REE, Uranium (U) and Thorium (Th) contents in Betula pendula leaf growing around Komsomolsk gold concentration plant tailing (Kemerovo region, Western Siberia, Russia)

D V Yusupov, Yu A Karpenko

Department of Geoecology and Geochemistry, Institute of Natural Resources, National Research Tomsk Polytechnic University, 30 Lenin Av., Tomsk, 634050, Russia

yusupovd@mail.ru , schaman734@gmail.com

Abstract. The article deals with the research findings of peculiarities of REE, Uranium and Thorium distribution in the territory surrounding the tailing of former Komsomolsk gold concentration plant according to the data from *Betula pendula* leaf testing. In the leaf element composition the slight deficiency of MREE and substantial excess of HREE are presented. In the nearest impacted area around the tailing, La, Yb, U and Th content, and Th/U ratio are lower than in the distant buffer area. It is shown, that value of Th/U ratio and REE can be an indicator for geochemical transformations of technogenic landscapes in mining districts. The results of the research can be used for biomonitoring of the territory around the tailing.

1. Introduction

For applied problem solving in geochemical researches, rare earth (REE) and radioactive (U, Th) elements are often used. The study of their distribution in natural and technogenic environments gives an opportunity for detecting of different classification features, determining of regularities, assessment of substance income sources and its differentiation degree [1-4]. For example, Th/U ratio, REE in plant and soil matters can reflect geochemical compound of underlying rocks in the conditionally background areas, they also allow detecting of the nature imbalance of these elements in technogenic landscapes [5-10].

The mining industry wastes affect negatively the environment and humans. The non-natural geological features – tailings – have the most negative impact, where the significant amount of waste with untreated mineral components is stored.

As a result of hypergenesis processes (decomposition, oxidation, solution, hydrolysis and others) primary ore minerals transform into secondary mineral forms. Heavy metals containing there migrate actively into the environment, pollute its components: atmosphere, surface water, ground waters, soil, flora, exceeding background concentrations and maximum permissible concentrations [11, 12].

The research purpuse is to study concentration distribution of rare earth elements, Uranium and Thorium in *Betula pendula* leaf as bioindicators in tailing areas of former Komsomolsk gold concentration plant for their usage in monitoring of polluted areas.

