

Dust dispersal and Pb enrichment at the rare-metal Orlovka–Spokoinoe mining and ore processing site: Insights from REE patterns and elemental ratios

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Abstract

Different geological, technogenic and environmental samples from the Orlovka–Spokoinoe Ta–Nb–Sn–W mining site and ore processing complex in Eastern Transbaikalia (Russia), were analysed for Pb, Y, Zr, Hf and rare earth elements (REE) to assess the effect of dust and metal dispersal on the environment within the Orlovka–Spokoinoe mining site. Potential source material analysed included ore-bearing and barren granites, host rocks, tailing pond sediments, and ore concentrates. Lichens and birch leaves were used as receptor samples. The REE enrichment relative to chondrite, the extent of the Eu anomalies, the enrichments of heavy REE (HREE), and Zr/Hf and Yb/Y ratios suggest that tailings, barren granites, and metasedimentary host rocks are the main sources of dust in the studied mining environment. In addition, calculated lead enrichment (relative to host rocks) suggests that the environment is polluted with Pb. Our results clearly demonstrate the potential of REE patterns and elemental ratios as a reliable technique to trace dust and metals sources and dispersal within a confined mining area offering a new tool for environmental assessment studies.

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Keywords: REE patterns; Elemental ratios; Enrichment factors; Metal dispersal; Orlovka–Spokoinoe rare-metal mining site

1. Introduction

Abandoned hard-rock metal mines have left a heavy legacy for potential environmental contamination across the world. Mined quarries, mine dumps and tailings (the material left over from the ore processing) as well as associated mineral processing and smelting plants, can contaminate the surrounding watershed and ecosystem by the release of metals and dust into the environment through wind blown dust particles [1–3], representing a serious threat to human health and local ecosystems, e.g. through accumulation of metals in food chains [4].

Dust dispersal represents a very important health hazard—due to both the small particle sizes and their effects on the respiratory system and to the dust's ability to carry potentially toxic trace elements such as Pb [5]. Dust carried away from the mine has a large surface area and is very susceptible to

chemical weathering. When sulphide minerals contained in dust from mine tailings are exposed to oxygen and water, they oxidise and dissolve [6].

If contamination from past and present mining or mineral processing is suspected, a thorough monitoring and an accurate source assessment are crucial to plan a cost efficient and targeted clean-up of the site. This, however, is often difficult given the many potential sources around a mining complex. Various microchemical, geochemical and mineralogical investigations of dust emitted by smelters have been conducted (e.g. [7,8]) and showed that precise and accurate source characterisation and thus assessments are possible. However, these methods are all very labour intensive and do not allow rapid screening of dust dispersal and characterisation on a larger scale [7].

Rare earth elements (REE) patterns have been used extensively in igneous, sedimentary and metamorphic petrology to trace sources of rocks and minerals during crustal and mantle evolution [9]. Due to its indicative and similar geochemical behavior Y, with an ionic radius similar to that of Ho, is sometimes included along with REE. The low atomic number

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members of the series are termed the light rare earths (LREE) and those with higher atomic numbers the heavy rare earth elements (HREE). A number of properties of the REE suggest that they should also be useful in the study of environmental processes as: (1) they are among the least soluble trace elements, and (2) they are relatively immobile during low-grade metamorphism, weathering and hydrothermal alterations [9]. There have been environmental geochemical studies using the REE patterns in the environment, e.g. in surface waters [10] and sewage water [11,12] to assess acid mine drainages, in oceanic waters to assess riverine inputs [13] or in peat bogs to assess sources of dust [14].

Trace element ratios are sensitive indicators to identify fractionation processes and fluid–rock interaction [15], and thus serve as a tool to discriminate groups of different origins and geneses. In previous research Zr/Hf, Y/Ho and Rb/Sr were used as diagnostic ratios for the investigation of the geochemical evolution of the deposit, i.e. to assess the evolution of the Orlovka granite intrusion [16,17], whereas Nb/U and Ce/Pb allowed constraining of crust–mantle input during the formation of the Orlovka–Spokoinoe ore-bearing granites [17]. In this study we use Zr/Hf and Yb/Y ratios as independent tool to trace dust sources within the mining site.

For biomonitoring environmental contamination around smelters and mining sites lichens have proved to be invaluable tools [18,19]. Lichens receive dust and pollutants from atmospheric deposition and consequently are regarded as suitable tools for monitoring levels of atmospheric contamination. However, despite these previous findings, studies using REE patterns in lichens to assess the impact of mining on the environment are very limited [20–22] and there is a clear potential to develop this source proxy further.

