Underwater Discharge of Fluids at the Bottom of Lake Baikal: Composition, Sources, and Migration Peculiarities within the MSU Structure

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Abstract—The paper presents geochemical study of bottom sediments from the MSU structure located on the large Gydratny Fault in the Central Basin of Lake Baikal at a depth of 1380 m. The first detailed data on the spatial variations in the qualitative and quantitative composition of the pore waters are presented. Pioneering data were obtained on Li, B, and Sr contents in the pore water of the sediments. It has been established that fluids are actively discharged within the MSU structure, and the main pathways of their near-surface migration are confined to the tops of hills of this structure on the downthrown fault block. The fluids are highly mineralized (up to 2900 mg/L), showing the highest mineralization ever found in Lake Baikal sediments. The waters are significantly enriched in Mg, Li, B, and Sr but depleted in K. The waters are thought to be generated by the processes of authigenic formation and illitization of smectite at depths of 1 to 2.5 km in the sedimentary sequence. The maximum values of concentration gradients are recorded in the pore waters of the sediments of the western hill, which may indicate a gradual westward shift of the center of the fluid seepage activity along the fault.

Keywords: structures of focused fluid discharge, bottom sediments, pore waters, chemical composition, fluid migration, Lake Baikal

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INTRODUCTION

Underwater structures of focused fluid discharge (such as mud volcanoes, gas seeps, and pockmarks) are widespread worldwide (Milkov, 2000; Dimitrov, 2002; Kopf, 2002). They are formed along active and/or passive continental margins, where sediments are rapidly accumulated, or in tectonically strained regions and/or those with actively generated hydrocarbons, where the sediments are affected by overpressure needed to force the deep fluids, which are sedimentary liquids saturated with gas, mostly methane, into bottom water (Judd and Hovland, 2007; Suess, 2018). Important pathways for the ascending migration of fluids are faults and fractures. The structures are widespread along active continental margins: in Cascadia (Rudebusch et al., 2023), on the Costa Rica margin (Han et al., 2004), in Chile (Scholz et al., 2013), Pakistan (Chen et al., 2024), Japan (Kawada et al., 2014; Ijiri et al., 2023), New Zealand (Turco et al., 2022), in the Mediterranean Sea (Shuhui et al.,

2021), the Sea of Okhotsk (Syrbu et al., 2024), and the South China Sea (Ai et al., 2022). Such structures also occur along the passive slopes of inland and marginal seas: in the Black Sea (Artemov et al., 2019), Baltic Sea (Pimenov et al., 2008), Barents Sea (Milkov et al., 2004), Laptev Sea (Baranov et al., 2020), and the Sea of Japan near South Korean shores (Kim et al., 2024). The structures are actively studied worldwide starting in the 1990s (Mazzini and Etiope, 2017).

Lake Baikal is the world's oldest and deepest lake and is constrained within a tectonically active rift zone. The confinedness of this lake to faults, its steep slopes, great depth, its sedimentary sequence several kilometers thick, and the richness of the sediments in organic matter (1.5-2.5% TOC) are responsible for conditions similar to those on continental margins. Hence, the hydrocarbon system of Lake Baikal is also similar in many respects to marine hydrocarbon systems (Aloisi et al., 2019). So far, 60 structures of focused fluid discharge have been mapped on the bottom of Lake Baikal. These structures are mud volcanoes, hydrate hills, gas seeps, and a pockmark (Khlystov et al., 2022). These structures are mostly constrained to deep active faults and are parallel to them or to their intersections (Cuylaerts et al., 2012; Seminsky et al., 2022). Two decades of the systematic comprehensive studies have shown that the cold seep systems of Lake Baikal are comparable in size and operation patterns to the systems of oceanic highproduction continental margins (Aloisi et al., 2019).

Structures of this type are in the focus of active geochemical investigations worldwide because fluids discharged through them provide information on the deep structural and diagenetic processes, which may significantly modify initial fluid chemical composition due to geochemical interactions between the ascending waters and sedimentary rocks. These processes may involve decomposition of organic matter and the formation of gas hydrates, reactions of mineral dissolution/precipitation, transformations of clay minerals, and high-temperature reactions with oceanic or continental crust (Hensen et al., 2007; Mazzini and Etiope, 2017). Depending on geological setting, the superposition of these processes may result in geochemically distinct fluids with complicated evolutionary histories. Filtration activity in a seepage field is generally heterogeneous in space, as well as in time and intensity. This leads to that even neighboring structures within a single field may contain pore waters of different composition (López-Rodríguez et al., 2019). When ascending, the waters may be affected by diverse processes that may occur either concurrently or successively in regionally variable environments. In this context, the geochemical characteristics, gradients of component concentrations, their relations, flows, and the isotope composition of various elements of the discharging fluids may provide an insight into the origin of the waters and the processes in cold seep system (Mazzini and Etiope, 2017; Ai et al., 2022; Ijiri et al., 2023).

