Rare-earth elements and isotopic geochemistry of thermal waters of the Okhotsk sea shore, Far East of Russia

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Abstract. New data on hydrogeochemistry of thermal waters of the Okhotsk sea-shore (Ulskiy, Annensky Tumnin, Talaya, Paratunka, Dagi and Lesogorsky) is presented in the paper. Sikhote-Alin ridge thermal waters with crystalline host rocks refer to sulfate-hydrocarbonate or hydrocarbonate sodium fresh waters with elevated silicon content (up to 41 ppm), lowest TDS (<0.3 g/L), alkaline (9.1<pH<9.3). Thermal waters of Talaya and Paratunka refer to sedimentary basins, resulting in presence of sulfate and chloride in main ions, higher TDS (1-1.2 g/L), lower pH (~8.6) values and reducing conditions (-82< E h >-157 mV). Geological conditions were proved by shapes of REE patterns (positive Eu-anomaly for sedimentary basins). Stable water isotopes led us to divide roughly studied waters into two groups, using peculiarities of moisture source for water recharge areas. First group: Tumin, Annensky and Talaya with more “continental” climate as for mainland thermal waters, forming isotopically lighter water and second group: Ulskiy, Paratunka, Dagi and Lesogorsky, with “marine” climate of Sakhalin and Kamchatka, forming isotopically heavier water.

1. Introduction
Groundwater forms it’s geochemical shape interacting with host rocks, borrowing numerous chemical elements. Thanks to the modern high-sensitive analytical detection methods, more than 80 chemical elements can be studied in groundwater. However, the limited solubility of minerals that make up the earth's crust significantly reduces the number of basic elements of natural waters. The main ions are usually Na+, Ca2+, Mg2+, K+, HCO3-, Cl-, SO42-, which form the main part of the mineral composition of the Earth. The total content of these ions in water is over 90-95% of all dissolved substances. The content of microcomponents (Br, I, F, B, Li, Rb, Sr, Ba, As, Mo, Cu, Co, Ni, Au and others) in waters does not exceed 10 mg/l.

The geochemical properties of N2-rich thermal waters are considered most fully by L.N. Barabanov and V.N. Disler [1]. According to their data, the general geochemical properties of N2-rich thermal waters include: the predominance of sodium in the cation composition and often hydrocarbonates or sulfates in the anionic; positive correlations between Na+K and Cl, SO4, F, T °C, HCO3, pH and negative correlations between Ca and HCO3, T °C; Ca and pH, as well as the dependence of the concentration of components on solubility products in the systems of Ca2+–CO3; Ca2+–F. Since the data concerning the hydrochemistry of the thermal waters of this area were obsolete or incomplete, analysis was carried out on the newest analytical equipment of samples of thermal waters, water-
bearing rocks, and also dissolved and associated gases. The purpose of the study was to determine the composition of the water (macro-, microcomponents, isotopic ratios), water-bearing rocks, and also the gas component.

The manifestations of thermal waters located on the coast of the continental part of the Far East of Russia attract a great deal of attention of a wide range of specialists [2-11], however, due to remoteness and inaccessibility, remain poorly understood.

The Ul’skiy thermal spring manifestation is located in the Nikolaevsky district of the Khabarovskiy region, 6 km southeast of the settlement of Mnogovershinnoe (Figure 1), on the left side of the right tributary of the Right Tyvlinka River. Manifestation looks like a small pool (1.5x1.5x0.8m), strengthened with wooden bars. Mineral water is used by local residents to take baths, without medical indications.

![Figure 1. Schematic map of studied objects. Far East of Russia.](image)

Annensky spa is located in the lower reaches of the Amur River, on its right bank, 120 km upstream from the town of Nikolaevsk-on-Amur, 6.5 km to the southwest from the Susanino pier (Figure 1). Modern balneary “Annenskie Vody” is using waters from borehole from this deposit, serving over 10000 people in need per year (80-120 patients in the winter and up to 200 people in the summer are treated monthly).

