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Biogeochemical Transformations of Sulphur in the Saline Lakes of Transbaikalia

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Abstract

Biogeochemical transformations of sulphur in the saline lakes of southeastern Transbaikalia have been studied. Quantitative measurements show that hydrogen sulphide is present in the water and bottom sediments of most of the lakes studied. In addition to hydrogen sulphide, the presence of sulphate, thiosulphate, and elemental sulphur was detected in the water column, while sulphate and elemental sulphur were found in the bottom sediments. It was established that elemental sulphur exists in the lakes primarily in the form of suspension and colloids, as well as polysulphidic sulphur, the amount of which increases with increasing water pH. It is concluded from the isotopic ratios of sulphur for sulphate, hydrosulphide ions, and elemental sulphur that sulphur in the studied natural systems is controlled by biological and geochemical processes. One of the processes controlling the behaviour of sulphate ions in the lakes is sulphate reduction, which leads to the enrichment of sulphate sulphur and depletion of sulphur in hydrogen sulphide with the ^{34}S isotope. It is shown that oxidation of reduced sulphur in the lakes proceeds with the participation of oxygen, iron, manganese, as well as various bacteria. The presence of an additional source of sulphur and/or absence of sulphur reduction causes ^{32}S accumulation in sulphate ions. It is determined that the loss of sulphate ions due to their bacterial reduction in bottom sediments is most pronounced in the chloride and soda lakes of the I and III subtypes. In the sulphate and soda lakes of the II subtype, an increase in the amount of sulphate ions was detected.

Keywords: sulphur cycle, sulphate lakes, sulphate reduction, sulphide oxidation, sulphur isotopes

INTRODUCTION

Sulphur is one of the essential kinds of chemical raw materials. It is widely used for the synthesis of many products (sulphuric acid, dyes, carbon disulphide, etc.) and for preparing various substances and materials (rubber, cellulose, fertilisers, pharmaceutical preparations, etc.). Investigation of natural sulphur-containing compounds enriches the theory of organic and inorganic chemistry, stimulates advancement of chemical technologies and initiates the studies of processes involved in substance transformation in the environments. One of the numerous processes determining biochemical transformations of sulphur is sulphate reduction assisted by sulphate reducing microorganisms [1–3]. Hydrogen sulphide (H_2S) can also be formed in anaerobic oxidation of

methane [4]. Independently of the route of hydrogen sulphide formation, it is oxidised through a complex network of microbiological and geochemical processes, with sulphate ion as the most oxidised product, and pyrite as the predominantly reduced product during burial [5]. Elemental sulphur (S^0) is formed as a result of hydrogen sulphide oxidation [6]. Among intermediate compounds, only elemental sulphur is accumulated to noticeable concentrations in most of natural environments [7]. It is known that elemental sulphur reacts with hydrogen sulphide to form polysulphides [8]. The latter compounds participate in microbial anaerobic methane oxidation in combination with sulphate reduction and are intermediates in phototrophic and chemotrophic sulphide oxidation processes [9].

Another stable sulphur-containing compound in natural water bodies is thiosulphate ion. It is formed as a result of hydrogen sulphide oxidation by dissolved oxygen or because of chemical and bacterial oxidation of pyrite [10], as well as in disproportionation of sulphite, elemental and polysulphide sulphur [11].

In spite of numerous studied of the biogeochemical transformations of sulphur in the lakes of various regions over the world, the questions related to sulphur behaviour in cycling still remain unanswered for the saline lakes of Transbaikalia. Determination of sulphate lake genesis is not a less important problem. In this connection, the goal of the work was to determine the main mechanisms controlling the behaviour of selected sulphur forms in the saline lakes of Transbaikalia related to different types and subtypes.

THE OBJECTS OF INVESTIGATION

Numerous shallow saline lakes are widespread in the south-east of Transbaikalia. These are the northernmost saline lakes of semi-arid and arid zones of Central Asia. All the studied saline lakes are confined to the forest-steppe and steppe landscape climatic zones and are situated in the catchment areas of the Ingoda, Onon, Argun rivers, and within the boundaries of the drainless Torey basin. The physical-geographical features of the region, its geological structure, hummocky terrain, dry sharply continental climate, perennial and seasonal frozen ground promote the formation of numerous saline lakes in the region under consideration. These lakes differ from each other in size, depth, and hydrochemical regime. Most of the lakes (72 %) are small water bodies with water area from 0.1 to 10.0 km^2. Large lakes (more than 10 km^2) are relatively few (4 %). With substantial variation of lake areas, their common feature is relatively small depth, as a rule, not more than several metres from water level. All lakes are undrained. They are situated in enclosed depressions which are most frequently terminal basins collecting groundwaters.

Previously we have distinguished three types of lakes [12]. Water bodies with pH ≥ 9.0 have been related to soda lakes; in turn, they were divided into three subtypes. Subtype I includes the lakes with $HCO_3^- + CO_3^{2-}$ anions prevailing in water, subtype II is for lakes with SO_4^{2-} anions prevailing, and subtype III – Cl^-. Lakes with pH < 9.0 in which Cl^- and SO_4^{2-}prevail among anions were related to chloride and sulphate types, respectively.

METHODS OF INVESTIGATION

Results of hydrogeochemical tests of the lakes during the years from 2013 to 2022 in summer (July – August) formed the basis for the studies. During field studies, 127 lakes were tested. Water was sampled in the central parts of lakes to carry out general chemical analysis, to investigate various forms of sulphur and its isotopic composition. It is necessary to stress that 99 % of the tested water bodies were shallow lakes with water column height <0.5 m, so water was sampled practically from the bottom water layer.

Rapidly changing parameters, namely hydrogen ion exponent (pH), oxidation-reduction potential (Eh), O_2 content, temperature, TDS in water (the total concentration of dissolved salts) were determined directly at sampling sites with the help of multiparameter analysers WTW Cond 340i (Germany) and Amtast AMT03 (USA). Sulphur in the form of sulphate ion SO_4^{2-} was determined using turbidimetric method and titration. Hydrogen sulphide was precipitated with $Zn(CH_3COO)_2$ or $Zn_5(CO_3)_2(OH)_6$ in the presence of glycerol from 100–2000 mL of water. Elemental sulphur S^0 together with ZnS was precipitated on a filter with pore diameter 0.45 μm. Silver salt Ag_2S was added in excess to the residual filtrate, and it was frozen. Prior to analysis, filters with precipitates were stored frozen. Thiosulphate ions ($S_2O_3^{2-}$), sulphite ions (SO_3^{2-}) and polythionate ions ($S_nO_6^{2-}$) were determined in the filtrate after thawing the sample in the laboratory.

In parallel, the samples of the upper layer of the bottom sediments were collected, tightly packed

and frozen. The samples were centrifuged under laboratory conditions. Then Cl^- and SO_4^{2-}, H_2S and S^0 were determined in silt water according to the scheme indicated above.

The procedures of reagent preparation and the sequence of operations during analysis have been described by us previously in [13] and used herein without any substantial changes. The evolved H_2S was determined quantitatively by means of spectrophotometry (Hach Lange DR 2800 spectrophotometer, USA). The detection limit of this method for reduced sulphur forms is 0.16 μmol/L.

The isotopic composition of sulphur in SO_4^{2-} and H_2S was measured in water layer, sulphur in H_2S and S^0 – in silt water using a Flash EA-1112 analyser (Thermo Scientific, Germany) in S configuration according to the standard protocol of sulphur conversion from sulphate and sulphide into SO_2. The $^{34}S/^{32}S$ isotope ratio was determined using a MAT-253 mass spectrometer (Thermo Scientific, Germany) at the Far East Geological Institute, FEB RAS (Vladivostok) with respect to the laboratory standard gas SO_2, calibrated according to international standards IAEA-S-1, IAEA-S-2, IAEA-S-3 and NBS-127. Result reproducibility for $\delta^{34}S$ was ±0.1 ‰ (1σ) both for standards (n = 10) and for samples. Results of $\delta^{34}S$ measurements are presented with respect to the international standard VCDT. Fractionation (ε) was calculated according to equation $\varepsilon = 1000 \cdot (\alpha - 1)$, where α is fractionation factor: for the system $SO_4^{2-} - H_2S$, $\alpha = (\delta^{34}S(SO_4^{2-}) + 1000) / (\delta^{34}S(H_2S) + 1000)$; for the system $S^0 - H_2S_{silt}$, the values of $\delta^{34}S(S^0)$ were put in the equation instead of $\delta^{34}S(SO_4^{2-})$, while for the system $H_2S_{silt} - H_2S_{water}$, $\delta^{34}S(H_2S)_{water}$ was put instead of $\delta^{34}S(SO_4^{2-})$.

To calculate the composition and amount of polysulphide ions, Geochemist's Workbench software was used. Sulphate parameter ($K_{SO_4/Cl}$) was expressed through the ratio of the mass concentrations of SO_4^{2-} and Cl^- ions. Results of the investigation are presented in Tables 1–4. In view of the enormous amount of data, the most typical data for specific types and subtypes of lakes were included in the tables.

