



## Background composition of pore waters in Lake Baikal bottom sediments



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### ABSTRACT

Bottom sediments were studied from 10 central sites within the pelagic zone of the three basins of Lake Baikal, and 16 sites in other regions of the lake. The composition of pore waters in the first two meters of the sedimentary cover was analyzed at 1–3 cm intervals. It was established that the salt composition of pore waters in the sediments was uniform across the entire lake. Background concentrations of each ion in the pore waters was determined from equations using concentration data profiles obtained from all sites of the three lake basins (1250 samples at 26 sites within the entire lake). Similar to the lake waters, background pore waters of Lake Baikal were dominated by calcium bicarbonate with low mineralization. The total concentration of ions in pore waters increased with depth during diagenetic transformations as did the concentrations of bicarbonate and calcium ions. Biogeochemical processes that affect the chemical composition of pore water in Lake Baikal sediments are discussed.

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### Introduction

At present, many studies are focused on the subaquatic discharge of oil, gas and deep waters occurring at the bottom of Lake Baikal (Matveeva et al., 2003; Klerkx et al., 2003; Granina et al., 2001, 2007; Zemskaia et al., 2010, 2015; Minami et al., 2010; Pogodaeva et al., 2013). However, there are very few data on the background composition of pore waters in the bottom sediments of Lake Baikal.

Lake Baikal, the world's largest freshwater body, is situated in Central Asia. It was formed as a result of intracontinental rifting (Mats et al., 2001). The basin, with a maximal depth of 1642 m, is situated in the center of the tectonically active rift zone and is filled with sediments (up to 7.5 km thick), the most ancient of which are approximately of Oligocene age (Hutchinson et al., 1992). The lake is morphologically divided into three deepwater basins (Southern Baikal, Central Baikal, and Northern Baikal), which are separated from one another by two underwater elevations: the Buguldeika-Selenga Isthmus and the Academicheskyy Ridge (Atlas of Lake Baikal, 1993).

The water column of Lake Baikal is an inertial system. It takes Baikal tributaries approximately 400 years to completely renew the lake waters. The time necessary for the surface waters to penetrate into the water column center (i.e., to a depth of 300 m from the surface or 100 m from the bottom) is approximately one decade (Weiss et al., 1991). Horizontal

water exchange is caused by cyclonic macrocirculations in all layers within each basin. Moreover, compensated water exchange occurs between neighboring basins (Shimaraev et al., 1995, 1996). Compared to the waters of shallow fresh lakes, each basin of Lake Baikal has an ion composition that is stable in time and space (Falkner et al., 1991; Grachev et al., 2004). A large amount of oxygen (9.6–12.8 mg/L) is observed at all depths of the lake, including the bottom water (Shimaraev et al., 1996; Killworth et al., 1996). Oxygen also penetrates into the bottom sediments, and a layer of oxidized sediment covers the entire lake bottom (Atlas of Lake Baikal, 1993).

The sediments in the three deepwater basins of Southern, Central and Northern Baikal have identical chemical composition as a result of the homogenization of fine fractions of incoming terrigenous material carried by steady currents (Gvozdkov, 1998). There are very few data on the composition of the liquid phase (pore water) of bottom sediments of Lake Baikal. Moreover, these data were mostly collected in anomalous areas and the Selenga River delta. According to these data, the pore waters of bottom sediments show heterogeneity in their chemical composition within the lake bottom area and are bicarbonate-sulfate, sulfate and chloride waters (Mizandrontsev, 1975; Granina et al., 2001, 2007).

This paper presents the results of a study on the background chemical composition of pore waters from bottom sediments in Lake Baikal to determine the extent of variability in pore water composition in this great lake. Equations of chemical composition variation as a function of sediment depth are also inferred from the obtained data to examine diagenetic changes with depth.

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**Material and methods**

*Sampling*

Bottom sediments were sampled from areas with regular sedimentation rates within the pelagic zones of the three basins of Lake Baikal (Fig. 1, Table 1), during expeditions between 2003 and 2006. Four cores ranging from 45 to 200 cm in length were collected in Southern Baikal (up to depth of 1480 m) at sites St2GC 2003, St97GC 2003, St1GC 2005, and St1BC 2005. Cores of 100 and 200 cm length were sampled in Central Baikal (up to 1600 m) at sites St81GC 2003 and StGC16 2006, respectively. In Northern Baikal, a 340 cm core was retrieved from site St12GC 2005 (depth of 940 m), and three benthic cores ranging in length from 16 to 40 cm were sampled from sites St12BC 2005, St12BC 2003, and St14BC 2003 (depths > 800 m).

Sediments were obtained using a gravity corer (GC) made by researchers from the Limnological Institute of the Siberian Branch of the Russian Academy of Sciences (LIN SB RAS). The 500–600 kg GC was 3 to 5 m long with an outer steel tube 128 mm in diameter and a 100 mm diameter plastic liner. The tubes had an upper valve and a leaf-type catcher to hold the core inside. Upon retrieval, the core-catcher cut the lower part of the core and the leaves closed tightly around the sediment core. The valve in the upper part of the corer also closed to

prevent bottom water percolation inside the liner, thus protecting the core surface from washing out. Sediments and bottom water above the sediments were also sampled with a benthic corer (BC) (100 mm in diameter, 1 m long).

In the summer expedition of 2009, on board the deepwater submersible “MIR”, sediments were collected throughout Lake Baikal (16 sites (Fig. 1, Table 1)) with a 30 cm long sealed corer. This sampling method provided the least disturbance to the uppermost sediment layer, allowing for sampling of the bottom water directly above the sediment.

To prevent contact with oxygen, all sediment cores were placed within an argon glove box onboard the ship immediately after coring. The sediment cores were opened and treated under an argon (O<sub>2</sub>-free) atmosphere using plastic disposable utensils. The middle section of the core cross-section was selected for analysis. Each centimeter of sediment was analyzed in the short cores, whereas the long cores were analyzed at 2–3 cm or 5–10 cm intervals. Pore waters were immediately extracted onboard the ship by centrifuging the sample for 20 min at 8000 rpm. Microparticles were separated from the pore water by subsequent ultracentrifugation (10 min, 14,000 rpm). The centrifuge tubes were opened anaerobically; the solutions were filtered with disposable syringes through a 0.20 μm filter (cellulose acetate, Vladisart, Russia) and then injected into chromatography tubes under

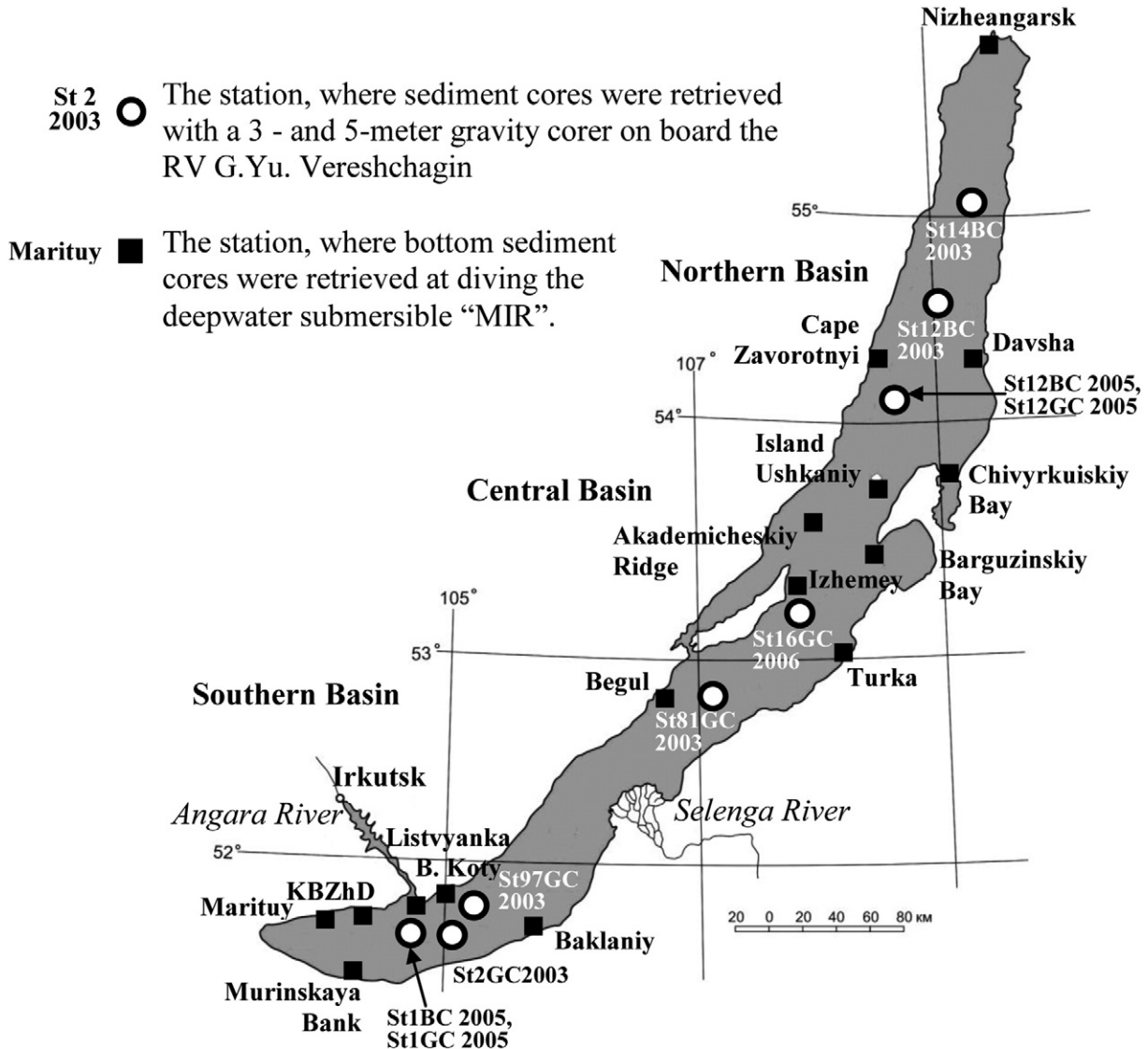


Fig. 1. Schematic map of the locality of sampling stations.