The Tumnin spa is located in the Vanino district of the Khabarovskiy region, 9 km from the Tumnin railway station, in the valley of the Chope River - the right tributary of the Tumnin River (Figure 1). Three balnearies are using groundwater from two boreholes for treatment. Around 8000 people use these springs annually. These spas are very popular among the population of other regions as well.
The Talaya spa is located in the Magadanskiy region, 270 km northward of the city of Magadan (Figure 1). Old-style balneary uses thermal water of this deposit since 1939. More than 5000 people from Magadan and Sakha (Yakutia) region get here treatment annually.

The Dagi spa area is located in the northern part of Sakhalin Island, 50 km northward of the city of Nogliki (Figure 1). The deposit is presented by the group of spa centers basically specializing on bath and pool swimming treatment and a group of natural springs occurring in the tidal zone of the Chaivo gulf. Small pools (2x2x1.5m) are dug on each natural spring, allowing more people to take treatments.

The Lesogorsky springs are located in the central part of Sakhalin Island, 40 km eastward the city of Telnovsk (Figure 1). Two groups of springs are merged into two pools (4x4x1m), covered with wooden houses. People from whole Sakhalin are excited to get free treatments on these springs all year round.

The Paratunka geothermal area is the largest debit deposit in Russia with more than 44000 m$^3$/day of high-enthalpy water (Figure 1). The deposit is presented by numerous boreholes and natural springs, was studied earlier by many researchers and is famous all over the world.

The main purpose of this work was to study the conditions for the formation and genesis of thermal waters and gases of the thermal waters of the Okhotsk Sea coast of the Khabarovskiy and Magadan regions and compare the data with previously studied regions of Sakhalin and Kamchatka. For this purpose, the springs and boreholes were monitored for the physical parameters of groundwater (temperature, electrical conductivity and water level), which together with isotope-hydrochemical data made it possible to understand the dynamics of processes that affect the genesis of thermal waters.

2. Materials and methods

Hydrochemical sampling was carried out according to a standard procedure. Unstable water parameters were measured at the sampling site, and the samples were filtered through 0.45 μm membrane filters. Gas was collected in glass flasks with rubber stoppers using displacement method. Water samples for the content of tritium were taken into 1-liter plastic bottles. Water samples were analyzed for macro- and microelements in a certified laboratory of the Analytical Center of Far East Geological Institute of the Far Eastern Branch of the Russian Academy of Sciences (AC FEGI FEB RAS). The main cations and anions were determined by the method of liquid ion chromatography (HPLC-10AVp, SHIMADZU, analyst O.V. Sukhanova), trace elements were determined by inductively coupled plasma (ICP-MS Agilent 7500 and 7500c) (analyst E.V. Elovskiy). The composition of the free gas was studied using a Shimadzu LC-20AD chromatograph. Samples for analysis of stable isotopes (δ18O, δ2H) were not filtered and sampled in glass vials, then performed on a high-temperature pyrolyzer TC/EA (ThermoQuest) connected to an isotope mass spectrometer model MAT 253 (ThermoQuest) via the ConFlo-IV interface (ThermoQuest). The TC/EA pyrolysis agent was used to produce CO and H$_2$ as a result of the reaction of water with carbon at a temperature of 1450 °C under reducing conditions and subsequent chromatographic separation of pyrolysis products. Water samples (0.5 μl) were introduced into the pyrolyzer reactor in automatic mode using the Combi PAL autosampler. To calibrate the analytical system, isotope standards distributed by the International Atomic Energy Agency (Vienna): VSMOW (Vienna Standard Mean Ocean Water) δ18O = 0.0 ‰; δD = 0.0 ‰. The results of the δD and δ18O analyzes are given in relation to the international standard VSMOW. The reproducibility of the results in the analysis of this series of samples was monitored by repeated measurements of the laboratory standard. The reproducibility of the results averaged ± 0.1 ‰ and ± 0.3 ‰ for δ18O and δD, respectively.