The aim of this investigation is to assess the potential of REE patterns, elemental ratios and enrichment factors in lichens and leaves to trace dust and metal dispersal within the environment of the Ta–Nb–Sn–W Orlovka–Spokoinoe mining site in Eastern Transbaikalia, Russia. To achieve this, we undertook REE, Y, Pb, Zr and Hf analysis of potential sources and receptors of the mining site. The selected samples included ore-bearing and barren granites from the magmatic intrusions, host rocks, tailings, ore concentrates and lichens and birch leaves. This work was conducted in the framework of the INTAS project 97-0721, which determined the geologic controls on the distribution of potentially toxic concentrations of elements and assess most of the environmental situation in the abandoned Orlovka–Spokoinoe mining site [23]. The Orlovka–Spokoinoe mining site is situated within a previously closed territory and provided strategic metal resources (Ta, Nb, W, Li, Be) for the former Soviet Union defense industries. The Orlovka plant had processed rare-metal ores from Orlovka deposit since the early sixties. In 1993, mining was temporarily stopped and only in recent years has work at the processing plant restarted sporadically. However, significant reserves of unsold potentially economic products, as well as low-grade, metal-bearing waste tailings are stored. Ores of the Orlovka deposit are enriched in Ta, Nb, Li, and F, whereas ores from the adjacent Spokoinoe deposit are also rich in W, Sn and Be. The list of associated toxic elements includes Pb, As, Cd, U, Th, Se, Bi, Hg, Sb, Zn, Mo, and Be. Two towns,

Novoorlovsky and Staroorlovsky, with 40,000 inhabitants in total are situated 5 and 10 km away from the ore processing plant, respectively.

2. Materials and methods

2.1. Orlovka–Spokoinoe mining site and geological setting

The Orlovka–Spokoinoe mining site is located in Eastern Transbaikalia 140 km SE of Chita, Russia. It consists of two major quarries (Orlovka and Spokoinoe) situated ~8 km from each other. Adjacent to the quarries is an ore crushing and processing facility that provides Ta–Nb and Sn–W ore concentrates, which are then transported for further processing outside of the mining site. The tailings from the mining activities are deposited in a large pond next to the ore processing complex.

The geology and the evolution of the ore-bearing granites of the Orlovka tantalum deposit and the Spokoinoe tin–tungsten vein quartz–greisen deposit within the Orlovka–Spokoinoe mining site have been discussed in all details elsewhere [17,24,25]. In summary, both deposits were formed from magmatic intrusions into the host rocks (felsic volcanics, metasediments and hornfels) during the late Jurassic. The Orlovka tantalum deposit is confined to the apical part of the Orlovka granite cupola. The tantalum minerals are represented by finely disseminated (0.01–1 mm) tantalite, tantalite–columbite, microlite and pyrochlore accumulated in the endocontact rocks of the granite cupolas. The Spokoinoe tin–tungsten deposit is characterized by tungsten (tin–beryllium) vein quartz–greisens and is composed of albite–muscovite granites similar to the Khangilay massif, but alaskitic leucogranites prevail. In the upper parts of the cupola the granites are albitized and greisenized with tungsten mineralization, major ore minerals being 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 through several low temperature physical and chemical separation steps. Firstly, the ore is crushed and milled to a particle size of 2 mm; then a further reduction of the particle size (down to 0.05 mm) is achieved using gravity concentration. The production of the raw ore concentrate consists of further gravity concentration, magnetic separation and sulphide flotation (Fig. 1). The tailings from the ore mining, ore crushing and extraction processes are deposited next to the complex in a shallow pond.

2.3. Sampling of representative source and receptor material

Whole-rock samples were collected in the field and from the quarries representing the granite intrusions of Orlovka and Spokoinoe deposits (ore-bearing and barren granites), classified according to the mineralogy (see details in [17,24]) and the host rocks. Samples from different stages of ore processing (gravitation, magnetic separation, flotation and the final Ta–Nb