**Table 1**  
Geographic location, water depth, and recovered core length for each site.

Site	Core no.	Latitude	Longitude	Water depth (m)	Core length (cm)	
Southern Baikal	St2GC 2003	51°42.0247'N	105°01.8534'E	1483	50	
	St97GC 2003	51°50.5111'N	105°03.7438'E	1475	140	
	St1GC 2005	51°42.1516'N	104°58.7340'E	1446	200	
	St1BC 2005	51°42.1185'N	104°58.7964'E	1442	45	
	Baklaniy	51°32.19'N	105°56.64'E	475	30	
	Murinskaya Bank	51°31.03'N	104°33.66'E	1025	30	
	Marituy	51°44.54'N	104°13.41'E	1400	30	
	KBZhD	51°48.95'N	104°43.20'E	1374	30	
	Listvyanka	51°50.52'N	104°58.91'E	1399	30	
	B. Koty	51°52.29'N	105°02.74'E	1030	30	
	Central Baikal	St81GC 2003	52°43.5615'N	107°06.7371'E	1511	100
		StGC16 2006	53°10.5732'N	107°46.5113'E	1608	200
		Begul	52°43.70'N	106°35.09'E	1100	30
Turka		52°56.33'N	108°00.87'E	780	30	
Izhemey		53°11.52'N	107°45.51'E	1608	30	
Barguzinskiy Bay		53°26.52'N	108°31.91'E	1214	30	
Akademicheskoy Ridge		53°32.69'N	108°00.17'E	490	30	
Is.Ushkaniy		53°53.68'N	108°37.22'E	685	30	
Civrykuiskiy Bay		53°52.01'N	109°07.34'E	505	30	
Northern Baikal		St12BC 2003	54°33.0713'N	109°05.8517'E	900	40
		St14BC 2003	55°08.8321'N	109°24.6609'E	880	25
	St12BC 2005	54°11.1547'N	108°43.4534'E	940	16	
	St12GC 2005	54°11.1681'N	108°43.5682'E	940	340	
	Cape Zavorotnyi	54°18.01'N	108°37.34'E	889	30	
	Davsha	54°19.55'N	109°24.95'E	350	30	
	Nizheangarsk	55°44.64'N	109°36.66'E	330	30	

an argon ( $O_2$ -free) atmosphere within an argon box. Contact with oxygen was eliminated during the pore waters separation and filtering.

#### Pore water chemical analysis

Pore water anion concentrations were measured onboard the ship immediately after preparation by means of liquid chromatography, on a Milichrom-2A chromatograph with a relative error of 5–10% (Baram et al., 1999). The most important advantage of this special Baikal water method is that it uses potassium hydrogen phthalate as an eluent, enabling  $SO_4^{2-}$ ,  $Cl^-$  and  $NO_3^-$  to be determined simultaneously, along with bicarbonate ( $HCO_3^-$ ) (Fig. 2). The detection limits are 0.1 mg/L for all anions. The measurement of one sampling point was accomplished in a maximum of 15 min.

The samples for cation analysis were stored in polystyrene vials pre-acidified with 50  $\mu$ L of ultrapure concentrated  $HNO_3$  and stored at 4 °C prior to analysis. Cation ( $Ca^{2+}$ ,  $Mg^{2+}$ ,  $Fe^{2+}$ ,  $Mn^{2+}$ ) concentrations were determined in the laboratory LIN SB RAS within a week by means of atomic absorption on an AAS-30 Carl Zeiss Jena spectrophotometer, as well as by flame emission methods (for  $Na^+$  and  $K^+$ ;

Fomin, 2000) with a relative error of 3–5%. The detection limits were 0.01 mg/L (for  $Na^+$ ,  $K^+$ ,  $Ca^{2+}$ , and  $Fe^{2+}$ ) and 0.001 mg/L (for  $Mg^{2+}$  and  $Mn^{2+}$ ).

The cation/anion balance was calculated in terms of R1 (%) by the following equation (Manual for Sampling and Chemical Analysis, 1999):

$$R1 = 100 * (\sum C - \sum A) / (\sum C + \sum A)$$

The ion balance discrepancy did not exceed 5–7%.

Nutrients ( $PO_4^{3-}$ ,  $NH_4^+$ ,  $NO_2^-$ ) and Si were determined onboard the ship immediately after preparation (within an argon glove box) using colorimetric methods (Fomin, 2000; Wetzel and Likens, 1991) with a relative error of <5%. The detection limits were 0.003, 0.05, 0.003, and 0.04 mg/L for  $PO_4^{3-}$ ,  $NH_4^+$ ,  $NO_2^-$  and Si, respectively. The pH was determined using standard method (Fomin, 2000).

All standard solutions were obtained from the Canto Chemical Company (Japan).

We note that the reliability of chemical analysis results, obtained with these methods and instruments, was repeatedly confirmed through participation in data quality control (QA/QC) as part of international programs (<http://www.qasac-americas.org/labic.html>; <http://www.acap.asia/~interlab/os/>; <http://www.nilu.no>; <http://kvina.niva.no/intercomparison2>). The data obtained largely deviate from true values by no >10–15%, indicating the high quality of personnel and reliability of results.

#### Additional analysis (methane)

For gas analysis, a headspace technique was applied, adapted for shipboard conditions (Bol'shakov and Egorov, 1987). A 5  $cm^3$  section of wet sediment was placed into a glass jar, 38  $cm^3$  in volume, with a screw cover and a rubber gasket. The sediment was flooded with distilled water, leaving 13  $cm^3$  of the jar volume free. A 24-h waiting period was used with periodic shaking of the jar to mix the water and gas phases and to establish phase equilibrium. For chromatographic analysis, 0.5 mL of the headspace gas was collected using a syringe running through a rubber gasket and a hole in the cover. Results were

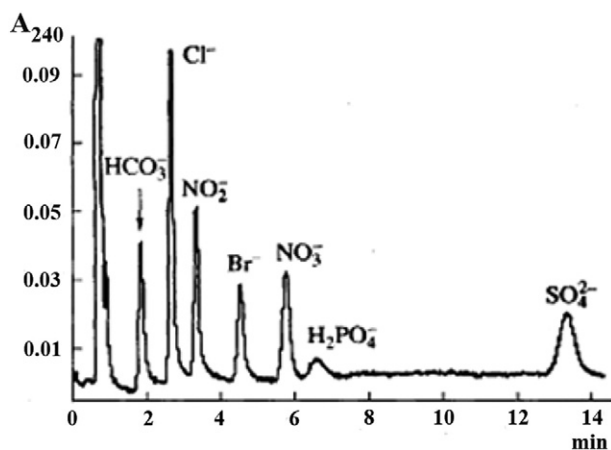


Fig. 2. A sample chromatogram of the mixture of anions (5  $\mu$ L at 10 mg/L).

recalculated according to the volume of wet sediment using Henry's law (Bol'shakov and Egorov, 1987). The Russian ECHO-PID chromatograph with a flame ionization detector was used. The limit of sensitivity for methane was 0.05 ppm. The detection limit in the sediment was

0.5  $\mu\text{L/L}$ . The total relative error of the determinations with this method (by parallel definitions) was 6.7%.

The water content was determined via the weight difference before and after freeze-drying.

