

## Sulfate Mineral Lakes of Western Transbaikalia: Formation Conditions and Chemical Composition of Waters and Bottom Sediments

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**Abstract**—The paper presents the formation of the chemical composition of water in the sulfate mineral lakes of western Transbaikalia. It is shown that sodium sulfate water in the regional lakes forms in two zones of continental salinization, the Barguzin and Gusinoe Ozero–Orongoi depressions. The average mineralization of the lakes reaches 30.8 g/L, pH = 7.90–8.84, the fractional content of sulfate ion is 55.2–81.8% eq, and the fractional content of sodium ion is 59.1–82.1% eq. The paper presents the major-ion and trace-element composition of lake waters and the chemical and mineral composition of bottom sediments. It is shown that groundwater enriched in sodium sulfate plays a major role in the lake formation.

**Keywords:** mineral lakes, evaporation, freezing-out, sulfate ion, trace elements, REE, isotope composition, bottom sediments

### INTRODUCTION

The conditions of formation of lakes with different chemical compositions and mineralization are the subject of the world's research. Numerous scientific publications are concerned with the hydrochemistry of lakes in the USA (Baker et al., 1991), Canada (Last and Ginn, 2005), Europe (Stojanovic and Kogelniga, 2009), Central Asia (Volkova, 1998), and other world regions. In Russia, such studies are performed in the European part of the country (Moiseenko and Ganshina, 2010), in West Siberia (Leonova et al., 2007; Taran et al., 2018), in the Baikal region, and in Transbaikalia (Sklyarova et al., 2002, 2011; Sklyarov et al., 2011; Borzenko et al., 2014; Strakhovenko and Gas'kova, 2018; Strakhovenko et al., 2018). Interesting results were obtained for the Great Plains in Canada, where about 500 lakes with different mineralization and chemical compositions of water were studied (Last and Ginn, 2005). Statistical analytical data show that the main factors controlling the chemical composition of the lake waters in this area are the composition of feeding groundwater, the humidification/evaporation ratio, and the altitude of the lakes within the catchment area. Processing of a large amount of data for the lakes in the European part of Russia led to the conclusion that the chem-

ical composition of their waters is determined by the regional geographical zonation, proximity to the sea, humification, salinization, and anthropogenic impact (Moiseenko and Ganshina, 2010).

Most researchers relate the chemical composition of mineral lake waters to evaporative concentration. Rocks interacting with water have a significant effect on its chemical composition (Shvartsev, 1982; Domrocheva and Lepokurova, 2015). Dynamic equilibrium–nonequilibrium interaction is established between water and the enclosing rocks. In this system, equilibrium between water and formed secondary minerals is established, whereas equilibrium is never reached between the water and primary aluminosilicates (Shvartsev, 1991, 1998; Shvartsev and Wang, 2006). Dissolution/precipitation processes lead to the accumulation of sodium and bicarbonate ion in the solution. The chemical composition of water changes to sodium hydrocarbonate–chloride and sodium chloride as the dissolved substances accumulate. As was assumed earlier, the chemical transformation to chloride water goes through the formation of sulfate water. It was commonly believed that sulfate water results from the direct metamorphization of the chemical composition of primary water, accompanied by an increase in its total salinity (Posokhov, 1969; Blake, 1989; Kimura, 1992; Parkhurst et al., 1996). However, the recently obtained data do not confirm this. The origin of zones of sulfate salinization stands apart from the general trend of the chemical transformation of mineral lakes. Formation of sulfate water requires additional sources of sulfur. Sulfur can be supplied into the lakes

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through the weathering of rocks with abnormally high contents of sulfide minerals, through dissolution of sulfate-containing rocks, and through discharge of fracture–vein and formation waters of deep aquifers.

The goal of this work was to establish the main factors determining the formation of sulfate lakes in western Transbaikalia and to study the geochemical composition of their waters.

## METHODS

The water and bottom sediments of lakes were sampled at a distance no less than 1.5–2.0 m from the shore, from a depth of 0.5–1.0 m. Temperature, electrical conductivity, pH, Eh, and the concentration of dissolved oxygen were measured at the sampling sites. Water for major-ion analysis was sampled into plastic 1.5 L bottles. Water for trace-element analysis was collected into polyethylene containers (15 ml) pretreated with 0.1N HNO<sub>3</sub> in the laboratory and washed with deionized water. The water samples were filtered through 0.45 μm Millipore filters and were preserved by acidification with purified 0.1N HNO<sub>3</sub> to pH = 1–2.

Major-ion analysis of the water was carried out in the certified laboratory of the Geological Institute, Ulan-Ude, following standard techniques for fresh and salt waters. Cations (Ca<sup>2+</sup>, Mg<sup>2+</sup>, Na<sup>+</sup>, and K<sup>+</sup>) were determined by atomic-absorption spectroscopy; F<sup>-</sup> and SiO<sub>2</sub>, by colorimetry; HCO<sub>3</sub><sup>-</sup>, CO<sub>3</sub><sup>2-</sup>, and Cl<sup>-</sup>, by titration; and SO<sub>4</sub><sup>2-</sup>, by the turbidimetric methods.

The trace-element composition of water was determined by ICP MS, using an ELEMENT XR (Thermo Finnigan, Bremen, Germany) double-focusing mass spectrometer with a magnetic sector and a cross-flow nebulizer, at the Common Use Center of the Geological Institute, Ulan-Ude. Calibration solutions were prepared by diluting the CLMS-1, CLMS-2, and CLMS-3 (SPEX, USA) multielement standard solutions with deionized water purified by an Elix-3/Milli-Q system (France). The accuracy of the analysis was monitored using a certified IQC solution (NIST, USA).

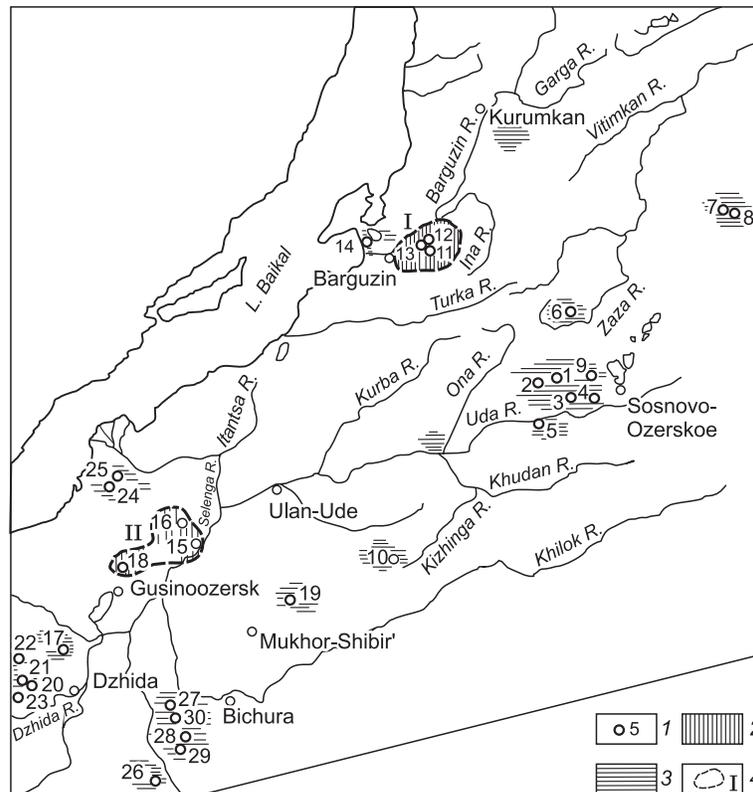
Bottom sediments were collected with a Patterson sampler from 0–20 cm thick sediment beds at depths of 0.4 to 3.5 m in different areas with diverse subaqueous lake landscapes. A total of 32 samples were taken. The pH and physicochemical parameters of the samples were measured in situ. In the laboratory, the samples were dried at 105 °C and ashed in a muffle furnace for organic-substance analysis. The major ions and trace elements of the bottom sediments were determined by XRF on an ARL Perform X-4200 (Switzerland) spectrometer. The mineral composition of the bottom sediments was determined by X-ray diffraction analysis on a DS Advance diffractometer (Bruker, Germany) with CuK radiation and a Vantec-1 detector. The obtained data were processed using the EVA software and ICDD database (2003).

## GENERAL REGULARITY OF MINERAL LAKE FORMATION IN WESTERN TRANSBAIKALIA

In the region under study, lakes with mineralization (total dissolved solids, TDS) of >1 g/L are common; they are called mineral or salt lakes. All of them are localized in forest–steppe and steppe landscape–climatic zones. The lakes get water and salts from atmospheric precipitation, during the weathering and subsequent leaching of the surrounding rocks, and through the discharge of groundwater.