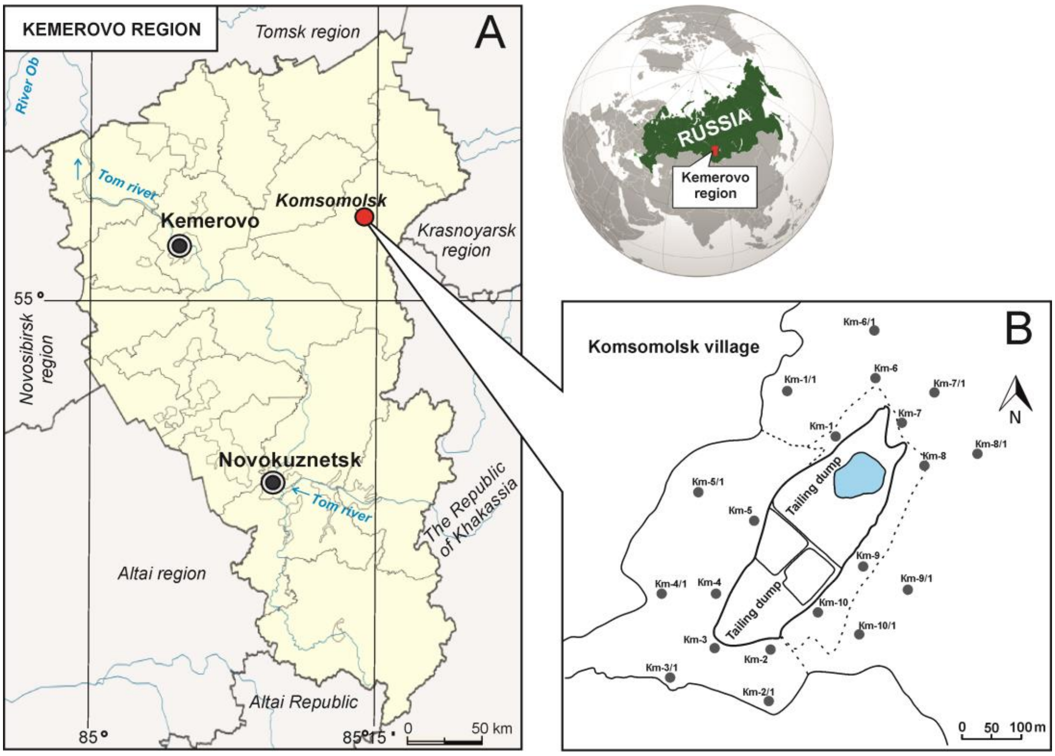

Figure 1. Map of the study area position **(A)**, location of Komsomolsk tailing and *Betula pendula* leaf testing scheme (Km, ●) **(B)** (latitude = 55°38'6.34", altitude = 88°11'52.51").

2. Materials and methods

The research area is the tailing of former Komsomolsk gold concentration plant in the Komsomolsk village of Kemerovo region (Western Siberia, Russia) (fig. 1, A). At the plant aurum-arsenic pyrit-quarz ores, as well as gold-containing wastes of Kadamzhaisk antimony plant (Kyrgyzstan) and Berikul gold-processing plant were recycled using cyanation method [13].

The tailing is situated in natural basin in 250-500 meter from residential area of the village. It takes 147 thous. m^2 and its volume is 810 thous. m^2, the tailing contains about 1,1 million m^3 of waste and it is a shrinkable technogenic lake (fig. 2, a). From the south-western side the tailing is bounded by filling dam. Oxidizing wastes (fig. 2, b) contain (first %) sulphidic minerals: pyrite, sphalerite, galenite, pyrrhotine, and arsenic pyrite [13].

The subject of study was *Betula pendula* leaf. It is a widespread species and wood edificator in Siberian region. Being a mesophyte, a birch-tree tolerates dry conditions well; it is light-demanding, but undemanding to soil capability. It often grows on the disforest places or burned forest areas. The birch is also often used in safeguarding foresting under the conditions of increased technogenic load.

Leaf testing was conducted in the second ten-days of July 2015 using radial network from the outer boundary of the tailing with a 150-200 meter pitch along 10 lines (fig. 1, B). The leaves were sampled from the approximately evenaged trees using middle sample method at a height of 1,5-2 m from the ground level. Totally, 20 samples were collected. The baseline sample was collected in the village Makaraksky by the side of the river Kiya in 10 km south-westwards from the tailing. For sample packing the strong envelopes “Sterit” were used. Sample preparation for quantitative element analysis includes drying by the environmental temperature, mechanical grinding, weighted portion taking and decomposition in concentrated nitric acid by standard methods.

a b
Figure 2. Photographs of the northern part (a) and of the southern part (b) of the tailing landscape.

The total content detection of chemical elements in the samples of dry solids of leaf was conducted using mass-spectrometry with inductively coupled plasma in the accredited chemical-analytical centre "Plasma" (Tomsk). For the control of analysis quality the standard sample of *Betula pendula* leaf content is used (SSS 8923-2007). The estimation error has not exceeded 10%. The experimental data were processed with the use of different software (MS Office 2003, Statistica 8.0, Surfer 10, Corel Draw X6).

3. Results and discussion

The REE content of *Betula pendula* leaf around Komsomolsk tailing is shown in fig. 3. REE distribution has serrate composition, deficiency of medium rare earths (MREE - Sm) is slightly expressed, and heavy rare earths (HREE – Ho, Er) are in sufficient excess. In comparison with the data [14], REE content (except Er) in *Betula pendula* leaf is 3-10 times lower.