RESULTS OF INVESTIGATION

Sulphur forms in silt waters

The content of H_2S, which was present mainly in the form of HS^- (80–99 %) in the silt water of lakes, varied within a broad range, from complete absence to 146.9 μmol/L in Lake Doroninskoye. In this lake, a relatively low Eh value equal to −423 mV was detected in the silt water of bottom sediments. Over all samples, the maximal Eh value in the sediments did not exceed 204 mV, which was determined in the sulphate lake Kuka-Azyrga. However, negative values of this parameter were detected in lake silt more frequently. According to averaged assessments, sulphate lakes were distinguished by higher H_2S concentration (9390 μm/L). In chloride lakes, the average H_2S concentration was 2635 μmol/L. In soda water bodies, the maximal H_2S content was detected in the lakes of subtype I (3398 μmol/L on average). Relatively lower H2S concentrations were determined in the soda lakes of subtypes III (1289 μmol/L) and II (1569 μmol/L) of soda lakes.

The concentration of the most oxidised sulphur form SO_4^{2-} in the silt waters of bottom sediments was also determined to vary within a broad range from 0.05 mmol/L in saline soda subtype I lake Baym-Bulak (2013 r.) to 587.7 μmol/L in the brine of the sulphate lake Shikhalin-Nuur (2020). Among lake types and subtypes under consideration, the ordered series in the descending order of average SO_4^{2-} (μmol/L) ion content in bottom sediments can be represented as sulphate → soda II → chloride → soda III → soda I. The sequence based on the average sulphate parameter ($K_{SO_4/Cl}$) is different: soda II → sulphate → soda I → chloride → soda III.

In addition to H_2S and SO_4^{2-}, elemental sulphur S^0 was also detected in silt waters. Its presence in the form of fine particles was also detected on the surface of bacterial fouling and directly on the water surface of lakes Kudzhertay, Khodatuy, Malye and Bolshye Yakshy, Doroninskoye, etc. The content of S^0 varied from its detection limit to 16 281 μmol/L. Relatively high concentration of S0 was detected in sulphate lake Barun-Shivertuy. In this respect, soda lakes of subtype II Busutu-Nur and subtype II Shvartsivskoye were also distinguished. Elemental sulphur content in chloride lakes and in soda lakes of subtype I did not exceed 43 μmol/L (Nizhniy Kaltan) and 284 μmol/L (Malye Yakshy).

Sulphur forms in water columns of lakes

In water columns of lakes with reducing environment, H_2S was detected (80–99 % in the form of HS^-), but its measured content was substantially lower in comparison with its content in the silt water of bottom sediments. In the presence of

TABLE 1

Eh, pH, concentrations of different sulphur forms and sulphur isotope ratios for SO_4^{2-}, S^0 and H_2S in soda I subtype lakes over the years

Lake	Year	Silt water							Water column								
		Eh, mV	SO_4^{2-}, mmol/L	$K_{SO_4/Cl}$	H_2S, μmol/L	S^0, μmol/L	$\delta^{34}S(H_2S)$, ‰	$\delta^{34}S(S^0)$, ‰	Eh, mV	pH	SO_4^{2-}, mmol/L	$K_{SO_4/Cl}$	H_2S, μmol/L	S^0, μmol/L	$S_2O_3^{2-}$, μmol/L	$\delta^{34}S(SO_4^{2-})$, ‰	$\delta^{34}S(H_2S)$, ‰
Dunda-Nur	2014	−238	5.47	0.60	194	–	−6.0	−3.9	11	9.6	8.00	0.87	<0.16	0.59	0.40	1.3	–
Tsagan-Nur (Urda-Aginskoye)	2020	149	1.71	10.30	156	23.01	−26.8	−24.0	−30	9.5	1.68	10.11	<0.16	0.47	68.57	6.5	–
Kuduk	2013	−243	17.96	1.62	500	2.00	−15.7	–	−62	9.6	17.65	1.59	4.66	2.22	<0.04	16.8	−11.8
	2019	−243	0.41	0.01	156	3.11	−18.2	–	–	9.4	40.00	0.04	12.81	2.19	<0.04	30.2	−15.3
Balyktuy	2015	−246	0.29	0.06	8931	–	13.0	–	−12	9.3	1.52	0.33	3.03	4.22	0.54	18.9	14.8
	2018	−248	1.04	0.16	4125	–	13.5	–	–	9.5	2.63	0.41	2.81	2.19	2.59	18.3	14.8
	2021	−203	1.52	0.14	4230	25.32	13.0	–	−66	9.6	2.95	0.26	5.69	9.34	1.88	19.2	14.6
Baym-Bulak	2018	−253	0.73	0.10	581	–	−5.3	–	–	9.5	1.36	0.16	2.50	1.88	0.63	15.1	−1.8
	2021	−256	0.35	0.04	200	–	−5.5	–	−137	9.3	0.46	0.05	7.53	11.31	1.63	22.0	−2.3
Kudzhertay	2018	−258	0.91	0.01	3719	–	20.3	–	−330	9.9	4.95	0.05	659.38	8.75	1.96	25.4	21
	2021	−249	9.38	0.03	3750	–	–	–	−401	9.9	14.55	0.05	659.38	7.41	0.28	31.7	21
	2022	−224	3.66	0.01	2250	–	20.1	–	−196	9.9	48.46	0.05	284.38	27.72	5.01	30.5	20.8
Malye Yakshy	2013	−380	4.84	0.22	1719	284.06	−17.1	–	−220	9.6	8.26	0.37	431.25	19.69	<0.04	15.0	−13.4
	2018	–	1.92	0.18	513	<0.16	−18.8	–	−84	9.6	2.24	0.21	14.06	2.19	2.68	15.0	−15.6
Zun-Torey	2013	−236	9.38	0.60	<0.16	<0.16	–	–	134	9.7	10.54	0.68	<0.16	0.03	<0.04	15.2	–
	2013*	−256	9.30	0.62	484	<0.16	−9.6	–	−81	9.5	12.60	0.78	0.44	1.47	<0.04	15.4	−9.0
	2015*	−232	18.66	0.61	8	<0.16	−8.8	–	−106	9.6	18.81	0.75	3.84	<0.16	<0.04	16.0	−8.2
	2015	−232	18.67	0.65	<0.16	<0.16	–	–	100	9.6	18.41	0.66	<0.16	<0.16	<0.04	14.6	–
Aru-Torum	2015	−140	12.16	0.44	3469	1.00	−20.7	–	−10	9.5	21.02	0.76	<0.16	0.53	<0.04	9.1	−9.9
	2017	−129	19.38	0.29	45	–	−19.6	2.1	−30	9.6	55.99	0.85	<0.16	6.56	0.36	8.9	–
Talutay	2015	−143	12.35	1.46	4	–	−20	−3.3	18	9.6	11.96	1.41	<0.16	<0.16	<0.04	13.3	–
Doroninskoye	2015	−423	0.31	0.01	146 900	–	–	–	−400	9.8	1.38	0.04	115 620	703.13	34.55	17.7	–
Batuy	2017	−311	0.42	0.31	213	–	−2.3	–	94	9.0	0.68	0.50	<0.16	0.00	<0.04	8.6	–
	2018	−245	1.40	0.35	431	<0.16	−2.3	–	–	9.1	2.27	0.57	1.88	2.50	0.80	8.9	0.9
17-19	2017	−243	13.61	0.35	18	–	−19.6	−2.2	−69	9.7	14.28	0.37	4.56	3.53	0.54	14.5	–
Khuzharnoye	2017	−146	134.38	1.78	14 688	–	−2.3	–	−186	9.8	132.57	1.76	135.00	7.50	2.32	30.2	2.6
Nizhniy Mukey	2021	−250	55.87	0.41	538	<0.16	−22.3	–	−150	9.9	70.02	0.52	226.09	73.75	31.47	15.8	−15.3

Note. Dash – no data.

* At the site of bacterial mat accumulation.

