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Biogeochemical processes at the Krasniy Yar seepage area (Lake Baikal) and a comparison with oceanic seeps

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Abstract

The expulsion of sedimentary, methane-rich fluids to bottom waters is a widespread process in Lake Baikal (eastern Siberia), resulting in deep water cold seep systems comparable in size and frequency to those of oceanic, high-productivity continental margins. Little is known, however, about how biogeochemical processes in Baikal cold seeps compare with those of oceanic cold seeps. In this paper, we present new pore water chemistry data from the Krasniy Yar seepage area located on the slope near the Selenga river delta. We compare biogeochemical processes deduced from these pore water chemical profiles with processes prevalent at oceanic cold seeps of highly productive continental margins. This comparison allows to draw the following conclusions: (1) in sediments not affected by seepage the fresh water mass of Lake Baikal results in a very low relative importance of the nitrogenous and sulfidic geochemical zones compared to the ocean; (2) diagenetic processes involving silicate minerals are, however, similar in Lake Baikal and the ocean; (3) fluid advection rates in cold seep sediments are similar in Lake Baikal and the ocean; (1) oxides, whereas in oceanic sediments the main methane-consuming process is the anaerobic oxidation of methane with sulfate. Lake Baikal cold seep sediments are therefore nearly devoid of authigenic carbonate minerals and have a reduced capacity to decrease the deep methane flux.

Introduction

Lake Baikal (eastern Siberia) is both the largest lake in terms of water volume and one of the lakes with the oldest and thickest sedimentary pile in the world (Logachev 2003). The organic matter productivity in the water column is low and comparable to that of oligotrophic water masses of the ocean (Weiss et al. 1991;

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Yoshida et al. 2003; Yoshioka et al. 2002). The organic content of Lake Baikal sediments ($C_{\text{org}} = 1.5-2.5 \text{ wt\%}$), however, is similar to that of oceanic sediments of highly productive continental margins (Prokopenko et al. 2007; Qiu et al. 1993; Vologina and Sturm 2009). This is due to transport of terrestrial organic matter (mainly humic acids and cellulose produced by land plants) from land, and to a minor component derived from organic matter produced by phytoplankton in the water column (Pogodaeva et al. 2017). The hydrocarbon system of this lacustrine basin bears many resemblances to marine hydrocarbon systems (Hovland et al. 2012; Moore et al. 2009; Yoshida et al. 2003). Methane of both microbial and thermogenic origin has been detected in Lake Baikal sediments (Kalmychkov et al. 2017). The resemblance of the hydrocarbon system with those of oceanic basins extends to shallow sediments and the benthic boundary, because, similar to the ocean, the expulsion of methane-rich fluids to bottom waters is widespread in Lake Baikal.

Shallow methane seeps in sediments of Lake Baikal have been known since the seventeenth century due to visual observation of free gas bubbling at the lake surface or trapped in the ice cover (Granin and Granina 2002). The expulsion at larger water depths (>400 m) of low-temperature methanecharged fluids to bottom waters has been observed for the first time in Lake Baikal in the Frolikha bay using temperature and heat flow measurements (Crane et al. 1991; Golubev 1982). Since this first discovery, cold seeps areas with acoustic free gas flares have been discovered more than 20 locations in the southern, central and northern basins (Granin et al. 2010). The seepage of methane-charged fluids is accompanied by venting of methane-gas bubbles that produce characteristic flares in echosounder images (Makarov et al. 2016b). Cold seeps occur in normally sedimented portions of the seafloor, but also in correspondence of mud volcanoes (Khlystov et al. 2013). Gas hydrates are widespread in cold seep areas located at a water depth greater than 380 m (Khlystov et al. 2013; Khlystov et al. 2014; Matveeva et al. 2003). The picture that emerges from the geological and geophysical observations carried out in Lake Baikal over the past 15 years is that of cold seep systems comparable in size and frequency to those of oceanic, highproductivity continental margins.