To explain distribution of rare earth elements (REEs) we used NASC-normalized concentrations. Calculations of Ce and Eu anomalies were done using formulas:

$$\text{Ce}^* = \frac{[\text{Ce}] - \frac{[\text{La}]+[\text{Pr}]}{2}}{[\text{Ce}]}$$

and

$$\text{Eu}^* = \frac{[\text{Eu}] - \frac{[\text{Sm}]+[\text{Gd}]}{2}}{[\text{Eu}]}$$

where [REE] – NASC-normalized concentration of the element.
3. Geological settings
Features of the geological evolution of the territory, the variety of types of water-bearing rocks, the presence of diverse fault tectonics led to very complex hydrogeological conditions, geothermal and hydrochemical conditions. Most of them were studied and presented in our earlier papers [2, 3, 9]. Talaya deposit of mineral thermal water is confined to Triassic or Jurassic shales of Noriysky suit, intruded by Cretaceous andesites. This area was tectonically affected during opening of the Okhotsk sea plate in Paleocene. Now it’s is still affected by neotectonic activity. All this conditions led to form a large geothermal reservoir with the debit of more than 500 m$^3$/day with the temperature ~75°C and TDS=~1g/L (Table 1).

4. Analytical data and discussion

Table 1. Geology, hydrochemistry, stable water isotopes.

| Unit          | Location | Host rock, Age | Age of intrusion | T °C | TDS mg/L | pH | Eh mV | $[K^+]$ mg/L | $[Na^+]$ mg/L | $[Ca^{2+}]$ mg/L | $[Mg^{2+}]$ mg/L | $[Cl^-]$ | $[SO_4^{2-}]$ | $[HCO_3^-]$ | Chemical type | Gas          | d-excess | δ D VSMOW | δ 18O ‰ VSMOW |
|---------------|----------|----------------|------------------|------|----------|----|-------|--------------|----------------|-----------------|-----------------|-----------|-------------|--------------|---------------|--------------|----------|----------|----------------|
| Ulskiy [6]    | N54 E140 | Granite P1     | P1               | 32   | 170      | 9.1| 0.7   | 2.1          | 57.3           | 58              | 0.05            | 4.9        | 26          | 58           | Na-HCO$_3$-SO$_4$ | N$_2$   | 10.6     | -113.4   | -15.5          |
| Annensky [4]  | N52 E140 | Qtz-porphyry K2| K2               | 49   | 235      | 9.2| 1.2   | 2.2          | 61             | 34.1            | 0.04            | 2.1        | 37          | 8            | Na-HCO$_3$     | N$_2$   | 18.5     | -135.9   | -19.3          |
| Tumnin [4]    | N49 E140 | Granite P2     | P2               | 44   | 195      | 9.3| 0.6   | 1.8          | 34.1           | 4.9             | 0.04            | 2.1        | 10          | 78           | Na-HCO$_3$-Cl-HCO$_3$ | N$_2$   | 15.5     | -120.5   | -17.4          |
| Talaya        | N60 E152 | Shale J$_2$-T$_2$ | K$_2$             | 75   | 980      | 8.69| 12.7  | 11.1         | 200            | 282             | 0.2             | 2.1        | 282         | 84           | Na-SO$_4$-Cl-HCO$_3$ | N$_2$   | 9.3      | -177.9   | -23.4          |
| Paratunka [5] | N53 E158 | Tuff-sandstone P3 | P$_3$             | 72   | 1200     | 8.55| 6.6   | 11.1         | 206            | 663             | 0.06            | 4.9        | 663         | 27           | Na-Ca-SO$_4$  | N$_2$   | 11.2     | -112     | -15.4          |
| Dagi [8]      | N52 E143 | Sandstone N$_1$ | N$_1$             | 45   | 1670     | 6.53| 4.5   | 113.4        | 587            | 405             | 1.28            | 709        | 405         | 405         | Na-Cl-HCO$_3$ | CH$_4$N$_2$ | 7.6      | -105.2   | -14.1          |
| Lesogorsky [8]| N49 E142 | Tuff-sandstone P$_3$ | P$_3$             | 31   | 410      | 9.2 | 4.5   | 19.8         | 120            | 86              | 1.28            | 86         | 86          | 86          | Na-Cl-HCO$_3$ | CH$_4$N$_2$ | 10.7     | -94.1    | -13.1          |