The dissolved substances in the Transbaikalian lake waters concentrate as a result of evaporation and freezing-out (Dzyuba et al., 1999). Evaporative concentration is related to the arid summer climate here. Evaporation from the water surface averages 1000 mm/year (Ivanov and Trofimov, 1982). In the arid period, this leads to a significant decrease in the lake water level and concentration of salts. Many lakes, especially small ones, dry out in arid seasons (Zamana and Borzenko, 2010). As a result, salts are removed with wind from the lake basins, and the loss of lighter sodium sulfate is greater than the loss of sodium chloride. Low air temperature and a thin snow cover in winter lead to the freezing of small lakes to the bottom. When the lake freezes, the concentration of salts in the water gradually increases and its freezing temperature correspondingly decreases. The first solid phase precipitated from water during freezing is calcium carbonate; its precipitation begins at ~0 °C. With a further temperature decrease, the sequence of the precipitation of salts is determined by their eutectic temperatures and the composition of the solutions. Sodium and magnesium chloride salts are usually removed last from the solutions. Under complete freezing of the salt lake, all salts present in the water precipitate. When the ice cover melts and water arrives from other sources, recently precipitated calcite, mirabilite, soda, and halite sometimes stay undissolved over a year. In this case, they form a salt bed on the lake bottom. These salts mix with silt, become overlapped by terrigenous sediments, and thus become bedrock deposits, which can consist of several beds of different salts. The indigenous salt sediments no longer participate in the annual precipitation/dissolution cycle. Their formation is favored by frosty weathering of rocks resulting in a significant mass of finely dispersed particles. The weathering products are carried into lakes, where they form terrigenous and silt sediments over the salt beds. The intricate processes of salt concentration in water in summer and winter and the precipitation of various poorly soluble compounds from the solution led to the formation of several zones of continental salinization in western Transbaikalia (Fig. 1) (Plyusnin and Peryazeva, 2005).

Figure 2 shows a diagram of the anionic composition of the studied mineral lakes of western Transbaikalia. These lakes are divided into two groups: (1) with a predominantly bicarbonate–carbonate anionic composition, HCO<sub>3</sub><sup>-</sup> + CO<sub>3</sub><sup>2-</sup> = 53–99% eq, and (2) with a predominantly sulfate anionic composition, SO<sub>4</sub><sup>2-</sup> = 59–85% eq. This division indicates radically different conditions of metamorphization of the chem-



**Fig. 1.** Scheme of the location of mineral lakes in western Transbaikalia. 1, water sampling sites; 2, zones of sulfatization; 3, zones of sodification of surface waters (the list of the studied lakes is given in the Fig. 2 captions); 4, location of: I, Alga Lakes; II, sulfate mineral lakes in the Gusinoe Ozero–Orongoi depression.

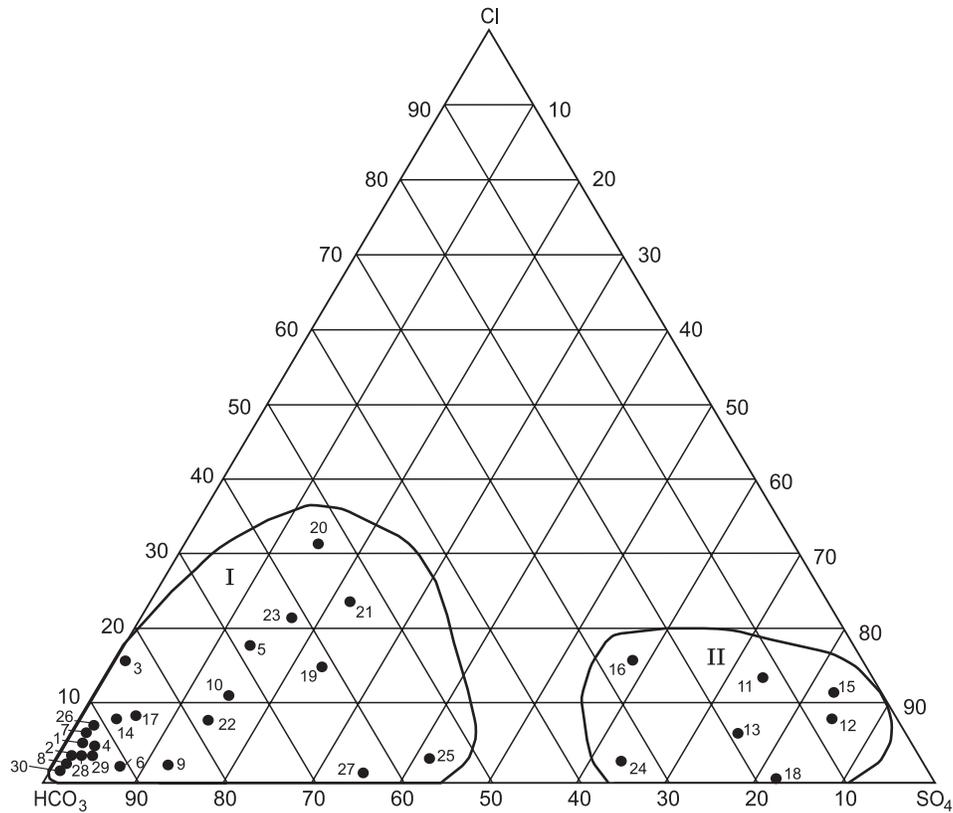
ical composition of waters in the region. Soda lakes are more common; the most saline ones are located in steppe landscapes. Waters of this type are also found in forest–steppe landscapes, but they have TDS < 1 g/L. Predominantly sulfate waters form in only two areas. In the Barguzin intermontane depression such waters are typical of the Alga Lakes. We studied lakes Bol’shoe (Great) Alginskoe, Maloe (Small) Alginskoe, and Gudzhirchan of this lake group. Earlier this group comprised seven lakes, but in recent years small lakes have dried out because of drought; their former location is marked by deposits of hydrogenous salts. In the Gusinoe Ozero–Orongoi depression, the sulfate waters are typical of lakes Sul’fatnoe, Stepnoe, and Beloe and several small lakes located in their vicinity.

#### FORMATION OF THE CHEMICAL COMPOSITION OF SULFATE MINERAL LAKES OF THE BARGUZIN DEPRESSION

The area of the Barguzin depression is characterized by intense discharge of nitric thermal waters. Thermal springs are localized mainly at the edges of the depression. The springs that discharge at the boundary between the depression and the Barguzin Ridge bordering it to the west have a

predominantly bicarbonate composition, and the springs localized at the foot of the Ikat Ridge are of sulfate type (Plyusnin et al., 2013). Among the latter is the Alga spring, which discharges in the southeast of the Barguzin depression in a well-expressed local topographic low (Fig. 3). This spring feeds the Alga Lakes and determines the chemical composition of their waters (Dzyuba et al., 1999).

As seen from the space image (Fig. 3), the Alga spring and mineral lakes are located within the same subsided block of rocks, which has sharp boundaries with the surrounding area. At the same time, the spring does not have a well-expressed washout basin; its discharge is low, 0.1 L/s (according to our measurement), and cannot exert a significant effect on the water resources and chemical composition of the lakes. We think that the lakes are fed by fracture–vein waters discharging along the faults located beneath the lake water area and in its vicinity. The entire area of the subsided block is swamped, which suggests a ubiquitous discharge of fracture–vein waters within it. The chemical composition of these waters is similar to that of the thermal spring; therefore, we will use the composition of the spring water to determine the degree of metamorphization of the lake waters (Table 1). The latter are weakly alkaline, except for rare cases of waters with pH > 9. Under these conditions, the chemical composition of the lake waters transforms to sul-



**Fig. 2.** Diagram of the anionic composition of mineral lakes of western Transbaikalia. Fields of: I, soda mineral lakes; II, sulfate mineral lakes. Lakes: 1, Maloe Okunevoe; 2, Bol'shoe Okunevoe; 3, Dolgoe; 4, Shchuch'e; 5, Nyudune Arshan; 6, Turkhul; 7, Vitlaus; 8, Vitlaus 2; 9, Ukyrskoe; 10, Kuorka; 11, Maloe Alginskoe; 12, Gudzhirchan; 13, Bol'shoe Alginskoe; 14, Bormashevoe; 15, Stepnoe; 16, Beloe; 17, Torm'; 18, Sul'fatnoe; 19, Olon' Shibir'; 20, Nizhnee Beloe; 21, Verkhnee Beloe; 22, Kamennyi Klyuch; 23, Tsaidam; 24, Nikitino; 25, Dolgoe; 26, Kiranskoe; 27, Ambon; 28, Chernoe; 29, Rybnoe; 30, Zhambalushkina.

fate. The predominance of sulfate ion in the anionic composition determines the stability of calcium in water, because the latter is not saturated with calcium sulfates during evaporative and freezing-out concentration. Calcium is not completely removed from the solutions but is present in significant concentrations, thus competing with sodium. The change in the chemical composition of the lake waters is an intricate process, because the weather conditions in the region are unstable: The amount of atmospheric precipitation, the average air temperature, and the intensity and direction of wind permanently change. This leads to changes in the proportion of the contribution of fracture–vein, surface, and atmospheric waters to the lake resources, in the intensity of evaporative and freezing-out concentration of the solutions, and in the deposition of authigenic minerals.

We have established that the water of Lake Gudzhirchan is the most mineralized; in 2010, its TDS reached 81.3 g/L. At that time, the water had a maximum concentration of sodium and a minimum concentration of calcium, and its pH reached 9.06. In 1954, N.A. Vlasov determined the total concentration of salts in the lake water, 107.67 g/L, with a predominance of sodium sulfate. In winter, mirabilite precipitated from the solution. The bottom of Lake Gudzhirchan

is covered with a 30–40 cm thick bed of silt mixed with mirabilite crystals. The silt bed rests upon an up to 3.5 m thick mirabilite bed. Mirabilite precipitates from highly concentrated solutions in winter (Tkachuk and Tolstikhina, 1961). More often, the lake waters are saturated with calcium and magnesium carbonates. Calcite and low-Mg calcite were found in the upper 40 cm thick silt bed; the content of these authigenic minerals in silty sediments reaches 40–45% (Solotchina et al., 2013; Solotchin et al., 2017). Rapid oxidation–reduction processes at the lake bottom cause reduction of sulfate ion to sulfide. As a result, hydrogen sulfide is produced, and iron sulfides are deposited. Crystalline hydrates are deposited on the shore of Lake Gudzhirchan, covering argillaceous sediments. Mineralogical analysis of these salts showed the presence of astrakhanite (blödite) ( $\text{Na}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot 4\text{H}_2\text{O}$ ) and enargite ( $\text{Cu}_3\text{AsS}_4$ ).