But while the geological and sedimentary prerequisites for the presence of cold seep systems might be similar in Lake Baikal and in the ocean, little attention has been given to possible differences in biogeochemical processes. In fact, the very different chemical composition of Lake Baikal water masses and seawater likely has important consequences on cold seep biogeochemical processes. In particular, the very low dissolved SO_4^{2-} concentration of Lake Baikal, where SO_4^{2-} is 500-fold less abundant than in seawater (Falkner et al. 1991; Pogodaeva et al. 2017), will strongly limit the anaerobic oxidation of methane with sulfate (AOM) (Boetius et al. 2000), a major methane sink at oceanic cold seeps. This is bound to have consequences on the chemical environment of cold seep shallow sediments. With the geophysical and geological investigations of Lake Baikal cold seeps being recently complemented with geochemical and microbiological investigations (Lomakina et al. 2018; Zemskaya et al. 2015; Zemskaya et al. 2010), a first comparison of biogeochemical processes of Lake Baikal and oceanic seeps can be made.

The goal of this paper is to describe the biogeochemical processes taking place in the Krasniy Yar deep water cold seepage area of Lake Baikal and compare them with the processes active at seepage areas in highproductivity continental margins of the ocean. Because of the very different chemical composition of Lake Baikal and oceanic water masses, also the biogeochemical processes in sediments unrelated to methane seepage will differ. We therefore include oceanic continental slope sediments and Selenga river delta slope sediments in our comparison, with the goal of providing a comprehensive view of the similarities and differences between Lake Baikal and oceanic cold seeps that will help guide future research in Lake Baikal.

The Krasniy Yar seepage area

The Krasniy Yar gas and fluid seepage area was discovered during a geophysical survey in the delta front of the Selenga River in 2007 at a water depth between 740 and 780 m (Fig. 1). On side-scan sonar records, it consists of several areas of strong backscatter compared with the surrounding seabed. Gas-bearing feeder channels were imaged on profiler records. The first geological sampling campaign for "Krasny Yar" structures was conducted in 2012. Sediment cores and heat flow measurements were obtained during cruise TTR-BL15 from the central and peripheral parts of the Krasniy Yar seep area, both within and outside of the high backscatter areas seen on the side-scan sonar records (Fig. 1). Five cores (092G, 093G, 094G, 096G and 102G) were taken outside of the strong side-scan backscatter areas; four cores (088G, 097G, 099G and 100G) were taken near the border of strong side-scan sonar backscatter areas and one core (095G) was taken at the centre of the largest side-scan sonar strong backscatter area.

Methods

The side-scan sonar image shown in Fig. 1 was obtained during cruise VER-07-01 as detailed in Khabuev et al. (2016). Gravity cores were obtained with a core barrel assembled at the Limnological Institute, Irkutsk. The 128-mm diameter steel core barrel was used with 100-mm diameter plastic liner. The barrel has an upper valve and a leaf-type core catcher to keep the sediment inside the barrel during core retrieval. The maximum sub-bottom penetration of the gravity cores was 350 cm.

Bottom sediments for chemical analysis of pore water were taken from the middle part of the core every 2–3 cm and every 5–10 cm from cores with an undisturbed structure. The sediments were centrifuged at 8000 rpm followed by another ultracentrifugation at 14,000 rpm to remove microparticles from pore waters. The solutions were filtered with disposable syringes through a 0.20- μ m filter (cellulose acetate, Vladisart, Russia) and then injected into chromatography tubes. 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 method is that it uses potassium hydrogen



Fig. 1 The location map of the Krasniy Yar seepage area discussed in this work. (a) Geographical location. (b) Side-scan sonar backscatter map showing the location of cores and heat flow measurements. (c) Sub-bottom profiler across the Krasniy Yar seepage area

phthalate as an eluent, enabling SO_4^{2-} , Cl^- and NO_3^- to be determined simultaneously, along with bicarbonate

 (HCO_3^-) . The detection limits are 0.1 mg/L for all anions. The measurement of one sampling point was

accomplished in a maximum of 10 min. The samples for cation analysis were stored in polystyrene vials preacidified with 50 μ L of ultrapure concentrated HNO₃ and stored at 4 °C prior to analysis. Cation (Ca²⁺, Mg²⁺, Fe²⁺, Mn²⁺) 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⁺, Ca²⁺ and Fe²⁺) and 0.001 mg/L (for Mg²⁺ and Mn²⁺).

