Geochemistry of Rare Earth Elements in Volchansky CO₂-Rich Mineral Water and Mineral Precipitations (Sakhalin Island, Far East of Russia)

K Yu Bushkareva¹, G A Chelnokov¹, I V Bragin¹

¹Far East Geological Institute FEB RAS, prospect 100-letnya 159, 690022, Vladivostok, Russia

E-mail: datace@mail.ru

Abstract. Distribution and abundance of rare earth elements in Volchansky Spa of CO₂-rich mineral waters and REE fractionation during the formation of Fe₂O₃ precipitates on the Sakhalin Island (the Far East of Russia) were studied. The main common features of waters are Na-Cl-HCO₃ hydrochemical type, high total dissolved solids (5.4–6.5 g/L), a slightly alkaline pH (6.4–6.5), and reduced conditions (Eh from -181 to -110 mV). The NASC-normalized patterns of groundwaters are characterized by HREE enrichments, negative Ce and positive Eu anomalies. The explanation for the HREE-enriched pattern is that the HREEs form stronger complexes with ligands in solution than do the LREE. Mineral precipitates are presented by Fe-oxides and ΣREE concentrations significantly higher compared to those of the original waters. The slight negative Ce and positive Eu anomalies are also found in the precipitates and these values are very similar to those of the original CO₂-rich waters. It is point out that mineral precipitates are unfractrated or slightly fractionated in comparison to the mineral waters.

1. Introduction
On the Sakhalin Island (the Far East of Russia) the CO₂-rich mineral waters are represented by two major manifestations - Sinegorsky Spa on the south and Volchansky Spa on the west part of the island. The first attempt to elucidate the genesis of mineral waters on the Sakhalin Island has been made in recent years [3, 4], but Vlochansky Spa had not been analyzed previously with regard to rare earth elements content.

The REE are considered as powerful tracers for detecting contamination from anthropogenic sources and characterizing fluid-rock interactions as their distribution and concentration in water is not only ruled by the type of primary minerals being dissolved by the fluid, but also by the precipitation of secondary minerals and reactions of complexation [1, 8, 9, 12, 14]. The mobility of REE in waters mainly depends on: physical-chemical condition, the aqueous composition that drive the stability of dissolved REE complexes, dissolution of rocks and the processes of precipitation / dissolution of secondary minerals [11]. For the last years, the study of the geochemistry of REE in different types of waters of the Far East of Russia was more active [2, 10]. Presently, we have indicated new results of REE contents and distributions in Volchansky Spa cold high pCO₂ mineral waters and associated mineral precipitates located on the Sakhalin Island.
The main objective of this study was to analyze the abundance and distributions of REE in the aquifer and mineral precipitates of Volchansky Spa in order to evaluate the behaviour of REE during water-rock interaction at low temperature and high CO$_2$ content.

2. Study area
Volchansky Spa of a high pCO$_2$ mineral water located in the western part of the Sakhalin Island within the West-Sakhalin fault has been studied. The research objects are CO$_2$-rich groundwaters from two boreholes, natural pool and their mineral precipitates (Figure 1, Table 1).

![Figure 1. Geographic setting of the study area. 1-Volchansky Spa CO$_2$-rich mineral water area; 2- boreholes; 3-tectonic dislocations.](image)

The Sakhalin Island is owed to the Sakhalin-Hokkaido orogenic belt and is characterized by tectonic zonality fully represented on the Hokkaido Island (Japan) and reflects the successive accumulation of continental crust from the middle Jurassic to Neogene [4]. The sedimentary rocks had been accumulated in marine environment. The geological structure of the Volchansky Spa has been studied during the drilling in 1991. Boreholes disclose the sandstone aquifer of Arakai formation of Upper Paleogene. The mineral water manifestations are located within the one of the large tectonic dislocations of the island- West Sakhalin Fault.

Hydrogeological conditions of the territory are very complex and caused by a zone and block structure, fracture permeability. The zone of an active water exchange makes not more than 100 m
from the surface and is caused by weathering. Water of the aquifers is free-flow, fresh, hydrocarbonate. The associated gases are presented by CO$_2$ (60 vol.%) and CH$_4$ (31 vol.%).

