Study on rare-earth elements distribution in surface waters of Primorsky region

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Abstract. Data obtained by the authors show that the background level of the rare-earth element (REE) content in the surface waters of southern Russian Far East is irregular and varies from 0.1 to 1.3 µg/l. The highest concentration of REE (0.48–1.3 µg/l) is characteristic for the rivers of Eastern Sikhote-Alin and Central Sikhote-Alin, catchment areas which are situated within the Sikhote-Alin volcanic belt. The lowest REE concentration was noted in the waters of Western Sikhote-Alin (0.09 µg/l). The profile of REE distribution in fresh waters of different areas of the region is uniform and is characterized with the deficit of Ce and enrichment of medium group REE.

1. Introduction
Interest in rare-earth element (REE) distribution in the environment and, especially in natural waters, is related to their possible use as geochemical processes tracers [1], which requires understanding of certain elements’ behavioural peculiarities and fractionation rules.

A considerable number of studies are dedicated to the research of REE in the surface waters of the Russian Far East [2, 3]. Studies on fluvial REE transportation carried out by a number of foreign researchers [4–7] allowed establishing a weighted form prevalent in REE transportation and significant difference in REE accumulation in the rivers depending on pH value, colloidal particles presence, etc. Data on REE content as suspended solid particles are reviewed in the following studies [8].

Concentration of dissolved REE in the river streamflow is, as a rule, much lower than of the suspended ones. Dissolved REE (fraction of less than 0.45 µm) are really dissolved forms and colloidal compounds. Composition of dissolved REE is to a great degree determined with individual chemical properties of REE [4, 7, 9]. In this regard it seems that research of REE distribution in the dissolved form may, most probably, reflect indirectly main peculiarities of their behaviour in the area of hypergenesis within interaction water-rock.

2. Materials and methods
Study of REE in the surface waters of Primorye was carried out for the purpose of revealing and
assessing the general geochemical background of the dissolved forms of REE in fresh waters and
determining the main patterns of REE concentrations and distribution change in water environments of
separate large hydrogeological structures of Primorye.

REE distribution character and concentration in fresh waters of surface stream-flows have been
studied. According to physical-geographical location of their catchment areas and peculiarities of
geological structure the following areas have been set out in Primorye: Eastern Sikhote-Alin, Central
Sikhote-Alin; Western Sikhote-Alin, Southern Primorye, Prikhankaikaya.

Samples of surface streamflows were taken between 2007 and 2012. Water samples were filtered
through the cellulose filter with the pore size of 0.45 µm on the sites of sampling and collected to
plastic test tubes. Samples to analyse REE content in water were further preserved by adding nitric
acid to them.

REE content in water environment was determined with inductively coupled mass spectrometer
Agilent 7500c (Agilent Technologies, USA) in the analytical centre of Common Use Center
(Primorsky Center of Local Element and Isotopic Analysis) of the Far East Geological Institute of Far
Eastern Branch of Russian Academy of Sciences (analyst: E.V. Elovskiy).

3. Research results and their discussion

The summary of research on REE content in streamflows of different areas of Primorye shows that the
regional level of dissolved forms concentration in fresh surface waters varies between 0.092 and 1.297
µg/l (see Table 1), with an interval of content fluctuation in separate rivers equal to 0.014–1.56 µg/l.

The highest REE concentration is common for the rivers of Eastern and Central Sikhote-Alin,
catchment areas of which are situated within the Sikhote-Alin volcanic belt. The lowest concentration
is common for the rivers of Western Sikhote-Alin. In all streamflows studied, concentration of light
REE is significantly higher than of heavy ones. They constitute 77–86% of total REE with stream-
flows of Prikhankaikaya plain being enriched most of all and waters of Eastern Sikhote-Alin being
depleted most of all (see Table 1). In Eastern Sikhote-Alin, samples were taken from the largest
streamflows, the main part of which are not affected by man-induced activities. REE dissolved forms
in the waters were revealed to be within relatively narrow limits, between 0.21 and 0.60 µg/l (see
Table 1). In this context, the highest REE concentration is common for Tayozhnaya River and the
lowest – for Mineralnaya River.