For the majority of the coring stations, the corer has been equipped with 5 autonomous high-precision temperature loggers (type THP/NKE®, temperature resolution of better than 5/1000K) to measure thermal gradients in the sediments at four intervals of 0.5 m. The corer has to stay at least 7–10 min in sediment without tension on the corer in order to allow the main dissipation of frictional heat. An S2IP logger (NKE®) monitored water depth and tilt angle of the corer. The sediment equilibrium temperatures are obtained using the THPread software (F. Lucazeau). Heat flow is determined as the product of the vertical temperature gradient in the surface sediments and the thermal conductivity of the sediments. For the latter, a regional average of 0.8 W/m K from previous studies is applied (Golubev 1982; Poort and Klerkx 2004).

Results

A summary of the core positioning with respect to the sidescan record and of the lithological heat flow and pore water characteristics of the sediments included in this study is given in Table 1.

Lithology of sediments and heat flow in the Krasniy Yar seepage area

The lithologies sampled from the Krasniy Yar seepage area show features that are characteristic of both normal background sedimentation in the southern Baikal basin, as well as evidence for the seepage of methane-charge fluids. These features correlate well with the position of the cores with respect to patches of strong backscatter on the side-scan sonar. The five cores taken outside of the areas of strong backscatter (cores 092G, 093G, 094G, 096G and 102G) contain the normal background recent sedimentary sequence of the southern Baikal basin. This consists of a 100- to 170-cm thick layer of clavey diatomic ooze with an upper, <10 cm thick, oxidised and watery interval containing a poorly lithified Mn- and Fe-oxide crust. The portion of this top layer beneath the oxidised interval often contains hydrotrolite laminae and some pure diatomic laminae a few cm thick. The clayey diatomic ooze is the typical Holocene sediment of Lake Baikal (Grachev et al. 1998). Below the clayey diatomic ooze, the cores have retrieved butter-like, consolidated clay sediments, often bearing hydrotrolite laminae that are the typical Pleistocene sediment of Lake Baikal (Kachukov et al. 1998). The four cores taken near the border of strong side-scan sonar backscatter areas (088G, 097G, 099G and 100G) also contain the Holocene clayey diatomic ooze (75 to 150 cm in thickness) and the underlying Pleistocene clay typical of the background southern Baikal sedimentary succession. However, compared to the cores that were taken outside from the area of strong backscatter, the cores taken near the border of

Table 1 Summary of main sedimentary and geochemical features of cores from the Krasniy Yar seepage area taken during cruise TTR-BL15

Gravity core	Lat. (°N)	Lon. (°E)	Water depth (m)	Side-scanner backscatter	Lithology	Heat flow (mW/m^2)	Pore water
92	52.35606	105.96345	756	Low	Background Baikal ^a	Background (49)	Background Baikal ¹
93	52.35989	105.96952	725	Low	Background Baikal	Background (72)	Background Baikal
94	52.36231	105.96998	725	Low	Background Baikal + gas	Background (55)	Background Baikal
96	53.35983	105.96263	756	Low	Background Baikal	Background (64)	Background Baikal
102	52.36164	105.96868	726	Low	Background Baikal	Background (52)	Background Baikal
88	52.35914	105.96535	736	Border	Background Baikal + gas		Background Baikal
97	53.36123	105.96363	749	Border	Background Baikal + gas + gas hydrates		Background Baikal
99	52.35913	105.96440	744	Border	Background Baikal	Background (78)	Inflow
100	52.35371	105.96113	764	Border	Background Baikal + gas	Background (60)	Inflow
95	52.36077	105.96601	732	Inside strong backscatter area	Clay + gas hydrates	Elevated (170)	Upwards advection of fluids