Geochemical peculiarities of rare earth and radioactive elements distribution in the territory of Komsomolsk tailing according to the data of *Betula pendula* leaf testing are shown in the diagrams of indicator ratios of Th/U and La/Yb (fig. 4). By consideration of La and Yb distributions in the leaf samples, we separate two groups of samples (fig. 4, a). The samples from the first group collected in the impacted area at the tailing border, by comparison with the samples from the second group collected in the buffer area far from the tailing are characterized by the lower contents of La and Yb, but by higher values of La/Yb ratio (from 16 till 122, average - 42).

The similar regularity appears by the consideration of Th and U distributions (fig. 4, b). It is found, that Th/U ratio has lower values (1,1 – 1,2) in the leaf samples collected in the impacted area at the tailing border than in the samples collected in the buffer area at a distance of 150-200 m from the outer tailing border (2,3 – 3,7). The Th/U ratio for the average content of these elements in the selection is 2,2. The low values of Th/U ratio indicate that the natural balance of radioactive elements is upset towards the increased U content determined by the technogenic transformation of the environment. High values of Th/U reflect probably the natural factor of the environment – the impact of igneous granitoidal ore complex developed in the territory on the U and Th content in flora. These values of Th/U ratio are comparable with the values obtained by the other researchers for soils (4,0), grassland vegetation ash (3,1) and *Betula pendula* leaf ash (2,7) in the background areas of the southern part of Western Siberia [15].

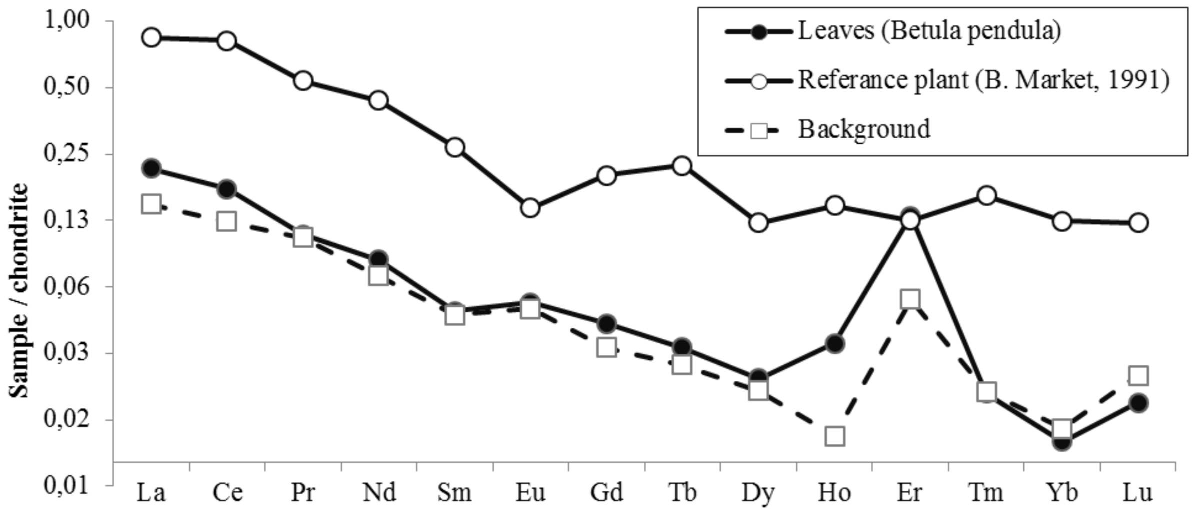

Figure 3. The rare earth element content of leaves (*Betula pendula*) around the Komsomolsk gold concentration plant in comparison with the baseline data and published data[14].

