

# Rare earth element contents in high pCO<sub>2</sub> groundwaters of Sakhalin Island (the Far East of Russia)

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**Abstract.** The geochemistry of rare earth elements in cold, high pCO<sub>2</sub> mineral waters was studied through the sampling of springs and boreholes of Sakhalin Island (the Russian Far East). The main common features of studied waters are the Na-Cl-HCO<sub>3</sub> hydrochemical type, high TDS (6–20 g/L), alkaline pH (6.2–7.4), and reducing environment (-195 to +62 mV). The North American Shale Composite-normalized patterns of groundwaters exhibited a heavy REEs enrichment with high positive Eu anomalies. Both, positive and negative Ce anomalies were detected in CO<sub>2</sub>-rich mineral waters. The distinct positive Eu/Eu\* in waters indicates water-rock interaction processes and positive Ce/Ce\* corresponds to reducing conditions. The various processes responsible for negative Ce anomaly in reducing environment are described.

## 1 Introduction

The cold CO<sub>2</sub>-rich mineral waters of Sakhalin Island are represented by two major manifestations – the Sinegorsky Spa on the south and the Volchansky Spa on the west part of the island. The first attempt to elucidate the genesis of mineral waters on Sakhalin Island has been made in recent years [1, 2]. It has been established that the CO<sub>2</sub>-rich waters are related to Na-Cl-HCO<sub>3</sub> type groundwaters with TDS from 5 to 26 g/L. The main associated gases of the waters are CO<sub>2</sub> (~80 vol%) and CH<sub>4</sub>, flowing into shallow groundwaters through major fault systems [2]. The isotopic data indicate that CO<sub>2</sub> gas in the mineral waters may be mantle-derived and its presence is critical for the development of the high-pCO<sub>2</sub> groundwater.

The aim of this study is to characterize the REE concentrations and profiles in the pCO<sub>2</sub> mineral waters of Sakhalin Island and to explain the difference in Ce behaviour.

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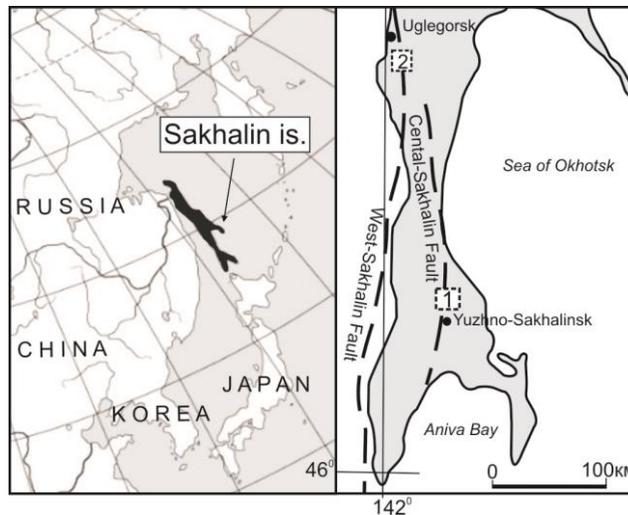
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## 2 Study Area

Sakhalin Island is owed to the Sakhalin-Hokkaido orogenic belt and is characterized by well-defined tectonic zonality fully represented on Hokkaido Island (Japan) and reflecting the successive accumulation of continental crust from the middle Jurassic to Neogene [2]. The high  $p\text{CO}_2$  mineral waters of Sakhalin Island discharge over a wide range of geological settings, including continental back-arc rifting in the West Sakhalin uplift (the Volchansky Spa) and an ancient accretionary prism in the South (the Sinegorsky Spa). The mineral water manifestations are located within large tectonic dislocations of the island: the Central-Sakhalin and the West-Sakhalin faults (Fig. 1). The water fluid circulation is mainly localized in clastic sedimentary rocks (sandstones, siltstones) inducing the  $\text{HCO}_3\text{-Cl-Na}$  groundwater type.