We compiled all data about geology, hydrochemistry and stable water isotopes of studied waters in Table 1. The chemical and isotope composition of the thermal waters was studied earlier [4, 5, 6, 7, 8]. Depending on geological conditions, waters are being formed either within crystalline or sedimentary rocks. Borders of these reservoirs are being crushed by neotectonics and heat comes from relatively fresh intrusions of crystalline or volcanic rocks. The age of host rocks as well as intrusions depend on the age of latest volcanic activity in the region and varies from Jurassic to Paleocene for host rocks and from Paleocene to Miocene for intrusions. According to the basic ionic composition, the Sikhote-Alin ridge thermal waters with crystalline host rocks refer to sulfate-hydrocarbonate or hydrocarbonate sodium fresh waters with elevated silicon content (up to 41 ppm), lowest TDS (<0.3 g/L), alkaline (9.1<pH<9.3). Geochemical conditions are reductive gley or slightly oxidizing (0<Eh<150 mV). The water temperature on the spout varies from 31.8 to 49 °C. Waters are weakly gasified, nitrogen predominates in the gas component (up to 72.5–97.2 vol. %). Thermal waters of Talaya and Paratunka refer to sedimentary basins, resulting in presence of sulfate and chloride in main ions, higher TDS (1-1.2 g/L), lower pH (~8.6) values and reducing conditions (~82<Eh~157 mV). Temperature is relatively high (72-75 °C) and gas composition is still nitrogen-rich. When sedimentary basins are
being influenced by granitic rocks as well as marine water intrusions, as we observe for Sakhalin waters, first of all, we see appearance of hydrocarbons in gas composition, i.e. methane. For more marine waters more gley conditions are being observed (-42 > Eh > -315 mV), higher TDS with Na-Cl prevalence and lower pH (6.5-9.2) values. Granitic intrusions, influencing more on the Lesogorsky waters reflect in lower TDS (0.4 g/L) (Table 1).

The main contribution to the overall mineralization of water (TDS) is made by sodium, sulfate, bicarbonate ion and partly silicon, whose content depends on water temperature. It should also be noted that the increase in the content of sulfate ion in areas where water supply is highly susceptible to water exchange with sedimentary rocks rich in sulfides. The inverse relationship between the content of sodium and calcium is explained by the fact that during the formation of the chemical composition of water, sodium overtakes calcium by leaching from rock-forming plagioclases. In turn, the content of calcium in waters is limited by the carbonate barrier, because of which all excessively released calcium precipitates in the form of secondary calcite.

### Table 2. Rare earth elements in thermal waters of Okhotsk sea shore (ppt).

|          | Ulskiy | Annensky | Tumin | Talaya | Paratunka | Dagi | Lesogorsky |
|----------|--------|----------|-------|--------|-----------|------|------------|
| La       | 0.0104 | 0.0179   | 0.0167| 0.0031 | 0.0089    | 0.0118| 0.0105     |
| Ce       | 0.0238 | 0.0281   | 0.0244| 0.0043 | 0.0281    | 0.0616| 0.0215     |
| Pr       | 0.0025 | 0.0054   | 0.0114| 0.0006 | 0.0014    | 0.0023| 0.0017     |
| Nd       | 0.0116 | 0.0211   | 0.0150| 0.0026 | 0.0063    | 0.0110| 0.0088     |
| Sm       | 0.0028 | 0.0049   | 0.0118| 0.0011 | 0.0015    | 0.0027| 0.0014     |
| Eu       | 0.0007 | 0.0011   | 0.0109| 0.0009 | 0.0029    | 0.0037| 0.0005     |
| Gd       | 0.0031 | 0.0051   | 0.0118| 0.0012 | 0.0017    | 0.0039| 0.0017     |
| Tb       | 0.0004 | 0.0009   | 0.0111| 0.0002 | 0.0002    | 0.0006| 0.0003     |
| Dy       | 0.0026 | 0.0046   | 0.0130| 0.0010 | 0.0010    | 0.0029| 0.0014     |
| Ho       | 0.0006 | 0.0009   | 0.0124| 0.0002 | 0.0002    | 0.0005| 0.0002     |
| Er       | 0.0018 | 0.0030   | 0.0130| 0.0006 | 0.0005    | 0.0014| 0.0005     |
| Tm       | 0.0003 | 0.0004   | 0.0126| 0.0001 | 0.0001    | 0.0003| 0.0001     |
| Yb       | 0.0019 | 0.0022   | 0.0123| 0.0009 | 0.0005    | 0.0016| 0.0005     |
| Lu       | 0.0004 | 0.0004   | 0.0129| 0.0004 | 0.0001    | 0.0002| 0.0001     |
| Ce*      | 0.021  | -0.614   | -1.941| -0.506 | 0.415     | 0.611 | 0.089      |
| Eu*      | 0.078  | -0.016   | 0.762 | 0.718  | 0.879     | 0.801 | 0.311      |
| ΣREE     | 0.0626 | 0.0961   | 0.1893| 0.0172 | 0.0535    | 0.1047| 0.0491     |