TABLE 2

Eh, pH, concentrations of different sulphur forms and sulphur isotope ratios for SO_4^{2-}, S^0 and H_2S in soda II subtype lakes over the years

Lake	Year	Silt waters							Water column								
		Eh, mV	SO_4^{2-}, mmol/L	$K_{SO_4/Cl}$	H_2S, μmol/L	S^0, μmol/L	$\delta^{34}S(H_2S)$, ‰	$\delta^{34}S(S^0)$, ‰	Eh, mV	pH	SO_4^{2-}, mmol/L	$K_{SO_4/Cl}$	H_2S, μmol/L	S^0, μmol/L	$S_2O_3^{2-}$, μmol/L	$\delta^{34}S(SO_4^{2-})$, ‰	$\delta^{34}S(H_2S)$, ‰
Tsogan-Nur	2013	−332	1.06	0.02	266	1.09	−6.5	–	55	9.9	49.48	0.83	0.56	3.16	<0.04	14.4	–
Khara-Torum	2015	−144	5.47	0.32	313	–	−4.3	–	−233	9.2	14.75	0.86	6.97	38.25	<0.04	6.4	–
Kharanor	2015	156	0.41	1.73	<0.16	–	–	–	34	9.4	9.24	1.73	<0.16	<0.16	<0.04	−8.4	–
Kholbon	2015	−341	0.10	0.01	15	–	−15.6	–	81	9.6	24.07	0.30	5.06	18.66	<0.04	17.0	–
Khara-Nur	2016	−343	3.67	0.11	49	<0.16	−23.6	–	−120	9.1	28.68	0.89	10.31	11.25	2.68	11.2	−23.0
Malaya Bulugunda	2018	−340	0.98	0.01	2656	<0.16	–	–	−136	9.8	8.13	0.10	8.13	8.75	1.61	21.3	13.2
Narym-Bulak	2018	−360	0.81	0.04	3097	<0.16	−9.6	–	−55	9.6	8.24	0.37	2.19	7.19	6.07	14.0	–
Ara-Torum	2018	−360	1.05	0.02	2016	<0.16	−35.4	−39.6	−35	9.7	31.42	0.48	<0.16	3.28	1.07	4.9	–
Khonkho-Torum	2019	−350	0.47	0.05	909	<0.16	−27.3	–	−23	9.6	1.20	0.13	4.69	15.94	3.21	13.1	−25.30
Bolshoy Chindant	2020	−132	25.17	0.17	1097	1097	−48.8	−49.3	−44	9.6	71.74	0.48	6.88	9.38	4.73	2.5	–
Ukshinda	2020	−242	0.66	0.10	102	<0.16	−9.2	–	113	9.3	19.65	0.20	6.00	8.41	2.10	18.1	−7.0
	2021	−242	0.55	0.01	106	<0.16	−9.4	–	−17	9.5	7.09	0.19	1.66	2.84	0.37	18.5	−7.4
	2022	−258	0.49	0.01	289	12.02	−9.7	–	−97	9.6	8.79	0.16	9.31	12.06	6.06	18.9	−7.7
Shvartsivskoye	2016	−352	3.23	1.20	3678	<0.16	−31.8	–	−248	9.2	86.53	1.18	593.75	153.13	37.95	11.0	−30.8
	2020	−309	14.53	0.69	9869	9869	−31.9	−21.3	−138	9.3	90.94	0.80	6.50	11.41	66.88	11.9	−31.0
	2022	−356	14.37	0.56	<0.16	<0.16	−31.9	–	−129	9.5	53.80	0.71	8.88	9.72	1.18	11.6	−30.8
Borzinskoye	2013	−333	183.11	1.18	619	–	−30.3	–	−125	9.6	174.48	1.12	2.34	0.59	<0.04	12.0	–
	2015	−228	64.50	0.05	2988	–	−31.6	–	−42	9.3	649.38	0.47	1.50	3.59	0.34	12.8	−28.0
	2018	−285	66.67	0.14	2566	<0.16	−31.6	–	−128	9.4	159.68	0.34	55.00	101.25	10.98	10.9	−28.2
	2019	−258	238.28	0.16	2988	299.00	−34.0	−39.6	−187	9.2	737.60	0.48	<0.16	60.00	<0.04	11.3	–
	2020	−237	16.39	0.01	106	<0.16	−30.9	–	−97	9.3	124.27	0.10	6.25	14.69	0.45	12.4	–
	2021	−233	241.05	0.25	222	<0.16	−31.4	−29.6	−59	9.4	392.25	0.41	<0.16	9.34	0.78	12.8	–
	2022	−289	25.19	0.04	1594	<0.16	−31.4	–	−225	9.5	391.50	0.05	19.41	16.22	0.71	13.1	−31.0
Khotochey	2018	−385	3.58	0.05	5975	<0.16	−16.6	−21.3	−44	9.7	10.10	0.15	5.31	4.38	2.59	12.1	–
Khodatuy	2018	−350	5.88	0.11	5169	<0.16	−2.1	–	−80	9.5	10.10	0.20	13.13	11.88	1.25	27.4	0.7
	2015	−353	0.21	0.01	5169	<0.16	−2.3	–	–	9.5	1.50	0.05	12.84	7.38	0.07	28.4	0.7
Bolshie Yakshy	2018	−370	1.78	0.07	2313	<0.16	16.0	–	−296	9.6	3.09	0.13	47.81	14.06	1.07	16.9	16.6
Bayn-Tsagan	2022	−170	69.06	0.17	1019	<0.16	−18.7	−19.2	−117	9.6	2.43	0.20	6.50	9.56	0.71	14.6	−16.3

Note. Dash – no data.

TABLE 3

Eh, pH, concentrations of different sulphur forms and sulphur isotope ratios for SO_4^{2-}, S^0 and H_2S in sulphate and soda subtype II lakes over years

Lake	Year	Silt waters							Water column								
		Eh, mV	SO_4^{2-}, mmol/L	$K_{SO_4/Cl}$	H_2S, μmol/L	S^0, μmol/L	$\delta^{34}S(H_2S)$, ‰	$\delta^{34}S(S^0)$, ‰	Eh, mV	pH	SO_4^{2-}, mmol/L	$K_{SO_4/Cl}$	H_2S, μmol/L	S^0, μmol/L	$S_2O_3^{2-}$, μmol/L	$\delta^{34}S(SO_4^{2-})$, ‰	$\delta^{34}S(H_2S)$, ‰
Soda type, subtype II																	
Zhilino	2016	−161	23.37	9.0	2159	–	−14.2	–	−178	9.2	20.07	6.2	300.94	481.25	64.02	8.8	−13.5
	2016	−152	54.09	8.6	1228	–	−19.3	–	−93	9.2	38.40	6.1	260.94	293.44	21.70	8.6	−18.6
	2020	−193	26.40	10.9	1310	25	−19.6	−18.6	28	9.0	20.41	8.4	7.94	29.69	46.34	8.2	−18.9
Busutuy-Nur	2019	−245	33.55	14.7	4969	9438	–	–	100	9.2	30.75	13.5	18.97	17.94	4.59	–	–
Kharaganash	2013	−232	23.75	2.7	<0.16	<0.16	–	–	98	9.5	17.50	2.4	<0.16	1.59	0.14	4.9	–
	2022	130	20.32	3.1	<0.16	12	–	–	103	9.3	16.23	3.0	<0.16	<0.16	<0.04	0.5	–
Sheluta	2013	−121	25.72	1.7	1141	–	−2.6	–	200	9.5	22.52	1.5	<0.16	<0.16	<0.04	4.9	–
	2022	–	23.51	2.3	855	27.05	−2.2	–	182	9.5	17.58	2.0	<0.16	<0.16	<0.04	4.6	–
Sulphate type																	
Tsagan-Torom	2014	239	7.75	1.9	<0.16	–	–	–	285	8.9	6.58	1.1	<0.16	0.78	0.32	1.1	–
Barun-Shivertuy	2016	−120	110.25	5.2	21 250	16 281	−24.4	–	−320	7.5	78.96	3.7	8703.13	4665.63	186.61	14.3	−23.6
	2020	−444	334.44	2.2	28 365	7407	−24.9	−18.8	−132	7.3	285.95	1.7	<0.16	7.81	2.41	16.0	–
	2022	−440	335.00	2.2	293	18.23	−24.4	−29.6	−267	7.9	200.51	1.9	<0.16	153.75	1.12	13.9	–
Kuka-Azyrga	2016	204	8.28	1.9	<0.16	–	–	–	204	8.7	5.12	1.8	<0.16	<0.16	<0.04	–	–
Shikhalin-Nuur	2016	−247	219.03	3.3	20 631	1594	−30.5	−39.6	−100	8.6	143.33	2.1	<0.16	525.00	9.55	6.7	–
	2020	−359	587.70	1.8	20 183	3418	−40	−39.6	−220	7.3	456.71	1.4	<0.16	484.38	168.75	7.3	–
	2022	−301	286.52	1.9	16.00	<0.16	−41.0	–	−95	8.3	82.04	1.5	4.28	4.91	0.54	7.3	−40.3

Note. Dash – no data.