Formation of solid phases is accompanied by a change in the chemical composition and pH of the lake water. We established dispersion of these parameters in the lake waters sampled in different years. At the site of the discharge of the Alga thermal spring, its water is not saturated with carbonates and other compounds; therefore, the concentrations of dissolved substances remain relatively constant (Table 1).

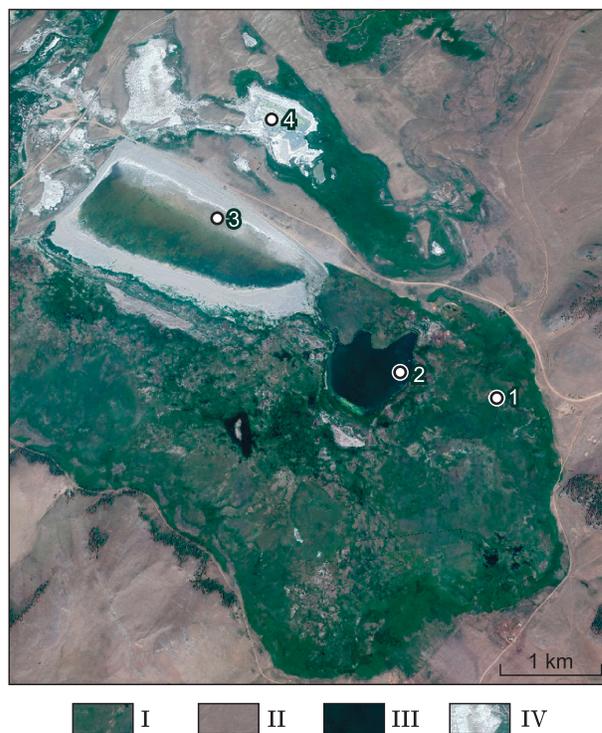
**Table 1.** Major-ion composition of the Alga thermal spring and sulfate sodium lakes of the Barguzin depression, mg/L

Water object	pH	TDS	Na <sup>+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	HCO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	Cl <sup>-</sup>	F <sup>-</sup>
Alga spring, 2003	8.0	658.6	159.2	36.1	8.5	64.1	336.3	20.6	15.1
Alga spring, 2012	7.9	693.4	156.4	45.1	1.2	91.5	322.7	18.1	5.0
Alga spring, 2016	7.37	597	104.2	74.3	0.8	53.5	338	15.5	3.15
Average	7.76	650	139.9	51.8	3.5	69.7	332	18	7.75
Lake Maloe Alginskoe, 2003	8.97	15,675	4950.3	7.5	86.5	1421.3	7764.5	1130.8	19.2
<i>n</i> -Fold concentration of components in the solution	–	24.1	35.4	0.14	24.7	20.4	23.4	62.8	2.5
Lake Bol'shoe Alginskoe, 2003	7.96	1518.6	388.6	66.6	13.4	250.1	743.1	43.9	10.5
Lake Bol'shoe Alginskoe, 2016	7.5	9411.8	2415.7	363.8	84.2	154.9	5860	372.5	19.0
<i>n</i> -Fold concentration of components in the solution	–	2.3–14.5	2.8–17.3	1.28–7.02	3.82–24.06	3.5–2.2	2.24–17.6	2.4–24.0	1.35–2.4
Lake Gudzhirchan, 2003	8.84	43,268	14,311.9	72.1	97.2	2775.2	23,817.5	1956.8	14.21
Lake Gudzhirchan, 2010	9.06	81,324	26,175.6	30.1	224.8	3600.0	47,663.3	2778.6	17.48
<i>n</i> -Fold concentration of components in the solution	–	66.5–125.1	102.3–187.1	1.4–0.6	27.7–64.2	39.8–51.6	71.7–143.5	95–154.4	1.8–2.2

Since the lake catchment area is small, we assume that dissolved substances are supplied into the lakes mainly with atmospheric precipitation and discharged fracture–vein waters. Atmospheric precipitation has low mineralization and thus does not contribute to changes in the chemical composition of the lake waters. In wet years it dilutes the lake waters, and the formation of authigenic minerals ceases. Fracture–vein waters make the main contribution to the chemical composition of the lake waters; they have the same chemical components as the studied thermal spring. The degree of concentration of dissolved substances in the lake waters can be evaluated using components stable in these solutions. Chloride ion is the best chemical element for this purpose. It is stable in the waters of this type over a wide range of concentrations, does not form poorly soluble compounds in them, and is quantitatively determined. The spring-normalized contents of chloride ion in the lakes testify that it accumulates in all the studied mineral lakes. Water evaporation and freezing-out increased the concentration of dissolved chloride by a factor of 2.4–24.0 in Lake Bol'shoe Alginskoe (data as of 2003 and 2016), 62.8 in Lake Maloe Alginskoe, and 95.0–154.4 in Lake Gudzhirchan (data as of 2003 and 2010) (Table 1). The degree of evaporative concentration of the solutions in the studied lakes is probably determined by the proportion of atmospheric precipitation and surface waters involved in the lake formation.

Sulfate ion and magnesium also intensely accumulate in the lake waters during evaporative concentration and freezing-out. The degree of concentration of sodium in Lake Gudzhirchan is higher than that of chloride ion. This is possibly due to the additional inflow of Na as sodium bicarbonate with surface waters from the lake catchment area. The contents of other components in the solution during evaporative concentration do not increase so intensely, and the content of calcium in the mineral lakes becomes lower as compared with the thermal spring. The proportion of dissolved components in the lake–spring system changes because of the formation of solid phases. In the lake waters,

equilibrium of dissolved substances with iron hydroxides, calcite, clays, and other poorly soluble compounds is reached. The concentration of fluoride ion in the lakes does not increase as intensely as the concentration of chloride; its maximum, 19.2 mg/L, is observed in Lake Maloe Alginskoe located near the Alga thermal spring. The other lakes, including Gudzhirchan with the maximum mineralization of water, have lower concentrations of fluoride ion. Probably, this ion cannot be significantly concentrated in sulfate wa-



**Fig. 3.** Satellite image of the Alga spring and mineral lakes area. I, lowland bog landscapes; II, steppe landscapes with steep slopes; III, mineral lakes; IV, salt deposition on the soil surface; 1, discharge of the Alga thermal spring; 2, Lake Maloe Alginskoe; 3, Lake Bol'shoe Alginskoe; 4, Lake Gudzhirchan.

**Table 2.** Trace-element composition of the Alga spring and sulfate mineral lakes of the Barguzin depression,  $\mu\text{g/L}$ 

Element	Alga spring	Lake Bol'shoe Alginskoe	$K_1$	Lake Maloe Alginskoe	$K_2$	Lake Gudzhirchan	$K_3$
Li	97.7	569.1	5.8	2670.3	27.3	2595.8	26.6
B	63.1	324.8	5.1	6845.8	108.5	12243.6	194.0
Rb	26.66	74.84	2.8	70.74	2.6	60.86	2.3
Cs	3.90	0.52	0.13	0.12	0.03	0.389	0.09
Sr	1332.2	4136.9	3.1	2725.0	2.04	3150.6	2.4
Ba	16.28	21.62	1.3	18	1.1	72.19	4.4
Al	11.3	23.4	2.07	309.1	27.3	95.5	8.4
P	36.2	71.6	1.97	N.d.	N.d.	4060.2	112.2
Ti	0.68	1.55	2.3	24.4	35.9	10.22	15.0
V	1.28	1.06	0.8	37.99	29.6	44.10	34.4
Cr	1.61	3.57	2.2	2.64	1.6	2.54	1.6
Mn	3.35	5.47	1.6	32.62	9.7	N.d.	N.d.
Fe	81.03	307.8	3.8	438.29	5.4	194.21	2.4
Co	0.018	0.04	2.2	1.75	97.2	0.22	12.2
Ni	0.81	1.06	1.3	6.7	8.3	33.18	40.9
Cu	1.71	3.46	2.0	66.21	38.7	44.93	26.3
Zn	9.54	15.98	1.7	27.89	2.9	16.64	1.8
Cd	0.02	0.11	5.35	0.63	31.5	0.70	35.1
Pb	0.94	1.36	1.4	0.6	0.6	26.54	28.0
Bi	0.018	0.134	7.4	N.d.	N.d.	0.269	14.9
As	0.39	1.76	4.5	45.2	115.9	64.41	165.1
Mo	12.07	16.48	1.4	249.8	20.7	188.2	15.6
Sn	0.158	0.278	1.7	0.20	1.3	N.d.	n.o
Sb	0.11	0.12	1.06	2.89	25.3	5.69	49.9
W	20.36	95.74	4.7	424	20.8	1161.9	57.0
Th	0.014	0.035	2.5	0.11	7.8	0.92	65.4
U	4.29	1.12	0.3	17.0	3.9	34.58	8.1

Note. N.d., not determined.  $K_1$ ,  $K_2$ , and  $K_3$  are the coefficients of trace-element concentration in the waters of lakes (Bol'shoe Alginskoe, Maloe Alginskoe, and Gudzhirchan, respectively) relative to the Alga spring water.

ters, because they always have relatively high concentrations of calcium; therefore, fluoride ion is removed from the solution through crystallization of fluorite. Earlier we established that equilibrium between dissolved components and fluorite in nitric thermal waters is reached at  $\text{TDS} = 0.2\text{--}0.3 \text{ g/L}$  if  $\text{pH}$  is  $>8.2$  (Shvartsev et al., 2015). The concentration of fluoride in soda mineral lakes, which contain much less calcium, can reach  $414 \text{ mg/L}$  (Borzenko and Fedorov, 2019).