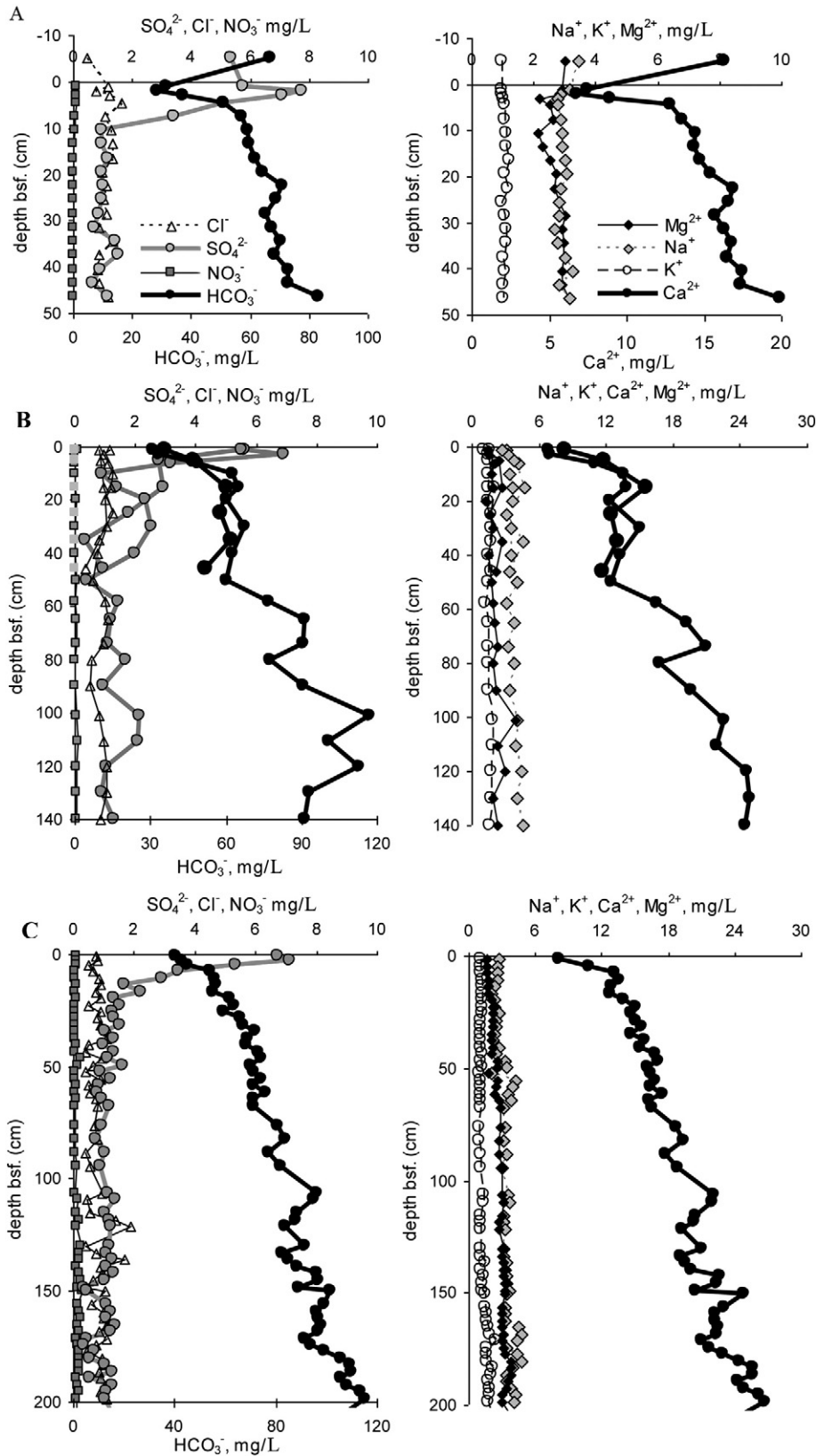


Fig. 3. Concentration vs. depth profiles of the main ions in pore waters of bottom sediments of Southern Baikal: A – St1BC 2005; B – St2BC 2003, St97GC 2003; C – St1GC 2005; depth as cm bsf (below lake floor).

### Saturation indexes

Saturation indexes (SI) of pore waters were calculated with respect to carbonates (aragonite, dolomite, calcite, rhodochrosite and siderite) using the formula:

$$SI = \lg \frac{[Me^{2+}] \cdot [CO_3^{2-}]}{K_{sp}}$$

where  $[Me^{2+}]$  and  $[CO_3^{2-}]$  are the ion activities ( $Me^{2+}$  are the cations incorporated in the crystal lattice of the carbonates) and  $K_{sp}$  the solubility product of carbonates. The ion activities are a function of their concentration in the pore water, and solution ionic strength at the measured in situ temperature (4 °C) and a pressure corresponding to a water depth. The  $CO_3^{2-}$  ion concentrations were calculated from the measured

$HCO_3^-$  concentrations using the measured pH. Crystallization of carbonates is possible when  $SI > 0$ . Calculations were performed using a specialized computer program PHREEQC-3.3.8.11728 (Parkhurst and Appelo, 2013).

### Experiments

The reversible absorption of pore water ions by iron hydroxides experiments were conducted according to the Bruevich method (Bruevich, 1978). The iron hydroxide paste was obtained by mixing solutions of  $FeCl_3$  and  $NaOH$ , and then washed with distilled water. The 90 mL natural Baikal water was mixed with:

- 1- 10 g fresh paste  $Fe(OH)_3$ ;
- 2- 10 g dry weight the unwashed oxidized natural Baikal sediment;
- 3- 10 g dry weight the washed oxidized natural Baikal sediment.

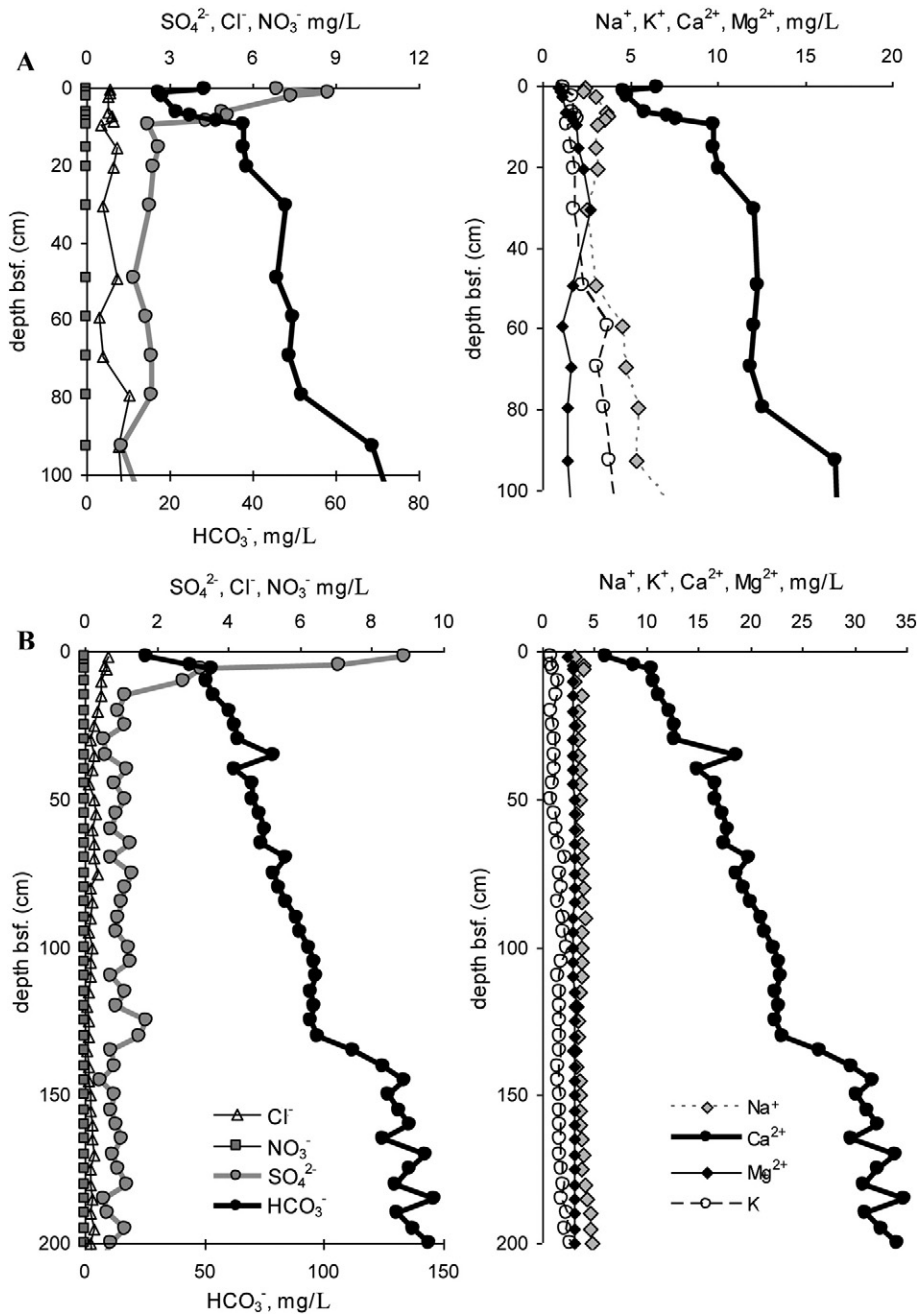
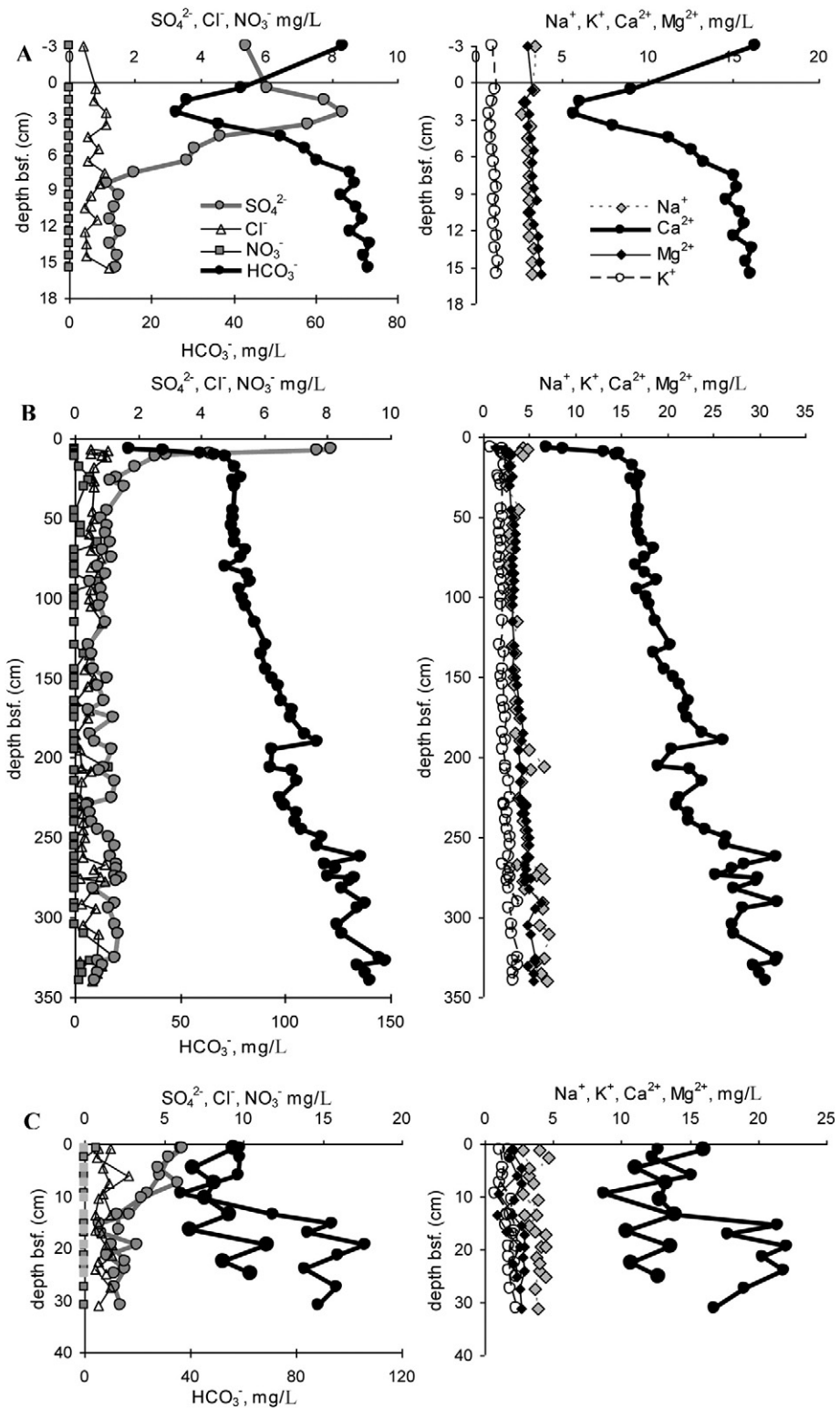


Fig. 4. Concentration vs depth profiles of the main ions in pore waters of bottom sediments of Central Baikal: A – St81GC 2003; B – St16GC 2005; depth as cm bsf (below lake floor).