The geological structure of a cretaceous complex within the Sinegorsky Spa is well known [3]. There are no natural springs but six boreholes disclose the sandstone aquifer of Maruyamsky formation of Pliocene - middle Miocene age. All sediments of the cretaceous system accumulated under marine conditions [2]. It should be noted, that two shallow wells (№17, №18 with depth of 15-20 m) are being operated and periodically pumped and other two (№ 22, №33 with depth of 70-90 m) have not been used for more than 10 years.

The Volchansky spring and two boreholes (with depth of 15-20 m) are located in the western part of Sakhalin, in the Ulegorsk region. The high  $p\text{CO}_2$  mineral waters are associated with fractured sedimentary rocks of Arakayski formation of upper Paleogene (sandstones and tuffs), which are covered with a clay cap at the surface. The formation of the spa is caused by the deep fluids enriched with carbon dioxide, bromine and iodine. The mineralization of water is 6-8 g/L.



**Fig. 1.** Locations of the investigation sites: 1-Sinegorsky area, 2-Volchansky area.

Hydrogeological conditions of the territory are very complex and caused by the fractured bedrocks, which plays a role of groundwater path to flow considerable lateral and/or vertical extend, frequently shows high permeability. The fractures or fracture zones control the bulk permeability of the rock mass and are usually a few hundred order of magnitude higher in hydraulic conductivity than the background matrix. A confined aquifers are artesian mostly occurs at depth intervals of 10–300 m, piezometric levels are vary from +0.5 to - 1.0 m from the ground surface, well water discharge range between

0.04 and 0.5 l/s. Mineral waters from the deep aquifers located between 300 and 500 metres have higher mineralization of 10-30 g/l and present Cl-Na or HCO<sub>3</sub>-Cl-Na compositions.

The <sup>3</sup>H concentrations of deep wells (№ 22, №33) are below the detection limit, indicating a mean transit time greater than 60 years. Whereas other Sinegorsky and Volchansky boreholes show higher <sup>3</sup>H amount (2.1-4.7 TU), which indicates mixing of submodern and modern groundwater [2].

### 3 Results and discussion

Water samples were being collected over a three-year period. Fresh shallow groundwaters and main river waters were also analyzed. Locations of investigated areas are indicated on Fig. 1, concentrations in REE are given in Table 1.

#### 3.1 Hydrogeochemistry

The high pCO<sub>2</sub> mineral waters have low temperature (8-10°C), high TDS (6-20 g/l) and pH varying from 6.2 to 7.4. All waters are characterised by reducing conditions (Eh values ranges from -195 to +62 mV) and show higher concentrations in sodium than in chlorine. The Na/Cl molar ratio varies from 1.06 to 4.73. A greater Na/Cl ratio may be ascribed to the feldspar weathering and the dissolution of other Na-containing minerals [2]. Increased [Na<sup>+</sup>] concentration coupled with decreased [Ca<sup>+2</sup>] and [Mg<sup>+2</sup>] concentrations also indicate the cation exchange (clay minerals etc.) [4]. The Cl/Br mass ratios range from 318 to 400 and indicate both fresh waters and NaCl dissolution components [2]. The concentrations of iodine (3.0–3.7 mg/L) in high pCO<sub>2</sub> waters either may be related to high organic enrichment or may be linked to complex geological history as well as may be associated with old seawater incursion. As a result of diagenesis and consolidation, iodine moves from the sediment to the pore fluid. Base-exchange softening and the consequent enhanced boron desorption can take place in aquifers with sufficient exchange surfaces (e.g., clay minerals) to permit base-exchange, and sufficient water-rock interaction to allow that process to change the calcium and sodium contents significantly and, consequently, to change the pH.

Thermodynamic calculations indicate that all groundwater samples are undersaturated with respect to halite, which proves the conservative nature of sodium and chloride. On the opposite, all groundwaters are oversaturated relative to the primary aluminosilicate minerals (SI<sub>albite</sub> = 1.2–2.8), quartz (SI<sub>quartz</sub> = 0.4–1.2) and hydroxides (SI<sub>hematite</sub> = 9.2–17).

