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Isotopic Composition of Dissolved Carbonates Meromictic Soda Lake Doroninskoe (Eastern Transbaikalia, Russia)

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1 Introduction

Meromictic soda Lake Doroninskoe localized in the intermountain area, filled with continental sediments of the Mesozoic, in the upper basin of the river Amur. Coordinates of its location are N51°14'42" E112°14'40", 860 m altitude. Lake area refers to the arid zone of the steppe. Annual rainfall does not exceed 330 mm and almost twice lower evaporation from the surface of the water and soil. Lake is drainless with water area of about 5 km² and a depth of 6.5 m.

In the summer due to melting ice and rain upper oxygen zone desalted water column up to 12-15 g/l and drops to a depth of 3.0-4.5 m below it abruptly from the anaerobic zone. Salinity of the bottom layers varies, but does not go beyond 28-37 g/l. Density stratification of the water column provides stability anaerobic conditions. Chlorides, carbonates and sodium bicarbonates dominate in the chemical composition of the water in both layers. In the seasonal dynamics of growth of carbonate complex recorded in autumn and spring. Chlorine contents depend on climatic event associated with atmospheric precipitation and the formation of ice. Sulfates in lake water contain small amounts (up to 295 mg/l). Their contents depend on the intensity of bacterial processes, especially from sulfate reduction (Borzenko, Zamana, 2011). In the lower layer the content of hydrogen sulfide, which is due to the high alkalinity of the medium (table) is mostly a hydrosulfide ion to the latest data reaches 370 mg/l. Hydrogen sulfide at concentrations up to 4.2 mg/l is found in the upper oxygen-bearing layer (Zamana, Borzenko, 2007). In anoxic layer installed elemental sulfur (Zamana, Borzenko, 2011) that demonstrates the simultaneously occurring there in oxidation and reduction processes with sulfur disproportionation (Poser et al, 2013).

Table 1 Isotopic composition of carbon and oxygen dissolved carbonates Lake Doroninskoe.

Number sample	pH	HCO ₃ ⁻ , mg/l	CO ₃ ²⁻ , mg/l	δ ¹³ C _{PDB} , ‰	δ ¹⁸ O _{PDB} , ‰	δ ¹⁸ O _{SMOW} , ‰
DO-09-09-0	9.82	6771	5520	0.25	-4.96	25.8
DO-09-09-1	9.81	6954	5520	0.05	-5.25	24.9
DO-09-09-2	9.80	7198	5460	0.12	-5.25	26.1
DO-09-09-3	9.80	6039	6060	0.23	-5.05	25.7
DO-09-09-4	9.75	9516	6660	0.12	-4.67	25.5
DO-09-09-5	9.72	8052	6120	-0.17	-5.83	25.5
DO-09-09-6	9.78	8967	6360	0.27	-4.96	25.8
DO-10-08-1	10.15	4209	4440	1.47	-4.47	26.30
DO-10-08-2	10.15	4209	4440	1.10	-5.00	25.76
DO-10-08-3	10.07	7015	8100	1.07	-5.20	25.55
DO-10-08-4	10.05	8052	8160	1.38	-4.85	25.91
DO-10-08-5	10.04	8540	8280	1.23	-4.59	26.18
DO-11-06-0	9.93	2928	4560	0.24	-6.44	24.27
DO-11-06-1	9.93	2928	4560	0.18	-6.57	24.14
DO-11-06-2	10.02	3538	4920	0.04	-7.03	23.66
DO-11-06-3	9.94	7564	7260	0.52	-7.37	23.31
DO-11-06-4	9.91	8296	8100	0.75	-7.15	23.54
DO-11-06-5	9.88	8357	8220	0.64	-7.01	23.68
DO-12-4-0	9.81	8784	8880	1.6	-2.34	28.5
DO-12-4-1	9.81	9028	9000	1.5	-2.43	28.4
DO-12-4-2	9.82	8906	8880	1.4	-2.43	28.4
DO-12-4-3	9.82	9028	9000	1.5	-2.43	28.4
DO-12-4-4	9.83	8784	9120	1.4	-2.53	28.3
DO-12-4-5	9.82	8906	9000	0.6	-3.50	27.3
DO-12-08-0	9.86	5246	4920	0.70	-5.44	25.3
DO-12-08-2	9.88	5368	4920	0.70	-5.54	25.2
DO-12-08-3	9.88	9516	9120	0.80	-4.67	26.1
DO-12-08-4	9.81	9394	8160	0.70	-4.18	26.6
DO-12-08-5	9.82	10126	8880	0.80	-3.21	27.6

Note: Digit in the sample: -10 – year (2010 etc), -08 – month, -1 – depth of sampling, m.