**Fig. 5.** Concentration vs. depth profiles of the main ions in pore waters of bottom sediments of Northern Baikal: A – St12BC 2005; B – St12GC 2005; C – St12BC 2003 and St14BC 2003; depth as cm bsf (below lake floor).

The washed oxidized natural Baikal sediment was obtained by aging the sediment in distilled water for 10 days with daily change of distillate.

The anion, cation concentrations and pH were measured after water separation and filtering by standard method (Fomin, 2000).

## Results

### Lithology of bottom sediments

Bottom sediments sampled from deepwater sites in Southern, Central, and Northern Baikal were gray, homogeneous, diatomaceous silts,

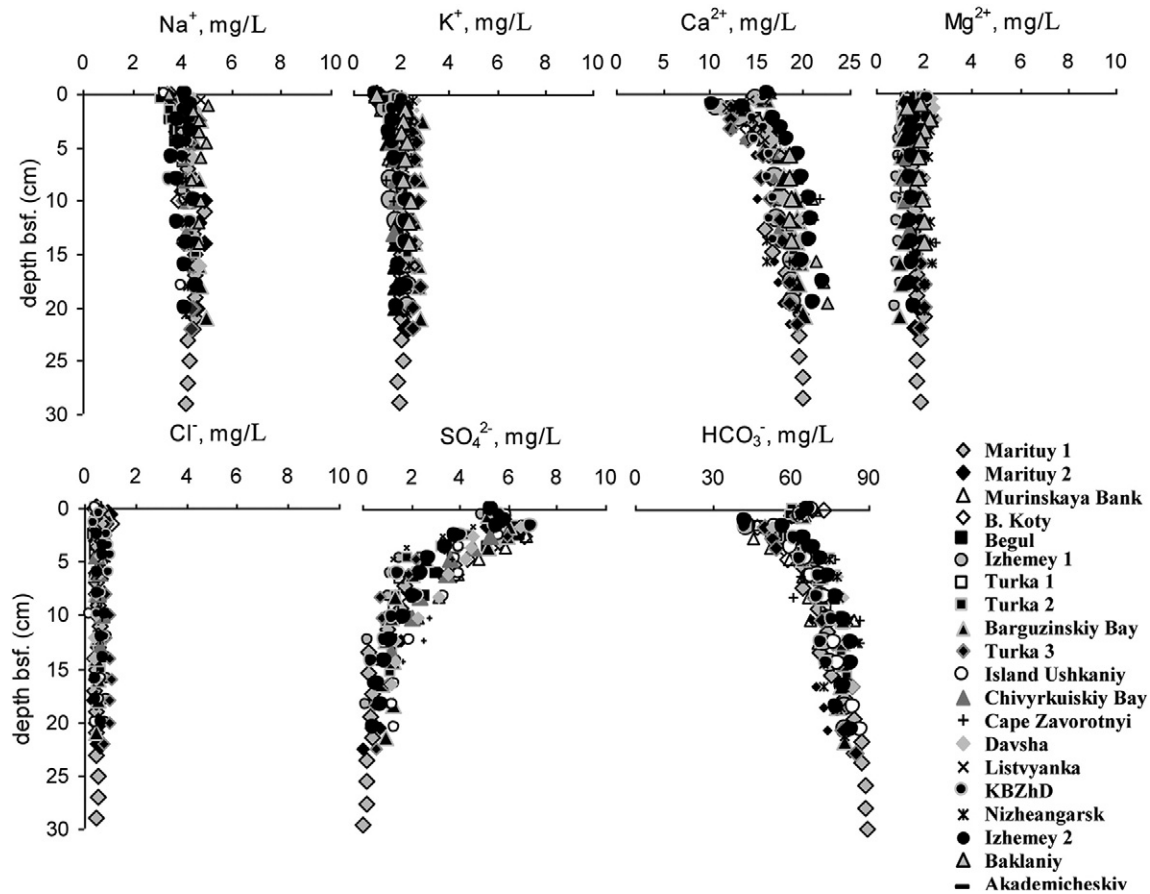


Fig. 6. Concentration vs. depth profiles of the main ions in pore waters of surface bottom sediments where bottom sediment cores were retrieved at diving the deepwater submersible "MIR".

with distinct horizontal layering (black hydrotroilite intercalations). Turbidites were either absent in the sediments or had minimal thickness (<5 cm). The uppermost layer of all cores (5–15 cm) was oxidized and of a reddish-yellow-brown color. Fe-Mn crusts were found on the boundary between the upper oxidized and lower reduced sediments. The position of the boundary was judged by color. Fe-Mn crusts buried within the reducing part of the sediments were present in some cores.

#### Chemical composition of pore waters

The chemical compositions of pore waters from deep bottom sediments of the pelagic zones in Southern, Central, and Northern Baikal are shown in Figs. 3, 4 and 5.

#### Southern Baikal

Bicarbonate ( $\text{HCO}_3^-$ ) was the major anion (98% of the total weight amount of anions) in the pore waters in both cores sampled from Southern Baikal. The concentration of bicarbonate ions in the surface oxidized layer of the sediments was 30 mg/L, which was half that of the lake and bottom water (Fig. 3). In the lower section of the oxidized sediment layer, at a depth of 8–10 cm, the concentration of bicarbonate ions reached values typical of Baikal water (66 mg/L) (Falkner et al., 1991), and its concentration increased with depth in the sediment layer to 120 mg/L. A high correlation was observed between the concentrations of bicarbonate and calcium ions throughout the entire depth of the cores (correlation coefficient  $r = 0.95$ ).

The concentration of  $\text{Ca}^{2+}$  in the oxidized layer was half that in the bottom water of the lake. The  $\text{Ca}^{2+}$  concentration increased at a depth of 8–10 cm in the oxidized layer to values close to those of Baikal water (16 mg/L). This concentration increased with depth in the

reduced layer to 25 mg/L (Fig. 3). The  $\text{HCO}_3^-/\text{Ca}^{2+}$  ratio remained close to that of the Baikal water: 4.2–4.5.

The maximal concentration of sulfate ions (7–8 mg/L) was recorded in the pore waters of the uppermost oxidized layer of the sediments (Fig. 3),

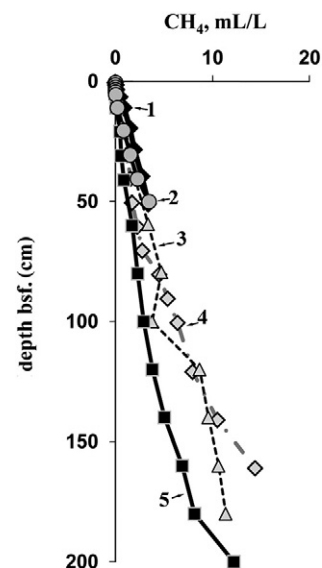


Fig. 7. Concentration vs. depth profiles of methane in the bottom sediments of the three basins of Lake Baikal: 1 – St1BC 2005 (Southern Baikal); 2 – St12BC 2005 (Northern Baikal); 3 – St16GC 2005 (Central Baikal); 4 – St1GC 2005 (Southern Baikal); 5 – St12GC 2005 (Northern Baikal).

while the concentration of sulfate ions in the bottom water of the lake was 5.3 mg/L. The concentration of  $\text{SO}_4^{2-}$  decreased to 1–2 mg/L on the boundary of the oxidized and reduced layers but then remained unchanged down to the lower horizons of the core. The concentrations of sulfate and bicarbonate ions showed a negative correlation ( $r = -0.70$ ). The concentration of chloride ions in the pore waters varied between 0.7 and 2 mg/L. No correlation was found between the distribution of chloride ions within the core and other anions or cations. The concentrations of  $\text{NH}_4^+$ ,  $\text{NO}_3^-$ , and  $\text{NO}_2^-$  in the pore water throughout the entire depth of the cores remained at 0.3, 0.1, and 0.01 mg/L, respectively. The concentrations of  $\text{PO}_4^{3-}$  did not exceed 0.1 mg/L. The concentrations of  $\text{Na}^+$ ,  $\text{K}^+$ , and  $\text{Mg}^{2+}$  in the pore waters were similar to those in the Baikal water and changed insignificantly throughout each of the cores (Fig. 3).

According to the classification by Alekin (Alekin, 1970), and similar to the lake water, pore waters in Southern Baikal contained primarily calcium bicarbonate.

#### Central Baikal

Low concentrations of  $\text{HCO}_3^-$  (20–25 mg/L) were recorded in the pore waters of the uppermost-oxidized layer of sediment in Central Baikal.  $\text{HCO}_3^-$  concentrations abruptly increased to 40–50 mg/L at the boundary of the oxidized layer and then continued to increase with depth to 150 mg/L (Fig. 4). A positive correlation was observed between the content of  $\text{HCO}_3^-$  and  $\text{Ca}^{2+}$  ( $r = 0.91$ ).