The content of trace elements in the lakes located in the studied salinization zones increases disproportionately to the degree of concentration. Table 2 presents results of trace-element analysis of the lakes and Alga thermal spring.

The highest degrees of concentration in the sulfate lakes have been established for trace elements present as anions in the solution, with the maximum concentration being specific to boron. Compared with the spring, the concentrations of boron, arsenic, and phosphorus in Lake Gudzhirchan are 194, 165, and 112 times higher, respectively. Moreover, the absolute contents of boron and arsenic are the highest here

as compared with other mineralized lakes of Transbaikalia. The reason is that nitric thermal waters, which are the main supplier of dissolved substances into the lakes, are rich in these elements. The established enrichment of sulfate lake waters with tungsten has the same explanation. Since thermal waters feeding the lakes have high contents of this element, its content after evaporation and freezing-out of the lake water reaches a few milligrams. In addition, the studied sulfate lakes are enriched in heavy metals (Ni, Cu, Pb, Cd, and Bi), which is also due to their high concentrations in fracture–vein waters feeding the lakes (Voitkevich et al., 1990; Plyusnin et al., 2008; Doroshkevich et al., 2017).

The concentrations of rare-earth elements (REE) in the lakes are slightly higher as compared with the Alga spring (Table 3). With increasing lake water mineralization, the portion of LREE increases initially, but then LREE and HREE reach an equal proportion. For example,  $\Sigma\text{LREE}$  (La–Eu) = 91% (of the total REE content) in the Alga spring, 95.8% in Lake Bol'shoe Alginskoe, and 92.3% in Lake Ma-

**Table 3.** REE concentrations in the Alga spring and sulfate mineral lakes of the Barguzin depression, µg/L

Element	Alga spring	Lake Bol'shoe Alginskoe	Lake Maloe Alginskoe	Lake Gudzhirchan
La	0.1938	1.08	0.74	N.d.
Ce	0.0466	0.62	0.37	N.d.
Pr	0.3387	0.068	0.033	0.1251
Nd	0.0205	0.25	0.42	0.2346
Sm	0.0012	0.038	0.104	0.3305
Eu	0.0008	0.0104	0.0129	0.0385
Gd	0.0541	0.0342	0.0273	0.4076
Tb	0.0004	0.0054	0.0097	N.d.
Dy	0.0095	0.0214	0.0186	N.d.
Ho	0.0006	0.0067	0.0002	N.d.
Er	0.0061	0.0131	0.0481	N.d.
Tm	0.0003	0.0019	0.0067	0.0463
Yb	0.0223	0.0104	0.0295	N.d.
Lu	0.001	0.0019	0.0045	N.d.
∑LREE	0.60	2.07	1.68	–
∑HREE	0.06	0.10	0.14	–
∑REE	0.69	2.16	1.82	–
(Ce/Ce*) <sub>N</sub>	0.03	0.43	0.40	–
(Eu/Eu*) <sub>N</sub>	0.12	1.34	0.96	–
(La/Yb) <sub>N</sub>	0.64	7.65	1.85	–

Note. PAAS-normalized,  $(Ce/Ce^*)_N = 2Ce_N/(La + Pr)_N$ ,  $(Eu/Eu^*)_N = 2Eu_N/(Sm + Gd)_N$ .

loe Alginskoe. The  $(La/Yb)_N$  ratio varies over a wide range of values, from 0.64 in the spring to 7.65 in Lake Bol'shoe Alginskoe. These variations reflect the influence of several factors on the behavior of REE in the solution. The most significant factors are the redox and acid–base conditions, the element species in the solution, and the rate of formation of authigenic minerals. Carbonate complex compounds are the main migrating species of many REE in the solution. Since the studied waters are poor in carbonate ion, carbonate complex compounds of REE do not play a great role in their chemical composition, and the contents of many REE are low. The most significant contribution of this migrating REE species is observed in the Lake Gudzhirchan water, which has pH >8.3 and contains much carbonate ion. As a result, the contents of some REE in the water are higher.

### SULFATE MINERALS LAKES OF THE GUSINOE OZERO–ORONGOI INTERMONTANE DEPRESSION

Another group of sulfate lakes of western Transbaikalia is located in the Gusinoe Ozero–Orongoi intermontane depression of Mesozoic age. This depression lies in the central part of western Transbaikalia and is bordered by the Khambin Ridge to the northwest and by the Monostoi Ridge to the southeast. The region has a severely continental climate with negative average annual temperatures (–2 to –3 °C), a short frost-free period (95–100 days), and a relatively small amount of precipitation (200–300 mm). The negative average monthly air temperature keeps for six months; therefore, the lakes freeze to a significant depth (to 1.2–1.4 m) (Obozhin et al., 1984).

Mineral lakes are located in closed microdepressions, where water evaporation and freezing-out lead to the concentration of dissolved substances.

**Geology and hydrogeology of the study area.** The Gusinoe Ozero–Orongoi intermontane depression is part of the rift system that existed here in the Mesozoic. Alkali and subalkalic flood basalts are widespread in the area. Magmatic melts were enriched in K, Na, F, Cl, S, Sr, Li, Mo, Ni, and V.

A specific geologic feature of the study area is the presence of late Mesozoic carbonatites on the northwestern flanks of the Gusinoe Ozero–Orongoi and Ivolga depressions (Ripp et al., 1999). Carbonatites are present as dikes, sheet-like deposits, and steeply dipping breccias; they are associated with alkaline high-K rocks and are referred to as REE (Arshan and Yuzhnoe (Southern) occurrences) and essentially Ba–Sr (Khalyuta and Oshurkovo) types. The carbonatites are enriched in sulfate sulfur. The content of their sulfate minerals often reaches 20–30%. The total content of SO<sub>3</sub> is 2.85–13.60% in the Khalyuta carbonatite field, 0.68–8.82% in the Oshurkovo field, 1.42–10.82% in the Arshan field, and 0.83–3.08% in the Yuzhnoe field. Sodium and potassium sulfates well soluble in water are the most widespread sulfate minerals here. Therefore, carbonatites of the above occurrences have surficial caverns resulted from the leaching of well-soluble alkali-metal sulfates (Doroshkevich et al., 2003). According to a personal communication by G.S. Ripp, alkali-metal sulfates are readily extracted from carbonatites by leaching with distilled water. His study of the sulfur isotope composition in these extracts showed  $\delta^{34}S_{CDT} = 10.9, 11.7, \text{ and } 12.6$ .

The Gusinoe Ozero–Orongoi depression is filled with continental sediments including rocks of different lithology, from coarse-pebble conglomerates and inequigranular sand-

**Table 4.** Chemical composition of groundwater of the Selenga Formation, mg/L (Borisenko et al., 1994)

Sampling date	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Na <sup>+</sup> + K <sup>+</sup>	HCO <sub>3</sub> <sup>-</sup>	CO <sub>3</sub> <sup>2-</sup>	SO <sub>4</sub> <sup>2-</sup>	Cl <sup>-</sup>	F <sup>-</sup>	TDS	rSO <sub>4</sub> <sup>2-</sup> /rCl <sup>-</sup>
6 August 1991	36	41	388	610	0.1	438	85	2.6	1609	3.81
10 December 1991	44	41	384	635	18	425	82	0.05	1638	3.83
8 April 1992	48	39	384	676	12	418	82	0.05	1665	3.77
13 August 1992	22	45	570	1031	42	427	85	0.05	2227	3.72

stones to silts and coals of the Lower Cretaceous Gusinoe Ozero Group (Borisenko et al., 1994; Bulnaev, 2006; Lunina, 2009). The sediments of this group are subdivided into four formations (from bottom to top): Murtoi, Ubukun, Selenga, and Khobol'dzhe. All the formations conformably rest upon each other. The Murtoi Formation overlies the Ichetui Formation volcanics.

The tectonic setting of the study area is determined by its location within the Dzhida–Vitim structural suture separating the areas of Mesozoic and Cenozoic tectonomagmatic activity. This tectonic suture was active for a long time. Deep regional faults here are of NE strike and are fracture, crush, brecciation, shearing, and mylonitization zones. In the inner field of the depression, there are several transverse faults mostly of NW strike, with near-vertical planes (Bulgatov et al., 1978). These are mainly normal faults and strike-slip faults formed in extension setting. The water abundance in the fault sediments increases by several orders of magnitude, being the highest at the intersection of two or more faults (Borisenko et al., 1990).