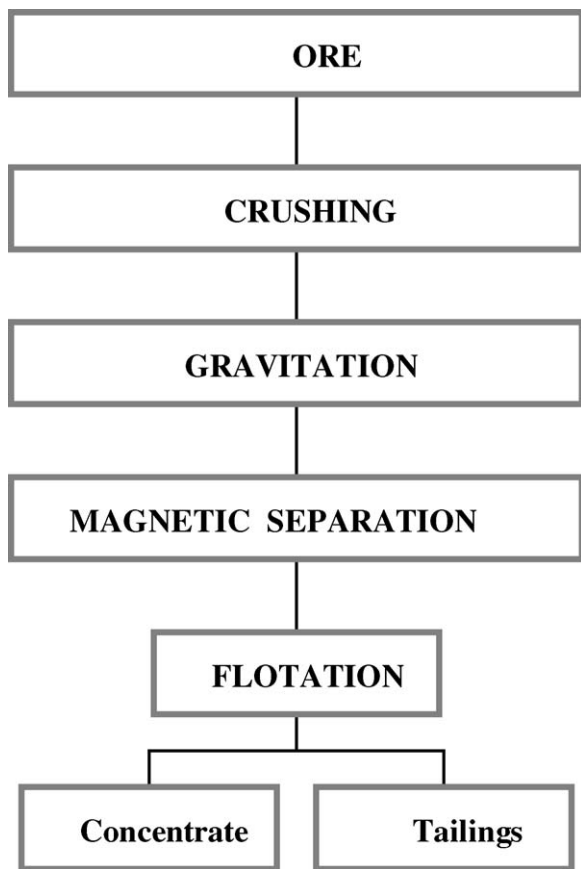


Fig. 1. Processing stages of the Ta–Nb ore from the Orlovka deposit.

concentrate) were collected in the processing plant and tailings were collected from the tailing pond shore.

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 Novoorlovsky settlement.

In the laboratory, ore processing plant samples, tailings, lichens and leaves were placed into previously cleaned ceramic beakers and dried at 40 °C overnight. Lichen and leaf samples were ground in an agate mortar using liquid nitrogen. Samples were sieved through 100 µm stainless steel sieve, placed in ceramic beakers and dried overnight at 40 °C prior to analysis. Whole rock samples, tailings and ore concentrates samples were prepared by milling them in a Tema agate mill. Samples

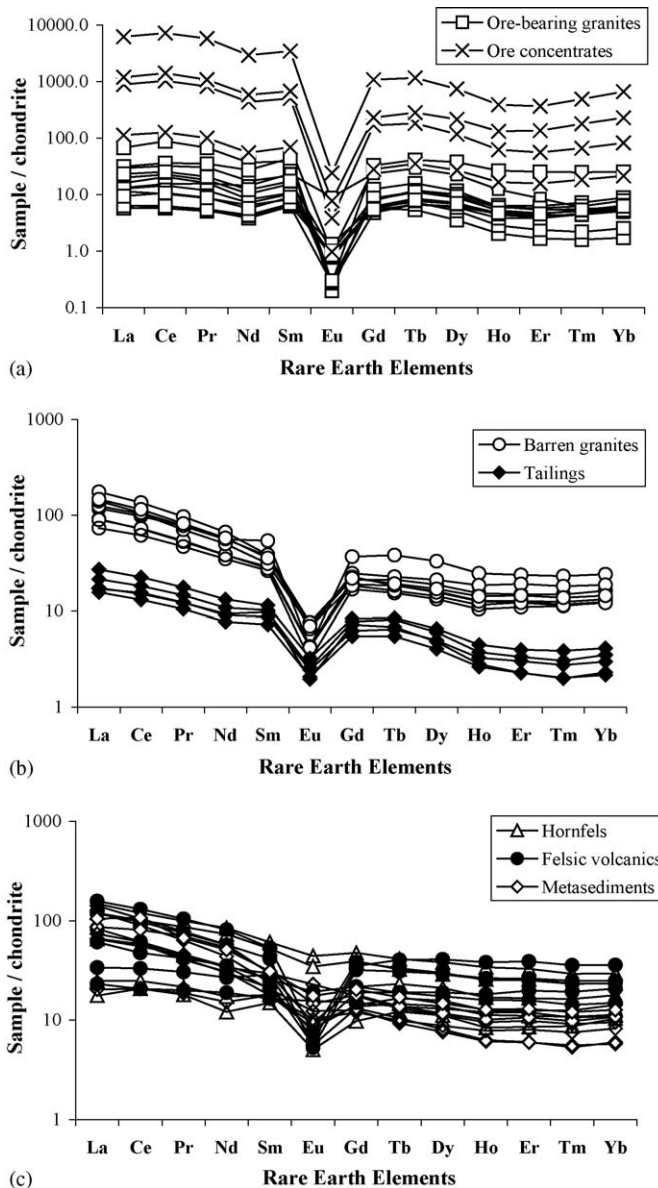


Fig. 2. The REE patterns of possible pollutant sources including geologic suites with ore-bearing granites and ore concentrates (plot a); barren granites and tailings (plot b); different host rocks (plot c).