As in Southern Baikal, elevated concentrations of sulfate ions (9 mg/L) were recorded in the pore waters of the uppermost-oxidized layer of sediment. Similarly, the sulfate ion concentrations also decreased to 1–2 mg/L close to the lower boundary of the oxidized layer, at a depth of 10–13 cm. The content of chloride ions (0.5–1 mg/L) changed insignificantly along the entire 2 m core. The concentrations of  $\text{NH}_4^+$ ,  $\text{NO}_3^-$ , and  $\text{NO}_2^-$  in the pore water, throughout the depth of all cores, did not exceed 0.4, 0.1, and 0.01 mg/L, respectively. The concentrations of  $\text{PO}_4^{3-}$  were 0.1 mg/L. The  $\text{K}^+$ ,  $\text{Mg}^{2+}$ , and  $\text{Na}^+$  content in the pore waters changed insignificantly throughout the entire depth of the sediment profile (Fig. 4).

#### Northern Baikal

Pore waters of sediments sampled in Northern Baikal were also characterized as being rich in calcium bicarbonate. Low concentrations of  $\text{HCO}_3^-$  (Fig. 5) recorded in the surface oxidized layer of the sediment increased with depth in the reduced layer to 150 mg/L. As in Southern Baikal, elevated concentrations of sulfate ions were recorded in the surface oxidized layer and decreased with depth to 2 mg/L (Fig. 5). The content of chloride ions varied along the entire 3 m core by approximately 1 mg/L.

The ion concentrations of  $\text{NH}_4^+$ ,  $\text{NO}_3^-$ , and  $\text{NO}_2^-$  were close to the detection limit in the pore waters and did not exceed 0.2, 0.1, and 0.01 mg/L, respectively. The concentration of  $\text{PO}_4^{3-}$  was 0.1 mg/L.

As in the two other basins, in Northern Baikal a positive correlation ( $r = 0.96$ ) was observed between concentrations of  $\text{HCO}_3^-$  and  $\text{Ca}^{2+}$ . The  $\text{HCO}_3^-/\text{Ca}^{2+}$  ratio changed insignificantly and was similar to that of the Baikal water, with a value of 4.3.

The concentrations of  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$  also changed insignificantly, increasing only at the bottom of the 3 m core (Fig. 5).

Using a manned submersible “MIR” (scientific program “MIRs at Lake Baikal-2009”), surface sediments were sampled at 16 deepwater stations throughout the most diverse areas of the lake (Fig. 1). The chemical composition of pore waters in these sediments and the rate of change with increasing depth corresponded to the data obtained from the deepwater sites of the pelagic zones (Fig. 6).

The methane concentration profiles of deep bottom sediments of the pelagic zones in Southern, Central, and Northern Baikal are shown in Fig. 7. The methane concentrations in the sediments increased almost linearly with depth up to 10–12 mL/L.

#### Discussion

Similar chemical compositions were measured in the pore waters of bottom sediments from 10 central sites in the three basins of Lake Baikal and 16 sites from other areas of the lake. The concentration profiles are of the same type at each site in the three basins (Fig. 8).

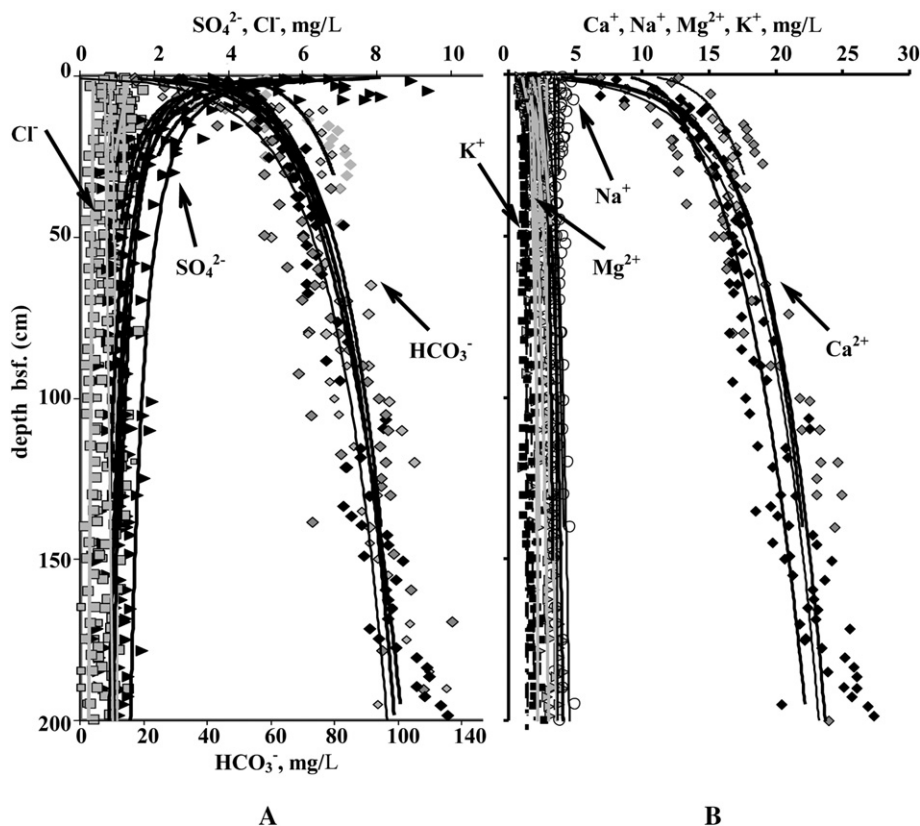


Fig. 8. Trends in concentration vs. depth profiles of the main ions in pore waters at each site of the three basins of Lake Baikal: A – anions, B – cations.



In deepwater areas with more uniform sedimentation rates of the three basins of Lake Baikal, the pore waters have a similar chemical composition. This is attributed to stable chemical parameters of the water column in both time and space, and a similar chemical composition of the sediment solid phase in all three basins.

In the pore waters of the three basins of the lake, as in the lake water,  $\text{HCO}_3^-$  is the major anion (Fig. 9). A high correlation ( $r = 0.95$ ) is observed between concentrations of bicarbonate ions and calcium, which is the major cation in the pore waters (Fig. 9).

Common patterns of variation in the chemical composition of pore waters were found at some sampling sites, for example, in Southern Baikal at St97GC 2003 (Fig. 10) and Northern Baikal at St12BC 2005 (Fig. 11). Variations in chemical composition across the *water – oxidized sediment – reduced sediment* boundaries are clearly seen in Fig. 11, which is representative of sediment data obtained by a benthic corer. Preservation of the surface layer of sediment and bottom water above were achieved when using the benthic corer.

As mentioned above, the major anion in the pore waters is  $\text{HCO}_3^-$ . The  $\text{HCO}_3^-$  concentrations are two- to three-times lower in the uppermost-oxidized sediment layer than in the bottom water of the lake. The  $\text{Ca}^{2+}$  profile has the same shape. One would assume that precipitation of calcium carbonate occurs near the sediment surface;

however, we found no trace of calcium carbonate in the sediments. The diatomaceous (40%–60% biogenic  $\text{SiO}_2$  (Mizandrontsev, 1975; Vykhristyuk, 1980; Fagel et al., 2005)) bottom sediments of Lake Baikal are carbonate-free due to the low alkalinity and calcium content of the lake water (Knyazeva, 1954). The theoretical possibility of carbonate crystallization is established based on saturation indexes. We calculated saturation indexes (SI) of pore waters with respect to carbonates (aragonite, dolomite, calcite, rhodochrosite and siderite) using all our data and a specialized computer program PHREEQC-3.3.8.11728 (Parkhurst and Appelo, 2013). Negative SI values (Fig. 12) indicate that the formation of carbonates in background Lake Baikal sediments is impossible. But the uppermost-oxidized sediments contain about 10% of an amorphous hydroxide of Fe(III) (Gvozdkov, 1998). Iron hydroxides have huge sorption surface (about  $600 \text{ m}^2 \text{ g}^{-1}$ ) and absorb both positive and negative ions from solutions (Schwertmann et al., 1984).

The decrease of alkalinity is likely due to the reversible absorption of pore water ions by iron hydroxides. Bruevich (1978) came to similar conclusions regarding alkaline reserves of ground solutions in the deep regions of the World's Oceans. We conducted experiments according to the Bruevich method (Bruevich, 1978) whereby iron hydroxide paste was obtained by mixing solutions of  $\text{FeCl}_3$  and  $\text{NaOH}$ , and then