TABLE 4

Eh, pH, concentrations of different sulphur forms and sulphur isotope ratios for SO_4^{2-}, S^0 and H_2S in chloride lakes over years

Lake	Year	Silt waters							Water column								
		Eh, mV	SO_4^{2-}, mmol/L	$K_{SO_4/Cl}$	H_2S, μmol/L	S^0, μmol/L	$\delta^{34}S(H_2S)$, ‰	$\delta^{34}S(S^0)$, ‰	Eh, mV	pH	SO_4^{2-}, mmol/L	$K_{SO_4/Cl}$	H_2S, μmol/L	S^0, μmol/L	$S_2O_3^{2-}$, μmol/L	$\delta^{34}S(SO_4^{2-})$, ‰	$\delta^{34}S(H_2S)$, ‰
Bilchir-Nur	2013	−213	78.13	0.29	200	–	−30	–	17	7.4	91.15	0.33	<0.16	0.00	<0.04	13.2	–
Usutuy	2019	−52	0.81	0.14	–	6	0.0	–	98	8.9	0.83	0.15	<0.16	6.25	<0.04	1.3	–
Maliy Chindant	2020	−115	75.82	0.31	300	25	−24.1	−26.5	–	8.5	78.81	0.32	25.00	25.00	9.55	7.8	–
Bishikhan	2020	−340	12.50	0.19	6097	8	−36.0	–	−20	8.5	14.15	0.22	14.06	8.44	23.75	1.5	−32
Nizhniy Kaltan	2020	−353	64.37	0.11	8870	43	−18.3	−22.9	−10	7.2	277.87	0.48	13.13	43.44	1.07	7.7	–
Babye	2018	−108	60.18	0.36	953	23	−28.1	–	−66	8.7	74.92	0.44	2.50	22.50	1.07	7.2	−25.8
Dabasa-Nor	2018	−395	5.44	0.09	3014	5	–	–	−11	8.4	7.11	0.36	5.63	5.00	10.00	5.8	−22.3
	2022	–	125.30	0.36	1305	<0.16	−32.6	–	−130	8.3	146.49	0.44	–	0.00	<0.04	5.8	–
Gorbunka	2013	−244	4.33	0.03	625	<0.16	−34.8	–	133	8.1	21.88	0.17	9.78	0.38	<0.04	10.4	−30
	2014	−229	8.38	0.01	1522	<0.16	−38.0	–	−10	7.2	142.50	0.14	0.63	1.22	<0.04	12.1	−33
	2018	–	1.52	0.02	0	<0.16	−38.0	−26.5	42	8.5	6.49	0.14	0.00	0.14	<0.04	12.1	–
	2020	−299	5.35	0.04	3200	<0.16	−35.2	–	−55	8.3	25.77	0.13	0.00	0.17	<0.04	12.8	−33.4
	2021	−342	9.30	0.04	828	5	−34.3	−22.9	15	8.2	63.25	0.23	17.56	0.23	7.99	9.6	−28.7
Khilganta	2013	−240	5.13	0.07	1844	–	−20.4	–	123	8.2	14.58	0.21	2.22	0.00	<0.04	6.0	−16
	2014	−235	26.53	0.18	875	–	−21.0	–	67	8.5	31.91	0.20	0.97	3.59	<0.04	9.4	−16.9
	2021	−244	11.67	0.07	220	19	−20.7	–	29	8.4	60.35	0.31	34.19	18.50	4.73	7.0	−16.8

Note. Dash – no data.

H_2S, Eh value varied from −437 to 100 mV. Relatively high H_2S concentration (μmol/L) was detected in the bottom layer of water in the soda meromictic lake Doroninskoye, as well as in shallow lakes (depth <0.5 m): sulphate (Barun-Shivertuy), soda subtype II (Zhilino and Shikhalin-Nuur), soda subtype III (Shvartsivskoye) and soda subtype I (Nuzhniy Mukey, Kudzhertay, Malye Yakshy, Khodatuy, etc.).

At the same time, there were some lakes in which H_2S content in water was below detection limit (Zasulan, Khoyto-Torum, Zagosutay, Busutuy-Nur, Kharanor, etc.). These lakes were distinguished by the presence of dissolved O_2 in water (>1.2 μmol/L) and relatively high Eh value (>200 mV) and, along with sulphate and soda II subtype lakes, were characterised by $K_{SO_4/Cl} > 1$ [14].

In addition to H_2S, the presence of S^0 and $S_2O_3^{2-}$ was detected in the water columns of lakes. The range of S^0 concentrations in the lakes varied from the detection limit (Zasulan, Balsoy, Khara-Torum, etc.) to 4665.63 μmol/L (Barun-Shivertuy). According to averaged estimates, S^0 was accumulated in large amounts in sulphate lakes (834.60 μmol/L). It relatively high content was also detected in soda subtype II lake Zhilino (481.30 μmol/L). The concentration of $S_2O_3^{2-}$ in lake waters varied from detection limit (Mongu-Tuy, Khara-Torum, etc.) to 186.61 μmol/L (Barun-Shivertuy). Relatively high $S_2O_3^{2-}$ content was also detected in sulphate lake Shikhalin-Nuur (168.75 μmol/L) and in soda subtype II lake Zhilino (64.02 μmol/L). Among chloride lakes, relatively high $S_2O_3^{2-}$ content was detected in lakes Nizhniy Kaltan (23.75 μmol/L), soda subtype I lakes Tsagan-Nur (Urda-Aginskoye) (68.57 μmol/L) and III subtype − lake Shvartsivskoye (66.88 μmol/L).

As far as SO_4^{2-} is concerned, its highest concentrations (mmol/L) were detected in self-settling lakes, in which settling was observed: soda (Kudzhertay − 48.46), thenardite (Shikhalin-Nuur − 456.71, Barun-Shivertuy − 285.95, Borzinskoye − 737.60). The value of $K_{SO_4/Cl}$ in the water column of chloride and soda subtype I and III lakes is higher on average than in silt waters, while, quite contrary, in sulphate and soda subtype II lakes it is lower. The ranged sequences of average SO_4^{2-} and $K_{SO_4/Cl}$ concentrations in descending order agree with the distribution of these values in silt waters.

Analysis of the distribution of most oxidised and reduced sulphur forms in the water column of each lake tested during different years shows that the amounts of these species are not constant in each lake. Moreover, either growth or decrease in the concentrations of these species can be observed in the same lake at different times, which is evidence that different processes govern the behaviour of these species. The behaviour of H_2S is mainly determined by sulphate reduction and the process of its chemical and/or bacterial oxidation, while the behaviour of SO_4^{2-}, in addition to its bacterial reduction and oxidation of reduced sulphur forms, can be also governed by evaporative concentrating processes or dilution of waters that take part in salt feeding of lakes. The value of $K_{SO_4/Cl}$ is also non-constant in a specific lake.

Isotope composition of sulphur

As a rule, a single chemical analysis of sulphur compounds is insufficient to understand the relative significance of various processes in the sulphur cycle. It is known that transformations of sulphur compounds cause measurable fractionation of sulphur isotopes, which sheds light on the routes of sulphur reduction and oxidation.

In the water columns of soda subtype I and II lakes, the values of $\delta^{34}S(SO_4^{2-})$ varied from −8.4 ‰ in lake Kharanor, where H_2S was not detected, to 31.7 ‰ in lake Kudzhertay with relatively high H_2S content (659.38 μmol/L) in water. In soda subtype II lakes, the value of $\delta^{34}S(SO_4^{2-})$ varied within a narrower range: from 0.5 ‰ in the oxidative environment of lake Kharaganash to 8.8 ‰ in lake Zhilino with the presence of hydrogen sulphide. In sulphate lakes, SO_4^{2-} is less enriched with ^{34}S in lake Tsagan-Torom (1.1 ‰), in which H_2S was not detected, and higher enriched in hydrogen sulphide waters of lake Barun-Shivertuy (16.0 ‰). In chloride lakes, the minimal $\delta^{34}S(SO_4^{2-})$ value was determined under oxidative environment in lake Usutuy (1.3 ‰), and the maximal one − under reducing environment of lake Bilchir-Nur (13.2 ‰).

In general, variations of sulphur isotope composition in SO_4^{2-} in the lakes under consideration fit within ^{34}S content in the waters of continental water bodies [5, 14]. According to the obtained data, in the water column of some soda lakes of subtype I (Kudzhertay, Baym-Bulak, Kuduk, Khuzharnoye, Doroninskoye) and III (Khodatuy), $\delta^{34}S(SO_4^{2-})$ varies from 27.4 to 31.7 ‰, which is higher than $\delta^{34}S(SO_4^{2-})$ for ocean water (20.1±0.8 ‰) and modern evaporates (24.3 ‰), as well as for the upper limit of the range for acid rocks (26.7 ‰), being inferior only to $\delta^{34}S(SO_4^{2-})$ for saline domes (62 ‰).

Broad data scattering over the whole set of samples was also revealed for $\delta^{34}S(H_2S)$ in the water column and in silt sediments of lakes. In this respect, soda subtype I and II lakes were distinguished, in the waters of these lakes this parameter varied from 21.0 ‰ in lake Kudzhertay (water layer is 0.1 m under the salt crust) to −48.8 ‰ in lake Bolshoy Chindant.

Results of the studies of sulphur isotope ratios in H_2S and SO_4^{2-} for lakes tested during different years show that, in spite of changes in water volume and SO_4^{2-} concentration for each water body, the measured $\delta^{34}S(SO_4^{2-})$ and $\delta^{34}S(H_2S)$ values exhibited relatively small standard deviation (SD). For example, for sulphur in SO_4^{2-} for all samples, the average value was SD = ±0.8 ‰, while for sulphur in H_2S it was SD = ±2.5 ‰.