Table 1
Source/receptor description indicating the sample type, number of samples analysed and sampling location within the Orlovka–Spokoinoe mining district (see text for details)

Source/receptor	Sample type	N	Sampling location
Barren granites (BG)	Biotite and biotite/muscovite granites	7	Khangilay pluton, Orlovka stock
Ore-bearing granites (OG)	Mineralized topaz/amazonite/albite granites	5	Orlovka open pit
Host rocks (HR)	Hornfels, metasediments, felsic volcanics	13	Orlovka open pit, Spokoinoe open pit
Ore concentrates (OC)	After crushing (SM), gravitation (SM4), magnetic separation (SM5), flotation (SM3)	14	Ore processing plant
Tailing pond sediments (TP)	Surface sediments	5	Tailing pond
Lichens and leaves (LL)	Lichens and leaves	13	Orlovka quarry, Spokoinoe quarry, tailing pond, settlement, ore processing plant

were then homogenised, and transferred into the acid cleaned plastic bottles for further use. Table 1 summarizes the type of samples used and sampling location.

Lichens and birch leaves were digested using a MARSX high pressure/high temperature microwave oven system and a $\text{HNO}_3/\text{HF}/\text{H}_2\text{O}_2$ acid mixture [26]. 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 from lichens and birch leaves. Pb analysis was performed using Fison's Instruments ARL 3508B ICP-AES at Imperial College London. Precision and accuracy were assessed using standard reference materials of lichens and leaves and were within 10%.

Y, Zr, Hf and the REE in lichens and leaves were determined by inductively coupled plasma mass spectroscopy (ICP-MS) using a Perkin-Elmer Elan 6000 instrument at the Acme Analytical Laboratories, Vancouver. 0.5 g of samples was digested in HNO_3 and Aqua Regia. The V6 vegetation standard of the Geological Survey of Canada was used as the standard reference material to control analytical reproducibility and accuracy that were within 12% for all measurements. The barren and ore-bearing granites, host rocks, tailing pond sediments and ore concentrates were dissolved using hot plate digestion with a standard HNO_3/HF acid mixture in closed Teflon beakers [17]. Pb, Y, Zr, Hf and the REE in rock samples, tailings and ore concentrates were determined by quadrupole based inductively coupled plasma mass spectrometry (ICP-MS) at the GFZ Potsdam using an ELAN 5000A ICP-MS (Perkin-Elmer/SCIEX, Canada). Detailed description of the instrumental parameters

and method and typical analytical precision and accuracy of the method are given elsewhere [27]. Briefly, about 0.1 g of sample powder was dissolved using mixed acid digestion (HF/HClO_4) under pressure and filled up with 0.5 M HCl up to 50 ml of final volume. 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 inductively coupled plasma mass spectrometer (ICP-MS) (Perkin-Elmer/SCIEX, Canada). Samples were measured in batches of five. Quantitative determination of element concentrations was performed applying external calibration using two calibration solutions, which bracketed each batch of samples. Interference corrections were routinely applied to correct analyte isotopes for molecular and isobaric interferences [27]. Precision and accuracy were within 5–10%. The full list of geological standard reference materials used during the measurements can be found in [27].

3. Results and discussion

3.1. REE patterns—tracing the dust sources

Fig. 2 shows the REE patterns from the granites (ore bearing and barren), the ore concentrates, the tailings, and the host rocks (hornfels, metasediments and felsic volcanics). The REE concentrations were normalised relative to the average chondritic value taken from Boyton [28]. The REE patterns of all samples form a monazite-type pattern (Fig. 2), where the light REE (LREE) are more abundant than the heavy REE (HREE).

