Geochemistry of Rare Earth Elements in the Rivers and Groundwaters of Chistovodnoe Thermal Area (Primorye, Far East of Russia)

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Abstract. The behaviour and hydrogeochemistry of rare earth elements were investigated in the surface and groundwaters of Chistovodnoe thermal area (Far East of Russia). The waters were classified according to the pH into neutral waters with pH ranging from 6.6 to 7.3 and alkaline waters with pH between 7.5 and 9.3. The REE concentrations in the river waters with pH = 6.6-6.8 are markedly higher than those from the thermal groundwaters with pH = 7.9-9.3. The surface water mass in the Chistovodnoe area has similar REE patterns reflected in negative Ce and Eu anomalies. The cold and thermal groundwaters are influenced by the water-rock interaction processes. Such correlations are explained by the redox changes with depth within the area. The oxidizing conditions in the shallower aquifer generate a larger Ce anomaly. The low concentrations of REE in groundwater suggest that the elements are relatively immobile during weathering and transport, being carried partly in heavy detrital minerals, especially zircon and titanite, and partly adsorbed onto clay particles. Heavy REE enrichment is explained by successive water-rock interactions supplying REE to the water in which differential scavenging of light REE by particulate matters occurs.

1. Introduction
The Chistovodnoe low-temperature thermal area is located in the Southern Primorye (the Far East of Russia) and represents by Chistovodnoe spring and Goriachii Kliuch spring. The first hydrogeochemical investigation of this group was carried out in 1995 [1]. It was established that thermal water has an atmospheric genesis and their chemistry is controlled by water-rock interaction with granite reaching equilibrium at relatively low temperature. The temperatures and depths of the thermal water formation and the residence time were determined by previous work [2, 3]. The REE actively investigated in natural groundwaters as an effective tool for tracing groundwater flow and understanding of water-rock interactions processes [4, 5]. For the last years, the study of the geochemistry REE in different types of waters of Primorye was more active [6, 7, 8]. Presently, we indicated new results of REE contents and distributions in surface and groundwater (fresh and thermal) spread within Chistovodnoe geothermal area.

The main aim of this study is to increase the understanding of the mobility and fate of REE in different geochemical types of groundwaters.
2. **Study area**

The Chistovodnoe geothermal area is located in Primorsky Region in the southern part of Far East of Russia (Fig. 1), 30 km away from the Sea of Japan represented by two groups of springs: Chistovodny and Goryachiy Kljuch. The geology of south Primorye is dominated by the Sikhote-Alin Ridge and has been previously studied by Khanchuk [9]. According to the tectonic scheme, the geothermal area is located within the bounds of the Samarka terrain within the Central Sikhote-Alin fault - the largest tectonic dislocation in Primorye. Bedrock in the Chistovodnoe thermal area consists mainly of Paleozoic sedimentary rocks (sandstones, siltstones) and Mesozoic granitoid (biotite granite, porphyritic granite, and acidic dikes). Nearest mafic rocks (basalts) are located on the ridges about 50 km on the north.

Chistovodnoe thermal field is the area with the densest river net (Fig. 1). The Kievka River (105 km long) and its right tributary - Krivaia River (71 km) are the principal rivers of the study area. Kievka River rises in Southern Sikhote-Alin and flows to Kievka Bay of Sea of Japan. The main watershed of the area - Partizansky Ridge is located on the NW of territory with maximum elevation points 1489 m. asl. The territory is characterized by a monsoon climate, therefore, the rivers there are predominantly rain-fed.

Thermal springs are located on the slopes of hills and connected with rivers and slopes erosion. It is typical low elevation springs about 150-300 m above sea level. Goriachy Kliuch Spring (#1) are low-flow (0.1 l/s) spring assumed to be flowing from the sedimentary rocks of the Upper Permian-Mesozoic age (sandstones, siltstones). Chistovodny (#2) thermal spring is located 16 km to the SW from the Goriachy Kliuch Spring (#1) on the west valley side of Chistovodnaya River and flowing from crumbling granites of Upper Cretaceous age. The flow rate of the spring is 0.1 l/s.