For example, in 2015 $\delta^{34}S$ values in SO_4^{2-} and H_2S in the water column of soda subtype I lake Balyktuy were 18.9 and 14.8 ‰, respectively. Gradual decrease in the amount of water in the lake by 2018 was accompanied by an increase in SO_4^{2-} concentration and $K_{SO_4/Cl}$, as well as by accumulation of ^{32}S in SO_4^{2-}. The situation changed in 2021: an increase in water area was observed in the lake, ^{32}S was detected to accumulate in H_2S, and ^{34}S in SO_4^{2-}, $K_{SO_4/Cl}$ decreased substantially. In lake Baym-Bulak, a decrease in SO_4^{2-} concentration by the last test date was accompanied by enrichment with ^{34}S in SO_4^{2-} and accumulation of ^{32}S in H_2S; the value of $K_{SO_4/Cl}$ was observed to change synchronously with $\delta^{34}S(H_2S)$. In the year-to-year observation section, SO_4^{2-} was changing substantially in the waters of lake Kudzhertay, while the values of $K_{SO_4/Cl}$, $\delta^{34}S(SO_4^{2-})$ and $\delta^{34}S(H_2S)$ were less prone to changes. Saline lake Zun-Torey was tested in two sites: with the mass development of bacterial mats (2013* and 2015*) and in their absence (2013 and 2015). Results show that in the sites where bacterial mats were accumulated (the mats had a layered structure, with purple upper layer and black bottom), in the presence of H_2S in silt waters of bottom sediments, sulphur in SO_4^{2-} was enriched in ^{34}S to a higher extent than sulphur in SO_4^{2-} in the sample taken for analysis from the site where no mats were detected. In the year-to-year section by 2015, a substantial increase in SO_4^{2-} concentration, a decrease in $K_{SO_4/Cl}$ (from 0.68 to 0.66 and from 0.78 to 0.75, respectively) and accumulation of ^{34}S in SO_4^{2-} and ^{32}S in H_2S were detected I at both test sites against the background of a sharp decrease in water volume in the lake.

Among soda subtype II lakes, in the year-to-year section, for example in lake Ukshinda against the background of a sharp change in SO_4^{2-} concentration, we detected changes in $K_{SO_4/Cl}$ and sulphur isotope ratios in SO_4^{2-} and in H_2S. By the last observation date, an increase in $\delta^{34}S(SO_4^{2-})$ was accompanied by a decrease in $K_{SO_4/Cl}$ and accumulation of ^{32}S in H_2S. In the self-settling salt lake Borzinskoye, tested in 2013, 2015, 2018–2022, in spite of substantial variations of SO_4^{2-} and H_2S concentrations in the bottom layer, SD was only 0.7 ‰ for $\delta^{34}S(SO_4^{2-})$ and 3.9 ‰ for $\delta^{34}S(H_2S)$. In 2015 and 2019–2022, thenardite settling was observed in the lake. The determined values were $\delta^{34}S(Na_2SO_4)$ = 13.3 ‰ and $\delta^{34}S(SO_4^{2-})$ = 13.1 ‰. In 2018, an increase in water volume in the lake and its desalination were observed. During the period with water abundance, sulphur in SO_4^{2-} isotopically lighter than during the low-water period, but still it remained isotopically heavier than sulphur in SO_4^{2-} in groundwaters (1.8 ‰) and in atmospheric precipitation (6.7 ‰) taking part in lake feeding. In less saline water bodies of this subtype (Shvartsivskoye, Khodatuy, etc) a decrease in $K_{SO_4/Cl}$ was accompanied by the accumulation of ^{34}S in SO_4^{2-} and ^{32}S in H_2S in each lake.

The mirror-symmetric distribution of $\delta^{34}S(SO_4^{2-})$ and $K_{SO_4/Cl}$, $\delta^{34}S(H_2S)$ was also conserved in chloride lakes Gorbunka and Khilganta. A distinguishing feature of chloride lake Dobasa-Nor was the constant isotope ratio $^{34/32}S$ in SO_4^{2-} against the background of varying SO_4^{2-}, H_2S and $K_{SO_4/Cl}$.

In soda subtype II lakes (Zhilino, Kharaganash, Sheluta) and in sulphate lakes (Shikhalin-Nuur and Barun-Shivertuy), in the year-to-year section, water desalination was accompanied by a decrease in SO_4^{2-} concentration but an increase in $K_{SO_4/Cl}$ and ^{32}S accumulation in SO_4^{2-}. In sulphate lakes Barun-Shivertuy and Shikhalin-Nuur, in 2020 against the background of a decrease in their water area, SO_4^{2-} concentration increased, while $K_{SO_4/Cl}$ decreased, ^{34}S was accumulated in SO_4^{2-}, and H_2S was enriched with ^{32}S. That year, thenardite settling was observed in these lakes. In lake Barun-Shivertuy, $\delta^{34}S(Na_2SO_4)$ = 16.2 ‰ and $\delta^{34}S(SO_4^{2-})$ = 16.0 ‰, while in lake Shikhalin-Nuur the corresponding values were $\delta^{34}S(Na_2SO_4)$ = 7.5 ‰ and $\delta^{34}S(SO_4^{2-})$ = 7.4 ‰.

To achieve a better understanding of processes that provide sulphur behaviour, we determined isotope ratio $\delta^{34}S(S^0)$ in silt waters. The measured $\delta^{34}S(S^0)$ values varied within a broad range from −49.3 ‰ in lake Bolshoy Chindant

(soda subtype III) to 2.1 ‰ in lake Aru-Torum (2017, soda subtype I). In this situation, in some lakes $\delta^{34}S(S^0) > \delta^{34}S(H_2S)$ (lakes Talatuy, Dunda-Nur, Aru-Torum, Tsagan-Nur (Urda-Aginskoye), Barun-Shivertuy, Zhilino, Shikhalin-Nuur (2020), Borzinskoye (2021), Shvartsivskoye, Gorbunka, lake encoded as 17-19). In other lakes, $\delta^{34}S(S^0) < \delta^{34}S(H_2S)$ (lakes Narym-Bulak, Ara-Torum, Borzinskoye (2020), Bayn-Tsagan, Maliy Chindant, Nizhniy Kaltan).

DISCUSSION OF RESULTS

The results presented above show that S^0 is accumulated on a large scale in sulphate and soda subtype II lakes in the sum of reduced sulphur ($\Sigma S_{red} = S^0 + S_2O_3^{2-} + H_2S$), while H_2S prevails in chloride and soda I and II subtype lakes (Fig. 1). Different ratios of hydrogen sulphur and the products of its incomplete oxidation are determined by different scales of two oppositely directed processes: bacterial sulphate reduction and oxidation of hydrogen sulphide [15]. The scale of these processes can be also traced in the changes of SO_4^{2-} concentrations and $K_{SO_4/Cl}$. In chloride and soda subtype I and III lakes, a decrease in SO_4^{2-} concentration and $K_{SO_4/Cl}$ values was observed in the direction of water column → silt. An opposite dependence was observed for sulphate and soda subtype II lakes.

The amount of SO_4^{2-} can change due to lake water dilution with atmospheric precipitation and by groundwaters, or due to evaporative water concentrating [16]. Water concentrating, dissolution and settling of thenardite, as shown above, does not have a substantial effect on $^{34/32}S$ in SO_4^{2-}. According to our data, $\delta^{34}S(SO_4^{2-})$ in atmospheric precipitation in this region is 6.7 ‰, while the value for groundwaters and river waters varies from −2.3 to 8.4 ‰. As a result of simple water dilution, $\delta^{34}S(SO_4^{2-})$ in lake water should vary within these limits. However, in most of cases, this value goes beyond the boundaries of the assigned range.

It is known that microbial reduction of SO_4^{2-} leads to isotope fractionation, characterised by the difference between $\delta^{34}S$ in H_2S and SO_4^{2-} from 3 to 70 ‰ [17]. The degree of sulphur isotopic fractionation ε in the system $SO_4^{2-} - H_2S$ in lakes with hydrogen sulphide varies generally over all samples from 5 to 54 ‰. In the water column of soda lakes Balyktuy, Kudzhertay (2018, 2021), Batuy, Zun-Torey, Bolshie Yakshy and Sheluta, we obtained $\delta^{34}S(SO_4^{2-}) \geq 8.3$ ‰, while $\varepsilon \leq 18$ ‰. It may be assumed that incomplete oxidation of organic matter has occurred, so sulphur in H_2S had relatively close $^{34/32}S$ to sulphur in initial SO_4^{2-} in water [18].