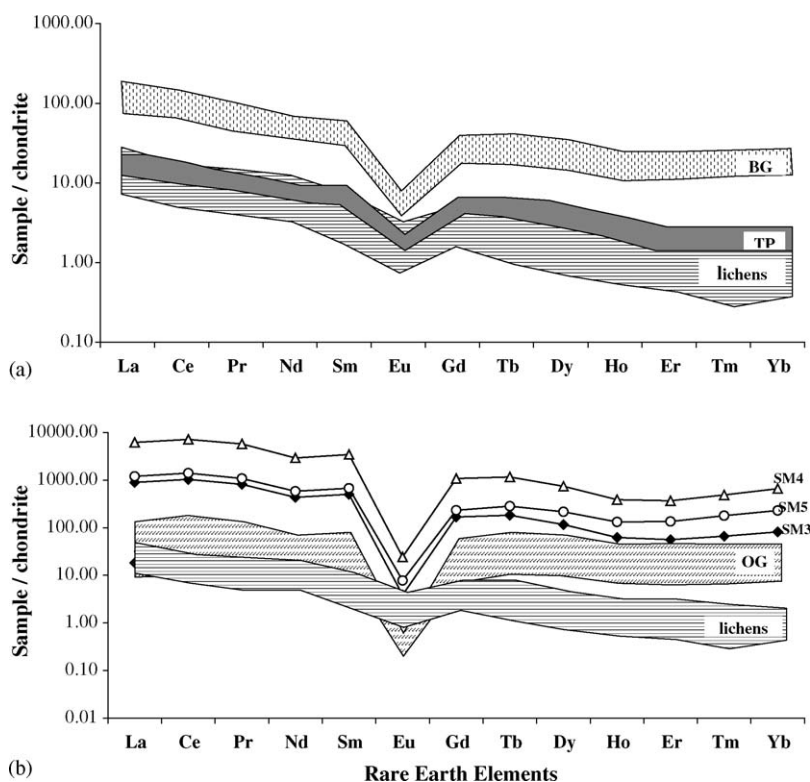


Fig. 3. The REE patterns of lichens (horizontal shading) compared to the REE patterns of barren granites + tailings (plot a); to the REE patterns of ore-bearing granites + ore concentrates (plot b).

Within the geological samples suite, the ore-bearing granites, represented by highly evolved amazonite granites [17,29], show the strongest developed Eu anomaly and REE tetrad effects (i.e. rounded segments or tetrads of the pattern) become more apparent (Fig. 2a). This is in agreement with previous work showing that the tetrad effect develops parallel to granite evolution, and significant tetrad effects are strictly confined to highly differentiated samples.

The REE patterns of different ore concentrates fractions inherit the general pattern of the ore-bearing granites—including the tetrad effect, negative Eu anomaly and [LREE] > [HREE], even though after the concentration steps of gravitation, magnetic separation and flotation, the Eu anomaly has become significantly larger and most importantly, the REE are strongly

enriched up to two orders of magnitude relative to the original granites (Fig. 2a).

The REE patterns of the tailing pond sediments (Fig. 2b) strongly resemble the barren granites—no large variations in REE enrichment (all less than 40 times average chondrite values) and slightly developed Eu anomalies. Although tailing pond sediments plot within the ore samples reflecting some of the naturally inherited characteristics of the latter, they show a specific REE pattern, which can be used as their identification tool.

The REE patterns of the host rocks, represented by hornfels, felsic volcanics and metasediments, show in general flat patterns apart from a few hornfels samples from the Orlovka deposit (Fig. 2c).