3. Sampling and analytical procedures
The materials obtained by the authors as a result of their field works carried out in 2017-2018 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 HNO$_3$. 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 7500) analysis. Trace element and REE concentrations were analyzed by ICP-MS (Agilent 7500 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 and Eu anomalies, such as the Ce anomaly $= 2\text{Ce}/(\text{La}_{\text{N}}+\text{Pr}_{\text{N}})$ and the Eu anomaly $= 2\text{Eu}/(\text{Sm}_{\text{N}}+\text{Gd}_{\text{N}})$, with N equal to the normalized abundance.

4. Results
4.1. Fluids chemistry and rare earth elements in water
The chemical composition of studied waters and REE contents in water after filtration through filter 0.45 µm are presented in Table 1. Groundwaters are represented with Na-Cl-HCO$_3$ water type with TDS varying from 5.4 to 6.5 g/L. All waters are cold, with stable pH = 6.4 and negative Eh values vary from -195 to -110. Na$^+$ dominates as cation species ranging from 1400 to 1650 mg/L. Local enrichments occur in relatively immobile elements, mg/L: I (3.7), Br (4.0) and B (24.5) [5]. While a value of Al is low (0.04 mg/l) and Mn (0.5 mg/l) relatively high compared with other analyzed water types [4]. The main sources of the elements in mineral waters are CI-rich fluids, rock dissolution and dissolved gases (CO$_2$). It is well known that the presence of dissolved CO$_2$ enhances the extent of water-rock interactions, particularly at the low temperature. Therefore, associated CO$_2$ gas increases the water-rock interactions and more intensely leaches elements from the bedrock. Thermodynamic calculations indicate that all mineral waters are undersaturated relative to the primary aluminosilicate minerals (SI$_{\text{abite}}$=1.1), sulfates BaSO$_4$ (SI$_{\text{barite}}$=8.0), CaSO$_4$ (SI$_{\text{gypsum}}$=9.8) and carbonate minerals (SI$_{\text{calcite}}$=0.2); oversaturated relative to Fe-hydroxides (SI$_{\text{hematite}}$=11.6), SiO$_2$ (SI$_{\text{quartz}}$=0.15), and FeS$_2$ (SI$_{\text{pyrite}}$=8.9).

The studied waters had not been analysed previously with regard to rare earth elements content. It is specified that: 1) the concentrations of total REE of natural mineral spring are almost two times higher than in the boreholes (Table 1); 2) the light REE (from La to Eu) dominate on heavy REE (from Gd to Lu) and 3) Eu, Ce and La have maximal content.

To more conveniently view inter-element trends, the REE analyses have been normalized to North American Shale Composite [7] in order to investigate the differences between the REE distribution patterns removing the Oddo Harkins effect. The NASC-normalized patterns of groundwaters are characterized by weak HREE enrichment, negative Ce (Ce/Ce*=0.5-0.6) and positive Eu/Eu* (2.0-2.5) anomalies (Figure 2). Anomalies of Ce and Eu were of particular interest following the anomaly’s potential use as an indicator of water/rock interaction processes or as a hydrological tracer [5]. The explanation for the HREE-enriched pattern is that the HREEs form stronger complexes with ligands in solution than do the LREE. This has two consequences: the HREEs will be preferentially released to
solution during weathering of source rocks; and the LREE will be preferentially adsorbed at particle surfaces in adsorption/equilibria reactions in waters. The presence of CO$_2$ gas also enhances the concentration of HREE [10].

It is known that negative Ce anomalies require near-surface partitioning of Ce due to the oxidation of Ce$^{3+}$ to Ce$^{4+}$ and precipitation under oxidative conditions [14, 18]. Starting with undifferentiated scavenging of all REE, most of these elements are released during aging, only Ce is retained as Ce$^{4+}$ leading to the positive Ce anomaly in the final precipitate and a corresponding negative one in waters. By analytical comparison with the other REEs and normalization to a shale standard, the well-known negative cerium anomaly in the oxidized waters of the world oceans, and a number of continental waters [6] is observed. Whereas, the positive Eu-anomalies are common for fluids considerably more reduced conditions [5, 15], reflecting weathering reactions with host rocks or for hydrogeological systems (aquifers) which has not yet reached static equilibrium [12]. The literature data indicate that problem of coexistence of the negative Ce and positive Eu anomaly in reduce conditions actual for iron-formations of the world [16].