* – anomaly of the element

![Figure 2](image_url). NASC-normalized patterns for REE concentrations in thermal waters of the Okhotsk seashore.
Data on REEs is presented in Table 2 and Figure 2. Here we can find low concentrations of REEs, which is common for alkaline waters with low TDS. NASC-normalized patterns show positive Eu-anomaly (Eu*) for Talaya, Paratunka Dagi and Lesogorsky, which is common for mineral waters, forming within sedimentary basins. More flat pattern is usual for waters circulating in crystalline rocks, i.e. Ulskiy and Annenskiy. Concentrations of REEs in Tumnin waters are too low, resulting in saw-shape pattern, so we omitted it. Ce-anomaly (Ce*) is usually explained by redox conditions of the water. If Eh value is higher than 0 mV, then Ce is oxidized to Ce$^{4+}$ form which is less mobile and precipitate with secondary clay minerals or organic matter particles, leading to negative Ce anomaly in solution (Annensky). If Eh value is negative, the Ce is reduced to Ce$^{2+}$ form, which is more mobile, leading to accumulation of Ce in solution (Dagi, Paratunka, Lesogorsky and Ulsky). Case of Talaya should be studied more deep, because here we observe negative Eh value and negative Ce*, which can be also explained by lack of Ce in Jurassic sediments, where Talaya waters circulate.

5. Stable water isotopes

The obtained values of oxygen and hydrogen isotopes for the studied waters correspond to the meteoric genesis (Figure 3). A comparison with the available data shows that the isotopic composition of the thermal spring as a whole reflects latitudinal dependence [4]. The calculated facilitation factor for this type of water is 4.84 ‰ for 1° of latitude for deuterium and 0.59 ‰ for 1° of latitude for δ18O. [4]. Tumin, Annensky and Talaya follow this theory, while Ulskiy, Paratunka, Dagi and Lesogorsky don’t. Here we have to divide thermal waters roughly into two groups, using peculiarities of moisture source for water recharge areas. First group: Tumin, Annensky and Talaya with more “continental” climate as for mainland thermal waters, forming isotopically lighter water and second group: Ulskiy, Paratunka, Dagi and Lesogorsky, with “marine” climate of Sakhalin and Kamchatka, forming isotopically heavier water. For more detailed fractionation of precipitation and moisture source future investigations should be carried out.

![Figure 3](image-url)

**Figure 3.** Diagram of δ18O vs δD in thermal waters of Okhotsk sea shore. VSMOW – Vienna standard mean ocean water. GMWL – global meteoric water line.

6. Conclusions

We can conclude that features of the geological evolution of the territory, the variety of types of water-bearing rocks, the presence of diverse fault tectonics led to very complex hydrogeological conditions, geothermal and hydrochemical conditions. Geology and tectonics created stocks and regime for thermal waters of Okhotsk sea shore.
Usage of sensitive markers as REEs led us to separate water-bearing rocks for thermal waters as well as redox conditions during water circulation. 

Stable water isotopes indicate meteoric origin of thermal waters from one side and difference in moisture source and recharge conditions from the other one.

Monitoring for the physical parameters of groundwater (temperature, electrical conductivity and water level), which together with isotope-hydrochemical data made it possible to understand the dynamics of processes that affect the genesis of thermal waters.

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