![Figure 1](image_url). Geographical location of Chistovodnoe thermal area and sampling points. Numbers according to Table 1.
3. Sampling and analytical procedures
The materials obtained by the authors as a result of their field works carried out in 2015-2018 are used in the paper. The water samples were filtered through 0.45 µm mixed cellulose ester filters (Advantec, Japan) and collected in acid-washed, high-density polyethylene sample bottles. Waters for the cation analysis were acidified to pH < 2 with ultrapure HNO₃. Water temperature, conductivity, and pH were measured directly in the field using Hach Lange HQ 40D probe. Major cations and anions were analyzed by the ion chromatography. Carbonate species were titrated in-situ with 0.1 N HCl. Trace elements concentrations in groundwater were determined by ICP-MS (Agilent 7700) analysis. Trace element and REE concentrations were analyzed by ICP-MS (Agilent 7700 and ELEMENT XR) in the Analytical Department of FEGI FEB RAS (Vladivostok, Russia) and Activation Laboratories company (Canada, www.actlabs.com). Analytical precision for the REEs, except for Ce and Pr, was better than 5% RSD; for Ce and Pr, the precision was 7% and 10% RSD, respectively. Solid mineral phase has been investigated in the Far East Geological Institute, the Far Eastern Branch of the Russian Academy of Sciences (Primorsky Centre of Local Elemental and Isotope Analysis). It was performed using the method of mass-spectrometry with inductively coupled plasma at the Agilent 7500 spectrometer (the analyst: Elovsky E.V.). The anomalous behaviors of Ce and Eu are quantified via Ce anomaly = 2Ce/(La₈+Pr₅) and the Eu anomaly = 2Eu/(Sm₅+Gd₅), with N equal to the normalized abundance.

4. Results

4.1. Background hydrogeochemistry
The chemical composition of studied waters is presented on the Piper diagram, (Fig. 2), which demonstrates the proportions between the water components of the area. According to the pH, the studied waters were classified into two groups: 1- neutral waters with pH values ranging from 6.6 to 7.3 and 2- alkaline waters with pH values between 7.5 and 9.3. The first group including river waters (#6, #7, #8) and cold groundwater springs (#4, #5) are represented by cations and anion mixed type Ca-Na-HCO₃. The typical total dissolved solids concentration for this waters is 0.03-0.04 g/L. Eh, values indicate typical oxidizing hydrochemical conditions (+176 - +325 mV).

The second group is low-temperature thermal groundwaters (25.1 – 31.1°C) and cold water (13.3°C) from the borehole №3 (interval 73 m). There is typically a sodium bicarbonate water, with low mineralization (133-157 mg/l) and increased concentrations of Si (6.7-13 mg/l) and F (7.5-33.4 mg/l). Redox potential changed from +85 to +190 mV. A major component of associated gasses is nitrogen (up to 72.2–97.2%). The radon concentrations up to 200 Bq/L. Geochemistry of thermal water from this area was discussed in previous works [1, 2, 3, 4, 5].

4.2. Rare earth elements geochemistry
The row REE data represents in Table 1. To more conveniently view inter-element trends, the REE analyses have been normalized to North American Shale Composite [10]. The data on the content of rare earth elements (REE) in the surface and groundwaters of the Chistovodnoe area divided waters into three groups: 1) high concentrated river waters; 2) middle REE concentrated shallow cold groundwaters, and 3) low REE concentrated deep thermal and cold groundwaters (Fig. 3). All groups have Ce anomalies as are the result of oxidation of Ce³⁺ to Ce⁴⁺ and precipitation under oxidative conditions (Eh=85–400 mV). But the negligible Ce anomalies in cold deep water (#3) could be connected with limited precipitation of Fe-oxyhydroxides under Eh=85 mV, allowing higher amounts of Fe (2.1 ppm) dissolved in this water. Whereas Eu anomaly is different for fresh groundwaters, thermal waters, and river water.
Figure 2. Piper divided groundwaters into two major groups: I - alkali carbonate Na-HCO$_3$ groundwaters (gray circles) and II - cation mixed Ca-Na-HCO$_3$ groundwaters (white circles).

Figure 3. Shale-normalized REE patterns dissolved in different types of water. Numbers according to Table 1.