However, in most of the cases, $\varepsilon > 18$ ‰ in the system $SO_4^{2-} - H_2S$. Relatively high sulphur fractionation value in SO_4^{2-} was determined in the soda lakes Bolshoy Chindant (54 ‰), Borzinskoye (up to 44 ‰), Ukshinda (up to 46 ‰), Shvartsivskoye (up to 44 ‰), Grishkino (up to 52 ‰), Khoyto-Torum (up to 44 ‰), Barun-Kholvo Bolshoye (46 ‰), etc. This separation is possible as a result of com-

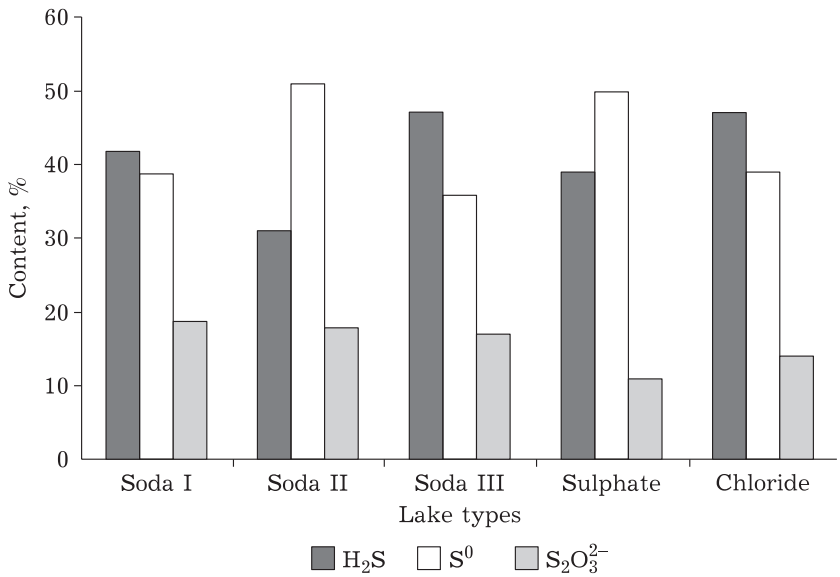

Fig. 1. Relative content of H_2S, S^0, $S_2O_3^{2-}$ in different types and subtypes of lakes.

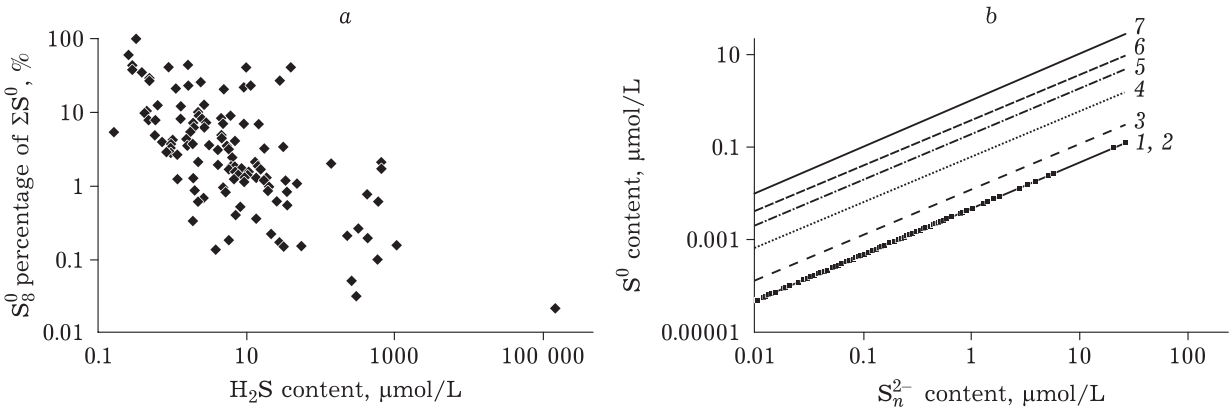

Fig. 2. Dependence of H_2S concentration on S_8^0 percentage (*a*) and various forms of S^0 (*b*) in the water column of lakes. *b* – S_2^{2-} (*1*), S_8^{2-} (*2*), S_3^{2-} (*3*), S_7^{2-} (*4*), S_6^{2-} (*5*), S_4^{2-} (*6*), S_5^{2-} (*7*).

plete mineralisation of the organic matter, because oxidation to CO_2 leads to higher degree of sulphur isotope fractionation because of lower rates of sulphate reduction [19]. At the same time, other possibilities related to higher sulphur fractionation in SO_4^{2-} cannot be excluded [20].

Previously, in the upper layers of bottom sediments in the lakes under investigation we detected the representatives of *Desulfosarcina*, *Desulfonatronum*, *Desulfobacterium*, *Desulfobacca*, *Desulfuromusa*, *Desulfurivibrio* and *Desulfobulbus* genera belonging to the physiological group of sulphate-reducing bacteria, responsible for bacterial reduction of sulphate ions with the formation of hydrogen sulphide. Moreover, the identified alkalophilic sulphate-reducing bacteria *Desulfonatronum lacustre*, *Desulfonatronumaceae* δ-*subclass Proteobacteria*, *Alkaliphilus namsaraevii* [21–23] used S^0, $S_2O_3^{2-}$ and SO_3^{2-} as alternative electron acceptors.

In the series of transition states of sulphur in aqueous solutions, sulphur S^0 occupies a special position because this species is formed only during oxidation of hydrogen sulphide or its derivatives. Hence, its indicative role in geochemical processes is evident. Under normal conditions, it is present in the form of orthorhombic cyclooctasulphur (α-S_8^0), its solubility in sea water at pH 8.2 and temperature 25 °C is only 0.152 μmol/L [24]. According to our calculations, the relative amount of dissolved sulphur S_8^0 with respect to ΣS^0 decreases with an increase in H_2S concentration in the lakes (Fig. 2, *a*). According to [24], the joint presence of S^0 and H_2S at neutral and alkaline pH leads to the formation of soluble polysulphides S_n^{2-}. It is known that inorganic S_n^{2-} species and their protonated forms contain (at least formally) one sulphur atom with oxidation degree −2 and one or several sulphur atoms with oxidation degree 0 ($S_n^{2-} = [S_n^0 - S^{(-2)}]^{2-}$). The expected S_n^{2-} concentrations were calculated using thermodynamic values of constants [24] taking into account the fact that lake waters are saturated with S_8^0.

According to thermodynamic calculations, with an increase in pH of water the amount of S_n^{2-} increases, and at pH 10.7 it may achieve 35 % of ΣS^0 in water (see Fig. 2, *b*). For this reason, S_n^{2-} is accumulated in large amount in soda lakes (2.5 % of ΣS^0) in comparison with sulphate (0.3 % of ΣS^0) and chloride (0.2 % of ΣS^0) lakes. Everywhere, the form prevailing in S_n^{2-} is S_5^{2-} ($[S_5^{2-}] > [S_4^{2-}] > [S_6^{2-}] > [S_7^{2-}] > [S_3^{2-}] > [S_8^{2-}] > [S_2^{2-}]$) (Fig. 3). The species S_4^{2-} and S_6^{2-} are present in comparable amounts, and the total $[S_4^{2-}] + [S_5^{2-}] + [S_6^{2-}]$ content is 87 % of S_n^{2-}. The relative amount of suspended and colloid sulphur (S_{SM}^0), calculated as $S_{SM}^0 = \Sigma S^0 - S_n^{2-} - S_8^0$, is within the range from 54 to 100 %.

Experimental data show that different mechanisms of H_2S oxidation lead to different isotope effects for $^{34/32}S$ in S^0. For instance, in the bottom sediments of lakes Talatuy, Aru-Torum, Gorbunka (2019 and 2021), Shvartsivskoye (2020) and the lake encoded as 17-19, S^0 and H_2S were detected at the same time, with $\delta^{34}S(S^0) > \delta^{34}S(H_2S)$, and fractioning value for this system was within the range $10.9 \le \varepsilon \le 21.1$ ‰. High sulphur fractionation in H_2S can be explained by repeated numerous reduction, oxidation and disproportionation reactions participated by different sulphur forms in lakes. It is known that biological disproportionation of intermediate sulphur forms (S^0, SO_3^{2-} and $S_2O_3^{2-}$) leads finally to H_2S depletion in 34S by 5–7 ‰ and to SO_4^{2-}enrichment with ^{34}S by 17–21 ‰ [25].

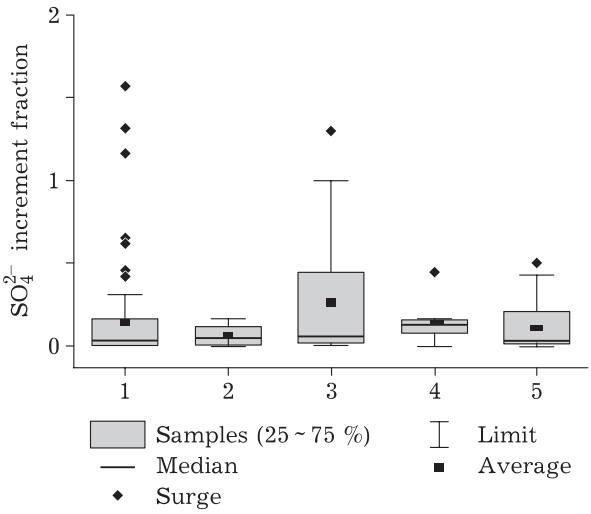

Fig. 3. Fraction of SO_4^{2-} increment in the water column due to H_2S oxidation in silt waters (S_n^{2-} formation) in different types and subtypes of lakes: 1, 2, 3 – soda subtype I, II, III lakes, respectively; 4 – sulphate; 5 – chloride.