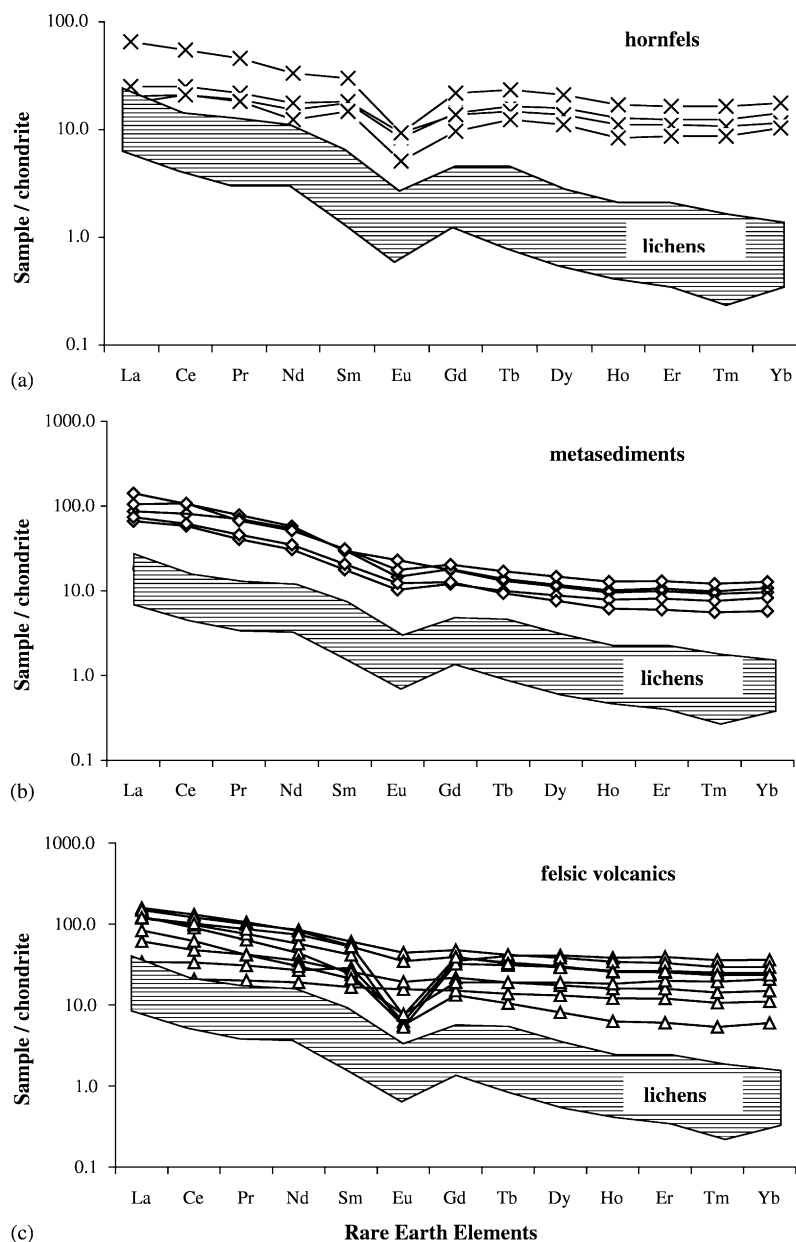


Fig. 4. The REE patterns of lichens (horizontal shading) compared to the REE patterns of host rocks: hornfels (a), metasediments (b) and felsic volcanics (c) to assess the influence of the geological background on dust deposition.

Among lichen and leaf species the average total concentrations of REE range from 9 to 32 $\mu\text{g/g}$ with the highest concentrations found in lichens and leaves sampled around the ore processing plant (17–32 $\mu\text{g/g}$) and lowest around the settlement, quarry and the tailing pond (9–22 $\mu\text{g/g}$). These concentrations are of a similar range reported for the lichens before [22]. All lichen and leaf samples included in the study are depleted in REE with respect to average crustal REE abundances [30]; some by more than 20 times.

Assuming that REE patterns are congruent or parallel if linked to each other, we plotted the REE pattern of lichens and leaves with the REE patterns of the potential sources (Fig. 3a and b). The lichens pattern is very similar to the REE patterns of the tailing pond sediments (Fig. 3a), showing similar slopes and shallower Eu anomaly compared to ore-bearing granites and ore concentrates (Fig. 3b) described above. Despite some depletion of REE contents in lichens and leaves (likely reflecting dilution effects due to the organic matter), their REE patterns are similar to REE patterns of barren granites (Fig. 3a). Comparison between REE patterns of lichens and leaves and those of host rocks (felsic volcanics, metasediments and hornfels) are shown in Fig. 4a–c. Beside the depletion of REE contents in lichens and leaves, the HREE show stronger depletion (fractionation?) relative to the volcanic and hornfels host rock groups resulting in a more inclined REE pattern in lichens and leaves (Fig. 4a and c). However, the REE patterns of the lichens and leaves are very similar to the metasediments and consequently, this host rock cannot be excluded as a potential dust source (Fig. 4b).

3.2. Zr/Hf and Yb/Y—additional evidence on the dust dispersal

The Zr/Hf ratio has been used previously during the study of the geochemical evolution of the Orlovka and Spokoineo deposits as a diagnostic ratio to assess the evolution of granite intrusions [17]. In contrast to their behavior in common magmatic rocks, the ratios of pairs of chemically coherent elements such as Hf/Zr, Ta/Nb and heavy REE/light REE are found to increase in minerals of granitic pegmatites [31] typical of the Orlovka system. Extreme differentiation of melts is required to achieve changes of these ratios because of the nearly identical chemical behavior of the related elements, which is largely the result of their correspondence in ionic radii and valence. Such patterns permit the application of trace element ratios to discriminate groups of different origin and genesis. Use of these indicative ratios allows assessment of the relationship between the sample groups of different origins. Zr/Hf plotted against Pb/Hf permitted: (1) distinction between two different sample groups such as (a) ore-bearing granites and ore concentrates, (b) lichens, leaves, tailings, barren granites and host rocks (Fig. 5a and b); (2) identification of the main dust sources such as tailings, barren granites and host rocks, with which lichens and leaves form a clearly distinguished group.

