Geochemistry of Rare Earth Elements in Sinegorsky Spa of CO_2-rich Mineral Water (Sakhalin Island, Far Eastern Russia)

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Abstract: Distribution and abundance of rare earth elements for Sinegorsky Spa of CO_2-rich mineral waters and their mineral precipitates on the Sakhalin Island (the Far East of Russia) were studied. The main common features of waters from six boreholes are Na-Cl-HCO_3 hydrochemical type, high total dissolved solids (16.2–23.1 g/L), a slightly alkaline pH (6.2–7.7), and Eh (-181 to 63 mV). The NASC-normalized patterns of all groundwaters are characterized by HREE enrichments and positive Eu anomalies, whereas some fluids are characterized by positive Ce anomaly and others have moderate negative Ce anomaly. The distinct positive Eu/Eu* in mineral waters indicates the nature of their water-rock interaction whereas Ce anomaly could be the result of the difference in groundwater circulation. Mineral precipitates are enriched with light REE and show a negative Eu/Eu* and positive Ce/Ce* anomalies which indicate redox controlled processes. The main processes controlling dissolved trace element behaviour in water were established. It is argued that bicarbonate ion-pairs can also play an important role for the solution chemistry of HREE which explains the significant relative fractionation between REE observed in CO_2-rich water. This work was supported by grants from Russian Science Foundation (RSF), project № 18-17-00245.

1 INTRODUCTION

On the Sakhalin Island (the Far East of Russia) the CO_2-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 cold mineral waters on the Sakhalin Island has been made in recent years (Chelnokov, et al. 2015; Chelnokov et al., 2018). It was established that the studied waters belonged to two main water types: 1) Na-HCO_3-Cl alkali carbonate waters with TDS less than 1.0 g\L and 2) Na-Cl or Na-Cl-HCO_3 saline groundwaters with TDS up to 26 g/L. The isotopic data indicate that CO_2 gas in the mineral water may be mantle-derived and its presence is critical for the development of the high-pCO_2 groundwater.

The processes controlling the fate and transport of rare earth elements in fluids are poorly understood because a complex set of variables affects rare earth element solubility including solution chemistry, pH, Eh, solid phase mineralogy and composition, temperature, and pressure (De et al. 1988; Johannesson et al.1997). 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 (Bragin et al. 2016; Chudaev et al. 2016; Kharitonova et al. 2016) . Presently, we have indicated new results of REE contents and distributions in Sinegorsky Spa cold high pCO_2 mineral waters and associated mineral precipitates located on the Sakhalin Island.

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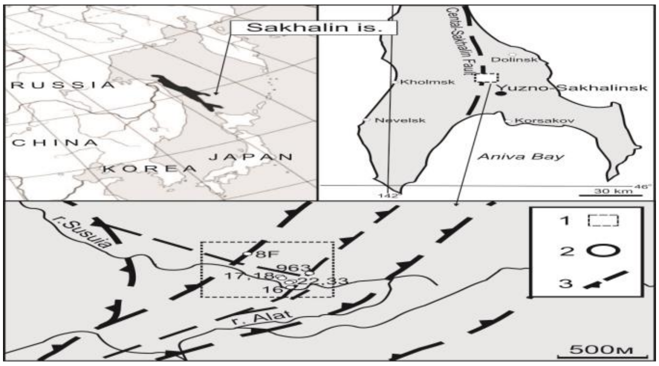

Figure 1: Geographic setting of the study area. 1-Sinegorsky spa high pCO2 mineral water area; 2- boreholes; 3-tectonic dislocations.

Table 1: Chemical composition of Sinegorsky high pCO2 mineral waters.