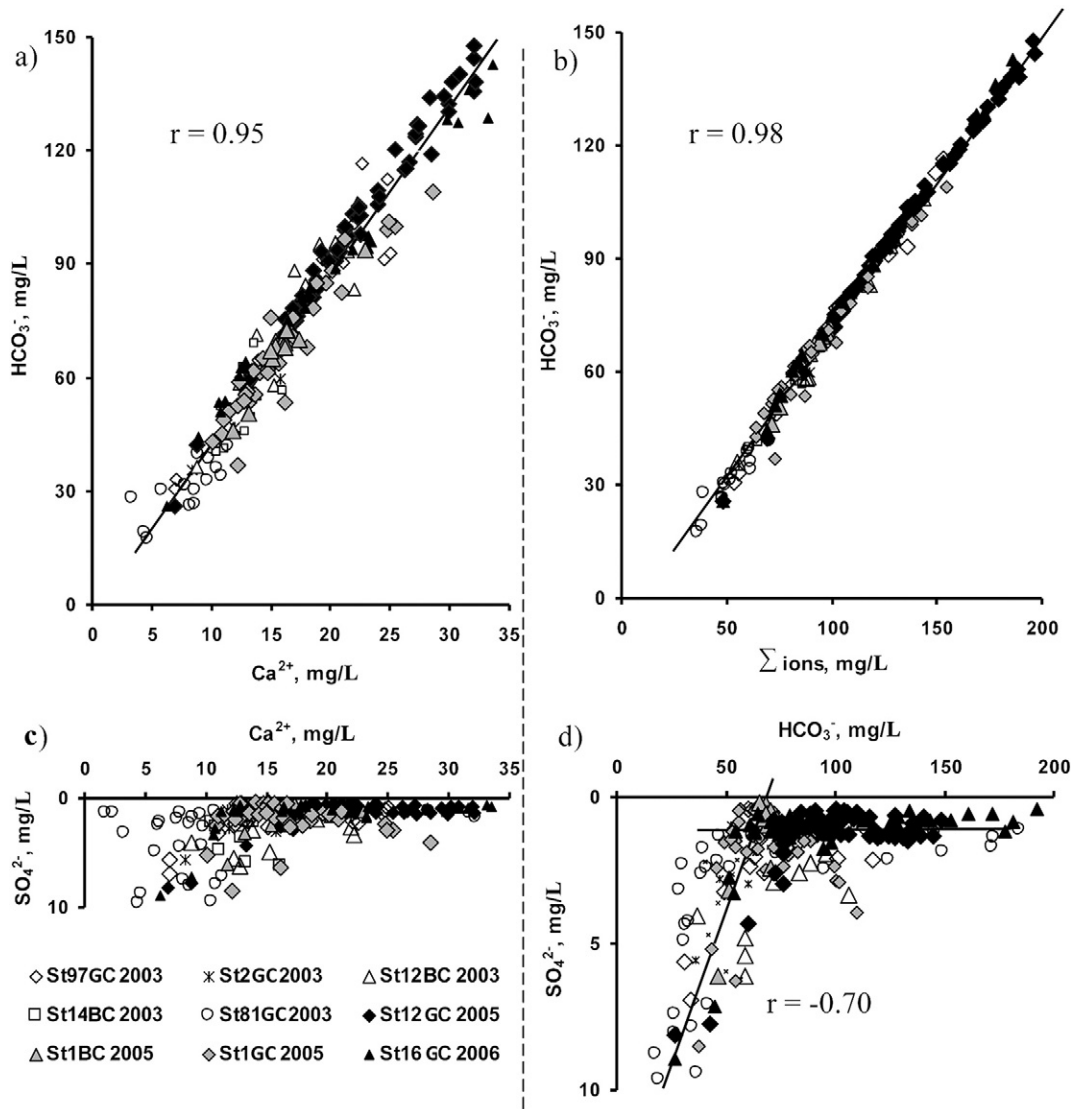
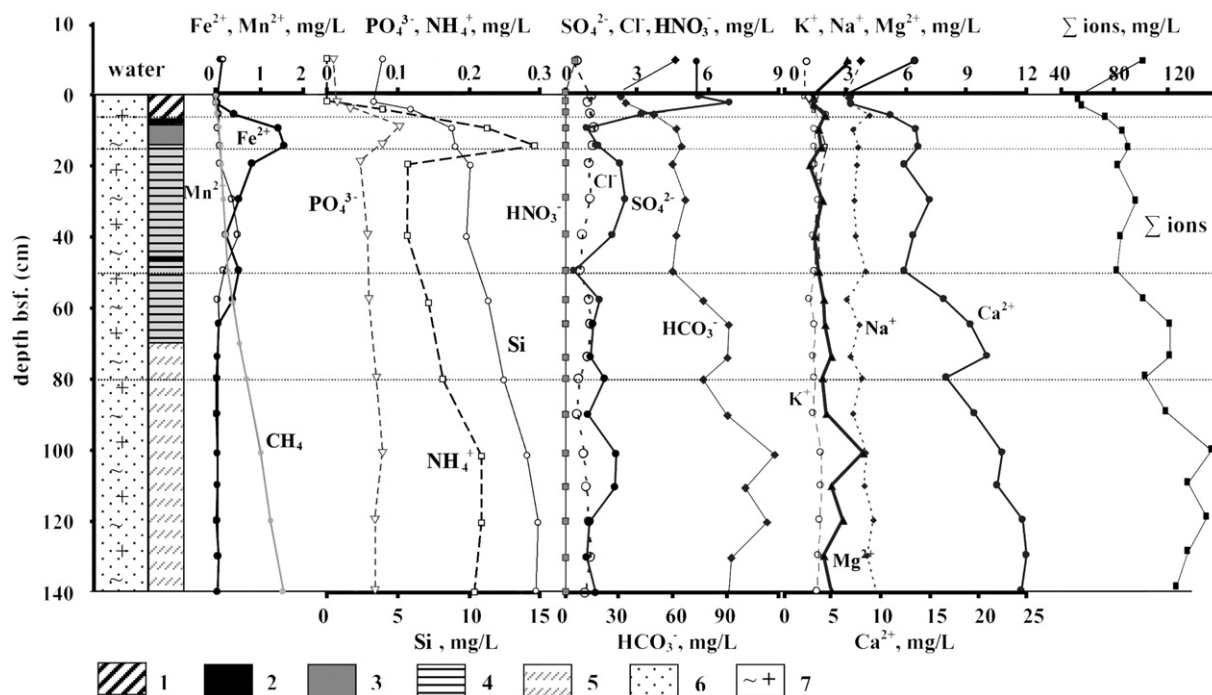


Fig. 9. Dependency graphs: a - calcium content of the content of bicarbonate ions and sulfate ions, b - the overall ion concentration ( $\Sigma$  ions) of the content of bicarbonate ions, c - the content of sulfate ions on the content of calcium ions and d - the content of sulfate ions on the content of bicarbonate ions in the pore waters of sediments of the three basins of Lake Baikal.



1 – oxidized layer; 2 – Fe-Mn crusts; 3 – solid black hydrotroilite; 4 – layering, black hydrotroilite intercalations; 5 – hydrotroilite traces; 6 – aleuropilite; 7 – diatomaceous silts.

Fig. 10. Chemical composition of pore waters vs. depth of sediments and mineral phases of Southern Baikal (S97GC 2003).

washed with distilled water. These experiments demonstrated the significant absorption of  $\text{HCO}_3^-$  on the iron (III) hydroxide. The treatment of Baikal water with fresh  $\text{Fe}(\text{OH})_3$  caused complete removal of  $\text{HCO}_3^-$ ,  $\text{Ca}^{2+}$ , and  $\text{Mg}^{2+}$  from the solution and decreased the concentrations of  $\text{SO}_4^{2-}$ ,  $\text{Na}^+$ , and  $\text{K}^+$  by factors of 3, 1.3, and 1.3, respectively. The contact of Baikal water with the unwashed oxidized sediments decreased the concentrations of  $\text{HCO}_3^-$ ,  $\text{Ca}^{2+}$ , and  $\text{Mg}^{2+}$  by a factor of 1.4, with a concurrent reduction of pH from 7.8 to 6.6 (Table 2). According to Bruevich (1978) mainly  $\text{CO}_3^{2-}$  ions are adsorbed in bicarbonate adsorption and the equivalent amount of  $\text{H}^+$  remains in solution and subsequently decreases the pH (Fig. 11). Accordingly, an equivalent amount of cations are adsorbed by iron hydroxides. Below the oxygen permeation zone the reduction process begins to develop (reduction of nitrate, sulfate, iron and manganese); pH increases (Fig. 11). The reduction of iron hydroxides contributes to desorption of ions, the concentrations of which increase and become equal to the concentrations of Baikal water near the boundary of the oxidized sediment – reduced sediment (Fig. 11). Further investigations are required for reliable determination of these processes.

The concentration of  $\text{HCO}_3^-$  increases in the reduced-sediment layer (Figs. 10, 11). Bicarbonates in pore waters are the direct product of the decomposition of buried organic matter (Mizandrontsev, 1990). Decomposition of organic matter is the driving force of early diagenesis and is described by the Redfield reaction (Redfield et al., 1963). The Redfield reaction shows production of bicarbonate, ammonia, phosphate and reduction of sulfate to sulfide during organic matter decomposition. Within freshwater sediments bicarbonate and methane are commonly produced with the molar ratio of 1:1 (Capone and Kiene, 1988; Reeburgh, 2007) that we observe within the Baikal bottom sediments (Fig. 13). Lake Baikal is a cold oligotrophic lake with low biological productivity and low contents of nutrient ions (0.48 mg/L ( $\text{NO}_3^-$ ), 0.05 mg/L ( $\text{PO}_4^{3-}$ )) in the water column (Weiss et al., 1991). Because the content of oxygen in the Lake Baikal water column is high (11 mg/L) (Weiss et al., 1991), the labile autochthonous organic matter and labile fraction of allochthonous organic matter is almost completely

mineralized in the water column and at the sediment–water interface. Only 13% of the total export organic matter from the epilimnion is finally buried in the sediment (Müller et al., 2005). According to Vykhristyuk (1980) and Afonina and Karabanov (2001), the buried organic matter is primarily humic acids and cellulose, much degraded remains of higher terrestrial plants and refractory phytoplankton organic matter, highly resistant to further degradation. The C/N ratio of the buried organic matter is high (16–50), while the content of organic nitrogen is very low (0.03–0.08%) and varies little with the depth of sediment due to high resistance to further degradation of persistent nitrogen-containing organic compounds (Vykhristyuk, 1980; Afonina and Karabanov, 2001). As a result, the sediment pore water concentrations of  $\text{NH}_4^+$ ,  $\text{NO}_3^-$ , and  $\text{NO}_2^-$  do not exceed 0.4, 0.1, and 0.01, respectively, and the typical C:N ratio for lacustrine sediments (10–12) is not observed.

The low concentrations of  $\text{PO}_4^{3-}$  (<0.1 mg/L) are attributed to the absorption of P onto iron (III) hydroxide. This is a well-known process during the oxidative diagenesis in Lake Baikal sediments (Müller et al., 2002; Fagel et al., 2005).

