with work of Wilkinson et al. (2005) on sphalerites in the Irish ore field, which suggested that the dominant processes controlling Zn isotopic variability operate on a deposit scale. There seems also an apparent temporal control in that the less evolved granites (biotite-muscovite granites) and hornfels (hornfels, mineralized hornfels, biotite hornfels) have tentatively lighter Zn compared to the most evolved mineralized granites (e.g., sample 2163, a mineralized topaz–amazonite–albite granite has a  $\delta^{66}\text{Zn}$  value of 1.20). This agrees again with Wilkinson et al. (2005), who found the heaviest Zn in late stage sphalerite minerals. Compared to the geological material, the lichens from the Orlovka–Spokoinoe mining district tend to exhibit heavier Zn isotopic compositions (up to 1.38 for  $\delta^{66}\text{Zn}$ ), and they only partly overlap with the geological samples (Fig. 4). The highest  $\delta^{66}\text{Zn}$  values ( $>1\%$ ) are found in lichens from the tailing pond area, quarry, processing plant and from the pristine environment of Lake Baikal situated about 500 km away from the mining area.

While some of  $\delta^{66}\text{Zn}$  values of lichens agree with measured values from the surrounding geological sources, the heaviest Zn signatures cannot be derived from those sources and we can consider four

possibilities for the enrichment in  $^{66}\text{Zn}$ : (1) selective adsorption of heavier Zn on the lichen surface from a dissolved Zn fraction; (2) isotopic fractionation of Zn through plant uptake; (3) long range transport of aerosols characterized by a heavy Zn isotopic composition and (4) a regional unidentified anthropogenic or geological source.

While we cannot rule out option 1 and 2, we believe they are not important. Firstly, controlled lab experiments of Zn uptake in plants suggests that adsorption of dissolved Zn on the root induced only a small positive fractionation (Weiss et al., 2005). Secondly, Zn isotope variations in deep-sea carbonates from the Pacific ocean (Pichat et al., 2003) and hydroponic plant uptake studies of higher plants (Weiss et al., 2005) suggest that biological uptake results in selective uptake of the light isotopes. Zinc derived from an unknown (long-range) aerosol source agrees with heavier Zn (up to 1.2 for  $\delta^{66}\text{Zn}$ ) found in peat bog sections representing aerosol deposition from pre-industrial times in Finland (unpublished data). Aerosols can have up to a hundredfold enrichment for Zn and Pb (Luck and Othman, 2002), so this additional source is possible and also agrees with the calculated Zn enrichment. Therefore, the source of isotopically heavy Zn within the Orlovka–Spokoinoe mining district could be potentially associated with earlier described long-

range atmospheric aerosols that also contributed Pb (see discussion on Pb).

## 6. Conclusions

A study using elemental ratios and Pb and Zn isotopes provided a unique possibility to identify Pb and Zn sources within the rare-metal Orlovka–Spokoinoe mining site and resulted in the following conclusions:

- (i) Significant Pb and Zn enrichment relative to the host rock was observed in lichen thalli and plant leaves, suggesting important contribution from sources other than natural dust derived from the host rocks of the local environment.
- (ii) Isotope ratios of Pb and Zn identify the contribution from additional, remote sources, for these elements potentially derived via long-range transport from other anthropogenic activities or dust.

Our work demonstrated the potential of isotopic tracer techniques to identify additional sources of potentially toxic elements, such as Pb and Zn. In addition, it is demonstrated that a given mining activity is not necessarily responsible for metal pollution nearby.

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