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GEOCHEMISTRY

Hydrogen Sulfide and Other Reduced Forms of Sulfur in Oxic Waters of Lake Doroninskoe, Eastern Transbaikalia

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Simultaneous occurrence of oxygen and hydrogen sulfide was established by hydrochemical investigations in the waters of the Black and Baltic seas at a depth of more than 50 m (c-layer) [1–3, 9, and others]. The most probable reason for the appearance of H_2S and other sulfur species with intermediate oxidation states (thiosulfates and sulfites) is sulfate reduction in situ, i.e., immediately in the c-layer. A great number of publications have been devoted to the problem of the formation of hydrosulfuric, especially underground, mineral waters [6, 11, and others]. However, the presence of H_2S in the oxic layer was reported only by few authors [8 and others], who believed that hydrogen sulfide can be supplied in part from bottom sediments. Data on other sulfur species (mainly, thiosulfates and sulfites) are rare [4]. The formation of suboxidized sulfur species (thiosulfates and sulfites) in waters during the oxidation of sulfide deposits has been studied in more detail [7].

The distribution of sulfur species in soda waters of Lake Doroninskoe has been studied since 2003. This work has been supplemented by determinations of oxygen since December 2005. The lake (4.5 km^2 in area and up to 6.5 m deep) is located at the bottom of the Mesozoic Chita–Ingoda intermountain depression in the Ingoda River basin, one of the sources of the Amur River. The lake is underlain by Early Cretaceous sandy–silty deposits intercalated with intermediate–basic effusive rocks. The bottom muddy sediments (up to 10 m thick) contain up to 0.4% iron sulfides [5]. The basin lacks drainage, and its water is characterized by high salinity due to evaporation.

Water was sampled from top to bottom using a plexiglas bathometer or peristaltic pump at two stations located in the central and coastal parts of the lake. Dissolved oxygen was determined by the conventional Ross–Winkler method using initial inflation of glass with CO_2. Thiosulfate and sulfite ions were determined by iodometric titration after precipitation of sulfides by a mixture of zinc sulfate and sodium carbonate: the ions were determined separately (after the removal of sulfites by formaldehyde) and jointly (based on the subtraction of thiosulfates). Macromeasurements of hydrosulfide ion in the bottom layer were carried out by the potentiometric method with preliminary fixation by an antioxidant buffer (a mixture of trilon B with ascorbic acid and caustic soda), while micromeasurements in the top layer were carried out by the photometric method using *NN'*-dimethyl-*p*-phenylenediamine. The sulfate ion was analyzed by the turbodimetric method in the form of $BaSO_4$. The content of elemental sulfur was not measured.

Lake Doroninskoe is classified as a meromictic basin showing a steady chemical stratification in the deepest water zone expressed in the two-layer distribution of salinity and major ions, which indicates the absence of significant turbulent mixing between water layers. Seasonal and perennial variations of salinity varied within 16–29 g/dm^3 in the top layer (depth up to 3.5–4.0 m) and only within 28–32.2 g/dm^3 in the bottom layer. The water in both layers has a chloride–carbonate composition.

Oxygen was established throughout the entire depth range in samples from the coastal station and only in the upper hydrochemical zone at the central station (table). The maximal concentrations (up to 2.86 mg/dm^3) were noted at a depth of 1.0 m in July. The shift of the maximum from the water table unambiguously suggests that O_2 is formed not only by diffusion from the atmosphere, but also by the biochemical process (photosynthesis). At the same time, vertical variations in the oxygen distribution could be related not only to its unequal biological production at different depths, but also to its uneven consumption. Oxygen shows the following seasonal variations: increase with the beginning of subice vegetation (February), complete consumption

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Oxygen and sulfur compounds (mg/dm^3) in the soda water of Lake Doroninskoe