Table 1. Chemical composition of Volchansky high pCO$_2$ mineral waters.

| Parameter | Unit | Spring | Mineral water boreholes |
|-----------|------|--------|-------------------------|
|           |      |        | Nº 92  | Nº 93  |
| TDS | g/L | 6.52 | 5.45 | 6.01 |
| T | °C | 9.9 | 9.9 | 10.0 |
| pH | Unit | 6.40 | 6.49 | 6.43 |
| Eh | mV | -114 | -110 | -195 |
| CO$_2$ | ppm | 1000 | 860 | 830 |
| Na | ppm | 1632 | 1520 | 1414 |
| Ca | ppm | 166 | 96 | 139 |
| Mg | ppm | 55.9 | 32.4 | 48.5 |
| K | ppm | 19.5 | 17 | 18.9 |
| Cl | ppm | 2085 | 1599 | 1763 |
| SO$_4$ | ppm | 2565 | 1428 | 1765 |
| HCO$_3$ | ppm | 3.5 | 3.9 | 2.6 |
| Fe | ppm | 15.9 | 3.7 | 4.3 |
| La | ppb | 0.225 | 0.0867 | 0.177 |
| Ce | ppb | 0.262 | 0.0751 | 0.189 |
| Pr | ppb | 0.030 | 0.0117 | 0.0229 |
| Nd | ppb | 0.125 | 0.0523 | 0.0980 |
| Sm | ppb | 0.056 | 0.0332 | 0.0439 |
| Eu | ppb | 0.334 | 0.231 | 0.257 |
| Gd | ppb | 0.081 | 0.0468 | 0.0664 |
| Tb | ppb | 0.006 | 0.0033 | 0.0046 |
| Dy | ppb | 0.042 | 0.0203 | 0.0310 |
| Ho | ppb | 0.010 | 0.0052 | 0.0074 |
| Er | ppb | 0.030 | 0.0141 | 0.0224 |
| Tm | ppb | 0.005 | 0.0028 | 0.0037 |
| Yb | ppb | 0.030 | 0.0164 | 0.0226 |
| Lu | ppb | 0.005 | 0.0033 | 0.0039 |
| $\sum$REE | | 1.240 | 0.602 | 0.949 |
| $\sum$LREE | | 1.032 | 0.49 | 0.788 |
| $\sum$HREE | | 0.209 | 0.112 | 0.162 |
4.2. Rare earth elements in mineral precipitates

Results of major and trace elements of bulk mineral precipitates are given in Table 2. The Fe₂O₃ is a main oxide of the sample (57%), whereas CaO and SiO₂ reach 3-5 %. The sum of the other constituents analysed (Al₂O₃, P₂O₅, MnO, MgO, Na₂O₂, TiO₂) is < 3.66 wt %.

| Parameter | Borehole № 93 [%] | Parameter | Borehole № 93 (ppb) | Parameter | Borehole № 93 (ppb) |
|-----------|-------------------|-----------|-------------------|-----------|-------------------|
| SiO₂      | 2.8               | La        | 9.07              | Tb        | 0.37              |
| TiO₂      | 0.002             | Ce        | 14.21             | Dy        | 2.27              |
| Al₂O₃     | 0.1               | Pr        | 1.96              | Ho        | 0.49              |
| Fe₂O₃     | 57.19             | Nd        | 8.38              | Er        | 1.36              |
| MgO       | 0.13              | Sm        | 2.18              | Tm        | 0.18              |
| CaO       | 5.49              | Eu        | 0.68              | Yb        | 1.23              |
| Na₂O      | 1.01              | Gd        | 2.15              | Lu        | 0.22              |
| H₂O       | 27.65             | ∑REE      | 44.75             |           |                   |

The data show that ∑REE concentrations of the precipitates are significantly higher compared to those of the original (i.e., prior to precipitation) waters (Table 2, Figure 2). This indicates that REEs are preferentially partitioned into Fe-precipitates. The slight negative Ce anomalies with Ce/Ce* values 0.73 are also found in the Fe-oxides and these values are very similar to those of the original CO₂-rich waters (0.49-0.66). The Eu anomalies are positive (1.3) and also similar for corresponding original CO₂-rich water (Eu/Eu=2.0-2.5).