#### 3.2 Rare earth element characteristics

Rare earth element concentrations vary considerably in the high pCO<sub>2</sub> mineral waters of Sakhalin Island. The maximal REE total concentrations are observed in the Volchansky Spa mineral waters ( $\sum\text{REE}_{\text{average}} = 0.93$  ppb) and are almost two times higher than in the Sinegorsky waters ( $\sum\text{REE}_{\text{average}} = 0.43$  ppb) (Table 1). The minimal concentrations are presented in wells № 17 and 18 of the Sinegorsky area. The REE data have been normalized to the North American Shale Composite [5]. The NASC-normalized patterns of groundwaters are characterized by HREE enrichments and positive Eu anomalies. The positive Eu-anomalies are observed in all studied waters and are supposed to reflect reducing conditions and weathering reactions [6]. The most important source of an inherited Eu anomaly is the alteration of feldspars, particularly plagioclase, which indicates water-rock systems that have not reached static equilibrium [6, 7, 8]. Moreover, Eu<sup>3+</sup> can be reduced to Eu<sup>2+</sup> (under reducing condition) and the Eu anomalies can be controlled during

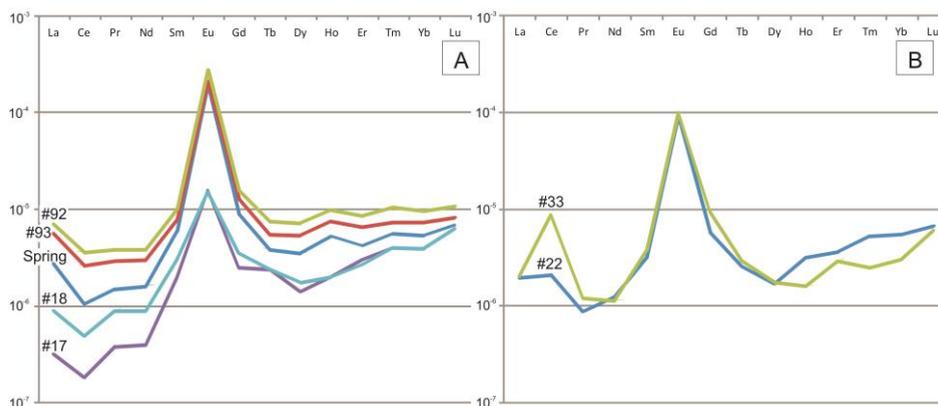
water-rock interaction by the preferential mobilization of  $\text{Eu}^{2+}$  in aqueous solution compared to trivalent REEs.

The main difference relates to the Ce anomaly: some fluids have moderate negative Ce anomaly ( $\text{Ce}/\text{Ce}^*=0.5-0.6$ ) (bh № 17, 18, 92, 93, Spring) and others are characterized by positive Ce anomaly ( $\text{Ce}/\text{Ce}^*=1.1-5.4$ ) (bh № 33, 22) (Fig. 2A, 2B). The disclosed Ce anomalies are considered to be of particular interest due to its potential use as an indicator of water-rock interaction processes or as a hydrological tracer [9].

The positive Ce anomalies in waters from Sinegorsky wells № 22 and №33 (Fig. 2B) can be explain by: i) accumulation of Ce in reducing environment (when  $\text{Ce}^{3+}$  does not oxidize to  $\text{Ce}^{4+}$  and not precipitate as  $\text{CeO}_2$ ) or ii) desorption on Fe-oxyhydroxides (for ex.  $\text{FeOOH}$ ) during the process of interaction of waters and sediments accumulating REE in oxidizing conditions [6].

