

REE in waters and bottom sediments of salt lakes of Southeastern Transbaikalia, Russia

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Abstract. This paper presents our analysis of the distribution of REE in mineral chloride and soda lakes of Southeastern Transbaikalia. With increasing water salinity, it was determined that concentrations of dissolved HREE increased. The prevalence in absolute concentrations of MREE and HREE was observed in lakes with the development of bacterial processes (sulfate-reduction). A geochemical barrier for accumulating the LREE in the waters can be fluoro-carbonates. The saturation degree of fluorcarbonates in soda lakes can be several orders higher than in chloride lakes. Under oxidizing conditions $Ce(OH)_4$ can be formed and, in a reducing environment – $Ce(OH)_3$.

1 Introduction

The distribution of rare earth elements (REE) in different types of natural waters is described in many publications and continues to be widely studied. Mineral lakes due to the diversity of their composition and salinity, and in such systems sedimentation provides great opportunities for research on hydrogeochemistry of rare earth elements and their participation in the modern sedimentation. The sorption of lanthanides by hydroxides of polyvalent metals (iron, manganese, cobalt), phosphorus compounds and others is typically considered as one of the processes, which limit accumulation of lanthanides in waters [1]. At the same time, the presence of authigenic REE minerals in the form of phosphate compounds, in particular, monazite, and fluorcarbonates of parisite and bastnäsite can be observed in sediment.

We studied REE in waters and bottom sediments of the salt lakes of Southeastern Transbaikalia to determine the dependence of the concentration on the chemical composition and salinity of the water. We also investigated the geochemical processes that limit the accumulation of REE in water, including the possibility of forming their own mineral phases as a result of their precipitation from saturated water solutions.

2 Area of Study

The salt lakes of southeastern Transbaikalia were tested in 2013-2016 during the driest period of the last two centuries of climatic conditions in the region, when the several hundred lakes existing in wet periods were partially filled with water [2]. The largest lake

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in the Barun-Torey area, which has an area up to 580 km² and a depth of 5 m at the maximum level, completely dried up. Most of the investigated lakes are located in the Onon-Torey plain, which was formed from Pleistocene lacustrine-alluvial sands (thickness is up to 100 m); these sands are whitish due to the presence of pelitomorph carbonates in their composition. Sandy stratum covers Mesozoic volcanic-sedimentary rocks (basalt, sandstone, siltstone) and Paleozoic metamorphic rocks (schist, metasandstone, limestone) rocks. The investigated lakes are located in the range of 600-800 m altitudes; they are endorheic and mostly confined to the internal drainage area within the boundaries of the Upper Amur basin. Lake salinity is determined by evaporation processes. The annual amount of precipitation within the plains is 300-400 mm and the evaporation from the water surface is more than 1000 mm. The groundwaters are fresh. Intrabasin hydrobiological processes [3], especially production of organic substances and sulfate-reduction [4] play an important role in the chemical composition of lake water.

The pH, Eh, O₂, electric conductivity in water samples for the study of the chemical composition were determined at the locations. Determination of macro- and some micro-components were performed in the Institute of Natural Resources, Ecology and Cryology, SB RAS. To define REE content we analyzed the samples, which were filtered through a filter paper with pores of 2-3 μm (total content) and a membrane filter 0.45 μm (dissolved form); a suspended form was calculated by difference. Samples were acidified by ultrapure nitric acid. Tests are done by using ICP-MS method on the instrument ELEMENT 2 (Finnigan MAT) with certified multielement solutions and standards in Geochemistry Institute, SB RAS (Irkutsk). The detection limits range from 0.00001 (Tm) to 0.001 (La) μg/L.

The bottom sediments (silt, calcareous crust) were taken from the coastal zone of lakes where the flow of terrigenous material from the shore was virtually excluded. REE tests in the bottom sediments was carried out by using ICP-AES method on the instrument OPTIMA 2000 DV at the Geological Institute of SB RAS (Ulan-Ude). The error analysis was less than 10%, the detection limit – 1.5×10^{-5} % with a minimum content of lanthanides in sedimentary rocks 5.0×10^{-3} - 2.5×10^{-5} % by [5].