In marine environments methane-saturated pore waters discharged through the structures are often highly alkaline (atypical of pore water outside the structures), but their concentrations of major ions $(Cl^{-}, SO_{4}^{2-}, Na^{+}, K^{+}, Ca^{2+}, and Mg^{2+})$ may be, however, relatively low resulting from the dehydration of clay minerals or the dissociation of gas hydrates, which contain low-salinity (almost distilled) water (Vanneste et al., 2011). The waters may contain much higher B and Li concentrations (Kopf, 2002; Hensen et al., 2007; Vanneste et al., 2011; López-Rodríguez et al., 2019; Hu et al., 2021). Both elements are contained in clay minerals but can pass into solution at temperatures of about 50°C via desorption or at the dehydration of the minerals (Aloisi et al., 2004; López-Rodríguez et al., 2019). At greater depths and higher temperatures, reactions with sedimentary and oceanic or continental basement rocks may give rise to very high Li and B concentrations (Vanneste et al., 2011).

Lake Baikal is unique in that its sediments contain oil hydrocarbons and accumulations of gas hydrates. Similar to marine environments, deep and fresh Lake Baikal hosts sediments that are saturated with methane of both microbial (both primary and secondary) and thermogenic origin (Hachikubo et al., 2023). The advection rates of gas-saturated waters in the sediments of cold seeps in Lake Baikal are comparable with those in oceanic systems (Aloisi et al., 2019). Similar to marine environments, ascending waters can be formed by the weathering of silicates (Aloisi et al., 2019) and dehydration of clay minerals (Minami et al., 2018). However, the low (500 times lower than in seawater) concentrations of sulfates in the fresh water of Lake Baikal and the pore waters of its sediments result in that practically no sulfate-dependent anaerobic methane oxidation occurs in the sediments. Because of this, sediments in structures of focused fluid discharge are devoid of authigenic Ca and Mg carbonates and can only weakly reduce the deep methane flux (Aloisi et al., 2019).

The high oxygen content in the bottom water of Lake Baikal near the water—bottom interface results in that the typical lacustrine sediments are ubiquitously oxidized to a depth of 5–20 cm below the lake floor (Och et al., 2012). The methane-saturated sediments of the structures are, on the contrary, devoid of the uppermost oxidized layer (Zemskaya et al., 2010; Minami et al., 2018; Aloisi et al., 2019).

It is known that the pore waters of Lake Baikal sediments outside the discharge structures have a similar typical background chemical composition, and their mineralization (TDS, total dissolved solids) typically slightly increases with depth (to 190 mg/L per 3.5 m of the sediment) due to the slight increase in the alkalinity and Ca^{2+} concentration (Pogodaeva et al., 2017). Pore waters in the sediments of the structures are strikingly different from the background ones. Their mineralization significantly increases (to 2 g/L) with depth, and high concentration gradients of components are observed. As in marine environments, these pore waters are highly alkaline and enriched in basic ions (Na⁺, K⁺, Ca²⁺, and Mg²⁺) and occasionally also in SO₄²⁻ and Cl⁻ (Pogodaeva et al., 2007; Zemskaya et al., 2010; Aloisi et al., 2019; Pogodaeva et al., 2020). The waters of sediments with gas hydrates display sawtooth-shaped geochemical profiles, and their mineralization is much lower than the background values (Zemskaya et al., 2010).

This publication presents our data on the major chemical composition of pore waters in the bottom sediments, and its distribution, of the recently discovered (Akhmanov et al., 2018) deep-water fluid discharge MSU (Moscow State University) structure, with these data first supplemented by information on deep markers of the fluids: B, Li, and Sr. The geochemistry of the pore water and gas is analyzed together with geological information, and we also ana-



Fig. 1. (a) Schematic location map of the MSU structure. The inset shown the Gydratny Fault in Lake Baikal. (b) 3D representation of the MSU structure and sampling sites within it (see Supplementary for their coordinates). Inset: sampling sites on the western hill. (c) Fragment of seismic profile through the MSU structure, with acoustic anomalies. Arrows indicate the tops of the hills (according to Akhmanov et al., 2018). (d) 3D representation of the bottom surface topography in the area of the MSU structure with (a) lines of the seismic profiles and (b) tops of the hills. (1) Eastern hill; (2) central hill; (3) western hill; (4) hillock on the upthrown blok of the tectonic scarp (according to Akhmanov et al., 2018).

lyze major diagenetic processes that might have modified the composition of the waters to elucidate details of the migration, discharge, and probable genesis of the methane-bearing fluids of the MSU structure.