Three aquifer systems have been recognized within the depression: (1) Quaternary sediments with pore–stratal groundwater. Pebbles, sands, and sandy loams are water-bearing rocks. These waters usually occur at a depth of 2–4 m, seldom reaching a depth of 22 m. They are fed by atmospheric precipitation, surface waters, groundwater of coal-bearing strata, and crystalline-rock water. The waters of this complex are mostly fresh calcium–magnesium bicarbonate. (2) Sediments of the Gusinoe Ozero Group with stratal and formation–fracture waters. The waters in the rocks of the Murtoi and Ubukun formations are sodium bicarbonate, with TDS ≤ 0.5 g/L. The rocks of the Selenga Formation enclose calcium–sodium sulfate–bicarbonate waters with TDS ≤ 2.2 g/L (Table 4). This aquifer system is fed by atmospheric precipitation and fracture waters of crystalline rocks. (3) The crystalline basement is formed by Paleozoic and Mesozoic granitoids and Triassic (Mesozoic) effusive rock complex. Fault zones are characterized by the highest water abundance, permeability, and porosity. Faults serve as major channels for the movement of groundwater discharging as ascending springs (Borkhonova, 2006). The spring water of Lower Cretaceous sediments contains up to 693 mg/L SO<sub>4</sub><sup>2-</sup> and up to 212 mg/L Cl<sup>-</sup>.

**Lake Sul'fatnoe** (Sulfate-bearing) is located in a tectonic microdepression in the interfluvium of the Zagustai and Ubukun rivers (Fig. 4). There are five large and several small lakes in this depression. Its surface slopes to the southeast, toward the Ubukun River valley. The lakes in the northern and northwestern parts of the depression are fresh. They are located at the boundary between a hydrogeologic massif and an intermontane depression and are fed by a weak surface and underground runoff from the hydrogeologic massif of the Khambin Ridge. These waters discharge in the SE direction, flowing via a system of shallow channels into the Ubukun River. In the satellite image (Fig. 4), the runoff direction is marked by bright green vegetation. These waters do not significantly contribute to the Lake Sul'fatnoe resources. The lake basin is located south of them, in the central part of the microdepression, and is separated from the fresh lakes by an isthmus. The basin is elongated to the northwest; its surface lies 50–60 m deeper than the surrounding area (abs. level 593 m). The tectonic origin of the lake basin is beyond doubt. The satellite images show faults of NW strike and the rectilinear shores of the lake. The catchment area of the lake is small and cannot ensure its long existence. Nevertheless, this lake has existed for over 100 years of its monitoring. Artesian waters play a significant role in its feeding. There



**Fig. 4.** Satellite image of the Lake Sul'fatnoe area. I, steppe landscapes; II, forest–steppe landscapes with shrubs; III, fresh and salt lakes; IV, faults identified from space images.

**Table 5.** Major-ion composition of groundwater within the catchment area of Lake Sul'fatnoe, mg/L

Parameters	Bulag Spring	Wells		
		1	2	3
pH	6.75	7.12	7.28	7.46
HCO <sub>3</sub> <sup>-</sup>	372.2	192.2	253.2	283.7
SO <sub>4</sub> <sup>2-</sup>	30.24	16.8	242.5	201.5
Cl <sup>-</sup>	8.16	5.32	8.16	51.41
Na <sup>+</sup> + K <sup>+</sup>	120.54	53.9	177.64	197.03
Ca <sup>2+</sup>	17.03	21.0	17.03	27.05
Mg <sup>2+</sup>	12.16	3.65	12.16	12.77
F <sup>-</sup>	1.16	0.54	2.0	1.96
SiO <sub>2</sub>	20.55	28.13	23.43	30.85
NO <sub>3</sub> <sup>-</sup>	4.37	0.9	2.43	34.2
TDS	560	293	711	773
rSO <sub>4</sub> <sup>2-</sup> /rCl <sup>-</sup>	2.73	1.52	21.9	2.89

is a spring in the southeast of the microdepression. In addition, three shallow wells were drilled here, which were earlier used for cattle watering (Fig. 4). The spring and well 1 seem to yield groundwater, which is weakly mineralized and has a sodium bicarbonate composition. Wells 2 and 3 penetrated deep waters; they have a much higher content of sulfate ion, and the water from well 3 is additionally enriched in chloride ion. The chemical composition of these waters is given in Table 5.

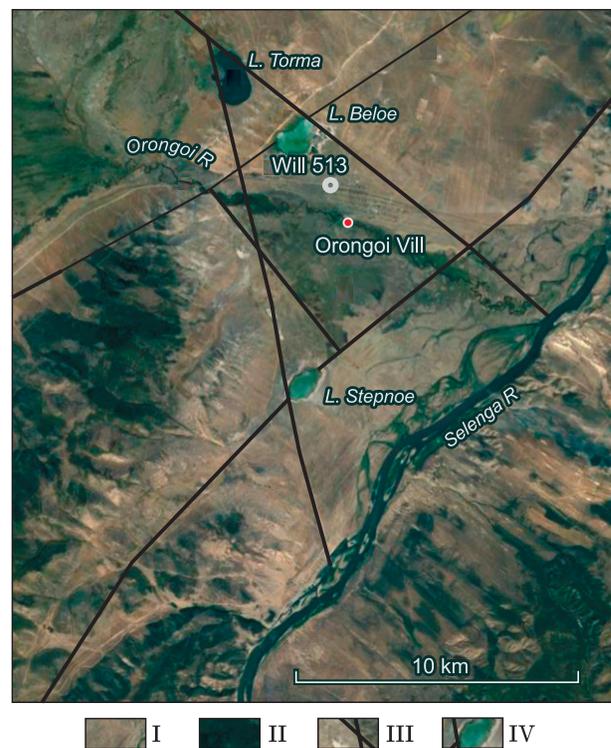
Bicarbonate is a predominant anion in the waters of the Bulag spring and well 1; its fractional content is 85 and 86% eq, respectively. The relative fractional contents of sulfate ion and chloride ion are within 8.8–9.5 and 3.2–4.0% eq, respectively. The main cation is sodium, 74.0 and 63.4 mg eq.%; the fractional content of calcium is 12.0 and 28.4% eq, and the fractional content of magnesium is 14.1 and 8.1% eq. The waters of the spring and well 1 are of sodium bicarbonate type. The main anion in the water from well 2 is sulfate, 52.7% eq; the fractional contents of bicarbonate and chloride ions are 43.3 and 2.4% eq, respectively. Sodium is a predominant cation, 80.1% eq, and calcium and magnesium are subordinate, 8.8 and 10.4% eq, respectively. In the water from well 3, the fractional contents of bicarbonate and sulfate ions are commensurate, 42.4 and 38.2% eq, and the fractional content of chloride ion is 13.2% eq. Sodium is the main cation, 78.12% eq, and the fractional contents of calcium and magnesium are 12.3 and 9.6% eq, respectively. These data permit us to assign the waters from wells 2 and 3 to sodium bicarbonate–sulfate and sulfate–bicarbonate types.

The waters penetrated by wells 2 and 3 might feed Lake Sul'fatnoe, because the confining bed is thin. Deep pressure water discharging along deep faults directly into the lake basin is probably the main lake feeder.

**Lakes Beloe (White) and Stepnoe (Steppe)** are located in the lowest part of the Gusinoe Ozero–Orongoi depression. The water surface of Lake Beloe has an absolute height of 521 m, and that of Lake Stepnoe, 517 m. The area of the mineral lakes has a flat relief with a slight slope to the east and southeast. Figure 5 shows a satellite image of this area

with identified faults. It is seen that the lakes are located at the intersection of faults of NE strike with cutting faults of NW and N–S strikes. The faults of NE strike are normal faults. The largest tilted fault block is observed along the northern fault. Here, the difference in height between lakes Torma and Beloe is 21 m over a distance of 1.5 km. This fault is clearly expressed in the relief as a ledge. The fault within which Lake Stepnoe is localized is marked by a ravine of NE strike. The ravine lies 2–3 m lower than the surrounding area. The next step in the fault system here is a fault along which the Selenga riverbed runs. In this place, the fault is of NE strike and is located parallel to the two above-mentioned faults. The river water level is 514 m. We think that the faults are hydraulically connected to each other and serve as channels for groundwater ascending from Jurassic sediments to the surface. In the zones of their intersection with transverse faults, where the rocks are highly crushed and well permeable, groundwater discharges at the surface and feed the lakes. The zone of deep pressure water is located at the boundary between the hydrogeologic massif and the intermontane depression in the northwest of the study area, which lies at much higher absolute heights.

In addition to the two lakes, there are other shallow mineral water shows in the study area (Lake Talyn-Nur etc.). The major factor that gave rise to these salt lakes is the subsidence of the block of rocks and, as a result, the ascent of



**Fig. 5.** Satellite image of the Lakes Beloe and Stepnoe area. I, steppe landscapes of the microdepression; II, forest–steppe landscapes of the surrounding crystalline-rock area; III, faults identified from space images; IV, mineral lakes.