In the analysis of REE distribution in the waters and sediments, values are normalized to NASC [6]. The strength of ionic solutions, activities of components, occurrence forms of chemical elements, the thermodynamic equilibrium of the lake waters with secondary minerals are calculated with the help of HG32 [7] computer program. To evaluate equilibrium we used the known solubility product (SP) of some of the mineral forms; SP for bastnäsite and parisite was calculated by us.

3 Results and discussion

According to basic physical and chemical indicators the studied salt lakes are divided into two geochemical types: soda ones with a predominance of the components of carbon dioxide (HCO₃⁻ and CO₃²⁻) in the anionic components and the value of pH > 9.0 and chloride ones with pH < 9.0 and the dominance of Cl⁻ ion [8]. The main cation in the waters of both types of lakes is sodium. Salinity of soda lakes ranges from 1.17 to 58.5 g/L; salinity of chloride lakes is substantially higher – from 44.5 to 339 g/L. The average values of the physical and chemical characteristics of lakes and groundwaters are presented in Table 1. Due to bacterial sulfate-reduction, there are no sulfate lakes on the territory of Transbaikalia. More intensive sulfate-reduction processes take place in the soda lakes. The total content of reduced forms of sulfur ($\Sigma S_r = S^{2-} + S^0 + S^{4+}$) is much higher than in chloride lakes (Table. 1), and SO₄²⁻ content is almost 3 times less. The content of dissolved organic carbon (DOC) is 3 times higher, because its production is associated with the sulfate reduction.

Data on the average content of REE are presented in Table 2. Σ REE concentrations in lake waters vary over a wide range, the maximum 155.3 $\mu\text{g/l}$ is set in the suspension of a soda lake with the highest turbidity (11500 units), contents of hydrolysate elements Al (17 mg/L), Fe (18 mg/L), Mn (0.8 mg/L) and suspended matter (11.5 g/L). The total content of lanthanides in the dissolved form does not exceed 82.3 $\mu\text{g/L}$. There is a linear relationship between REE and the mentioned hydrolysates (correlation coefficient $r_{\text{Al}} = 0.93$, $r_{\text{Fe}} = 0.88$, $r_{\text{Mn}} = 0.99$).

Table 1. Average values of the physical and chemical characteristics of lake and groundwaters, mg/L. Type waters: 1 – soda lakes, 2 – chloride lakes, 3 –groundwaters; n – number of samples.

Type water	Eh, mV	pH	O ₂	ΣS_i	DOC	CO ₃ ²⁻	HCO ₃ ⁻	SO ₄ ²⁻	Cl ⁻	F	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	TDS	P	Si
1 n=78	99	9.58	8.0	1.3	188	1110	1420	1170	2910	14	11	59	3630	65	10510	0.8	2.1
2 n=10	30	8.20	7.1	0.1	68	83	610	3451	17780	7	100	3470	22480	76	48070	0.5	0.6
3 n=97	217	7.88	6.5	-	1	89	345	42	31	2	33	25	84	1	562	0.1	7.6

Table 2. Average REE content in waters, ppb (1 – suspended, 2 – dissolved forms, GW – groundwaters) and bottom sediments (3), $\mu\text{g/L}$.