STUDY AREA AND ITS GEOLOGY

The structure named MSU was discovered on the bottom of the Central Basin of Lake Baikal in the course of joint fieldwork conducted by researchers of Lomonosov Moscow State University and Limnological Institute, Siberian Branch, Russian Academy of Sciences, under Project Class@Baikal (Akhmanov et al., 2018). The structure occurs at a depth of 1380 m, 31 km away from the northwestern slope of the basin (52°52' N, 107°07' E) and is constrained to the large Gydratny Fault (Fig. 1a), the main tectonic feature of the deep-water part of the Central Basin of Lake Baikal.

The fault stretches southwestward from Cape Ukhan of Olkhon Island to the pro-delta front of the Selenga River. The area is seismically active. In addition to the recent significant earthquake in 2020 (magnitude 7.6), whose epicenter was located 20 km away from the structure, the area is periodically impacted by smaller earthquakes (http://seis-bykl.ru). Tectonic data indicate that the Gydratny Fault extends from the basement to the top of the lake bottom, crosses the sedimentary sequence 7.5 km thick (Seminskii et al., 2022), and is a normal fault whose hanging (southwestern) wall is downthrown for a maximum of 100 m relative to the footwall (northwestern) block (Solovyeva et al., 2020). The downthrown block is cut by

numerous splay faults and fractures. In addition to the MSU structure, the fault is accompanied by several other mapped sites of focused gas discharge and by surface accumulations of gas hydrates, including Novosibirsk, Ukhan, and St. Petersburg mud volcanoes (Khlystov et al., 2022).

The fault is clearly discernible in the topography of the bottom surface as an escarp (Solovyeva et al., 2020), which is about 20 m high in the vicinities of the MSU structure.

Morphologically, the structure is a multisummit edifice about 500 m in diameter in its bottom part and consists of four underwater hills 5-10 m high, one of which was formed on the upthrown limb of the tectonic escarp, and the other three rest on the downthrown limb and are roughly parallel to the sole of the escarp (Akhmanov et al., 2018) (Figs. 1b, 1d).

Seismic profiles show acoustic anomalies beneath the structure, as is typical of zones of the focused discharge of hydrocarbons (Fig. 1c). They make up a "transparent" zone indicating that the sediments are rich in gas (Akhmanov et al., 2018; Vidishcheva et al., 2021). Layers within the structure are displaced and convex, which suggests vertical fluid migration, probably with the transfer of solid components (Akhmanov et al., 2018).

Gas-geochemistry data (Akhmanov et al., 2018; Vidishcheva et al., 2021) indicate that the sediments of the MSU structure contain much (~300 mL/L) methane with admixtures (up to 3.62 mL/L) of heavy hydrocarbons (C₂₊). The gases are generally of mixed genesis, but the heavy carbon isotope composition of the methane and its homologues ($\delta^{13}C(CH_4) \approx -57\%_0$; $\delta^{13}C(C_2H_6) \approx -29\%_0$; $\delta^{13}C(C_3H_8) \approx -22\%_0$; and $\delta^{13}C(C_4H_{10}) \approx -24\%_0$) indicates that the discharged gases contain much thermogenic catagenetic hydrocarbons (Vidishcheva et al., 2021).

Data on the MSU structure thus indicate that it is characterized by the intense focused discharge of hydrocarbons. It is highly probable that these hydrocarbons migrate along the Gydratny Fault from depths of the meso- to apocatagenesis zone (Akhmanov et al., 2018; Vidishcheva et al., 2021).

MATERIALS AND METHODS

The chemical composition of the pore waters was studied in 14 selected cores of the bottom sediments (Fig. 1b). The cores were taken from the upthrown block of the tectonic scarp (Site 13), at three underwater hills on the downthrown block (Sites 1 and 12 on the eastern hill, Site 2 on the central hill, and Sites 3, 4, and 7–11 on the western hill), the saddle between the tops of the western and central hills (Sites 5, 6), and away from the structure (Site 14), the latter as background site (Fig. 1b). In addition, sampling was performed on a denser grid (western hill) (Fig. 1b, inset) to identify the spatial distribution patterns of fluid within a single top.

Bottom sediments were sampled by gravity corers manufactured at LIN SB RAS (outer steel pipe 128 mm in diameter, inner plastic insert 100 mm in diameter, pipes 3–5 m long, total weight 500–700 kg). The pipes were equipped with a top valve and a petal core-catcher to retain the sampled sediments in the pipe. The top valve was closed and did not allow water into the insert to protect the sediment surface from erosion and not to allow bottom water in. Bottom waters were sampled by benthic corer 100 mm in diameter and 1 m long.

The sediments thus obtained were studied at intervals of 10-20 cm. Immediately upon sampling, pore water was separated from sediment on board the vessel by centrifugation (for 20 min at 8000 rpm, 5000 g) and ultracentrifugation (for 10 min at 14000 rpm, 12000 g), and the sub-samples were then filtered using disposable syringes and 20-µm filters (acetyl cellulose Vladikart filters, Russia).

Redox potential (Eh) was determined in wet sediment using a ProfLine pH 3310 (Germany) pH-meter.