Depth, m	pH	E_h, mV	O_2	HS^-	$S_2O_3^{2-}$	SO_3^{2-}	SO_4^{2-}
Central zone, Dec. 10, 2005							
0.0*	9.80	102	0.64	0.027	7.96	1.59	173
1.0	9.83	103	0.36	0.025	7.96	1.31	130
1.5	9.80	114	0.42	0.020	8.62	1.60	108
2.0	9.85	114	0.35	0.020	8.12	1.34	113
2.5	9.88	120	0.30	0.020	8.62	1.90	126
3.0	9.85	112	0.37	0.020	7.29	1.35	130
3.5	9.85	118	0.47	0.023	9.28	1.89	130
4.0	9.86	103	0.23	0.030	7.96	3.37	122
4.5	9.85	–13	0.00	0.064	13.26	3.37	122
5.0	9.80	–163	0.00	6.40	18.56	3.67	85
5.5	9.79	–252	0.00	16.08	18.56	4.17	86
6.0	9.83	–67	0.00	2.44	19.89	3.97	85
Coastal zone, Dec. 10, 2005							
0.0*	9.87	69	0.47	0.030	8.62	1.34	121
1.0	9.86	80	0.38	0.023	9.28	1.10	124
1.5	9.88	88	0.38	0.022	8.62	1.08	123
2.0	9.88	91	0.41	0.023	9.95	1.08	110
2.5	9.88	96	0.38	0.027	9.95	1.08	108
3.0	9.88	96	0.39	0.023	9.95	1.08	122
Central zone, Aug. 2, 2006							
0.0*	9.82	48	2.15	0.62	10.75	0.32	136
1.0	9.78	56	2.15	0.42	10.75	0.32	156
2.0	9.78	71	2.56	0.15	10.75	0.32	112
3.0	9.72	72	1.61	0.44	10.75	0.32	178
4.0	9.73	49	0.50	0.65	10.75	0.32	138
5.0	9.70	–23	0.00	23.42	24.19	1.54	120
6.0	9.68	–283	0.00	26.28	24.19	1.54	110
Coastal zone, Aug. 2, 2006							
0.0	9.76	46	2.03	0.42	10.75	0.32	135
1.0	9.75	0	2.03	0.38	10.75	0.32	96
2.0	9.75	44	1.84	0.30	10.75	0.32	75
3.0	9.69	14	1.72	0.30	10.75	0.32	136

Note: (*) In hole.

for biochemical processes at the moment of ice cover disruption (April), gradual concentration of oxygen in water up to the maximum concentration in summer, and decrease of its concentration up to February owing to the oxidation of organic matter dissolved in water. In addition to the presence of O_2, the oxic zone can be reliably identified by a positive redox potential. The underlying hydrosulfuric zone shows a steplike change of E_h into the negative region at practically constant pH values (table).

Owing to high pH values in the medium, hydrogen sulfide dissolved in water occurs in the dissociated form (mainly HS^-) year round in the oxic zone. Its content varied within 0.01–0.62 mg/dm^3 at the beginning of oxygen measurements and reached 3.86 mg/dm^3 during the observation period. The maximum H_2S contents were found at the water surface in summer due to intensification of the activity of sulfate-reducing bacteria in response to the increase in water temperature. This process is independent of the oxygen content in

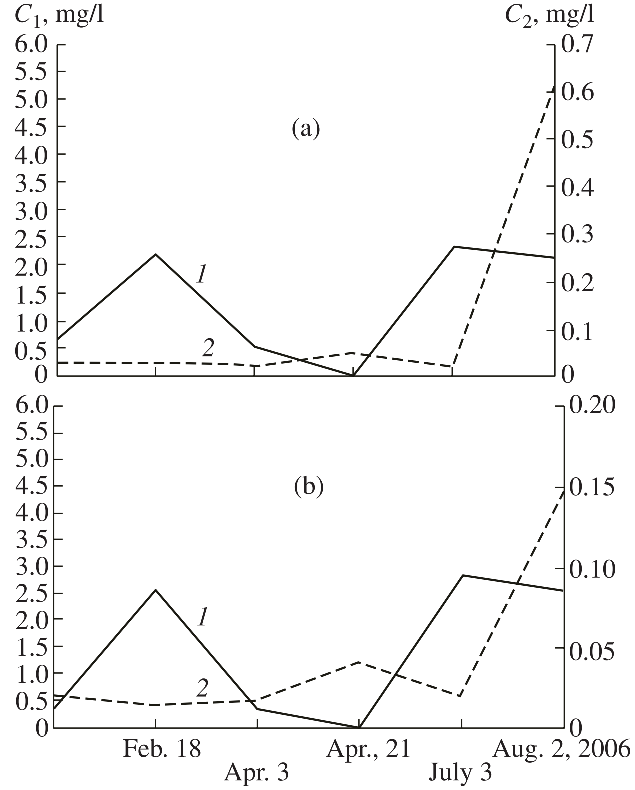

Fig. 1. Variations of (*1*) O_2 and (*2*) HS^- contents in water in the central zone of the lake (a) near the surface and (b) at a depth of 2.0 m.