Table 1: Average content of REE dissolved forms in fresh waters of surface streamflows of
different areas of Primorye, µg/l.

| Rare-earth element | Average for world rivers* | I | II | III | IV | V | Average for Primorye |
|-------------------|--------------------------|---|----|-----|----|----|---------------------|
| La                | 0.120                    | 0.088 | 0.230 | 0.021 | 0.059 | 0.068 | 0.085               |
| Ce                | 0.262                    | 0.087 | 0.299 | 0.017 | 0.080 | 0.062 | 0.098               |
| Pr                | 0.040                    | 0.028 | 0.075 | 0.005 | 0.016 | 0.016 | 0.025               |
| Nd                | 0.152                    | 0.127 | 0.329 | 0.023 | 0.071 | 0.068 | 0.111               |
| Sm                | 0.036                    | 0.032 | 0.082 | 0.005 | 0.015 | 0.013 | 0.026               |
| Eu                | 0.009                    | 0.006 | 0.017 | 0.002 | 0.005 | 0.005 | 0.006               |
| Gd                | 0.040                    | 0.035 | 0.087 | 0.005 | 0.018 | 0.013 | 0.028               |
| Tb                | 0.005                    | 0.005 | 0.011 | 0.001 | 0.002 | 0.001 | 0.003               |
| Dy                | 0.030                    | 0.027 | 0.068 | 0.004 | 0.011 | 0.009 | 0.021               |
| Ho                | 0.007                    | 0.005 | 0.013 | 0.001 | 0.002 | 0.002 | 0.004               |
| Er                | 0.020                    | 0.016 | 0.038 | 0.002 | 0.006 | 0.005 | 0.012               |
| Tm                | 0.003                    | 0.002 | 0.005 | 0.0001 | 0.001 | 0.001 | 0.001               |
| Yb                | 0.017                    | 0.014 | 0.034 | 0.002 | 0.006 | 0.005 | 0.011               |
| Lu                | 0.002                    | 0.002 | 0.005 | 0.0001 | 0.001 | 0.001 | 0.001               |
| ∑REE              | 0.745                    | 0.480 | 1.297 | 0.091 | 0.298 | 0.275 | 0.437               |
| LREE              | 0.619                    | 0.370 | 1.032 | 0.075 | 0.249 | 0.236 | 0.353               |
Profiles of REE distribution in the waters of Eastern Sikhote-Alin streamflows are normalized in relation to North American Shale Composite [4], relatively uniform, and are characterized with REE enrichment insofar as it concerns terbium neodymium with maximum values of europium or gadolinium (Fig. 1). The index of La/Ybn proportion varies within quite significant limits – from 0.56 to 1.20, which reflects a rather non-uniform character of the waters‘ enrichment with heavy and light REE. All spectra have clearly expressed negative ceric anomaly (Ce/Ce* = 0.19–0.58) and less clearly expressed negative europium anomaly (Eu/Eu* = 0.55–0.93). All spectra show inexplicitly expressed positive holmium anomaly (Ho/Ho* = 1.13–1.20).

In waters of the Southern Primorye they change within relatively narrow limits: between 0.11 and 0.51 µg/l (see Table 1). The highest concentration is common for Pinkanka River and the lowest – for Petrovka River. Prevalence of light REE over heavy ones is found in all waters of the streamflows studied – 80–86%, which is in the whole much higher than in the rivers of Eastern Sikhote-Alin.

Unlike the rivers of Eastern Sikhote-Alin, spectra of REE distribution in the waters of Southern Primorye show positive europium anomaly (Eu/Eu* = 1.10–1.58). Moreover two types of europium anomalies are determined for the waters under consideration: clearly expressed with index 1.45–1.58 and relatively poorly expressed (Eu/Eu* = 1.10–1.24). Spectra of the latter are pointed out with exceeding normalized values of gadolinium over europium.

In the waters of Prikhankaiskaya area, they vary within quite wide limits: between 0.04 and 0.51 µg/l (see Table 1). The highest REE concentrations are common for Grigorievka River, the lowest – for Krinichnaya River. Prevalence of light REE over heavy ones is found in all waters of the streamflows studied – 80–88% of total composition which is, in the whole, comparable to the Southern Primorye rivers.