^a See "Lithology of sediments and heat flow in the Krasniy Yar seepage area" for a description of background Baikal sediments

^b See "Pore waters in the Krasniy Yar seepage area" for a description of background sediment pore water composition

this area contain clear evidence for the seepage of methane-charged fluids. These include sediments that are extremely gas-saturated (core 088G), sediments bearing gas escape structures (cores 097G and 100G) and sediments containing lenticular gas hydrate accumulations (core 097G, depth interval 200–270 cm). The core taken at the centre of the largest area of strong back-scatter recorded by the side-scan sonar (095G) contains 58 cm of clay with abundant lenticular gas hydrate accumulations.

In the corer stations characterised by low backscatter and normal lithological stratification, a heat flow was measured in the range of 49–78 mW/m² (average $61 \pm$ 10 mW/m²), which is close to the background heat flow of 55–70 mW/m² reported for all Baikal (Poort and Klerkx 2004). In station 95G where the side-scan backscatter is high, a heat flow is measured that is three times higher than normal (170 mW/m²).

Pore waters in the Krasniy Yar seepage area

We present the pore water geochemical composition $(\text{HCO}_3^-, \text{Ca}^{2+}, \text{Mg}^{2+}, \text{K}^+, \text{Na}^+, \text{Cl}^-, \text{SO}_4^{2-} \text{ and NO}_3^-)$ of 10 sediment cores taken from the Krasniy Yar seepage area. Three patters of downcore pore water geochemistry can be observed: (1) the typical Baikal slope sediments diagenesis pattern, (2) geochemical profiles suggesting advection of fluids from below and (3) geochemical profiles suggesting inflow of bottom lake waters into the sediment. These three patterns will be described below.

Baikal slope sediments

Seven cores (088G, 092G, 093G, 094G, 096G, 097G and 102G) show a pore water geochemical signature that is very similar to that of typical Baikal slope sediments not influenced by fluid seepage or other depositional (e.g. turbidites) or geochemical (e.g. hydrothermalism) processes (Granina et al. 2001; Pogodaeva et al. 2017; Pogodaeva et al. 2007) (Fig. 2). These cores were taken either outside of the area of strong backscatter in the sidescan sonar images (cores 092G, 093G, 094G, 096G and 102G) or near its border (cores 088G and 097G). The cores taken outside from the strong backscatter area all contain normal background Baikal sediments (see "Lithology of sediments and heat flow in the Krasniy Yar seepage area"); those taken near the border contain normal background Baikal sediments that are gas-charged. In addition, core 097G contains gas hydrates in its lower part. These observations suggest that in the Krasny Yar seepage area, the seepage of methane-charged fluids is limited to the zone of strong backscatter seen on the side-scan sonar records. The presence of gas in cores 088G and 097G and of gas hydrates in core 097G does not modify the pore water signature that remains very similar to that of background Baikal slope sediments. We therefore conclude that no advection of methane-charged fluids is taking place in these two cores, because this would create convex upwards pore water profiles that are not observed in these cores (Fig. 4).