In the lakes under investigation, we detected chemolithoautotrophic micro-anaerobic thionic bacteria *Thioalkalivibrio* and purple sulphobacteria *Thioalkalicoccus limnaeus*, *Ectothiorhodospira variabilis*, *Ectothiorhodospira magna* and *Ectothiorhodospira shaposhnikovii* [26], which produce S^0 as a product of H_2S oxidation and are able (mainly green and purple sulphobacteria) also to oxidise S^0 and some other reduced sulphur compounds (including $S_2O_3^{2-}$) to SO_4^{2-} and to participate (in particular, some sulphate-reducing species) in disproportionation of sulphur S^0, $S_2O_3^{2-}$ and SO_3^{2-} [27].

The condition under which $\delta^{34}S(S^0) > \delta^{34}S(H_2S)$, and fractionation coefficient is within the range $0 \le \varepsilon \le 4$ ‰, agrees with the equilibrium isotope effect observed between elemental sulphur and sulphide in equilibrium with polysulphides (S_n^{2-}) [13], and can depict, with smaller ε, either abiotic formation of S^0 at the oxidation-reduction barrier, or intracellular equilibrium isotope effect connected with the oxidation of H_2S by anoxygenic phototrophs. In this case, sulphur isotope separation leads to S0 enrichment with ^{34}S and simultaneous depletion of H_2S in ^{34}S. Due to H_2S oxidation with anoxygenic phototrophs, the determined ε values range from 2 to 4 ‰ [28], while due to H_2S oxidation by chemotrophic bacteria and abiotic oxidation by iron oxides $\varepsilon < 1$ ‰ [29].

Abiotic formation of S^0 at the oxidation-reduction barrier with the participation of iron and manganese in the determined concentrations (from 10^{-9} to 10^{-5} mol/L) in most of the cases can provide a definite amount of ΣS^0. For sulphate and soda subtype II lakes, ε values for sulphur in H_2S in bottom sediments and water column of lakes were on average equal to 0.6 and 0.7 ‰, respectively, which confirms the possibility of oxidation as a result of abiotic reaction of H_2S with Fe-Mn-oxides and/or with the participation of chemotrophic bacteria.

According to the data reported in [30], in the presence of Fe-Mn-oxides, $S_2O_3^{2-}$ can also be formed. Definite concentrations of Fe-Mn-oxides provide analytically detected amount of $S_2O_3^{2-}$ in lake waters. At the same time, one cannot ignore the formation of $S_2O_3^{2-}$ due to biological processes driven by the strains of alkalophilic aerobic chemorganotrophic bacteria of *Halomonas* genus, identified in the samples of the top layer of water column, which can oxidise H_2S in the presence of organic substrates [31]. In turn, $S_2O_3^{2-}$ is oxidised to SO_4^{2-} by bacteriochlorophyll *a*-containing bacteria of *Roseinatronobacter* genus, identified in the aerobic zone, which are capable of chemolithoheterotrophic growth [32]. There are also other mechanisms of $S_2O_3^{2-}$ formation, but because of the absence of data on sulphur isotope ratios in $S_2O_3^{2-}$ it seems impossible to determine the major contribution from a definite process into its formation.

In lakes Bolshoy Chindant, Borzinskoye, Maliy Chindant, Bayn-Tsagan, Nizhniy Kaltan, Barun-Shivertuy, etc., the values $\delta^{34}S(S^0) < \delta^{34}S(H_2S)$, while ε varies from −1 to −9.4 ‰. This fact points to H_2S oxidation by O_2 and/or by the participation of chemoautotrophic microorganisms (non-anoxygenic photosynthetics) in H_2S oxidation. As a result, a mixture of products enriched with ^{34}S in H_2S and ^{32}S in S^0 is formed [28]. It may be assumed that, at a definite moment of time, oxygen got into the bottom sediments of these shallow lakes (wind-caused mixing), which resulted in abiogenic oxidation of hydrogen sulphide. This process caused ^{34}S accumulation in H_2S. It is possible that S^0 is a product of H_2S oxidation in the water column. Indeed, hydrogen sulphide of the water column is enriched with ^{34}S to a higher extent than hydrogen sulphide of silt waters. The value of ε in the system $H_2S_{water} - H_2S_{silt}$ is $-10.9 \le \varepsilon \le -0.3$ ‰ and close to the result obtained with bacterial and abiotic oxidation of H_2S.

Small variations of ε values in the system $H_2S_{water} - H_2S_{silt}$ in each lake in the year-to-year section of observations are likely to depict relative constancy of the composition and amount of organic matter and the corresponding microflora, as well as kinetic parameters at each stage of SO_4^{2-} reduction and H_2S oxidation during sum-

mer. At the same time, both over lake depth and in the season-to-season section, different versions of hydrogen sulphide oxidation can be expected. This may be confirmed by the measured values of sulphur isotope ratios in S^0 and H_2S in the bottom sediments of lakes Borzinskoye, Barun-Shivertuy, Shikhalin-Nuur, in which in one case $\delta^{34}S(S^0) < \delta^{34}S(H_2S)$, that is, H_2S oxidation in bottom sediments was mainly due to dissolved oxygen, while in another case $\delta^{34}S(S^0) > \delta^{34}S(H_2S)$, that is, H_2S oxidation was performed mainly by anoxygenic phototrophic bacteria and/or due to abiogenic oxidation in the presence of Fe-Mn-oxides.

The next question to be solved was: why SO_4^{2-} in water column is not replenished due to the oxidation of freshly formed H_2S. If we admit that the whole amount of hydrogen sulphide, calculated as the difference $H_2S_{silt} - H_2S_{water}$, is oxidised in water column to form SO_4^{2-}, then sulphate parameter $K_{SO_4/Cl}$ is calculated from the obtained SO_4^{2-} concentration, and thus obtained value is compared with the similar parameter for the water column, it will turn out that only insignificant fraction of SO_4^{2-} (0.34 on average) is formed due to H_2S oxidation, only in some cases H_2S oxidation can replenish SO_4^{2-} amount (see Fig. 3). However, calculations did not take into account the processes in which intermediate sulphur forms were generated, H_2S was bound with polyvalent metals, and metal sulphides were precipitated into bottom sediments: the presence of metals is confirmed, in particular, by a discovery of amorphous troilite in bottom silts. Moreover, as shown above, an increase in SO_4^{2-} in bottom sediments was detected in sulphate and soda II subtype lakes, and in sole soda subtype I and III lakes.

According to the data reported in [16], some selected sulphate and soda II subtype lakes are distinguished by relatively high aqueous concentrations of Fe, Co, Ni and Cu elements, originating from pyritised rocks. Ground and surface waters localised within these limits are enriched with SO_4^{2-} [16]. Being the major water-salt source for lakes, these waters brought SO_4^{2-} to lake waters, so during wet periods an increase in $K_{SO_4/Cl}$ values and accumulation of ^{32}S in SO_4^{2-} were observed as a result of lake water dilution. Evidently, if an additional source of SO_4^{2-} ions appears, the amount of ^{34}S isotope in these waters decreases, while the concentration of these ions under the conditions of evaporative concentrating increases till the formation of sulphate-type lakes or soda type with increased SO_4^{2-} content (subtype II).

CONCLUSION

Analysis of factual information shows that sulphur form prevailing in the bottom sediments of saline lakes in Transbaikalia is H_2S (HS^-). In the water column, S0 prevails in the sum of reduced sulphur forms in sulphate and soda subtype II lakes, while the species dominating in chloride and soda subtype I and III lakes is H_2S (HS^-). Thermodynamic calculations show that S^0 is present in water mainly in the forms of colloids and suspensions. The amount of $S_2O_3^{2-}$ in lake water is relatively low, the maximal fraction of these ions was detected in soda II subtype lakes. In the year-to-year observation section, substantial changes in SO_4^{2-} and H_2S content and in $K_{SO_4/Cl}$ value were detected in each lake. At the same time, $\delta^{34}S(SO_4^{2-})$ and $\delta^{34}S(H_2S)$ had relatively small standard deviations.

It is shown that the behaviour of SO_4^{2-} is complicated, because along with evaporation and dilution of lake waters it is controlled by two additional oppositely directed processes: sulphate reduction and hydrogen sulphide oxidation. It is determined that ^{34}S in SO_4^{2-} was concentrated in chloride and soda subtype I and III lakes as a result of sulphate reduction.