2 Isotopic composition of oxygen and carbon dissolved carbonates

The production and destruction processes in the lake are mostly run by microbial communities, among which are the strains of bacteria involved in the redox sulfur cycle (Gorlenko et al, 2010). Development in the lake of sulfate sulfur-oxidizing and chemo- and phototrophic microorganisms allows to transform not only a noticeable amount of sulfur, but also carbon. During bacterial activity only at the expense of sulfate in the bottom layer is formed to 56.8 mg/l per day HCO₃⁻. The relationship of sulfate

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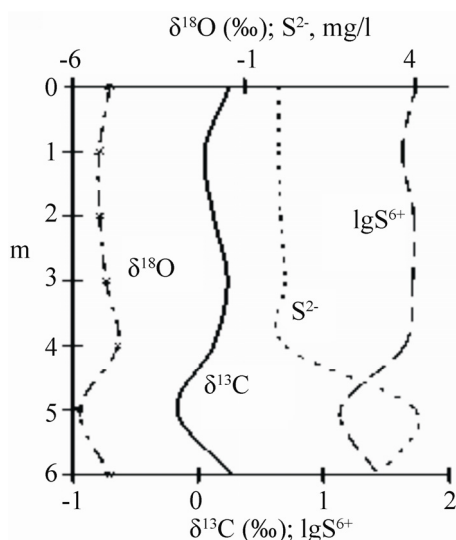


Fig. 1. Distribution of $\delta^{13}\text{C}_{\text{PDB}}$, $\delta^{18}\text{O}_{\text{PDB}}$ dissolved carbonates, sulfur concentrations of sulfates and hydrogen sulfide in the water column of the Lake Doroninskoe, September 2009.

reduction and formation of carbonates is clearly visible on the agreed distribution of the isotopic composition of carbon and form of sulfur in one of the sampling periods (Fig. 1). On the biogenic origin of the carbon in carbonates indicates some enrichment of its light isotope.

The obtained values $\delta^{13}\text{C}$ of bicarbonate and carbonate water column range from -0.17 to 1.60 ‰, which corresponds to the composition of carbonates deposited in seawater (Galimov, 1968). In relation to atmospheric CO_2 ($\delta^{13}\text{C}_{\text{PDB}} -5.0$ to -8.0 ‰), with coefficients of fractionation in the system carbon dioxide–the bicarbonates and carbonates of 1.014 and 1.012 respectively $\delta^{13}\text{C}$ values at least 3.4 ‰ richer light isotope compared to the equilibrium. It also suggests the involvement of biogenic carbon in the formation of carbonates dissolved in saline lakes.

Seasonal variations of the isotopic composition of carbon and oxygen carbonates expressed clearly (Fig. 2), with the difference largely due to variations in oxygen isotope ratios. After freeze-up (June) oxygen carbonates lightest, in August and September points on the diagram occupy an intermediate position, and by the end of the period freezing oxygen carbonates heaviest. Also mean values $\delta^{13}\text{C}$ change, but with a smaller amplitude. One reason may be a change of mineral equilibrium and composition of minerals produced, including those due to changes in temperature of the water column.

In one of the periods of testing clearly showed different dependence of both the isotopic ratios of the value $K = \text{CO}_3^{2-}/\text{HCO}_3^-$ (Fig. 3). The composition of the oxygen in the upper layer at a value of 1.39 – 1.56 K was heavier, while the heavier carbon structure is marked in the lower layer at K 0.96 – 0.98 . We explain the reasons for these

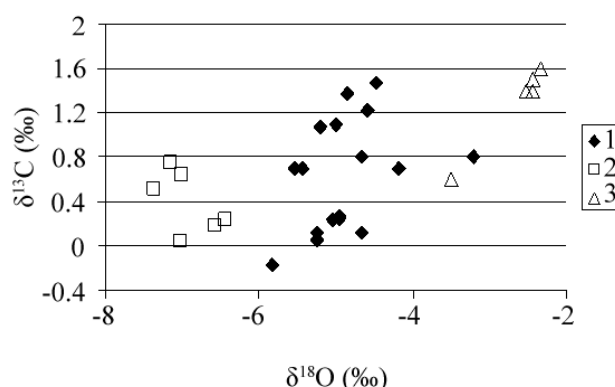


Fig. 2. Depending on the isotopic composition of oxygen and carbon: 1 - August-September, 2 - June, 3 - April.

opposite dependencies as follows. Formation of ions HCO_3^- and CO_3^{2-} occurs as a result of the hydrolysis reaction $\text{OH}^- + \text{CO}_2 \rightarrow \text{HCO}_3^-$. Because the water in the upper layer at this time the heavier oxygen due melted ice OH -group is also enriched O -18 isotope. At the same time the prevalence of CO_3^{2-} above HCO_3^- indicate greater fractionation his first of these ions. Enrichment of isotope $\delta^{13}\text{C}$ carbonates in the lower layer can be explained by an increase the bicarbonate proportion in sum of carbonic acid dissociate in which carbon higher fractionation coefficient compared with CO_3^{2-} .

Thus, marked seasonal and interannual variations of the carbon and oxygen isotopic composition of carbonates dissolved in the water column soda lake was revealed. Their causes are multifactorial, as well as the nature of the formation of soda brine.

Key words: Soda lake, dissolved carbonates, sulfate reduction, hydrogen sulfide, isotopic composition, carbon, oxygen.

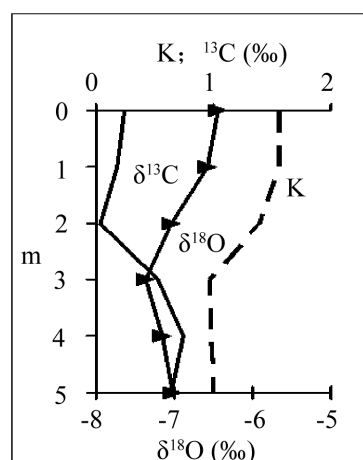


Fig. 3. Change in the isotopic composition of carbonates and the value K at a depth of sampling in June 2011.

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