NASC-normalized REE patterns for the river water and fresh groundwater with neutral pH are illustrated in Fig. 1A. It indicates that maximal concentrations of REE are typical for estuarine part of Kievka River - the main watercourse of the study area after all inflow (Fig. 1, Table 1). REE pattern of Kievka River (#8) is characterized by slightly HREE enrichments and moderate negative Eu anomalies. Its tributaries - Chistovodnaia (#6) and Goriachaia (#7) rivers have a lower content of $\Sigma$REE, similar negative Eu anomalies, and strong HREE enrichment. The negative anomalies in river waters usually explained by regional bedrock mineralogy and lithology [11, 12, 13, 14]. The main water quality issue of the River Kievka is high levels of suspended sediment via surface runoff and land use practices. It could be a reason of MREE enrichment of Kievka River against Chistovodnaia and Goriachaia rivers. Also, organic colloids contribute to the small MREE enrichments of the river water [15, 16]. Kievka River sample shows an abnormally high Gd value that in good correlation with anthropogenic Gd anomalies in river waters were first recognized by Bau and Dulski [17], and also have recently been reported for the river and seawater samples from the Asian region [18]. Altogether,
REE data on river waters of Chistovodnoe geothermal area in good correlation with typical river waters of the world [15].

Correlation analysis shows that REE in neutral waters correlating with Fe (r=0.9), Al (0.9), Mn (0.9) and Ba for river water. Probably barium and REE desorbs from clay minerals and making surface water enriched in [Ba$^{2+}$] [19].

Throughout shallow cold groundwaters (#4, #5) lowest concentrations of REE were observed for Chisty spring (#4). The level of REE could be compared with an alkaline group (Fig. 1). Small creek T'oply Kliuch (#5) flowing out close to the thermal spring Goriachy Kliuch (#1) nevertheless have different REE concentrations of REE compared to thermal spring. It could be evidence of absence mixing and dilution processes between thermal and cold groundwaters. That were proved by the data loggers monitoring also [3]. In contrast to river waters, all cold shallow groundwaters have positive Eu anomalies. As well as the positive Eu anomalies within shallow water likely reflect weathering reactions with granitic rocks as result of the preferential dissolution of a Eu-rich phase in the host rocks (e.g. plagioclase). Positive Eu anomalies correlate with high concentrations of Ca and Sr, pointing plagioclase dissolution.

Table 1. Representative data of the REE concentrations in studied water (ppb).

| Thermal springs | Cold waters | Rivers |
|-----------------|-------------|--------|
| Goyachy Kliuch | Chistovodny | Borehole №3 | Chisty spring | T'oply Kliuch | Chistovodnaia | Goria-chaiia | Kievka |
| № on map       | 1           | 2       | 3         | 4         | 5           | 6          | 7         | 8       |
| La              | 0.021       | 0.006   | 0.040     | 0.006     | 0.017       | 0.027      | 0.050     | 0.032   |
| Ce              | 0.030       | 0.007   | 0.058     | 0.011     | 0.025       | 0.030      | 0.098     | 0.030   |
| Pr              | 0.0043      | 0.0019  | 0.0064    | 0.0021    | 0.0045      | 0.0067     | 0.0132    | 0.0085  |
| Nd              | 0.0163      | 0.0049  | 0.0213    | 0.0069    | 0.0187      | 0.0261     | 0.0551    | 0.0380  |
| Sm              | 0.0037      | 0.0013  | 0.0039    | 0.0028    | 0.0048      | 0.0059     | 0.0138    | 0.0092  |
| Eu              | 0.0009      | 0.0003  | 0.0008    | 0.0007    | 0.00147     | 0.0008     | 0.0022    | 0.0014  |
| Gd              | 0.0042      | 0.0013  | 0.0032    | 0.0008    | 0.0048      | 0.0062     | 0.0151    | 0.0093  |
| Tb              | 0.0011      | 0.0001  | 0.0004    | 0.0001    | 0.00073     | 0.0009     | 0.0023    | 0.0013  |
| Dy              | 0.0047      | 0.0013  | 0.0028    | 0.0016    | 0.0041      | 0.0061     | 0.0155    | 0.0075  |
| Ho              | 0.0011      | 0.0004  | 0.0004    | 0.00005   | 0.00094     | 0.0012     | 0.0030    | 0.0017  |
| Er              | 0.0029      | 0.0012  | 0.0015    | 0.0095    | 0.00217     | 0.0039     | 0.0097    | 0.0051  |
| Tm              | 0.0003      | 0.0002  | 0.0001    | 0.0001    | 0.00034     | 0.0006     | 0.0014    | 0.0007  |
| Yb              | 0.0021      | 0.0009  | 0.0010    | 0.0019    | 0.00196     | 0.0043     | 0.0105    | 0.0049  |
| Lu              | 0.0003      | 0.0001  | 0.0001    | 0.0002    | 0.00025     | 0.0006     | 0.0015    | 0.0007  |