**Table 6.** Chemical composition of groundwater in Jurassic sediments of the Lower Orongoi depression, mg/L (Plyusnin and Gunin, 2001)

Sampling depth range, m	Discharge, L/s	NH <sub>4</sub> <sup>+</sup>	Na <sup>+</sup>	K <sup>+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	SO <sub>4</sub> <sup>2-</sup>	Cl <sup>-</sup>	HCO <sub>3</sub> <sup>-</sup>	CO <sub>3</sub> <sup>2-</sup>	TDS	rSO <sub>4</sub> <sup>2-</sup> /rCl <sup>-</sup>
82–143	2	0.6	259	2.2	22	36	289	78	347	48	918	2.74
146–250	0.23	5.6	1080	4.5	162	115	2315	453	213	18	4270	3.78
340–490	6.9	6.0	1184	4.9	252	200	3106	436	219	18	5329	5.27

groundwater to the surface along faults. The chemical composition of groundwater of Jurassic sediments is seen from the data of water sampling from well 513 drilled by the Selenga geological-survey expedition in 1996 (Table 6). The well depth is 504 m; the rocks enclosing groundwater within the sampled depth ranges are siltstones, mudstones, and sandstones.

As seen from Table 6, the total mineralization of groundwater and the fractional content of sulfate ion in aquifers increase with depth. The content of sulfate ion increases from 43.3% eq in the upper aquifer to 74.5% eq in the middle one and 80.3% eq in the lower aquifer. This is also reflected in the increase in the ratio of sulfate ion to chloride ion with depth, i.e., water becomes enriched in sulfate and depleted in chloride. The fractional content of calcium also increases with depth, from 7.2% eq in the upper aquifer to 12.5% eq in the middle one and 15.6% eq in the lower aquifer. This is probably due to the accumulation of sulfate in the solution, because the solubility product of calcium sulfate is much higher than that of calcium carbonate. The relative content of magnesium remains the same, and its absolute content increases, reaching a few grams in Lake Stepnoe. The lower aquifer is the water-richest (Table 6) and probably feeds the lakes with groundwater via faults.

**Major-ion and trace-element composition of the lake waters.** The sulfate lakes located in the Gusinoe Ozero–Orongoi depression show a wide variation in salinity, from 3.5 to 30.8 g/L (Table 7). The maximum salt concentration was found in Lake Stepnoe. The waters are weakly alkaline, with pH = 8.47–8.79, and are characterized by significant hardness, mostly due to magnesium rather than calcium. High magnesium contents are a distinctive feature of the

above lakes. In this parameter they differ strongly from the sulfate lakes of the Barguzin depression.

According to the classification by Alekin (1970), the waters of the lakes under study belong to the sulfate class sodium group. The maximum fractional content of sulfate ion is specific to the water of Lake Stepnoe (81.8% eq); the water of Lake Beloe contains 58.1% eq SO<sub>4</sub><sup>2-</sup>, and the water of Lake Sul'fatnoe, 55.5% eq SO<sub>4</sub><sup>2-</sup>. The maximum fractional content of chloride ion, 31.2% eq, was found in the water of Lake Sul'fatnoe. Sodium is a predominant cation in the lake waters; its fractional content in lakes Stepnoe and Beloe is 59.1 and 62.4% eq, respectively, and in Lake Sul'fatnoe it reaches 82.1% eq. The next abundant cation is magnesium; its fractional content varies from 39.8% eq in Lake Stepnoe to 33.6% eq in Lake Beloe and 16.5% eq in Lake Sul'fatnoe.

The sulfate lakes have relatively high contents of lithium, strontium, and boron, but in general, the concentration of trace elements is rather low despite the high salinity (Table 8).

Sulfate lakes Beloe and Sul'fatnoe are characterized by an absolute domination of LREE over HREE (Table 9). Lanthanum, cerium, and praseodymium are major LREE in their waters. Lake Stepnoe has a different REE pattern: a relative decrease in praseodymium content and an increase in erbium content. The serious difference in the REE patterns of the lake waters might indicate that the lakes are fed by groundwater from different aquifers, with different evolution of its chemical composition. The normalized REE patterns of the waters show a distinct negative Ce anomaly,  $(Ce/Ce^*)_N = 0.1–0.85$ , and a positive Eu anomaly,  $(Eu/Eu^*)_N = 3.99–22.57$ . The  $(La/Yb)_N$  ratio increases with water salinity: from 0.79 in Lake Beloe (TDS = 6.98 g/L) to 4.94 in Lake Sul'fatnoe (TDS = 16.27 g/L) and 1.06 in Lake Stepnoe (TDS = 30.81 g/L).

**Chemical composition of bottom sediments.** Let us consider the composition of the bottom sediments of the studied sulfate lakes in comparison with the fresh lakes in the same area (Table 10). This comparison will help us to recognize the processes responsible for the specific chemical composition of such sediments during sulfatization.

Analysis of the data in Table 10 shows that the contents of SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, and K<sub>2</sub>O in the salt lakes are almost half as high as those in the fresh lakes, whereas the contents of CaO and MgO are almost twice or thrice higher. The bottom sediments of salt Lake Beloe are characterized by high LOI values, and the sediments of Lake Sul'fatnoe are rich in sodium. The fresh lakes contain the element association Fe–Al–Ti–Mg–K and P. These elements show high positive correlations with each other ( $K_{cor} = 0.82–0.94$ ) and stable

**Table 7.** Major-ion composition of sulfate lake waters in the Gusinoe Ozero–Orongoi depression, mg/L

Parameter	Lake Sul'fatnoe	Lake Beloe	Lake Stepnoe
pH	8.79	8.67	8.73
HCO <sub>3</sub> <sup>-</sup>	1159.4	778.0	1525.5
SO <sub>4</sub> <sup>2-</sup>	3797.0	1413.0	18,306.9
Cl <sup>-</sup>	1579.8	302.3	2128.6
F <sup>-</sup>	2.58	3.5	9.9
Na <sup>+</sup>	2719.2	733.8	6389.3
Ca <sup>2+</sup>	40.0	40.1	100.2
Mg <sup>2+</sup>	285.5	206.5	2247.7
TDS	9654.8	3504.4	30,808.8
rSO <sub>4</sub> <sup>2-</sup> /rCl <sup>-</sup>	1.78	3.45	6.36

**Table 8.** Trace-element composition of sulfate lake waters in the Gusinoe Ozero–Orongoi depression,  $\mu\text{g/L}$ 

Trace element	Lake Sul'fatnoe	Lake Beloe	Lake Stepnoe
Li	1499	649.6	465
Be	0.09	1.06	0.002
B	641.33	506.8	230
Al	5.5	6.3	90
P	412.14	2.98	185
Sc	0.0046	0.036	0.033
Ti	5.64	2.82	36
V	4.15	5.62	27.5
Cr	0.9	4.49	1.45
Mn	0.18	0.22	22.05
Fe	93.12	88.8	61.5
Co	0.89	0.11	1.25
Ni	0.24	0.2	4.55
Cu	1.12	5.14	7.85
Zn	1.68	1.52	4.5
Ga	0.0061	0.0058	0.105
Ge	0.086	N.d.	0.485
As	37.3	7.04	31.5
Se	2.37	0.08	0.65
Br	18.3	6.8	N.d.
Rb	7.39	3.23	8.2
Sr	3656.2	5193	18890
Y	0.09	0.11	0.215
Zr	7.44	2.28	1.15
Nb	0.047	0.015	0.0465
Mo	11.02	6.39	80.0
Cd	0.047	0.05	0.48
Sn	0.33	1.217	0.26
Sb	11.1	1.17	3.0
Cs	0.038	0.086	0.265
Ba	44.61	17.79	125.0
Hf	0.15	0.1	0.037
W	3.56	0.39	14.4
Tl	0.0082	0.0214	0.13
Pb	3.68	8.68	15.5
Bi	0.018	0.022	0.32
Th	0.115	0.166	0.065
U	33.42	5.73	85

Note. N.d., not determined.

negative correlations with Si ( $K_{\text{cor}} = -0.82$  to  $-0.94$ ), which is due to the accumulation of clay minerals and iron, manganese, and aluminum hydroxides in the upper bed of the bottom sediments.

There are significant differences in trace-element composition between the salt and fresh lakes. The bottom sediments of the salt lakes contain 1.5–2.5 times less Sc, V, Cr, Co, Zn, Pb, and Rb than the sediments of the fresh lakes (Table 11). These elements are associated with terrigenous deposits that are ablated from the surrounding area. The mineral lakes are poor in them, i.e., the input of the ablation of weathering products from the surrounding area is much smaller. The bottom sediments of these lakes are predominantly authigenic. They are enriched in bromine, which probably gets into the lake through its leaching with groundwater from the sedimentary rocks of the basin and from coal beds rather than through the weathering of the catchment area rocks. The bottom sediments of Lake Sul'fatnoe are

**Table 9.** REE composition of sulfate and soda mineral lakes in the Gusinoe Ozero–Orongoi depression,  $\mu\text{g/L}$ 

Element	Lake Sul'fatnoe	Lake Beloe	Lake Stepnoe
La	0.402	0.397	0.195
Ce	0.108	0.336	0.250
Pr	0.142	0.209	0.0200
Nd	0.0021	0.151	0.150
Sm	0.0023	0.0023	0.0200
Eu	0.0018	0.0018	0.0265
Gd	0.0173	0.004	0.0135
Tb	0.0014	0.0014	0.0095
Dy	0.0023	0.0039	0.0115
Ho	0.0084	0.0177	0.050
Er	0.0014	0.0014	0.2150
Tm	0.0039	0.0018	0.0025
Yb	0.006	0.037	0.0135
Lu	0.0009	0.0009	0.0020
$\Sigma\text{LREE}$	0.66	1.10	0.66
$\Sigma\text{HREE}$	0.04	0.07	0.32
$\Sigma\text{REE}$	0.70	1.17	0.98
$(\text{Ce}/\text{Ce}^*)_N$	0.1	0.25	0.85
$(\text{Eu}/\text{Eu}^*)_N$	3.99	8.3	22.5
$(\text{La}/\text{Yb})_N$	4.94	0.79	1.06