Water samples were analyzed by HELC for major

ions (HCO₃⁻, CH₃COO⁻, Cl⁻, NO₂⁻, NO₃⁻, and SO₄²⁻) on board immediately after the waters were separated from sediments using a MilikhromA-02 microcolumn liquid chromatograph by the method described in (Baram et al., 1999), accurate to 5–7 rel %. The cation composition (Na⁺, K⁺, Ca⁺, and Mg²⁺) was analyzed, upon corresponding acidification (pH 2) in the laboratory as soon as possible after the fieldwork, by AAS on a ContrAA-800 Analytik Jena (Germany) accurate to 3–5 rel %. The completeness of the analysis was controlled by comparing the equivalent concentrations of cations and anions; the balance was accurate to no worse than 3%.

The mineralization (TDS) was calculated from the analysis for the ionic composition of the water as the total of ions.

The most representative cores (from Sites 9, 7, 12, and 13) were analyzed for B. Li, and Sr. The elements were determined in the acidified (pH 2) filtered pore water on an Agilent 7500ce quadrupole mass spectrometer at the Center for Microanalysis of the Limnological Institute, Siberian Branch, Russian Academy of Sciences. The samples were loaded using a microflow nebulizer (0.3 mL/min), which had been calibrated on the standard high-purity solutions ICP-MS-68A-A-100 and ICP-MS-68A-B-100 (highpurity standards, United States) (1, 2, 5, 10, 25 µg/dm³ of each element). The instrumental drift was controlled using an internal standard and reference sample (standard solution with 50 μ g/dm³ of each element), which was measured after analyzing every ten samples by ISO 17294-2:2016.

The quality of the analyses was controlled by including them in international correlation tests. The deviation of the test results from the true values were generally no greater than 10–15%, which verified the quality of the factual materials (https://proj-ects.nilu.no/ccc/intercomparison/index.html).

RESULTS

Description of the Sediment Samples

The bottom sediments sampled away from the MSU structure contain a surface oxidised layer, whose thickness (0.5-1 cm) was slightly lower than the typical background values (5-20 cm; Och et al., 2012). Otherwise the sediments are typical (Vologina et al., 2003) olive-gray diatom ooze, which gives way to dark gray silty clay down the sedimentary sequence. The boundary between these intervals occurs at a depth of 60 cm.

The bottom sediments sampled at the MSU structure are also olive-gray diatom ooze, which gives way to dark gray silty clay at a depth of 25–80 cm. The cores show thin beds of fine-grained sand and, in their lower parts, patches and beds of hydrotroilite. Throughout their whole vertical section penetrated by the corer, the sediments contain much gas and show degassing structures and large nearly vertical channels of fluid migration. The uppermost part of the sediment sequence recovered from the underwater hills and between them are reduced. The sediments have no upper oxidized layer.

Chemical Composition of the Pore Waters

Profiles of the distribution of major ion concentrations and those of Li, B, and Sr with depth in the pore waters of the bottom sediments within the MSU structure are shown in Fig. 2. Data on the background composition of pore waters of Lake Baikal bottom sediments from (Pogodaeva et al., 2017) were added to the presented results (see the results of the analyses in the Appendix).

The absolutely dominant anion of the pore waters in the sediments of all cores taken at the MSU structure is bicarbonate (HCO₃⁻), whose concentration increases with depth with high gradients, starting with a concentration of 72 mg/L. The concentrations of other anions, CH₃COO⁻, Cl⁻, NO₂⁻, NO₃⁻, and SO₄²⁻ occurred to be below the detection limits of 0.01 mg/L. High HCO₃⁻ concentrations were registered at the tops of the underwater hills (Sites 7, 2, 12, and 1), with the maximum concentrations found at the top of the western hill (Site 7), where the HCO₃⁻ concentration at a depth of 3 m reaches 2200 mg/L. Dense-grid sampling at the top of the western hill has also shown that HCO₃⁻ systematically decrease away

from the "central" point of Site 7 (Fig. 1) to Sites 9 and 11 and then to Sites 3, 4, and 10, although concentrations at these sites are still high (Fig. 2). Somewhat lower concentrations were registered within the zone between the tops of the western and central hills (Sites 5 and 6). The total ion concentrations in the waters are proportional to the contents of the bicarbonate ion $(R^2 = 0.99)$. The cations of the pore waters are calcium, magnesium, and sodium, whose concentrations increase (proportionally to anion) with high gradients with depth and reach 330, 190, and 90 mg/L, respectively (Fig. 2). The concentrations of the potassium ion do not exceed 13 mg/L even in the most mineralized pore waters.