![Figure 2. NASC-normalized concentrations of REE in mineral waters and its precipitates.](image-url)
It was expected that during the formation of precipitates by CO₂ degassing and redox changing, fractionation of REEs would occur and result in the Ce enrichment in the precipitates. However, such a fractionation pattern between the water and the Fe₂O₃ precipitates was not observed in this study. This may be caused by the fact that most of the REEs (80%) in CO₂-rich waters are complexed with carbonate ligands and hence coprecipitate with carbonate minerals [13] without causing significant fractionation effects.

It is point out that mineral precipitates are unfracated or slightly fractionated in comparison to the mineral waters. Because of neither mineral waters nor precipitates have not a positive Ce anomaly, no redox controlled processes leading to the formation of CeO₂ can be invoked. However, the cerium signal to be expected with iron oxide precipitation from deeper anoxic waters is unclear, whereas positive Eu anomaly can be related to strongly reducing condition during diagenesis.

5. Conclusion
Our investigation of slightly alkaline CO₂-rich Na-Cl-HCO₃ mineral waters of Volchansky Spa (Sakhalin Island) and precipitates lead to the following conclusions: 1) The NASC-normalized patterns of groundwaters are characterized by HREE enrichments, negative Ce and positive Eu anomalies. This observation can be explained largely by the preferential leaching of the HREEs from sedimentary bedrock during water–rock interaction in the presence of CO₂; 2) Mineral precipitates are presented by Fe-oxides and ΣREE concentrations significantly higher compared to those of the original waters. The slight negative Ce and positive Eu anomalies are also found in the precipitates and these values are very similar to those of the original CO₂-rich waters. It is point out that mineral precipitates are unfracated or slightly fractionated in comparison to the mineral waters; 3) precipitates has not a positive Ce anomaly, means that no redox controlled processes leading to the formation of CeO₂ can be invoked. The data showed that precipitates are unfracated or slightly fractionated in comparison to the mineral waters.

6. References
[1] Bau M and Koschinsky A 2009 J.Geochim. 43
[2] Bragin I, Chelnokov G, Chudaev O, Kharitonova N and Vysotskiy S 2016 Acta Geol. Sinica 90
[3] Chelnokov G, Bragin I and Zharkov R 2015 J. Geoscience and Environment Protection 3
[4] Chelnokov G, Bragin I and Kharitonova N 2018 J.Hydrology 559
[5] De Baar H, German C, Elderfield H and Van Gaans P 1988 Geochim. et Cosmochim Acta 52 5
[6] Elderfield H, Upstill-Goddard R and Sholkovitz E 1990 Geochim. Cosmochim. Acta 54 971
[7] Gromet P, Dymek R, Haskin L and Korotev R 1984 Geochim. Cosmochim. Acta 48
[8] Inguaigato I, Itiguz E, Peiffer L, Kretzschmar T, Brusca L, Mora-Amador R, Ramirez K, Bellomo S, Gonzalez G, Rouwet D 2018 Gondwana Research, 59 87
[9] Johannesson K, Palmore D, Fackrell J, Prouty N, Swarzenski P, Chevis D, Telfeyan K, White C and Burdige D 2017 Geochim. et Cosmochim. Acta 198 229
[10] Kharitonova N, Chelnokov G, Karabtsov A, Kiselev V 2007 Applied Geochemistry 22
[11] Lewis A J, Palmer M R, Sturchio N C, Kemp A J 1997 Geochim. Cosmochim. Acta 61
[12] Möller P 2000 Hydrology of crystalline rocks In Stober. I. and Bucher. K. (eds), Kluwer Acad. Press, 227-246
[13] Nêgre P H, Guerrot C, Cocherie A, Azaroual A, Brash M and Fouillac Ch 2000 Appl. Geochem. 15 1345
[14] Noack C, Dzombak D and Karamalidis A 2014 Environmental Science and Technology 48, 4317
[15] Sholkovitz E 1995 Aquat. Geochem 1
[16] Towe K 1991 Palaeogeograph, Palaeoclimatology, Palaeoecology (Global and Planetary Change Section) 97 113
Acknowledgment
This work was supported by grants from Russian Foundation for Basic Research, project № 18-35-00100.