Parameter	Unit	Mineral water boreholes						Fresh GW
		№ 963	№ 16	№ 17	№ 18	№ 22	№ 33	№8F
TDS	g/L	16.2	23.1	17.6	17.3	19.3	18.9	0.5
T	°C	15.3	9.6	10.8	8.6	10.3	9.6	9.5
pH	Unit	6.67	7.4	6.5	6.2	7.1	7	7.7
Eh	mV	-181	69	58	62	-60	-69	63
TOC	mg/L	-	107	27	-	-	-	-
CO2		2000	681	439	650	598	954	-
Na		4780	5612	4528	4282	6978	6298	143
Ca		146.00	270	209	188	245	261.6	13
Mg		91.08	182	114	124	211	221.7	1.46
K		107	29	37	53	59.7	58.17	20.2
Cl		6700	6073	6753	6846	6390	6240	65.2
SO_4		<<	59.6	7.2	7.5	68.2	51.5	1.02
HCO_3		5223	9543	4392	5587	10547	10114	268
Fe		1.0	4.0	1.6	1.6	8.4	8.7	0.3
NH_4		150	95.4	102	106	<<	<<	3
La	ppb	0.0139	0.023	0.010	0.028	0.062	0.063378	0.002
Ce		0.0254	0.032	0.013	0.035	0.152	0.639169	0.000
Pr		0.0013	0.005	0.003	0.007	0.0068	0.009554	0.0004
Nd		0.0169	0.016	0.013	0.029	0.0409	0.036748	0.0014
Sm		0.0114	0.010	0.011	0.017	0.0176	0.021086	0.0009
Eu		0.0501	0.012	0.019	0.018	0.11039	0.121292	0.00356
Gd		0.0131	0.012	0.013	0.018	0.0296	0.048218	0.0010
Tb		0.0016	0.002	0.002	0.002	0.00214	0.002459	0.00008
Dy		0.0084	0.007	0.008	0.010	0.0096	0.010213	0.0003
Ho		0.0016	0.001	0.002	0.002	0.00319	0.001592	0.00010
Er		0.0054	0.006	0.010	0.009	0.01228	0.009914	0.00033
Tm		0.0012	0.002	0.002	0.002	0.00260	0.001244	0.00005
Yb		0.0065	0.009	0.012	0.012	0.01687	0.009282	0.00018
Lu		0.0012	0.002	0.003	0.003	0.00322	0.002851	0.00000
∑REE		0.16	0.14	0.12	0.19	0.47	0.97	0.01
∑LREE		0.13	0.11	0.08	0.15	0.42	0.94	0.01
∑HREE		0.02	0.03	0.04	0.04	0.05	0.04	0.001

The main objective of this study was to analyze the abundance and distributions of REE in the aquifer and mineral precipitates of Sinegorsky Spa (the Sakhalin island) in order to evaluate the behaviour of REE during water-rock interaction at low temperature and high CO_2 content.

2 STUDY AREA

Sinegorski spa of a high pCO2 mineral water located within the southern part of the Central-Sakhalin fault has been studied. The research objects are the CO2-rich groundwaters from six boreholes and mineral precipitates from a borehole № 16 (Figure 1, Table 1). It should be noted, that three wells are being operated and periodically pumped (16, 17 and 18) and other three (№ 963, 22 and 33) are not being used for more than 10 years.

The geological structure of a cretaceous complex within Sinegorski spa has been studied well in the previous work (Chelnokov et al. 2018; Niida and Kito 1986). Boreholes disclose the sandstone aquifer of Maruyamsky formation of Middle-Pliocene and Miocene age. The oldest formation in the area is Mesozoic rocks which consist of micaceous and quartz shales, marble and quartzite, siltstones, mudstones, sandstones and tuffs. All sediments of the cretaceous system had been accumulated in marine conditions (Chelnokov et al. 2018). The southern part of the Central-Sakhalin fault is in the Susunayski artesian basin in terms of hydrogeology. 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 top aquifers is free-flow, fresh, hydrocarbonate. Mineral water of the deepest aquifer has mineralization of 10 - 30 g/l and Cl-Na or HCO_3-Cl-Na composition. The associated gases are presented by CO_2 (50-98 vol.%) and CH_4 (2-45 vol.%) (Chelnokov et al. 2015)

The boreholes objects of investigations are located within large tectonic dislocations of the island. 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 (Niida and Kito 1986).

3 SAMPLING AND ANALYTICAL PROCEDURES

The materials obtained by the authors as a result of their field works carried out in 2015-2017 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 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.).