Ln	Soda lakes			Chloride lakes			GW	Ln	Soda lakes			Chloride lakes			GW
	1 n=13	2 n=78	3 n=22	1 n=4	2 n=10	3 n=10	2 n=97		1	2	3	1	2	3	2
La	3.330	0.590	23.460	1.030	0.115	21.550	0.020	Er	0.140	0.092	1.890	0.100	0.003	1.750	0.003
Ce	6.590	1.268	50.080	2.260	0.206	48.200	0.020	Tm	0.020	0.011	0.310	0.010	0.002	0.300	0.001
Pr	0.690	0.146	5.000	0.290	0.025	5.020	0.002	Yb	0.080	0.082	1.620	0.080	0.014	1.600	0.003
Nd	3.070	0.732	21.910	1.110	0.155	19.850	0.017	Lu	0.010	0.016	0.190	0.010	0.003	0.180	0.001
Sm	0.460	0.156	4.470	0.270	0.128	3.975	0.004	Σ REE	15.48	3.42	117.50	6.44	0.71	110.53	0.09
Eu	0.110	0.034	0.860	0.630	0.021	0.795	0.006	LREE	13.68	2.74	100.45	4.69	0.50	94.62	0.06
Gd	0.440	0.112	3.520	0.290	0.018	3.350	0.004	MREE	1.55	0.49	13.04	1.55	0.21	12.08	0.02
Tb	0.070	0.024	0.560	0.050	0.005	0.550	0.001	HREE	0.25	0.20	4.01	0.20	0.02	3.83	0.01
Dy	0.410	0.122	3.010	0.260	0.020	2.830	0.004	La _n /Yb _n	5.45	0.25	1.41	1.39	0.74	1.15	1.02
Ho	0.060	0.039	0.620	0.050	0.014	0.580	0.001	Ce _{an}	0.22	0.88	1.01	0.93	0.067	1.01	0.58

Σ REE concentration in the dissolved fraction generally decreases and in the bottom sediments increases with increased salinity and pH in soda lakes. Primarily LREE (La-Nd) accumulate in the bottom sediments, the ratio of normalized values La_n/Yb_n go up from 0.94 to 1.65 with an increase in salinity from 2.2 to 42.9 g/L. When the salinity of the water is more than 30 g/L, REE in absolute concentrations have mainly MREE (Sm-Ho) and HREE (Er-Lu), and Σ REE content is tens of $\mu\text{g/L}$. As a rule the processes of bacterial sulfate-reduction are significantly manifested in these lakes; HS⁻ water content is up to 10.3 mg/L, DOC concentration is several hundred mg/L and Eh values decrease to -146 mV. La_n/Yb_n ratio in dissolved form decreases to 0.02 and increases to 1.64 and 17.4 in the suspension and in the sediments, respectively. In the profiles of distribution of the normalized values (not given in this article) REE differentiation is more pronounced than in lakes with oxidizing conditions.

Despite the presence in water of hydrosulfide HS⁻, lanthanides do not form their own sulphides Ln₂S₃. Saturation of solutions is impossible, when solubility product (SP) for sulfide La (10^{-26.3} by [9]) keeps minimum and its activities product (AP) (on the average is 10⁻³⁴) keeps maximum. Therefore, the absence of a pronounced positive Ce anomaly in the waters with reducing conditions (with 3⁺ oxidation state) can be explained by the formation

of poorly soluble hydroxide $\text{Ce}(\text{OH})_3$ ($\text{SP} = 6.43 \times 10^{-26.4}$ by [10]). In the oxidizing conditions stability of cerium in the waters can be controlled by hydroxide $\text{Ce}(\text{OH})_4$; its formation is possible for all lakes (AP is 10^{-41} and SP is 1.6×10^{-55} the same link).

The accumulation of LREE in sediments may be explained by the formation of their own carbonates, in particular, parisite $\text{CaCe}_{0.95}\text{La}_{0.6}\text{Nd}_{0.35}\text{Pr}_{0.1}(\text{CO}_3)_3\text{F}_2$ and bastnäsité $\text{Ce}_{0.5}\text{La}_{0.25}\text{Nd}_{0.1}\text{Pr}_{0.05}\text{CO}_3\text{F}$; their solubility product is calculated by us with data of Gibbs energies given in [11], and they are $10^{-93.6}$ and $10^{-34.9}$, respectively. According to the average content in the soda lakes, activities product of parisite is 10^{-36} and of bastnäsité is 10^{-16} , and for chloride lakes – 10^{-43} и 10^{-19} , respectively. These numbers show that a relatively small value of solubility of these minerals can control the LREE content in the waters. The degree of saturation in both minerals is higher in soda lakes than in chloride lakes. The possibility of precipitation of lanthanides carbonates is confirmed by data on the newly precipitated carbonate crusts, which were selected in the coastal zone of one of soda lakes; ΣREE content in these crusts is one order of magnitude more than in silt of the same lake. In this case, molar fractions of lanthanides (except Ce) in the formed carbonate precipitate are close to parisite (Ce – 0.75, La – 0.71, Nd – 0.40, Pr – 0.14) relative to their total content.