**Table 10.** Macrocomponent composition of lake bottom sediments in the Gusinoe Ozero–Orongoi depression, %

Component	Lake Shchuch'e	Lake Gusinoe	Lake Beloe	Lake Sul'fatnoe
SiO <sub>2</sub>	<u>51.3–64.2</u> 59.7(2.2)	<u>48.6–68.1</u> 63.8(2.3)	<u>19.3–24.7</u> 22.5(2.2)	<u>32.4–49.6</u> 42.4(2.3)
Al <sub>2</sub> O <sub>3</sub>	<u>11.4–15.8</u> 13.8(5.2)	<u>6.8–16.2</u> 12.1(4.8)	<u>4.4–7.8</u> 6.2(5.1)	<u>6.8–9.45</u> 8.7(4.9)
Fe <sub>2</sub> O <sub>3</sub>	<u>2.43–6.14</u> 5.17(16.1)	<u>1.72–6.2</u> 4.16(15.9)	<u>2.18–3.06</u> 2.34(15.8)	<u>1.27–1.89</u> 1.56(16.2)
MnO	<u>0.09–0.11</u> 0.11(18)	<u>0.07–0.12</u> 0.11(18)	<u>0.09–0.13</u> 0.12(18)	<u>0.11–0.14</u> 0.12(18)
CaO	<u>1.19–3.94</u> 1.72(20.4)	<u>1.92–12.81</u> 6.87(19.8)	<u>26.4–30.2</u> 28.4(19)	<u>13.6–23.2</u> 18.3(21)
MgO	<u>0.98–3.14</u> 1.17(35)	<u>0.62–1.81</u> 1.43(36)	<u>3.9–5.32</u> 4.9(37)	<u>1.85–2.15</u> 2.04(34)
TiO <sub>2</sub>	<u>0.85–1.54</u> 1.28(15)	<u>0.19–0.84</u> 0.58(16)	<u>0.21–0.42</u> 0.28(17)	<u>0.29–0.82</u> 0.63(15)
K <sub>2</sub> O	<u>1.97–3.12</u> 2.46(6.3)	<u>2.09–3.84</u> 2.52(6.5)	<u>0.93–1.36</u> 1.12(3.1)	<u>1.64–2.12</u> 1.87(6.6)
Na <sub>2</sub> O	<u>2.12–3.16</u> 2.72(24.8)	<u>1.32–3.2</u> 2.42(25.3)	<u>1.08–1.72</u> 1.26(17.8)	<u>2.89–3.64</u> 3.12(23.8)
P <sub>2</sub> O <sub>5</sub>	0.19–0.42	0.13–0.29	0.07–0.11	0.08–0.12
LOI	3.08–5.42	6.8–20.1	26.1–32.3	1.02–1.94

Note. The values in the numerator are the content range, the value in the denominator is the average content, and the parenthesized value is the determination error, %. Analyses were carried out for eight samples from each lake.

rich in strontium; its concentration shows a positive correlation with the concentration of calcium ( $K_{\text{cor}} = 0.72$ – $0.82$ ). Probably, it gets into the bottom sediments from the solution during the precipitation of authigenic carbonates. Authigenic minerals formed in different geochemical conditions de-

**Table 11.** Average contents of trace elements in lake bottom sediments, ppm

Element	Lake Gusinoe	Lake Shchuch'e	Lake Beloe	Lake Sul'fatnoe
	fresh		sulfate	
Sc	12(10.6–13.4)	14(12.3–15.7)	8.6(7.6–9.6)	9.5(8.4–10.6)
V	95(83.6–106.4)	104(91.5–116.5)	39.0(34.3–43.7)	47(41.4–52.6)
Cr	56(49.3–62.7)	43(37.8–48.2)	32.0(28.2–35.8)	22(19.4–24.6)
Co	12(10.6–13.4)	12(10.6–13.4)	6.2(5.5–6.9)	5.7(5.0–6.4)
Ni	7.2(6.3–8.1)	20.8(18.3–23.3)	6.2(5.5–6.9)	14.3(12.6–16.0)
Cu	10(8.8–11.2)	16(14.1–17.9)	11(9.7–12.3)	10.6(9.3–11.9)
Zn	34(30.0–38.0)	52(45.8–58.2)	21(18.5–23.5)	27(23.8–30.2)
Ga	14(12.3–15.7)	19.4(17.1–21.7)	5(4.4–5.6)	12.4(10.9–13.9)
As	5.2(4.6–5.8)	4.6(4.1–5.1)	6.2(5.5–6.9)	5.2(4.6–5.8)
Rb	131(115.3–146.7)	96(84.5–107.5)	11(9.7–12.3)	68(59.8–76.2)
Sr	399(351–447)	247(217–276)	21(18.5–23.5)	979(861–1096)
Y	13(11.4–14.6)	53(46.6–59.4)	5(4.4–5.6)	34(29.9–38.0–1)
Zr	165(145–185)	15(13.2–16.8)	6.2(5.5–6.9)	667(586–747)
Nb	11(9.7–12.3)	22(19.4–24.6)	11(9.7–12.3)	19(16.7–21.3)
Mo	1.5(1.3–1.7)	2(1.8–2.2)	21(18.5–23.5)	1.7(1.5–1.9)
Ag	4.5(4.0–5.0)	<0.6	5(4.4–5.6)	<0.6
Ba	932(820–14–043)	669(588–750)	270(237–302)	500(440–560)
La	21(18.5–23.5)	64(56.3–71.7)	37(32.5–41.5)	41(36.1–45.9)
Ce	55(48.4–61.6)	105(92.4–117.6)	48(42.2–53.8)	79(69.5–88.5)
Hf	2.3(2.0–2.6)	40(35.2–44.8)	4.2(3.7–4.7)	18(15.8–20.2)
W	2.4(2.1–2.7)	N.d.	7.3(6.4–8.1)	N.d.
Pb	19(16.7–21.2–3)	26(28.9–29.1)	8(7.0–9.0)	13.4(11.8–15.0)
Th	5.7(5.0–6.4)	15.7(13.8–17.6)	4.8(4.2–5.4)	14(12.3–15.7)
U	3.5(3.1–3.9)	7.8(6.9–8.7)	2.4(2.1–2.7)	8.2(7.2–9.2)
Br	<5	<5	7.3(6.4–8.2)	38 (33.4–42.6)

Note. Eight samples from each lake were studied. Parenthesized is the range of contents. N.d., not determined.

terminated by climatic changes. The 56 cm thick silt bed in Lake Sul'fatnoe is formed mainly by calcium and magnesium carbonates deposited over the last 6.6 kyr (Solotchin et al., 2017). Also, gypsum is sporadically present in the silty bottom sediments. In the southern part of the lake, the silt bed overlies mirabilite sediments up to 3 m in thickness (Tkachuk and Tolstikhin, 1961).

The XRD study showed significant amounts of calcium and magnesium carbonates in the bottom sediments of lakes Beloe and Sul'fatnoe. In addition, the sediments of Lake Beloe contain ankerite  $\text{Ca}(\text{Fe},\text{Mg})(\text{CO}_3)_2$ , calcite ( $\text{CaCO}_3$ ), and magnesite ( $\text{MgCO}_3$ ). Earlier, burkeite ( $\text{Na}_6(\text{CO}_3)(\text{SO}_4)_2$ ) was found on the shore of Lake Beloe (Doroshkevich et al., 2003). We have identified calcite and magnesite in the bottom sediments of Lake Sul'fatnoe.

The bottom sediments of the fresh lakes contain quartz (up to 45–50%), plagioclase (up to 25–30%), and K-feldspar (up to 15–20%). Clay mica aggregates are formed by biotite (up to 41%), muscovite (up to 6.2–7.8%), and chlorite (up to 1.2%).

## DISCUSSION

The above research data show that sulfate mineral lakes are unique natural objects. They form in extraordinary natu-

ral environments under the influence of several factors. One of the most crucial factors is the extra input of sulfur. In western Transbaikalia, sulfate mineral lakes result from the discharge of sodium sulfate groundwater.