4 RESULTS

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-HCO3 water type with TDS varying from 16.2 to 23.1 g/L. All waters are cold, the pH changes from 6.2 to 7.4 and Eh values vary from -181 to +63. Na+ dominates as cation species ranging from 4528 to 6978 mg/L. The concentrations of Si, Mn, I, Ba are relatively high (Chelnokov et al. 2018). Local enrichments also occur in relatively immobile elements such as As and Sr. While values of Al could be compared with other analyzed water types. Ammonium concentrations are remarkably high since organic matter which is oxidized by sulfate ions in pore water releases NH4+ and I- ions from entrained organic matter (e.g., Sholkovitz 1995). The main sources of the elements in mineral waters are Cl-rich fluids of a different origin, rock dissolution and dissolved gases (CO_2) (Chelnokov et al. 2018). It is well known that the presence of dissolved CO2 enhances the extent of water-rock interactions, particularly at the low temperature. Therefore, associated CO2 gas increases the water-rock interactions and more intensely leaches elements from the bedrock. Thermodynamic calculations indicate that all mineral waters are oversaturated relative to the primary aluminosilicate minerals (SIalbite =1.2–2.8), quarts (SIquartz =0.4–1.2), hydroxides (SIhematite =9.2–17) and carbonate minerals (SIcalcite =0.2–1.4).

The studied waters had not been analysed previously with regard to rare earth elements content. Typical for borehole №33 maximal concentrations of total REE are almost two times higher than in the bh № 22 and are remarkably higher than in other boreholes (Table 1). The minimal concentrations show fresh groundwaters (bh №8F). To more conveniently view inter-element trends, the REE analyses have been normalized to North American Shale Composite (Gromet et al. 1984). The NASC-normalized patterns of groundwaters are characterized by HREE enrichments and positive Eu anomalies. The interesting difference consists in Ce anomaly: some fluids are characterized by positive Ce anomaly (Ce/Ce*=1.1-5.4) (bh № 33, 22, 963) (Figure 2A) and others have moderate negative Ce anomaly (Ce/Ce*=0.5-0.6) (bh № 16, 17, 18) (Figure 2B). Anomalies of Ce were of particular interest following the anomaly's potential use as an indicator of water/rock interaction processes or as a hydrological tracer (Seto and Akagi 2008).

The positive Eu-anomalies are common for both groups and are likely reflecting weathering reactions with host rocks as a result of the preferential dissolution of a Eu-rich phase (e.g. plagioclase). Other way groundwater might reflect considerably more reduced conditions (De et al. 1988; Sholkovitz 1995). Also the Eh conditions of the waters could specify the difference in Ce anomalies. 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 (Eh>0) (Johannesson et al. 1997; Lewis et al. 1997). negative Ce anomalies do not occur in reduced fluids (Eh<0) since Ce^{3+} doesn't oxidize to Ce^{4+}.

Also it can be explained by regional bedrock mineralogy and lithology (Ce-depleted source minerals in the materials through which the water flows). Experimental data (Bau, 1999) indicate that variation in Ce anomaly magnitude could be a result of the difference in residence time of groundwater circulation. It is in a good agreement with behavior of Ce: in boreholes which are being operated (№ 16, 17, 18) we observe Ce minimum and unused boreholes (№ 963, 22, 33) have Ce maximum.

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 heavy REE (Kharitonova et al. 2007). Results of major and trace elements of bulk mineral precipitates are given in Table 2. The samples from the top of the well were limpid, white salt crystals.

The Al_2O_3 and Na_2O contents of the sample are consistently very high (~35%) and (~10%) correspondingly. Mineral precipitates are enriched with LREE (89%) compared to the HREE (11%), it is in good correlation with mineral water producing this precipitates (Bh №16) containing LREE -79% and HREE -21% (Tables 1, 2). Comparing the rare earth element signature of waters with its mineral precipitates reveals differences (Figure 2). NASC-normalized concentrations are higher for REE in solid phase than for the water. The respective NASC-normalized REE pattern decreases slightly from La to Nd, increases from Eu to Lu; and shows a small positive Ce and negative Eu anomalies (Table 2). Enrichment of Ce in solid phase (Bh №16 Ce/Ce*= 1.2) is clearly indicated by the depletion of this element in corresponding waters (Bh №16 Ce/Ce*= 0.6). Positive Ce anomaly can indicate redox controlled processes leading to the formation of CeO_2 (Aubert et al. 2001). Whereas Eu do not accumulate in mineral precipitates and demonstrates lowest level among REE (Table 2, Figure 2B).