Away from the MSU structure (Site 14), the pore water of the surface oxidized layer (0-1 cm) contains, in addition to the HCO_3^- ion, SO_4^{2-} (3.3 mg/L), NO_2^- (0.03 mg/L), NO₃ (0.35 mg/L), and Cl⁻ (0.43 mg/L). No CH₃COO⁻ has been identified (<0.01 mg/L), as is common to the typical background deep-water sediments of Lake Baikal (Pogodaeva et al., 2017). In the reduced sediments below the oxidized layer, bicarbonate is registered, whose concentrations increase with depth to 200 mg/L (Fig. 2), and chlorine, whose concentrations do not exceed 0.5 mg/L. Correlations between the concentrations profiles at Site 14 were detected only for the bicarbonate and calcium ions $(R^2 = 0.99)$. The concentrations of the magnesium, sodium, and potassium ions insignificantly increase with depth, which is also typical of background deepwater sediments.

The core from the upthrown block of the tectonic scarp (Site 13) contains only trace amounts of the oxidized layer. Down the sedimentary sequence, the pore waters of the reduced sediments contain bicarbonate as the only anion, whose concentration gradually increases from 72 mg/L near the surface to 300 mg/L at a depth of 450 cm below the bottom surface. Similar to Site 14, the only correlation between the concentrations was found for the bicarbonate and calcium ions ($R^2 = 0.99$). The concentrations of the magnesium, sodium, and potassium ions slightly increase with depth (Fig. 2).

The concentration profiles of B, Li, and Sr correspond to the distribution of the dominant anion at all sites (Fig. 2). The highest concentrations were found at the top of the western hill (Site 7), where the concentrations at a depth of 3 m below the bottom surface reach 93 μ g/L Li, 998 μ g/L B, and 2700 μ g/L Sr, which are 75, 100, and 50 times, respectively, higher than the concentrations in Baikal water (Grachev et al., 2004). Much lower values were found in the pore waters in sediments at the upthrown block of the tectonic scarp (Site 13), where the concentration in Baikal water was exceeded by no more than two to three times.

Redox Parameters of the Sediments and Pore Waters

Figure 3 shows pore water pH and sediment Eh at Sites 7 and 13, where pore waters with the highest and lowest mineralization were identified.



Fig. 2. Profiles of variations in total ion concentration, major ion and Li, B, and Sr concentrations with depth in the pore waters of bottom sediments of the MSU structure at Sites 1-14, where 3,4, and 7-11 are sites on the western hill, on whose top Site 7 is located; 2 is the site on the central hill; 1 and 12 are sites on the eastern hill; 5 and 6 are sites in the saddle between the western and central hills; 13 is a site on the upthrouwn block of the tectonic scarp; and 14 is a site away from the MSU structure. The background is the background composition data on pore waters in the bottom sediments of Lake Baikal (Pogodaeva et al., 2017).

The pH values vary within narrow range in both cases and decrease with depth from 7.5-7.4 to 7.3. The Eh values differ significantly: at Site 13, oxidizing conditions change to reducing conditions from +80 to -230 mV; at Site 7, reducing conditions from -360 to -390 mV are observed from the surface.

DISCUSSION

Formation of Pore Waters in the Background Areas of Lake Baikal

Due to the exceptional constancy of the content of major ions in the water column (both at a depth and in different basins) (Grachev et al., 2004), as well as the close chemical composition of bottom sediments (Gvozdkov, 1998), the sediments of Lake Baikal form

pore waters that are almost identical in composition and mineralization and are classified as background waters (Pogodaeva et al., 2017). An important role in the formation of their composition is played by weathering of silicates, during which the mineral constituent of the sediment is leached by CO_2 generated at methanogenesis as follows:

cation-enriched silicates + $CO_2 \rightarrow$ cation-depleted silicates + HCO_3^- + Na^+ + K^+ + Ca^{2+} + Mg^{2+} (Aloisi

sincates + HCO_3 + Na^3 + K^3 + Ca^{23} + Mg^{23} (Aloisi et al., 2019).

In this process, both alkali and alkaline-earth metals are extracted into solution, but due to cation exchange, Na^+ , K^+ , and Mg^{2+} are transferred to the adsorbing complex of the sediment, displacing Ca^{2+} from it, with the latter cation accumulated in the pore



Fig. 3. pH and Eh of the pore waters of bottom sediments at Sites 7 and 13.

water (Pogodaeva et al., 2007; Aloisi et al., 2019). In the surface sediments of a deep cold-water oligotrophic lake, in the presence of decomposition-resistant organic matter, methanogenesis is weak (Pogodaeva et al., 2017), and there is little CO_2 . There is favorable for the dominance of cation exchange processes. As a result, the pore waters are characterized by a slight uniform increase in mineralization with depth (up to 190 mg/L per 3.5 m of sediment depth) due to a slight

increase in HCO_3^- and Ca^{2+} ions (Fig. 2, background). Geochemical characteristics close to the background ones were identified in sediments sampled away from the MSU structure (at Site 14) and on the upthrown block of the tectonic scarp (Site 13) (Figs. 1, 2).