Y, commonly used as an analogue to the LREE is contained in xenotime, which plays a role in the magmatic fractionation

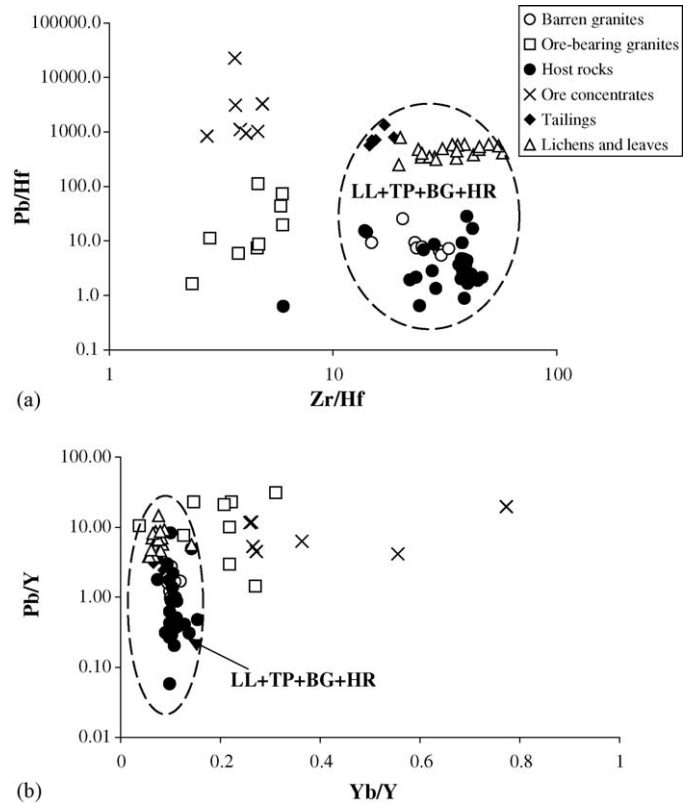


Fig. 5. Zr/Hf vs. Pb/Hf (a) and Yb/Y vs. Pb/Y (b) for barren granites, ore-bearing granites, host rocks, ore concentrates, tailing pond sediments and lichens and leaves. The lichen and leaves field is characterised by high Zr/Hf and Pb/Hf ratios, agreeing well with the tailings, host rocks, and barren granites but excluding most of ore concentrates and ore-bearing granites as possible dust sources. BG, barren granites; TP, tailing pond sediments; HR, host rocks; LL, lichens and leaves.

of the Orlovka–Spokoineo granite suite. Xenotime is known to be a stable accessory phase in the Khangilay pluton but unstable in the fluorine-enriched environment of the ore-bearing processes leading to the Orlovka Ta–Nb and Spokoineo W–Sn deposits. This explains the change from immobility to mobility of Y from the low fractionated Khangilay pluton to the highly fractionated Orlovka–Spokoineo ore-bearing granites and consequently their technogenic (anthropogenic) products, the ore concentrates. Yb represents the HREE. Therefore, the Yb/Y ratio is used to normalize the whole REE spectrum (Fig. 5b). Ore concentrates have the highest Yb/Y values compared to other sample groups. The highest Yb/Y value can be explained by xenotime (as the Y carrier) removal during different stages of ore processing leading to the highest values. Plot of Yb/Y versus Pb/Y (Fig. 5b) reflects different geologic and technogenic processes resulting in distinct sample groups. Lichens and leaves exhibit the closest link to the tailings, host rocks and barren granites (Fig. 5a and b) and form a group with them, whilst their relationship to the other sample groups is less clear. Pb/Y ratio of ore-bearing granites and ore concentrates is 10–100 times higher than that of the host rocks. Ore concentrates reflect features of the ore-bearing granites by forming one group with them; however, they exhibit a rather scattered pattern.