In the Barguzin depression, sulfate lakes form from discharging thermal fracture–vein waters of sodium sulfate type. Such waters occur mainly within the Ikat Ridge bordering the depression to the southeast (Plyusnin et al., 2013). Thermal waters discharging here are characterized by a heavy isotope composition of sulfur:  $\delta^{34}\text{S}_{\text{CDT}} = 28.7\text{‰}$  in the Alga spring, 24.0‰ in the Ina spring, and 22.6‰ in the Seyui spring. This isotope composition of sulfur is inherited from the rocks enclosing fracture–vein waters of the study area. Earlier we assumed that the inflow of sulfur to fracture–vein waters is not due to the oxidation of sulfide minerals that are often found in rocks but due to the dissolution of sulfate minerals that might be present in metamorphogenic–sedimentary deposits (Plyusnin et al., 2008; Shvartsev et al., 2015). A specific geologic feature of the Ikat Ridge is the presence of Cambrian carbonate sediments formed in a back-arc sea basin (Belichenko et al., 2006). This is why the rocks contain heavy sulfur isotope in the form of sulfates. The Ikat carbonate massif is traceable for 29 km, locally reaching 7 km in width and hundreds of meters in thickness. It is divided by tectonic movements into blocks. Surficial

**Table 12.** Carbonate and sulfate saturation index of lake waters

Lake	Calcite	Dolomite	Magnesite	Strontianite	Gypsum	Epsomite	Kieserite	Sakiite	Mirabilite
Sul'fatnoe	3.14	11.43	4.50	2.24	-1.81	-5.50	-59.45	-96.69	-131.33
Beloe	2.57	9.97	3.61	2.04	-1.73	-5.74	-59.70	-96.93	-131.281
Stepnoe	2.92	12.14	5.42	2.76	-1.22	-3.79	-57.72	-94.97	-129.539
Maloe Alginskoe	1.64	8.92	3.48	2.13	-3.32	-6.54	-60.49	-97.73	-129.901
Bol'shoe Alginskoe	1.15	3.89	-1.05	0.33	-1.23	-8.48	-62.45	-99.67	-135.64
Gudzhirchan	-7.42	1.35	4.99	2.78	-11.9	-7.12	-60.81	98.27	-125.90

karst caverns few millimeters to tens of centimeters in size are observed in all limestone outcrops. In addition, six caves, a karst funnel, and high-discharge (up to 40 L/s) karst springs were revealed in this area (Vasil'ev and Morozov, 2013). In one of the caves, the walls and floor are covered with prismatic and scalenohedral calcite crystals. The crystal shape indicates their formation from solutions. The Ikat Ridge is located in the continuous permafrost zone, with permafrost in watersheds reaching 500–600 m in thickness (Galazii, 1993). Only thermal water can be in the liquid state there. The thermal conditions in the caves also indicate the impact of thermal water: At their entrance negative temperatures prevail even in summer and the floor is covered with ice, whereas in the recess of the caves the temperature is positive and the water is in the liquid state. The caves were probably formed by thermal waters flowing along faults; under negative air temperatures prevailing in this area for most of the year, the subsurface caverns were filled with ice. Thermal waters flowing along limestone caverns are saturated with carbonate minerals: calcite, magnesite, siderite, etc. Calcium, magnesium, and carbonate ions are removed from the solution during the formation of these minerals; therefore, most of the waters have a sodium sulfate composition. These thermal waters, like all karst waters, are probably characterized by a high discharge. The resources of the thermal waters discharged within the Alga Lakes area cannot be calculated, because there are no reliable data on subaqueous discharge. Judging from the thickness of mirabilite sediments, reaching 3.5 m in the area of Lake Gudzhirchan, sodium sulfate waters significantly contribute to the lake resources.

The Alga Lakes have an unstable water regime. Carbonate sediments of Lake Bol'shoe Alginskoe formed irregularly; the climatic conditions changed many times over a period of 4.9 kyr, which is expressed as the nonuniform sedimentation of carbonate minerals (Solotchina et al., 2013). In the studied section, the content of carbonate minerals increases from bottom to top, which indicates climate aridization. Today, most of the Alga Lakes have dried up.

The established specific trace-element composition of the lake waters is directly related to the primary accumulation of certain chemical elements in thermal waters, whose composition formed during their prolonged filtration through fractured rocks and dissolution of the latter by heated waters. At the final stage, the drainless-lake water became concentrated as a result of evaporation and freezing-out. Tungsten and boron present as sodium tungstates and borates are the most stable trace elements in the solution. The initially

high tungsten contents are due to the interaction of thermal waters with scheelite mineralization found here by prospecting and exploration work. Four tungsten deposits and a number of ore occurrences were discovered within the Ikat Ridge (Vasil'ev and Morozov, 2013; Tikhomirov, 2015).

Sulfate salinization of groundwater and surface water in the Gusinoe Ozero–Orongoi intermontane depression was caused by the discharge of deep groundwater from aquifers of Jurassic and Cretaceous deposits.

The formation of sodium sulfate waters in these aquifers seems to have a long history. Oxidation of sulfide minerals in endogenous rocks surely makes some contribution to the formation of sulfate waters, but this contribution is not the governing factor. Oxidation of dispersed sulfide mineralization is related to weathering of rocks; therefore, not only sulfate ion but also other anions and cations formed during the hydrolysis of effusive and intrusive rocks accumulate in the solution. As a result, sodic waters form (Shvartsev, 1998). Sulfur in sulfides has a light isotope composition. The sulfur isotope ratio in sulfides is preserved during their oxidation to sulfates. In the Tsagan-Gol River feeding the Gusinoe Ozero depression, sulfate ion is also produced from the oxidation of sulfides. We have established that the river water has  $\delta^{34}\text{S}_{\text{VCDT}} = 3.8\%$ , whereas the studied sulfate lakes are characterized by a heavier sulfur isotope composition:  $\delta^{34}\text{S}_{\text{VCDT}} = 15.4\%$  in Lake Sul'fatnoe,  $15.9\%$  in Lake Beloe, and  $12.3\%$  in Lake Stepnoe.

The presence of carbonate rocks in the study area was noted above. In contrast to sulfides, carbonatites have a heavier sulfur isotope composition:  $\delta^{34}\text{S}_{\text{VCDT}} = 13.0\%$  in baryte of carbonatites of the Arshan deposit and  $13.2\%$  in barytocelestite (Doroshkevich et al., 2003). These  $\delta^{34}\text{S}_{\text{CDT}}$  values are close to those in the sulfate lake waters. Taking into account the high contents of sulfate sulfur in carbonatites, we assume their significant influence on the chemical composition of the regional groundwater. Sodium and potassium sulfates can be washed out of carbonatites by atmospheric precipitation, which was proved by their leaching with distilled water. For a long period, a large amount of sulfate passed into the solution, and part of sulfate was probably scattered. In the Mesozoic, tectonic movement resulted in depressions, in which mineralized groundwater rich in sulfate ion began to accumulate. The formation of groundwater runoff from carbonatite zones to the central part of the depression was favored by the tectonic setting, including widespread transverse faults.

The sodium sulfate phase of carbonatites was probably depleted in trace elements. Although its dissolution resulted in high-mineralization solutions, they were poor in trace elements. The waters of sulfate lakes Sul'fatnoe, Beloe, and Stepnoe inherit the low contents of trace elements. Despite the evaporative and freezing-out concentration of the solutions and the gradual formation of sulfatization zones, the contents of trace elements remained low, except for strontium and lithium, which were probably inherited from the primary sulfate melt of carbonatites. For the same reason, the lakes have high contents of magnesium. The presence of sulfate ion determines the stability of all alkali-earth elements, including Mg and Sr, in the lake waters. At the same time, the permanent precipitation of carbonates, primarily calcium carbonates, takes place in the lakes. Carbonate ion is the limiting factor for their formation. It is supplied into the solution during biogenic processes running in the lakes and also with surface waters.

The carbonate sediments of Lake Sul'fatnoe were examined to a depth of 57 cm (Solotchin et al., 2017). Isotope studies showed that the lake formed at 6.6 ka and was mineral throughout its lifetime. Calcium and magnesium carbonates and, sometimes, gypsum were deposited in it. Four stages of the lake water evolution were recognized, which were related to the climatic changes in the region and the lake water regime.

Sulfate lakes are located in drainage basins, where evaporation and freezing-out of water results in the concentration of the solutions and their equilibrium with relatively insoluble compounds. Chemical and XRD analyses of the bottom sediments reveal deposition of various carbonate minerals. Our equilibrium calculations using the HydroGeo32 software (Bukaty, 1997) show that the waters of all studied sulfate lakes are in equilibrium with carbonate minerals, such as dolomite and strontianite (Table 12). The waters of these lakes are saturated with calcite and magnesite, except for lakes Gudzhirchan and Bol'shoe Alginskoe with extremely low contents of calcium and magnesium. Despite the high content of sulfate ion in the lake waters, none of them are saturated with sulfate minerals. The waters are particularly far from being saturated with mirabilite. This mineral was probably deposited in the periods when the lakes completely froze over.

The bottom sediments of the sulfate lakes have low contents of lanthanum and cerium, although the carbonatites of the Arshan deposit are rich in REE, which are contained in bastnaesite, parasite, and allanite. This is due to the poor migration of REE in the solutions in the study area. The sulfate lakes of the Gusinoe Ozero–Orongoi depression have low contents of trace elements, because their waters weakly interact with the rock.

## CONCLUSIONS

There are two zones of sulfatization of surface waters and groundwater in western Transbaikalia. Sodium sulfate

groundwater plays a major role in the formation of sulfate lakes here. The chemical composition of this groundwater results from the leaching of sulfate ion and sodium from the enclosing carbonate rocks.

Evaporative and freezing-out concentration of the solutions in mineral lakes located in drainless basins leads to further transformation of their chemical composition. The waters become saturated with carbonates, whose mineral composition is controlled by the climatic conditions. Mirabilite is deposited in winter, when the lakes freeze over.

The trace-element composition of the mineral lakes is determined by the geochemical conditions and the history of formation of the feeding groundwater and its chemical composition. The highest contents of B, As, P, W, and heavy metals have been established in the lakes located in the Barguzin depression. The sulfate lakes of the Gusinoe Ozero–Orongoi depression are poor in trace elements, except for Sr, Li, and B, despite the high water mineralization.

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