As mention above the alkaline group of deep groundwaters has high TDS, F, Si and usually temperature, but lowest REE concentrations (ΣREE up to 0.099 ppb). This is primarily caused by the alkalinity of the water environment where the REE display strong sorption characteristics onto mineral surfaces limiting their role as true conservative tracers [16, 20].

Instead of other waters, NASC-normalized REE patterns of thermal springs (#1, #2) show negligible negative Eu anomaly. For sedimentary aquifer of Goriachy Kliuch and Borehole №3 Eu/Eu$^*=$0.003 and 0.0008 correspondingly. The main differences of water from borehole №3 compared to the other waters belonging to the alkaline group are the higher ionic strength, the lower Eh value, low temperature and no discharge (Table 1). It suggests that weathering reactions with sedimentary rocks are very slow. According to thermal investigations in the well, we fixed interval of waters with temperature 13$^{°}$C inflow at the 73 m depth. Then mixing processes between different aquifers occur that could influence on REE geochemistry.

Contrary to above mentioned thermal waters discharge from granite (#2) do not indicate positive Eu anomalies (Eu/Eu$^*=$0.0003). In general, it is customary for mafic and ultramafic rocks. The
possible explanation for the absence Eu anomalies reported here is the preferential mobilization of Eu during weathering of host lithologies. From the other hand, if the REE patterns indicate the recharge area [21], the REE investigation of the thermal water demonstrates that the recharge zone for the initial water has to be connected with another source (e.g. mafic rocks).

Speciation calculations of aqueous REE complexes were carried out by the computer program SELECTOR- Windows with the SPRONGS88 database of thermodynamic parameters [22]. In fresh groundwaters concentrations of REE[CO₃]²⁺ are 92–95% and REE³⁺ is second in significance (0.5–8%). In thermal groundwater REE[CO₃]²⁺ complex is strongly uppermost (at about 99%) and all other complexes are negligible. The saturation indexes (SI) obtained using WATERQ software [23] reveal that REEs are leached from the same phases as the relatively high quantities of Si, Al, Nb. Obtained data suggest that the REE in alkaline conditions are relatively immobile during weathering and transport, being carried partly in heavy detrital minerals, especially REE-bearing andradite and chlorite, and partly adsorbed on to Fe, Al, Mn-oxides and clay minerals.

5. Conclusion
We carried out research on REE behaviour in river water, cold groundwater and thermal water within Chistovodnoe thermal area (Eastern Russia). It is found that maximal concentrations of REE are typically for surface waters with neutral pH and lowest for groundwater with an alkaline environment. Strong positive correlations were observed between REE content and Al and Ba in both groups. Negative correlations for Fe, F, K and Th for thermal springs only. The negative Ce anomalies present in all studied waters and caused by redox conditions. The behaviour of Eu likely reflects not only the relative mobility of Eu but also a host-rock signal inherited from the positive Eu anomalies of the local rocks. REE[CO₃]²⁺ is predominant species in studied groundwaters although its content (%) being dependent on hydrogeological conditions.

Obtained data suggest that the REE in alkaline conditions are relatively immobile during weathering and transport, being carried partly in heavy detrital minerals, especially REE-bearing andradite and chlorite, and partly adsorbed on to Fe, Al - oxides, zeolites, and clay minerals. Thus concentrations of REE and their NASC-normalized patterns to the change as the function of processes occurring on the surface, cold groundwater and the geothermal system.

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**Acknowledgment**

This work was supported by grants from Russian Foundation for Basic Research, project № 18-05-00445 and 19-55-50002 and grant from Far East Branch of Russian Academy of Sciences № 18-5-089.