**Table 1.** Rare earth element contents of high  $\text{pCO}_2$  mineral waters of Sakhalin Island.

Parameter	Unit	Volchansky Spa			Sinegorsky Spa			
		Natural Spring	Boreholes		Boreholes			
			# 92	# 93	#17	#18	#22	#33
La	ppb	0.225	0.0867	0.177	0.010	0.028	0.062	0.0634
Ce		0.262	0.0751	0.189	0.013	0.035	0.152	0.6392
Pr		0.030	0.0117	0.0229	0.003	0.007	0.0068	0.0095
Nd		0.125	0.0523	0.0980	0.013	0.029	0.0409	0.0367
Sm		0.056	0.0332	0.0439	0.011	0.017	0.0176	0.0211
Eu		0.334	0.231	0.257	0.019	0.018	0.1104	0.1213
Gd		0.081	0.0468	0.0664	0.013	0.018	0.0296	0.0482
Tb		0.006	0.0033	0.0046	0.002	0.002	0.0021	0.0025
Dy		0.042	0.0203	0.0310	0.008	0.010	0.0096	0.0102
Ho		0.010	0.0052	0.0074	0.002	0.002	0.0032	0.0016
Er		0.030	0.0141	0.0224	0.010	0.009	0.0123	0.0099
Tm		0.005	0.0028	0.0037	0.002	0.002	0.0026	0.0012
Yb		0.030	0.0164	0.0226	0.012	0.012	0.0168	0.0093
Lu		0.005	0.0033	0.0039	0.003	0.003	0.0032	0.0028
$\Sigma\text{REE}$		1.24	0.60	0.95	0.12	0.19	0.47	0.97
$\Sigma\text{LREE}$		1.03	0.49	0.79	0.08	0.15	0.42	0.94
$\Sigma\text{HREE}$		0.21	0.11	0.16	0.04	0.04	0.05	0.04



**Fig. 2.** NASC-normalized concentrations of REEs in high  $\text{pCO}_2$  mineral waters. A- operated wells with negative Ce anomaly; B- not operated wells with positive Ce anomaly.

The explanation for the HREE-enriched pattern is consistent with Fe-oxyhydroxides dissolution and adsorbed REE release. This is in good agreement with the results relating to the high pCO<sub>2</sub> waters on the continent [10].

Opposite, the negative Ce anomalies are common in oxygen rich waters (rivers, seas) because this require the oxidation of Ce<sup>3+</sup> to Ce<sup>4+</sup> (Eh>100) [6]. Unusual negative Ce anomalies in reducing high pCO<sub>2</sub> waters (Fig. 2A) can be explained by: i) the regional bedrock mineralogy and lithology (host rocks with Ce-depleted source minerals); ii) when Ce<sup>4+</sup> (for ex. CeO<sub>2</sub>) is reduced to Ce<sup>3+</sup> [11] and iii) as a result of the difference in residence time of groundwater circulation [12].

At now, there are no data about rocks REE geochemistry and mineralogy. But negative Ce anomaly is common for boreholes with shallow depth of 15-20 m or wells which are being operated (№ 17, 18). Isotopic and geochemical data reveal [2] that the processes of the groundwater-seawater mixing are also possible. Thus the dynamics of this system are not fully understood and are the focus of ongoing research.

## 4 Conclusions

The present investigation indicates that high pCO<sub>2</sub> mineral waters of the Sakhalin Island have different REE patterns with the Ce anomaly. The NASC-normalized patterns of all groundwaters are characterized by HREE enrichments and positive Eu anomalies, whereas some fluids are characterized by negative Ce anomaly which is unusual for reducing conditions. All the data are interpreted to be a result of the following processes: 1. REE leaching in a reducing environment in presence of CO<sub>2</sub> which enhances weathering; 2. accumulation of Ce<sup>3+</sup> in reducing environment when Ce<sup>3+</sup> does not oxidize to Ce<sup>4+</sup> (form positive Ce anomaly); 3. pumpage, mixing, CO<sub>2</sub> outgassing change in the redox conditions and mineral precipitates deposition can influence negative Ce anomaly forming.

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