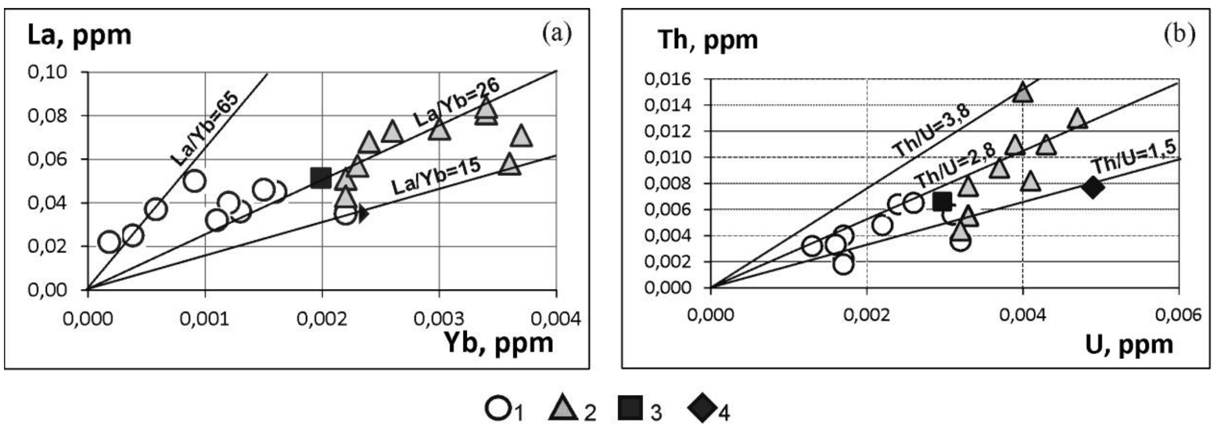

Figure 4. La/Yb (a) and Th/U (b) ratios diagrams for leaves (*Betula pendula*). Legend: 1 – samples taken at the border of the tailings; 2 – samples taken at a distance of 150-200 meters from the boundary of the tailings; 3 – the average content in the samples (n = 20); 4 – background value.

The peculiarities of spatial structure of geochemical fields around Komsomolsk tailing according to the indicator ratios of La/Sm, La/Er, La/Yb and Th/U are presented in the figure 5. Halos with contours 9-12 of La/Sm ratio cover most of the area around the tailing, maximal ratio is 12,5; it is shown in the central part (fig. 5, 1). Halos with maximal values 60-85 of La/Er ratio takes the north-western and western part of the tailing (fig. 5, 2). In the northern part of the tailing the halo with maximal value of La/Yb ratio – 122 is detected (fig. 5, 3). When the plant was in operation, there was a sludge pond near this area, but now it is a shrinkable lake (fig. 2, a), which is used by local children for swimming. In the southern part of the tailing the halo with minimal La/Yb ratio – 16 is detected. The oxidation zone of sulphide-containing wastes with the removal of sulfur, ferrum oxide and hydroxide formation is developed here (fig. 2, b). The halos with minimal Th/U ratio are detected in the basin in the impacted area, where the tailing bed is situated; the halos with maximal Th/U ratio are detected in the buffer area, on watersheds with natural landscape (fig. 5, 4).