On the basis of sulphur isotope ratios in H_2S and S^0, different mechanisms of hydrogen sulphide oxidation were established. In some lakes substantial sulphur fractionation in S^0 can be connected with repeated use of H_2S in the reactions of oxidation and/or disproportionation of intermediate sulphur compounds (S^0, SO_3^{2-} and $S_2O_3^{2-}$), while in other lakes H_2S oxidation proceeds due to oxygen or Fe-Mn-oxides, as well as with the participation of various bacterial, including anoxygenic phototrophs.

The existence of an additional source of SO_4^{2-} ions and/or absence of the process of their bacterial reduction lead to an increase in ^{32}S content in SO_4^{2-} and allows SO_4^{2-} to be concentrated till the formation of sulphate lakes of soda subtype II lakes.

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REFERENCES

1 Sulfate-Reducing Bacteria, L. L. Barton (Ed.), Plenum Press, New York, 1995. P. 217–241. (Biotechnology Handbooks; Vol. 8).

2 Ecophysiology and Biochemistry, M. Dworkin, S. Falkow, E. Rosenberg, K.-H. Scheifer, E. Stackebrandt (Eds.), 3th ed., Springer, Berlin, 2006. P. 659–768. (The Prokaryotes : A Handbook on the Biology of Bacteria; Vol. 2).

3 Past and Present Water Column Anoxia, L. N. Neretin (Ed.), Springer, Dordrecht, 2006. P. 69–104.

4 Boetius A., Ravenschlag K., Schubert C. J., Rickert D., Widdel F., Gieseke A., Amann R., Jørgensen B. B., Witte U., Pfannkuche O., A marine microbial consortium apparently mediating anaerobic oxidation of methane, *Nature*, 2000, Vol. 407, P. 623–626.

5 Sulfur Biogeochemistry – Past and Present, J. P. Amend, K. J. Edwards, T. W. Lyons (Eds.), Geological Society of America, Boulder, 2004. P. 97–116. (Special Paper; 379).

6 Avetisyan R., Eckert W., Findlay A. J., Kamyshny A. J., Diurnal variations in sulfur transformations at the chemocline of a stratified freshwater lake, *Biogeochemistry*, 2019, Vol. 146, No. 1, P. 83–100.

7 Milucka J., Ferdelman T. G., Polerecky L., Franzke D., Wegener G., Schmid M., Lieberwirth I., Wagner M., Widdel F., Kuypers M. M. M., Zero-valent sulphur is a key intermediate in marine methane oxidation, *Nature*, 2012, Vol. 491, P. 541–546.

8 Kamyshny A. Jr., Goifman A., Rizkov D., Lev O., Kinetics of disproportionation of inorganic polysulfides in undersaturated aqueous solutions at environmentally relevant conditions, *Aquat. Geochem.*, 2003, Vol. 9, P. 291–304.

9 Dahl C., Schulte A., Stockdreher Y., Hong C., Grimm F., Sander J., Kim R., Kim S.-H., Shin D. H., Structural and molecular genetic insight into a widespread sulfur oxidation pathway, *J. Mol. Biol.*, 2008, Vol. 384, No. 5, P. 1287–1300.

10 Jørgensen B. B., Bak F., Pathways and microbiology of thiosulfate transformations and sulfate reduction in a marine sediment (Kattegat, Denmark), *Appl. Environ. Microbiol.*, 1991, Vol. 57, No. 3, P. 847–856.

11 Zhang J.-Z., Millero F. J., The products from the oxidation of H_2S in seawater, *Geochim. Cosmochim. Acta*, 1993, Vol. 57, No. 8, P. 1705–1718.

12 Borzenko S. V., Shvartsev S. L., Chemical composition of salt lakes in East Transbaikalia (Russia), *Appl. Geochem.*, 2019, Vol. 103, P. 72–84.

13 Dubinin A. V., Demidova T. P., Rimskaya-Korsakova M. N., Semilova L. S., Ocherednik O. A., Determination of the reduced sulfur species in the water of anoxic basins, *Phys. Oceanogr.*, 2019, Vol. 26, No. 1, P. 32–46.

14 Borzenko S. V., Principal parameters controlling water composition in saline and brakish lakes in Eastern Transbaikalia, *Geochem. Int.*, 2020, Vol. 65, No. 12, P. 1356–1373.

15 Borzenko S. V., Fedorov I. A., Geochemical transformations of sulfur and their role in the formation of different types and subtypes of saline lakes in Southeastern Transbaikalia, *Appl. Water Sci.*, 2024, Vol. 14, Art. 32.

16 Borzenko S. V., The main formation processes for different types of salt lakes: evidence from isotopic composition with case studies of lakes in Transbaikalia, Russia, *Sci. Total Environ.*, 2021, Vol. 782, Art. 146782.

17 Canfield D. E., Farquhar J., Zerkle A. L., High isotope fractionations during sulfate reduction in a low-sulfate euxinic ocean analog, *Geology*, 2010, Vol. 38, No. 5, P. 415–418.

18 Detmers J., Brüchert V., Habicht K. S., Kuever J., Diversity of sulfur isotope fractionations by sulfate-reducing prokaryotes, *Appl. Environ. Microbiol.*, 2001, Vol. 67, No. 2, P. 888–894.

19 Brüchert V., Knoblauch C., Jørgensen B. B., Controls on stable sulfur isotope fractionation during bacterial sulfate reduction in Arctic sediments, *Geochim. Cosmochim. Acta*, 2001, Vol. 65, No. 5, P. 763–776.

20 Canfield D. E., Isotope fractionation by natural populations of sulfate-reducing bacteria, *Geochim. Cosmochim. Acta*, 2001, Vol. 65, No. 7, P. 1117–1124.

21 Zakharyuk A. G., Ryzhmanova Ya. V., Avtukh A. N., Shcherbakova V. A., Iron-reducing microbial communities of the Lake Baikal low-temperature bottom sediments, *Microbiology*, 2019, Vol. 88, No. 2, P. 156–163.

22 Kozyreva L. P., Egorova D. V., Ananyina L. N., Plotnikova E. G., Namsaraev B. B., Microbial diversity of cellulose-degrading sandy mats community from lake Zun-Torey (Southern Transbaikal region), *Inland Water Biology*, 2014, No. 2, P. 40–46. (In Russ.).

23 Dagurova O. P., Garankina V. P., Dambaev V. B., Namsaraev B. B., Biogeochemical processes of formation of methane and hydrogen sulfide in coastal sediments of lake Baikal, *Bulletin of Buryat State University*, 2013, No. 3, P. 36–38. (In Russ.).

24 Avetisyan K., Kamyshny A. Jr., Thermodynamic constants of formation of disulfide anion in aqueous solutions, *Geochim. Cosmochim. Acta*, 2022, Vol. 325, P. 205–213.

25 Canfield D. E., Thamdrup B., The production of ^{34}S-depleted sulfide during bacterial disproportionation of elemental sulfur, *Science*, 1994, Vol. 266, No. 5193, P. 1973–1975.

26 Saline and Brine Lakes of Transbaikalia: Hydrochemistry, Biology, A monograph, B. B. Namsaraev (Ed.), Buryat State University Publishers, Ulan-Ude, 2009. (In Russ.).

27 Cypionka H., Smock A. M., Bottcher M. E., A combined pathway of sulfur compound disproportionation in *Desulfovibrio desulfuricans*, *FEMS Microbiol. Lett.*, 1998, Vol. 166, No. 2, P. 181–186.

28 Fry B., Gest H., Hayes J. M., $^{34}S/^{32}S$ fractionation in sulfur cycles catalyzed by anaerobic bacteria, *Appl. Environ. Microbiol.*, 1988, Vol. 54, No. 1, P. 250–256.

29 Zerkle A. L., Farquhar J., Johnston D. T., Cox R. P., Canfield D. E., Fractionation of multiple sulfur isotopes during phototrophic oxidation of sulfide and elemental sulfur by a green sulfur bacterium, *Geochim. Cosmochim. Acta*, 2009, Vol. 73, No. 2, P. 291–306.

30 Luther G. W., Pyrite synthesis via polysulfide compounds, *Geochim. Cosmochim. Acta*, 1991, Vol. 55, No. 10, P. 2839–2849.

31 Erdyneeva E. V., Radnagurueva A. A., Dunaevsky Ya. E., Belkova N. L., Namsaraev Z. B., Lavrentieva E. V., Aminopeptidase activity of haloalkalophilic bacteria of the genus *Halomonas* isolated from the soda-saline lakes in the Badain Jaran desert, *Microbiology*, 2018, Vol. 87, No. 4, P. 538–548.

32 Thamdrup B., Finster K., Hansen J. W., Bak F., Bacterial disproportionation of elemental sulfur coupled to chemical reduction of iron or manganese, *Appl. Environ. Microbiol.*, 1993, Vol. 59, No. 1, P. 101–108.