Formation of Pore Waters at the MSU Structure

Quantitative composition of pore waters within the MSU structure. Sediments in the MSU structure itself contain pore waters of high (according to the classification of O.A. Alekin) mineralization, which rapidly increases with depth and reaches 2900 mg/L (Fig. 2), i.e., up to 20 times higher than the background values at the same depth (Pogodaeva et al., 2017). These are the highest mineralization values ever found in the pore waters of sediments in Lake Baikal throughout the whole period of its studies. Concentration of the bicarbonate ion at Site 7, depth 3 m, reaches 2200 mg/L, which is 2.7 times higher than concentrations in the bottom sediments of the subaquatic hydrothermal vent in Frolikha Bay (Granina et al., 2001).

The MSU structure is spatially constrained to the central portion of a deep basin, far away from any sources of terrigenous material, in an area with typical sedimentation at relatively low rates (0.69 mm/year;

Och et al., 2012). Anomalous pore waters, different from background ones, cannot be formed here as a result of in situ diagenetic transformations alone, without inflow from outside. The absence of a typical oxidized layer, the fact that the pore water contains no sulfate ion, the anomalously low Eh (-360 mV), the high methane concentration with a thermogenic component in the sediments (Vidishcheva et al., 2021), acoustic anomalies seen in the seismic profiles (Akhmanov et al., 2018), the occurrence of the MSU structure within a fault zone (Solovyeva et al., 2020), and the high δ^2 H (as in deep-sitting waters; Hachikubo et al., 2023) of the pore waters of the sediments suggest that fluids should come to this structure from below.

Investigations performed on deep-sea bottom fluid discharge structures have demonstrated that the configuration of the concentration profiles of components in the pore waters and their gradient characteristics are highly informative for studying fluid seepage (Vanneste et al., 2011; Ai et al., 2022). The concentration profiles of components and the mineralization of pore waters at Sites 7, 9, and 11 of the MSU structure are convex upward (Fig. 2), as is typical of the ascending advection of fluids from deep buried strata (Aloisi et al., 2004; Vanneste et al., 2011; Chatterjee et al., 2011; Aloisi et al., 2019; Kinoshita et al., 2019; Ai et al., 2022) and suggests advective liquid transfer from below. We detected high mineralization gradients at the tops of the underwater hills (Sites 7, 2, 12, and 1) (Fig. 4), the highest of which was registered at the top of the western hill (Site 7). Areas away from the MSU structure and those on the upthrown block of the MSU structure show low gradients correspond to the background values.



Fig. 4. Schematic map showing the distribution of the mineralization gradients of pore waters in the bottom sediments of the MSU structure at Sites 1-14, where 3, 4, and 7-11 are sites on the western hill, on whose top Site 7 is located; 2 is a site on the central hill; 1 and 12 are sites on the eastern hill; 5 and 6 are sites in the saddle between the western and central hills; 13 is a site on the upthrouwn block of the tectonic scarp; and 14 is a site away from the MSU structure.

The gradients consecutively decrease from the central part to peripheries of the hills and between them. Such trends from centers to peripheries are known to be typical of previously studied marine structures with focused fluid discharge (Vanneste et al., 2011). It is thus reasonable to suggest that the sediments of the MSU structure as those previously studied earlier at Lake Baikal bottom (Zemskaya et al., 2010; Minami et al., 2018; Aloisi et al., 2019; Pogodaeva et al., 2020) are characterized by active gas discharge associated with the intense discharge of gas-saturated waters. According to the mineralization gradients, the dominant discharge pathways seem to be the central channels of the hills.

Qualitative composition of pore waters within the MSU structure. Due to the absence of the any significant content of other anions, the pore waters of all of the studied sites show a strong correlation (R 0.99) between their mineralisation (TDS) and concentrations of the bicarbonate ion (Fig. 5). Therefore, the

ratios of Na, K, Ca, Mg, and Li, B, and Sr to the latter are indicative, reflecting changes in the qualitative composition of the pore waters. The waters, which are similar in composition at the water-bottom interface (and the composition of the lake water), diverge in composition the more, the greater the depth of the bottom sediments. In relation to the pore waters of the background composition (with increasing concentrations of the bicarbonate ion and mineralization), the waters are increasingly depleted in calcium, sodium and, more importantly, potassium. At the same time, the waters are enriched in magnesium, lithium, strontium, and especially boron. Changes occur in the direction of stations: 13, $14 \rightarrow 5$, 6, $\rightarrow 10$, 1, $2 \rightarrow 12 \rightarrow 8$, 3, $4 \rightarrow 9$, 11, 7. The maximum changes are recorded at sites 7. 9. 11.