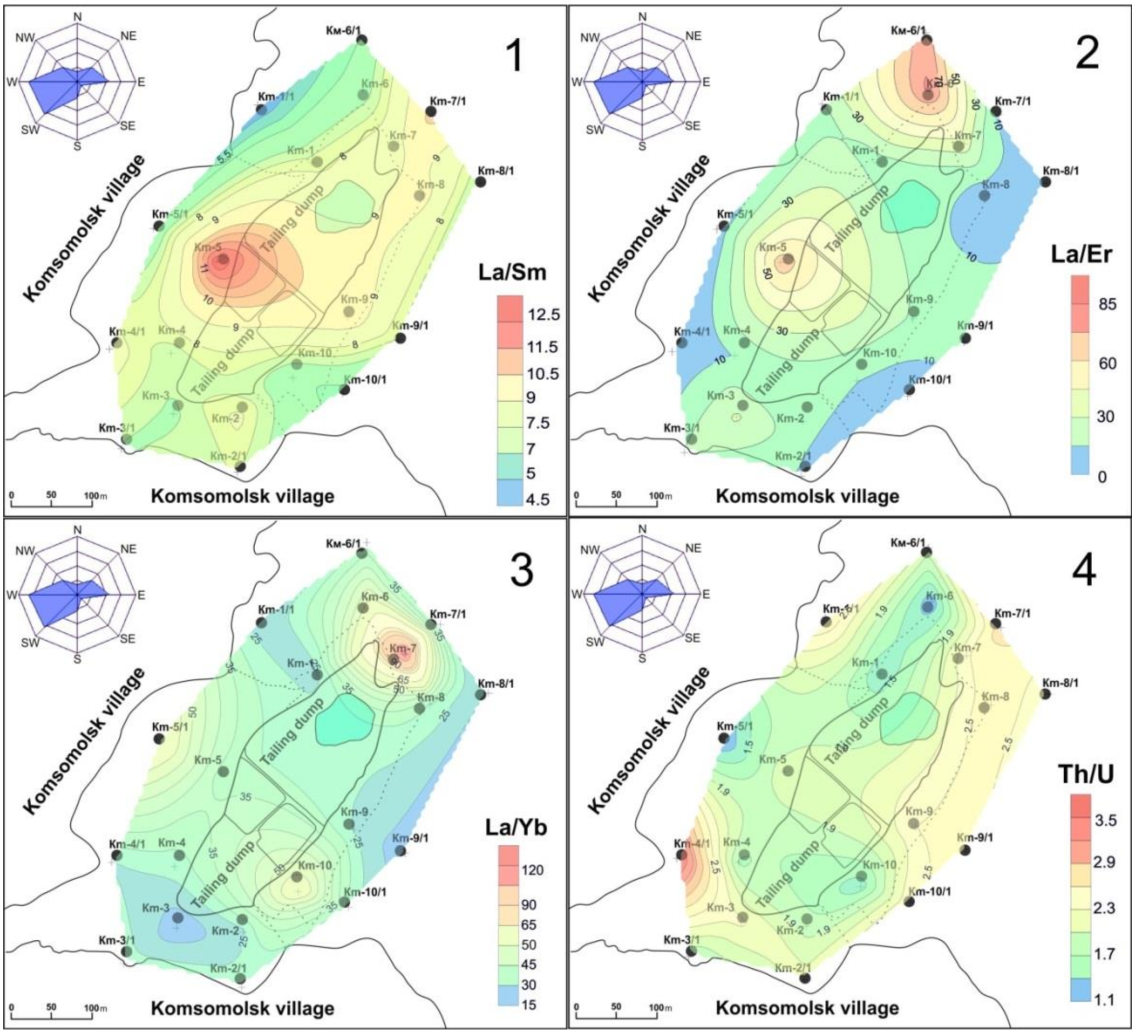

Figure 5. The maps of La/Sm (1), La/Er (2), La/Yb (3) and Th/U (4) ratios ("the nearest neighbor" method) showing the halos of geochemical transformation of landscape around the tailing of former Komsomolsk gold concentration plant

4. Conclusion

For the foregoing information, we can draw the following conclusions:

1. For the REE distribution in the territory of Komsomolsk tailing according to the *Betula pendula* leaf testing data the slight deficiency of MREE (Sm) and sufficient excess HREE (Ho, Er) are observable.

2. The distribution regularity of La and Yb and of U and Th in the *Betula pendula* leaf samples depending on the distance from the tailing is discovered. On the tailing border, in the impacted area the lower contents of La, Yb, U and Th, as well as low value of Th/U ratio were indicated. The halo with minimal value of La/Yb ratio maps the oxidation zone of sulphide-containing wastes. With distance from the tailing border, in the buffer area the La, Yb, U, Th contents and the value of Th/U ratio in growth samples increase.

3. The halos with maximal values of La/Sm ratio and La/Er ratio cover most of the area around the tailing bed.

4. The research findings confirm the conclusion, that values of Th/U ratio and REE can be indicators of the environment transformation degree in the limits of nature landscapes, and they can be used in biomonitoring.

Acknowledgment
This work was financially supported by the Russian Science Foundation grant №15-17-1001.

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