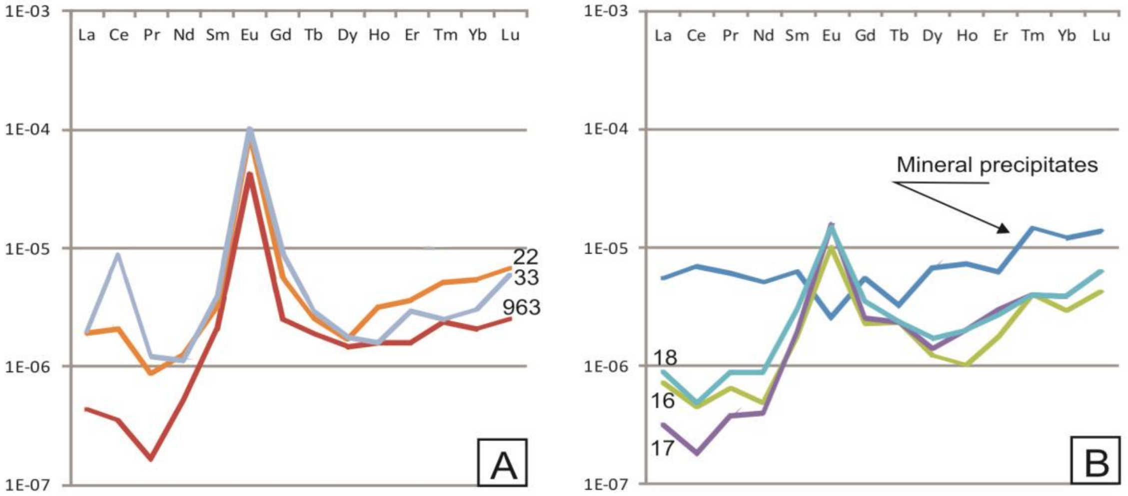

Figure 2: NASC-normalized concentrations of REE in mineral waters and precipitates. A-not operated wells with positive Ce anomaly; B- operated wells with negative Ce anomaly and their mineral precipitates.

Table 2: Bulk chemical composition of the studied mineral precipitates.

Paramerer	Borehole № 16 [%]	Parameter	Borehole № 16 (ppb)	Parameter	Borehole № 16 (ppb)
SiO_2	0.81	La	0.177	Tb	0.003
TiO_2	0.032	Ce	0.499	Dy	0.039
Al_2O_3	34.75	Pr	0.048	Ho	0.007
Fe_2O_3	0.4	Nd	0.164	Er	0.021
MgO	0.83	Sm	0.036	Tm	0.007
CaO	0.66	Eu	0.003	Yb	0.037
Na_2O	9.81	Gd	0.028	Lu	0.007
H_2O	48	∑REE	1.07		

5 CONCLUSIONS

Our investigation indicates that Sinegorsky CO_2-rich mineral waters have some unusual geochemical characteristics including different Ce anomaly. The NASC-normalized patterns of all groundwaters are characterized by HREE enrichments and positive Eu anomalies, whereas some fluids are characterized by positive Ce anomaly and others have moderate negative Ce anomaly. All the data are interpreted as the result of the following processes: 1. REE leaching in a reducing environment in presence of CO_2 which enhances concentration of heavy REE; 2. oxidation of Ce^{3+} to Ce^{4+} in an oxidizing environment; 3. deposition and accumulation of REE (such oxides have positive Ce anomalies indicating their adsorption of the insoluble Ce-phase).

The water pumping from boreholes, CO_2 outgassing, changes in the redox conditions and mineral precipitates deposition are the main processes thought to control dissolved trace element behavior by co-precipitation and/or adsorption. It is suggested that bicarbonate ion-pairs can also play an important role for the solution chemistry of HREE which explains the significant relative fractionation between REE observed in CO_2-rich water.

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