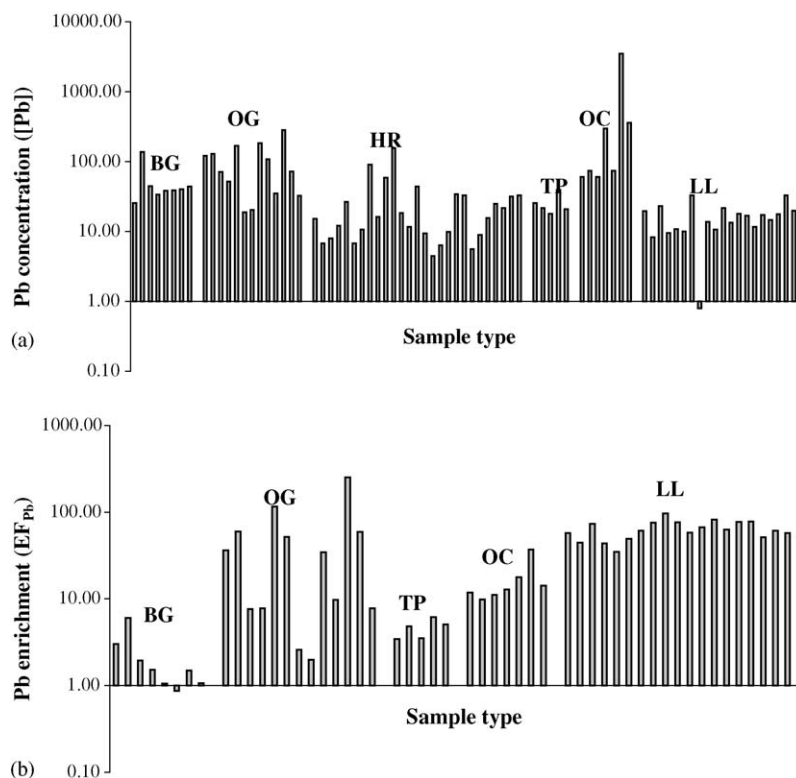


Fig. 6. Lead concentrations [Pb] (in ppm) (plot a) and Pb enrichment factors EF_{Pb} (plot b) of the different potential sources (host rocks, HR; barren granites, BG; ore-bearing granites, OG; ore concentrates, OC; tailings, TP) and receptors (lichens and birch leaves, LL) within the Orlovka–Spokoinoe mining site.

3.3. Pb concentrations and Pb enrichment

Fig. 6 shows the Pb concentrations (plot a) and Pb enrichment (EF_{Pb} , plot b) from the granites (barren, BG; ore bearing, OG), the host rocks (HR), tailing pond sediments (TP), the concentrates (OC), and the lichens and leaves (LL). The Pb enrichment (EF_{Pb}) was calculated using the equation:

$$EF_{Pb} = (Pb/Zr)_{\text{sample}} / (Pb/Zr)_{\text{background}}$$

where $(Pb/Zr)_{\text{sample}}$ is the ratio of the sample and $(Pb/Zr)_{\text{background}}$ is the ratio of the host rocks representing the local background value (arithmetic average of 0.207 ± 0.288 , $n = 27$).

The Pb concentrations are on average lowest in the host rocks ($26.6 \mu\text{g/g}$ including two high values of 155 and $90 \mu\text{g/g}$), tailings ($26.0 \mu\text{g/g}$) and lichens and leaves ($13.7 \mu\text{g/g}$) but are higher in the barren and ore-bearing granites (50 and $99 \mu\text{g/g}$, respectively) due to the presence of amazonite as the main Pb carrier. The range of Pb concentrations in the different ore concentrates is large, with highest values of 0.35% in concentrates after the gravitation stage, correlating with high Ta and W concentrations.

The Pb/Zr ratios are the highest in the ore-bearing granites (up to 52.1), lichens (up to 40) and ore concentrates (up to 7.7 after gravitation) but low (below 1) in all barren granites and tailings (0.7 – 1.3).

As seen in Fig. 6a, the Pb concentrations in lichens and leaves do not suggest any Pb contamination of the environment

despite the high concentrations of potential sources such as ore concentrates and ore-bearing granites. However, calculated Pb enrichment relative to host rocks shows slight Pb enrichment in the tailings (five to six times) and significant in lichens and leaves (between 35 and 191 times) despite the low Pb concentrations.

4. Summary

An environmental geochemical study has been conducted in the Orlovka–Spokoinoe mining site in Transbaikalia, Russia, to assess the sources of dust in the environment and the impact of the mining and ore processing activities. Measurements of REE, Pb, Zr, Hf, Yb and Y in possible sources (host rocks, tailings, ore concentrates, ore-bearing and barren granites) and receptors (lichens and leaves) were conducted. REE patterns normalised to average chondritic values, and Zr/Hf and Yb/Y ratios were used as geochemical tools to trace dust sources within the mining site. REE patterns were successfully used to link natural geological sources (ore-bearing amazonite granites of the Orlovka deposit) to their anthropogenic products (ore concentrates from different processing stages and tailings). This allowed identification of natural (geologic) and anthropogenic (ore concentrates, tailings) sources for particles dispersed within the mining area. Comparison between REE patterns of lichens and leaves and those of geological and anthropogenic origin showed that the tailing pond sediments, barren granites and metasedimentary host rocks can be considered as the main sources for the dust dispersion in the studied mining environment. We also showed that even though

Pb concentrations are not elevated, Pb is enriched in lichens and leaves relative to the host rocks. A detailed Pb source assessment is subject of another paper [32].

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