The content of sulfate ions in the bicarbonate fresh waters of Lake Baikal is not high (5.3 mg/L) (Falkner et al., 1991; Grachev et al., 2004). Low concentrations of sulfur (<0.2% (Lazo, 1980), 0.08% (Gvozdkov, 1998)) are recorded in the bottom sediments and low concentrations of sulfate ions are observed in pore waters. High-resolution chemical composition studies of pore waters (Fig. 11) revealed that higher concentrations of  $\text{SO}_4^{2-}$  (7–10 mg/L) are recorded in pore waters of the upper part of the oxidized-sediment layer than in bottom water of the lake. A probable source of this maximum is the decomposition of sulfur-containing organic matter and oxidation of sulfide compounds near the interface of the water and the oxidized sediment in aerobic conditions. The concentrations of  $\text{SO}_4^{2-}$  decreased by an order of magnitude at the boundary between the oxidized- and reduced-sediment layers and then retained this value down to the lower core horizons (Fig. 11). Sulfate-reducing bacteria are most abundant and show the largest activity at horizons where an abrupt decrease of sulfate ion concentration occurs (Namsaraev and Zemskaya, 2000; Pimenov et al., 2014). Namsaraev and Zemskaya

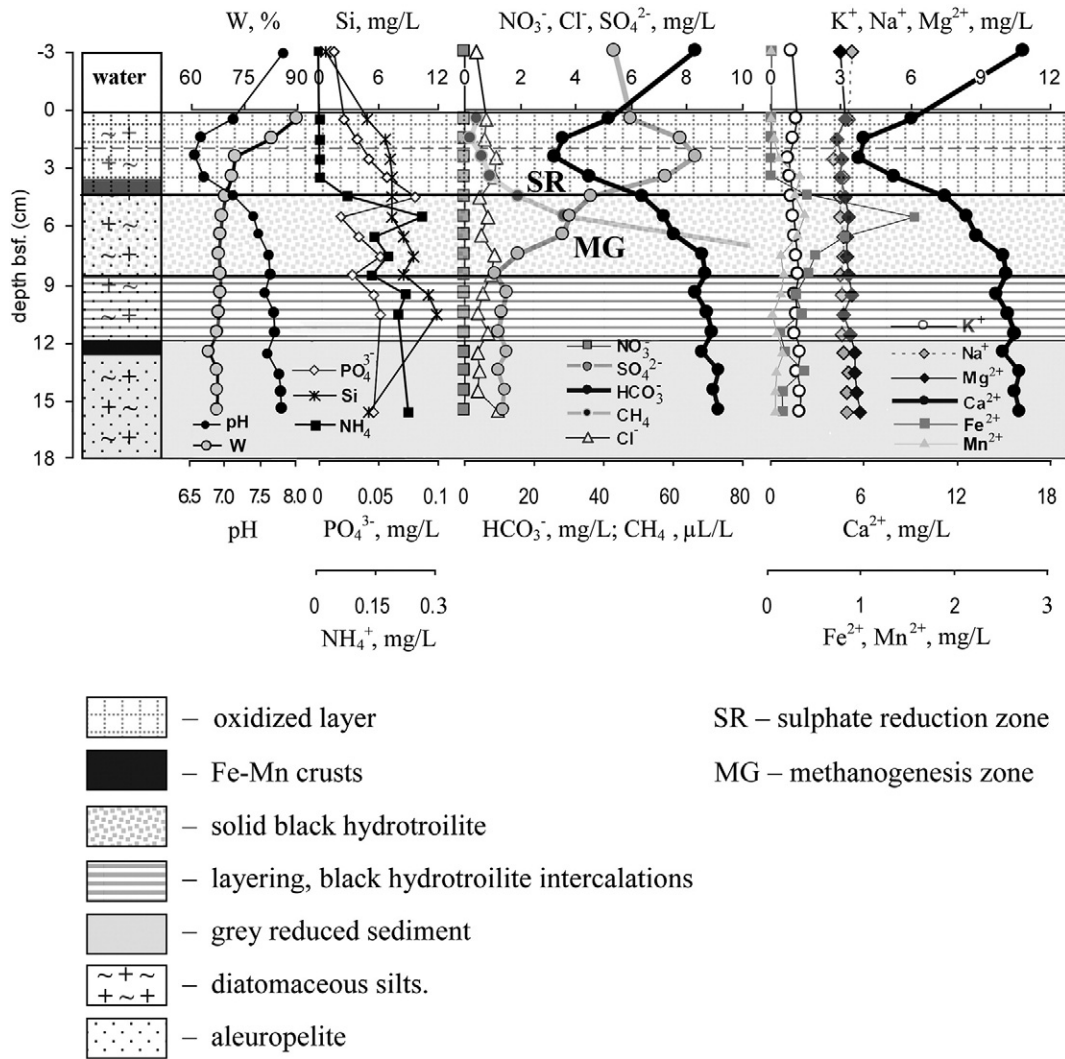


Fig. 11. Chemical composition of pore waters vs depth of sediments and mineral phases of Northern Baikal (St12BC 2005).

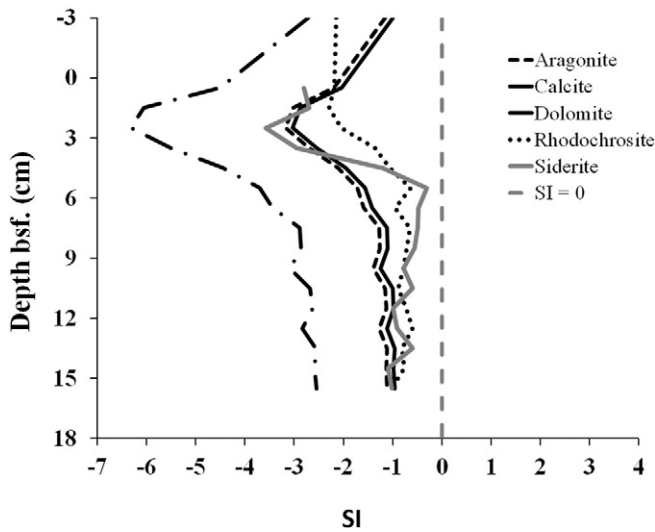


Fig. 12. Saturation indexes (SI) of pore waters of sediments of Northern Baikal (St12BC 2005) with respect to carbonates (aragonite, dolomite, calcite, rhodochrosite and siderite). SI equal to one or higher indicates saturation and likely crystallization of the mineral.

(2000) used radioisotope techniques to reliably demonstrate detectable sulfate reduction (SR) rates from 0.3 to 0.7 nmol/(dm<sup>3</sup> day) in the upper 15 cm of the sediments. Immunofluorescence analysis revealed the presence of *Desulfovibrio desulfuricans* and *Desulfotomaculum guttoideum* in the sediments (up to 3.3 × 10<sup>4</sup> cells/cm<sup>3</sup>) (Namsaraev and Zemskaya, 2000). In reduced sediments of seas and sulfate-rich lakes, sulfate-reducing bacteria are known to play a major role in organic matter mineralization (Jørgensen, 2006). In anaerobic horizons of freshwater basins, the biogeochemical activity of sulfate-reducing bacteria is

**Table 2**  
The decrease of the pH and concentrations of Baikal water ions (mg/L) in the interaction<sup>a</sup> with fresh Fe(OH)<sub>3</sub> and oxidized Baikal sediments.

Ion	pH	HCO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	Cl <sup>-</sup>	Na <sup>+</sup>	K <sup>+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>
Baikal water	7.8	66	5.5	0.4	3.6	0.9	16	3.0
The unwashed oxidized sediment	6.6	47	5.2	0.4	2.9	0.9	10	2.2
The washed <sup>b</sup> oxidized sediment	6.6	26	3.1	0.4	2.7	0.8	5.2	1.3
Fe(OH) <sub>3</sub> <sup>c</sup>	6.4	<0.01	1.7	0.3	2.2	0.7	<0.01	<0.01

<sup>a</sup> 90 mL (natural Baikal water) + 10 g dry weight (sediments or Fe(OH)<sub>3</sub>).  
<sup>b</sup> Aging the sediment in distilled water for 10 days with daily change of distillate.  
<sup>c</sup> Fresh Fe(OH)<sub>3</sub> was obtained by mixing solutions FeCl<sub>3</sub> and NaOH, and then water distilled washed (Bruevich, 1978).

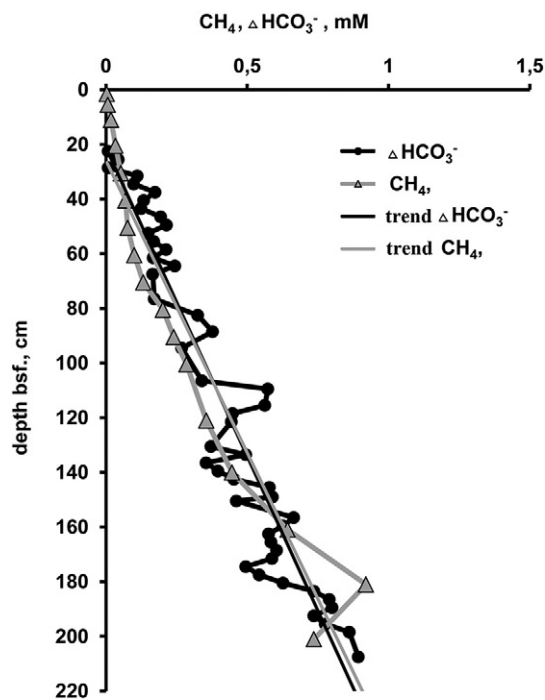


Fig. 13. Sediment depth profiles of increasing concentrations of methane and bicarbonate relative to Baikal water (Southern Baikal St1GC 2005).

limited by low concentrations of sulfate, where  $K_m$  for sulfate consumption varies from 5 to 30  $\mu\text{M}$  (Capone and Kiene, 1988). We detected incomplete sulfate reduction in freshwater sediments of Lake Baikal, which stopped at values ranging from 5 to 20  $\mu\text{M}$ . The most important factor affecting the intensity of sulfate reduction in sediments is the presence of easily digestible organic matter. The reactivity of the buried organic matter (Vykhristyuk, 1980), in spite of the high sediment content of organic carbon ( $\sim 2\% C_{\text{org}}$ ), due to its long exposure to oxic conditions, is very low in Lake Baikal sediments. Analysis of  $C_{\text{org}}$  consumption for sulfate reduction and  $\text{CH}_4$  formation (Namsaraev et al., 1995) indicated that methanogenic archaea usually played a major role in the terminal phase of organic matter decomposition in Lake Baikal sediments, while sulfate-reducing bacteria were actively involved in the degradation processes only in the narrow upper zone. The increased abundance and activity of methanogenic archaea, which compete for organic carbon and transform 99% of organic carbon into  $\text{CH}_4$ , is recorded down the sediment core (Namsaraev and Zemskaya, 2000; Zemskaya, 2007). According to the results of molecular methods methanogenic archaea are dominated in the subsurface sediments in some areas of Lake Baikal (Kadnikov et al., 2012). Fig. 11 shows that the zone of sulfate reduction is displaced by the zone of methane generation.