In chloride lakes accumulation of REE in the water and sediments is lower than in soda lakes. Correlations between dissolved REE and elements hydrolysates – Al, Fe and Mn are not significant ($r < 0.50$), but the bonds between biogenic elements, especially with phosphorus and heavy lanthanide group are getting stronger. In the bottom sediments REE content is higher than in aqueous filtrates, but in comparison to soda lakes the REE accumulation both in the bottom sediments and aqueous filtrates is lower. Graphs of the normalized values (not given) on the majority of the lakes are slightly differentiated. La_n/Yb_n ratio in dissolved form is 0.74, in sediments and suspensions is 1.31 and 1.15, respectively.

According to calculation, lanthanides occur in the lake waters mainly in the form of carbonate ions $(\text{LnCO}_3)^+$. The proportion of carbonate associate of lutetium significantly reduces in soda lakes, but the percentage of oxyhydroxide (27.3%) and acetate (7.8%) complexes increases, while its activity $(\text{LnCO}_3)^+$ in chloride lakes remains relatively high (above 80%). Both soda and chloride waters are saturated by dolomite $\text{CaMg}(\text{CO}_3)_2$, chlorite $\text{Mg}_{4.5}\text{Al}_3\text{Si}_{2.5}\text{O}_{10}(\text{OH})_8$, and iron hydroxide $\text{Fe}(\text{OH})_3$; chloride waters are saturated by magnesite MgCO_3 , and soda waters by calcite CaCO_3 and under reducing conditions by hydrotroilite $\text{FeS}_2(\text{H}_2\text{O})$.

4 Conclusions

Accumulation of REE in soda lakes is more intensive in comparison to chloride lakes. When the water salinity increases, total content of REE in the dissolved form decreases at a certain growth of HREE and it increases in sediments. LREE in dissolved form do not accumulate, it can be explained not only by their sorption on oxyhydroxide compounds of iron and manganese (formed in oxygen waters), but also by the formation of their own fluorcarbonate minerals (parisite and bastnäsité). Saturation in these minerals can be observed in all lakes, and the degree of saturation in soda lakes is several orders of magnitude larger than in chloride lakes, that is why REE accumulate more in the bottom sediments of soda lakes. According to the calculations equilibrium is achieved also with cerium hydroxide; in a reducing medium it forms sparingly soluble compounds $\text{Ce}(\text{OH})_3$ and in oxidative conditions – $\text{Ce}(\text{OH})_4$.

It is explained by the different genesis of the lakes. The chemical composition of soda lakes is formed mainly due to the process of water-rock interaction and sulphate-reduction

and to a lesser extent due to evaporation. This is confirmed by the presence of the highest pH values (9.0-10.7). The hydrolysis of aluminosilicates and sulfate-reduction provide an increase in pH and an increased content of HCO_3^- and CO_3^{2-} . High pH values and HCO_3^- and CO_3^{2-} contents, in turn, lead to maximum loss of calcite, gaylussite, bastnäsite, parisite, etc. All these processes contribute to the separation of REE and the accumulation of HREE. The degree of interaction between the chloride lake waters and aluminosilicates is relatively small, hence the low contents of HCO_3^- and CO_3^{2-} and REE, as well as a slight differentiation of REE.

This work was prepared under the project IX.137.1.2 “Geochemistry of rare and rare-earth elements in natural and geotechnogenic landscapes and hydrogeochemical systems”.

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