The greatest potassium depletion (four-fold in molar composition) was encountered in the waters with the maximum (also four-fold) enrichment in magnesium (Fig. 6a). These are Sites 7, 9, and 11, at



Fig. 5. Correlations between the mineralization, Na, K, Ca, Mg, Li, B, and Sr concentrations on that of the bicarbonate ion in the pore waters of bottom sediments at Sites 1–14 within the MSU structure. Dashed lines show the correlations in the background pore waters (Pogodaeva et al., 2017) and lines of Baikal water for Li, B, and Sr.

which the highest mineralization gradients were found (Fig. 4). It is known (Hensen et al., 2007) that the extent of depletion/enrichment is a function of the rate of advection, a process that determines the possibility of mixing between the pore and discharged waters. This mixing is at a minimum at a fluid advection rate >5 cm/year (Hensen et al., 2007).

The plot of this dependence (Fig. 6a) shows two clearly distinct groups of the waters: (I) background waters (and similar to them) at Sites 13 and 14 and (II) discharge waters at Sites 7, 9, and 11. Group III comprises mixed waters at all other sites (1, 2, 3, 4, 5, 6, 8, 10, and 12) and those in the upper levels (0-60 cm) at Sites 7, 9, and 11.

The similar relations in Mg, and Li, B, and Sr enrichment in the waters (Fig. 5) suggest their common source. Indeed, the B/Li ratio is constant at high Mg and Sr concentrations (Figs. 6e, 6f). The same groups of the waters can be distinguished based on relations between elements (Figs. 6b, 6c).

Evidence of the Probable Sources of the Discharged Fluid

The pioneering data on Li, B, and Sr concentrations in the pore waters of Lake Baikal bottom sediments show that concentrations of these elements at sites where waters are the most mineralization (Sites 7 and 9) are 75, 10, and 50 times, respectively, higher than in Baikal water. The enrichment levels are comparable to those in marine seep structures (Vanneste et al., 2011; López-Rodríguez et al., 2019; Hu et al., 2021). The concentrations in pore waters similar to the background ones (Site 13) are no more than two to three times higher.

Enrichment in B and Li is typical of cold seep structures along active continental margins round the world (Kopf, 2002; Hensen et al., 2007; Vanneste et al., 2011; López-Rodríguez et al., 2019; Hu et al., 2021). Both elements are contained in clay minerals but can be transferred into solution at temperatures of ~50°C by the dehydration/transformations of clay



Fig. 6. Correlations between (a) K mole fraction and Mg mole fraction; (b) K/Mg ratio and Sr; (c) K/Mg ratio and B/Li ratio; (d) B/Li ratio and depth in the sediments; (e) B/Li ratio and Mg concentration; (f) B/Li ratio and Sr concentration. Water groups: (I) background waters (and similar to them) at Sites 13 and 14, background; (II) discharge waters at Sites 7, 9, and 11; and (III) mixed waters, which are all others at Sites 1, 2, 3, 4, 5, 6, 8, 10, and 12 and the waters of the uppermost (0–60 cm) at Sites 7, 9, and 11.

minerals, increasing the concentrations with increasing temperature (Aloisi et al., 2004; López-Rodríguez et al., 2019). However, before 150° C is reached, sedimentary exchangeable B is completely released, which does not happen with Li (Aloisi et al., 2004). In contrast, at moderate to high temperatures ($150-350^{\circ}$ C), there is a preferential enrichment of waters with Li over B (Hensen et al., 2007).

The B/Li ratio in pore water at Sites 7 and 9 is, starting with certain depth, constant and amounts to 10-11 (6 if recalculated to mM) (Fig. 6d). According to (Hensen et al., 2007), this suggests that the waters may have been formed in deeper sources, where B and Li are leached from sediments at temperatures of ~50 to 150° C. The B/Li ratio decreases closer to the water—bottom sediment interface due to water mixing and reaches values determined for sites close to the background.

The identical B/L distribution at ratios with Mg and Sr (Figs. 6e, 6f) highlight the general release mechanism when the waters are formed.

It has been found out (Aloisi et al., 2004) that B release into solution and an increase in its concentration is related to illitization of smectites. This process

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is also related to K depletion, which can also be observed in the found dependences (Figs. 6a, 6b, 6c). A universal explanation of K depletion in the fluid structures of cold seeping is the incorporation of this element into illite when clay minerals are transformed (Aloisi et al., 2004; Hensen et al., 2007; Vanneste et al., 2011; Scholz et al., 2013; López-Rodríguez et al., 2019: Xu et al., 2021). Moreover, K is the main factor that controls the kinetics of smectite transformation into illite, and a K deficit may result in that this process will not come to completion (Hüpers and Kopf, 2012; Mills et al., 2023; Ohazuruike and Lee, 2023). It is also known that smectite illitization in marine environments is a dominant process forming migrating fluids for mud volcanoes and seeps (Judd and Hovland, 2007; Suess, 2018; Scholz et al., 2013; López-Rodríguez et al., 2019). The existence of this process in Lake Baikal bottom sediments has been proved by the oxygen and hydrogen isotopic composition of the pore waters of Kedr mud volcano (Minami et al., 2018).