Interestingly, the sulfate persisted into the methanogenesis zone. We suggest that this is possible due to the absence of sulfate-reducing bacteria and anaerobic methanotrophic archaea in the reduced sediments of Lake Baikal, which in a consortium with sulfate-reducing bacteria are responsible for anaerobic methane oxidation (Kadnikov et al., 2012). In the methane-enriched Lake Baikal sediments, microorganisms other than sulfate reducers (e.g.,  $\text{Fe}^{3+}$  or  $\text{Mn}^{4+}$  reducers, denitrifying bacteria) or the methane-producing archaea may be responsible for anaerobic methane oxidation (Pimenov et al., 2014).

A specific feature of sulfate reduction in Baikal sediments is the almost total absence of  $\text{H}_2\text{S}$ . As the sediments are poor in S and rich in Fe, the formation of  $\text{H}_2\text{S}$  occurs more slowly than the subsequent interaction with  $\text{Fe}^{2+}$  (Mizandrontsev, 1975). As a result, the decreasing sulfate concentration in the pore waters causes the appearance of black impregnations and layers of hydrotroilite in the sediment (Fig. 10).

The concentrations of chloride ions in the pore waters from the three basins do not exceed 2 mg/L. Moreover, no correlation was observed with the other ions analyzed which is consistent with its conservative behaviour, not participating in biogeochemical reactions.

Calcium is a prevailing cation in pore waters. Its concentration shows a high correlation ( $r = 0.95$ ) with the concentration of bicarbonate ions (Fig. 9). The  $\text{Ca}^{2+}$  concentrations, like the bicarbonate ion, are two- to three-times lower in the uppermost oxidized-sediment layer than in the bottom water of the lake. According to Müller et al. (2002), and to our experiments,  $\text{Ca}^{2+}$  is absorbed onto iron (III) hydroxide.

In the reduced-sediment layer, the main alkaline and alkali-earth metals are leached into the pore waters from the mineral sediment. According to Fagel et al. (2007) Lake Baikal sediments (the clay fraction) mainly consist of smectite (montmorillonite) and illite and have a high cation exchange capacity. According to Shimaraeva (1981) pore water cations are 1% of the cations of the absorbing complex of bottom sediment. This value slightly increases with the depth of sediments. Calcium is 90% of the total amount of absorbed cations. Experiments studying the absorption complex of sediments (Shimaraeva, 1981) demonstrate what  $\text{Na}^+$ ,  $\text{K}^+$ , and  $\text{Mg}^{2+}$  pass into the absorbing complex of the sediment via cation exchange, thereby displacing calcium ions. Thus, calcium ions accumulate in the pore water. A similar phenomenon is observed in lakes of the Putorano Plateau (Shimaraeva, 1981) and Lake Erie (Azcue et al., 1996).

The existence of the oxidized layer with Fe and Mn oxides at the water-sediment interface leads to diagenetic redistribution of elements such as P, Ca (Müller et al., 2002) and, according to our data (Table 2), sulfate and bicarbonate ions. The redistribution depends on the thickness of the oxidized layer. The latter depends on the mass accumulation rate of organic carbon,  $\text{O}_2$  supply to the sediment, sedimentation rate, and porosity (Granina et al., 2004). Special features of Lake Baikal sediments are the layers of Fe and Mn oxides buried within the reducing part of the sediments (Granina et al., 2004). Each pore water ion profile is defined by its specific conditions and is unique (Figs. 3–5). However, according to our data, differences in the pore water ion profiles occur in common patterns (Figs. 8, 14).

Hence, the pore waters of Lake Baikal bottom sediments are similar to the lake waters, with low mineralization and a primary composition of calcium bicarbonate.  $\text{HCO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ , and  $\text{K}^+$  are the major ions of pore waters. The similarity of the chemical composition of pore waters at all of the sites studied, including those from different basins, makes it possible to infer that pore waters of Lake Baikal have uniform composition. Using concentration profiles of the data obtained (1250 samples from 26 sites around the whole bottom area of the lake), shown in Fig. 14, we were able to determine the background concentration of each ion salt in the pore waters at a certain depth from 1 to 200 cm, as shown at the Table 3.

## Conclusions

The pore waters of Lake Baikal have uniform salt composition across the lake floor. Like the lake waters, the background pore waters of Lake Baikal have a calcium bicarbonate composition with low mineralization. The total concentrations of ions in the pore waters increases with depth during diagenetic transformations due to the increase in the concentration of bicarbonate and calcium ions; however, this occurs without changing the class and group of the waters. Equations of background concentrations can be used to determine the chemical composition of pore waters in the bottom sediments from 1 to 200 cm. The existence of uniform salt composition of Lake Baikal pore waters is another special distinguishing feature of the lake. Sulfate ions were detected in the reduced methanogenic sediment of the freshwater Lake Baikal as a result of incomplete sulfate reduction in sediments.

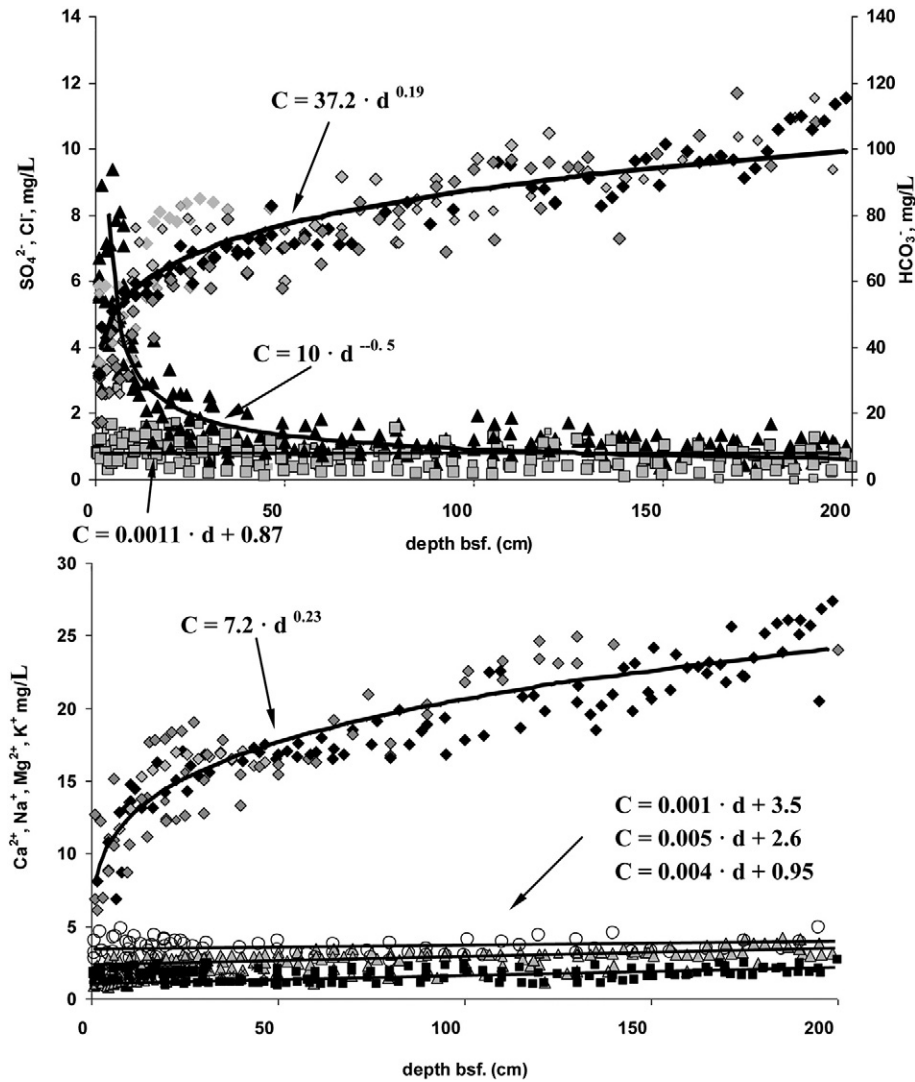


Fig. 14. Concentration vs. depth profiles of the major ions obtained (1250 samples from 26 sites around Lake Baikal) ( $1 < d < 200$  cm bsf). Equations for fitted lines also given in Table 3.

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**Table 3**

Fitted equations for each ion for estimating the background concentration (mg/L) of each ion of the Lake Baikal pore waters salt composition at a certain depth  $d$  (cm) ( $1 < d < 200$ ) based on data obtained (1250 samples from 26 sites around the lake).

Ion	Approximated equation
HCO <sub>3</sub>	$C = 37.2 \cdot d^{0.19}$
SO <sub>4</sub> <sup>2-</sup>	$C = 10 \cdot d^{-0.5}$
Cl <sup>-</sup>	$C = 0.0011 \cdot d + 0.87$
Na <sup>+</sup>	$C = 0.001 \cdot d + 3.5$
K <sup>+</sup>	$C = 0.004 \cdot d + 0.95$
Ca <sup>2+</sup>	$C = 7.2 \cdot d^{0.23}$
Mg <sup>2+</sup>	$C = 0.005 \cdot d + 2.6$
Overall ion concentration	$C = 54.5 \cdot d^{0.18}$

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