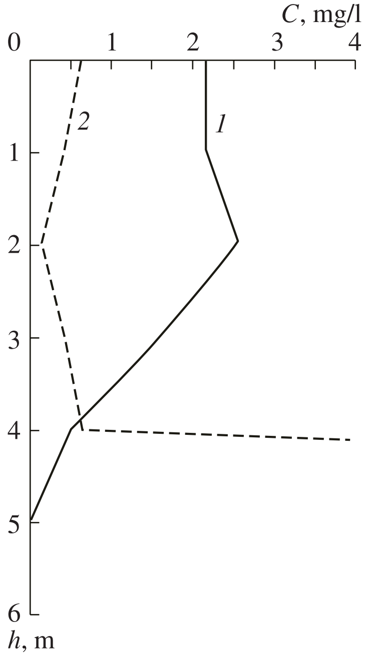

Fig. 2. Distribution of (*1*) O_2 and (*2*) HS^- in water at the central station on August 2, 2006.

the water. The HS^- and O_2 contents demonstrate mirror-symmetric distribution versus both time and depth (Figs. 1, 2). Previously, up to 4.2 mg/dm^3 H_2S were detected in the subsurface layer, but this layer was considered as an anoxic layer [4]. The decrease in the HS^- content from the water surface to deep zones was manifested most brightly at both stations in August (table) and definitely indicated its formation in the c-layer.

The H_2S content is higher under the anaerobic conditions of the lower hydrochemical zone, reaching maximum values of 50.2 mg/dm^3 in the bottom layer at the central station in July 2004. As in the oxic zone, the lower zone shows significant temporal variations of HS^-, which closely correlate with variations in the water temperature. Variations of the H_2S content can be influenced by the formation of iron sulfides in the water sequence and their accumulation in bottom sediments of the lake, as was found in the hydrosulfide zone of the Black Sea [10].

Thiosulfate and sulfite species of sulfur were established over the entire depth of the basin. Since December 2005, the $S_2O_3^{2-}$ content in the c-layer varied from 7.3 to 18.1 mg/dm^3; the SO_3^{2-} content, from 0.32 to 3.37 mg/dm^3. The maximum content of thiosulfate was noted at the coastal station in April, while the maximum content of sulfite was established at the central station in December. Variations in the $S_2O_3^{2-}$ content typically exhibit chaotic distribution along the vertical column, while the SO_3^{2-} content shows an increase with depth accompanied by a decrease of the redox potential. For the considered period, the concentrations of these ions reached 27.96 and 5.51 mg/dm^3, respectively, in the lower hydrochemical zone. They were also noted in the bottom layer in February. The annual cycle demonstrates consistent variations of the contents of hydrogen sulfide and thiosulfate (Fig. 3).

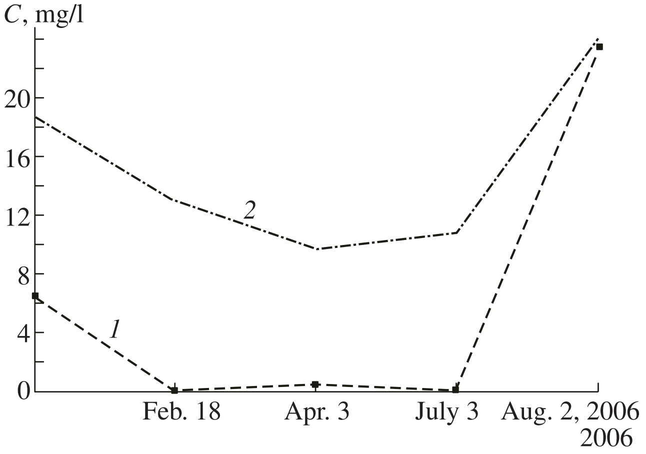

Fig. 3. Variations of (*1*) HS^- and (*2*) $S_2O_3^{2-}$ contents in water at a depth of 5.0 m (central station).

Thus, the results reported in this paper show that hydrogen sulfide and other reduced sulfur species can exist in oxic waters, which are in immediate contact with the atmosphere, under certain hydrogeochemical conditions. According to the conventional concept, the coexistence of geochemically incompatible oxygen and hydrogen sulfide is explained by the ratio of rates of atmospheric oxygen influx to water and the production of oxygen in the water, on the one hand, and by the consumption of oxygen during sulfate reduction by oxygen-tolerant bacteria discovered in 1980s [12], on the other hand.

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