Illitization of smectites (as well as the release of Li, B, and Sr) proceeds at temperatures of 60 to 150°C (Vanneste et al., 2011, Hüpers and Kopf, 2012). Given that the geothermal gradient in the Central Basin of

Lake Baikal is approximately 60°C km⁻¹ (Gel'mshtok et al., 1997; Golubev, 2007), fluids can come from depths of 1 to 2.5 km. With regard to that gases migrate through the sedimentary section not as individual bubbles but as dissolved gas-saturated fluids (Kopf, 2002; Judd and Hovland, 2007; Suess, 2018), this depth estimate well correlates with data on the deep sources of hydrocarbon gases discharging through the MSU structure, which migrate (Vidishcheva et al., 2021) from levels of the sedimentary sequence corresponding to the meso- to apocatagenesis zone, i.e., from depths of more than 1 km.

Superposition of Processes during Fluid Migration

It is known that the process of illitization, which is associated with the dehydration of clay minerals at the rearrangement of their smectite layers (Hüpers and Kopf, 2012; Mills et al., 2023; Ohazuruike and Lee, 2023), results in the release of significant volumes of interlayer water and, hence, in the freshening of the pore waters (Hensen et al., 2007; Vanneste et al., 2011; Hüpers and Kopf, 2012; Scholz et al., 2013; López-Rodríguez et al., 2019; Xu et al., 2021). However, the pore waters of the MSU structure are highly mineralization (up to 2900 mg/L), and no evidence of their freshening has been detected.

The likely explanation of this is geochemical interactions between the ascending waters and sediments. At a depth of hundreds of meters, according to (Scholz et al., 2013), processes of authigenic formation of smectites are common in sediments. This process is associated with water consumption by clay layers, which increases the mineralisation of the pore waters. This process was identified in the active margins off the coast of Central Chile, the Aleutian Islands, Cascadia, and in the Nankai Trough and is probably possible in the bottom sediments of Lake Baikal. Deep drilling materials on Lake Baikal indicate that silicates are the dominant component of bottom sediments at depths of hundreds of meters. This is despite the fact that the bottom sediments were drilled through in various parts of Lake Baikal, in which sedimentation parameters are principally different (Solotchina et al., 2001; Solotchina, 2009). Newly formed smectite was identified in these rocks in (Fagel et al., 2003).

When the deep waters migrate to the surface, water released at illitization may be consumed in processes that form authigenic smectite. This implies a balance of fresh water and a relatively low resultant freshening potential of the pore waters. Consequently, no integral freshening of the fluid occurs. This process was identified in studying deep-sea drilling materials offshore central Chile (Scholz et al., 2013).

An increase in the mineralization of waters ascending to the surface may also be facilitated by silicate weathering. At depths of tens of meters in sedimentary sequences, in the oxygen-free zone, high CO_2 concentrations can be generated in the course of methane generation (Wallmann et al., 2008), and they are favorable for the predominance of silicate weathering over other processes of water-sediment geochemical interactions. The possibility of such reactions in seeps in Lake Baikal has been recently demonstrated for the Krasnyi Yar seepage area (Aloisi et al., 2019). As a result of silicate weathering, the pore waters are enriched in bicarbonate ions and in Na⁺, K⁺, Ca²⁺,

and Mg^{2+} . Therewith cation exchange at high $HCO_3^$ concentrations is insignificant (Wallmann et al., 2008). These processes can occur in the sediments of the MSU structure, but it is difficult to identify them based on our data alone. Moreover, a linear positive correlation was found between conservative B and

nonconservative HCO_3^- (*R* 0.99) (Fig. 5), which is in conflict with the hypothesis that additional processes can be involved. This problem can be elucidated based on further studies with isotope data.

CONCLUSIONS

The first ever data have been obtained on the composition of pore waters in bottom sediments sampled within the MSU structure. These data indicate that waters of deep strata are currently actively discharged within the structure. The pore waters have a high mineralization (up to 2900 mg/L), whose values are the highest among those ever measured in such waters in Lake Baikal. The waters are significantly enriched in Mg, Li, B, and Sr but depleted in K compared to the water of the lake and pore waters in its areas outside zones of intense fluid discharge. Analysis of fluid composition data and its changes along the section allows us to connect the genesis of deep waters of the MGU structure with the processes of authigenic formation and illitization of smectites in intervals of the sedimentary section from 1 to 2.5 km, at temperatures from 60 to 150°C. Active fluid discharge processes are spatially constrained to hills on the downthrown block of the Gydratny Fault, near the foot of the tectonic scarp. The highest gradient of the mineralization is identified in the bottom sediments from the western hill, which may indicate that the major center of focused fluid seepage is moving westward along the fault.

SUPPLEMENTARY INFORMATION

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CONFLICT OF INTEREST

The authors of this work declare that they have no conflicts of interest.

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