Profiles of REE distribution in the waters of Prikhankaiskaya area normalized in relation to North American Shale Composite; though similar in configuration they may be divided into two types according to REE fractionation. Waters with high REE concentration explicitly show smooth profile of REE distribution (Fig. 1) and enrichment with light REE (La/Ybn = 1.31–1.81). They may have both negative and positive europium anomaly (Eu/Eu* = 0.92–2.01). Waters with a low REE concentration profile of REE distribution are characterized with the increase of heavy REE (La/Ybn = 0.45–0.57). It is ordinary for them to have europium peak (Eu/Eu* = 3.26–11.44). All spectra of waters of this hydrogeological area have clearly expressed negative ceric anomaly (Ce/Ce* = 0.26–0.50) and poor holmium anomaly (Ho/Ho* = 1.03–1.17).

REE distribution in the streamflows of Central and Western Sikhote-Alin is poorly studied. There are only three samples of the streamflows of the former and two samples of the streamflows of the latter. Significant REE concentration is found out in the streamflows of the former area – between 1.0 and 1.6 µg/l (see Table 1), with prevalence of light REE portion over heavy one 77–81% and REE content in the streamflows of the latter area is low – between 0.14 and 0.17 µg/l.
Figure 1: Spectra of REE distribution in surface streamflows of Primorye normalized in relation to North American Shale Composite (NASC). Eastern Sikhote-Alin: 1 – Maksimovka river, 2 – Kema river, 3 – Tayozhnaya river, 4 – Jigitovka river, 5 – Rudnaya river, 6 – Mineralnaya river; Southern Primorye: 7 – Volchanka river, 8 – Bolshaya Rudnevka river, 9 – Pinkanka river, 10 – Petrovka river, 11 – Sukhodol river, 12 – Loboga river, 13 – Shkotovka river, 14 – Artyomovka river; Central Sikhote-Alin: 15 – Arsenievka river, 16–17 – Pavlovka river (2008 and 2009); Western Sikhote-Alin: 18 – Avaga river, right-bank tributary of Bolshaya Ussurka river, 19 – Mikhailovka river, left-bank tributary of Bolshaya Ussurka river; Prikhankaiskaya area: 20 – Repievka river, 21 – Abramovka river, 22 – Grigorievka river, 23 – Blagodatnoye Lake, 24 – Krinichnaya river.

Profiles of REE distribution normalized in relation to North American Shale Composite have smooth convex shape in the former area, with REE enrichment insofar as it concerns terbium neodymium, and the latter one is characterized with an increase of heavy REE (La/Ybn = 0.23–0.91) and clearly expressed europium peak (Fig. 1).

All spectra of the Central and Western Sikhote-Alin waters have clearly expressed negative ceric anomaly (Ce/Ce* = 0.34–0.721) and positive holmium anomaly (Ho/Ho* = 1.13–1.17).

Summarized profiles of REE distribution in the streamflows of different areas of Primorye normalized in relation to North American Shale Composite have smooth convex shape with sharply expressed enrichment with REE within medium group of REE. All spectra of Primorye waters have clearly expressed negative ceric anomaly (Ce/Ce* = 0.26–0.50) and poor holmium anomaly (Ho/Ho* = 1.03–1.17).

4. Conclusions

Data obtained in the course of research allow making the following conclusions, which reflect main patterns of REE distribution in dissolved solid yield of fresh surface waters.

REE content in the dissolved solid yield of Primorye fresh waters significantly differs from North American Shale Composite and is characterized with an accumulation of REE of medium group. A number of authors point out the facts of the river waters enrichment with light and medium REE [1,
7.], though this rule is not always complied with. A number of publications mention depletion of light REE in the dissolved streamflow [4], which is explained with their higher degree of sorbing by solids of river waters at high values of pH.

Anomalies of europium behaviour in the surface waters are observed in all areas of Primorye and depend on water-bearing materials of catchment area.

Clearly expressed ceric anomaly in the fresh waters of Primorye is determined with chemical properties of this REE, which changes its oxidation degree from 3+ to 4+ in the hypergenesis area and contributes to the formation of low-soluble forms and its fast removal from solution.

The level of dissolved REE concentration in the surface waters is, most probably, determined by REE concentrations in materials of catchment area and peculiarities of technogenic pollution of waters during development of certain types of mineral deposits.

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