In the top 0-30 cm that corresponds to the oxidised portion of sediments, all of the mentioned cores show a minimum in the concentrations of HCO_3^- , Ca^{2+} and Mg^{2+} , suggesting a sink of these elements at this shallow depth. In the same interval, instead, the concentration of K⁺ and Na⁺ increases downcore (Fig. 2), suggesting a shallow source of these elements. Below 30 cm, the concentration of HCO₃⁻ and of all the above cited cations (Ca²⁺, Mg²⁺, K⁺ and Na⁺) increases linearly downcore, suggesting diffusion from deeper sediment intervals. Dissolved SO_4^{2-} is depleted in the top 20 cm while dissolved Cl⁻ varies irregularly downcore with concentrations that are often larger than those of bottom waters. Note that the pore water geochemical signature of Baikal slope sediments differs somewhat from that of typical Baikal pelagic sediments (Pogodaeva et al. 2017) because in the latter dissolved Mg, K, Na and Cl stay constant with depth in the first few meters of sediments. As explained in the "Discussion" section, this might be due to silicate weathering processes taking place at depth in Baikal sediments.

Concave upwards pore water profiles

Core 095G was taken near the centre of the area with strong backscatter on the side-scan sonar record; it contains gas hydrates immersed in a clay matrix throughout its length (58 cm) and lacks completely the oxidised layer and Fe-rich and Mn-rich layers of background Baikal sediments. In this core, the pore water concentration profiles of HCO3⁻, Ca²⁺, Na⁺ and K⁺ show a convex upwards shape that is typical for upwards advection of fluids from deeper sediment intervals (Aloisi et al. 2004a; Chatterjee et al. 2011; Luff and Wallmann 2003; Reitz et al. 2011; Wallmann et al. 2006b) (Fig. 3). The shape of the pore water profiles of HCO_3^- and Ca^{2+} , in particular, is in evident contrast with that of these elements in background Baikal sediments where a clear minimum in concentration is observed in the 0-30-cm depth interval.

Pore waters with Lake Baikal bottom water composition

Two cores have a peculiar pore water signature in that the top 100 cm (in core 100G) and 150 cm (in core 099G),



Fig. 2 Pore water concentrations of HCO_3^- , Ca^{2+} , Mg^{2+} , Na^+ , $C\Gamma$, SO_4^{2-} and K^+ (**a**–**g**) in cores 088G, 092G, 093G, 094G, 096G, 097G and 102G from the Krasniy Yar seepage area that show the typical geochemical signature of Baikal sediments not influenced by seepage; **h** and **i** show

the concentrations of HCO_3^- and Ca^{2+} in the top 80 cm of cores 088G and 096G. Note: the blue vertical dashed lines indicate the composition of Lake Baikal bottom waters

corresponding roughly to the Holocene interval, contain pore waters that have the same chemical composition of Lake Baikal bottom waters (Fig. 4). These two cores were taken near the border between the area of strong backscatter on the sidescan sonar and surrounding sediments; they contain normal background Baikal sediments (see "Lithology of sediments and heat flow in the Krasniy Yar seepage area"). Below this top layer with bottom water composition, chemical profiles are very similar to those of cores showing Baikal slope sediment diagenetic processes below the oxidised top layer, with HCO_3^{-7} , Ca^{2+} , Mg^{2+} , Na^+ and K^+ increasing downcore and the near absence of SO_4^{2-} .



Fig. 3 Measured (dots) and modelled (red and dashed black lines) concentration profiles of HCO_3^- , Ca^{2+} , Mg^{2+} , Na^+ , CI^- , SO_4^{2-} and K^+ in core 095G from the Krasniy Yar seepage area that shows the typical geochemical signature of upwards advection of fluids. Notes: numbers in

panels HCO_3^- and Ca^{2+} represent the advection rates (in cm year⁻¹) that correspond to the model profiles; the blue vertical dashed lines indicate the composition of lake Baikal bottom waters

Discussion

Background biogeochemical processes in Lake Baikal slope sediments

The background biogeochemical processes in Baikal sediments have been investigated by many authors (Granina et al. 2004; Och et al. 2012; Pogodaeva et al. 2017; Pogodaeva et al. 2007). Most of the efforts have been directed to understand the early diagenetic processes in the oxidised surface sediments ($\approx 0-25$ -cm depth) responsible for the formation of indurated Fe(III) and Mn(IV) layers between 3- and 8-cm depth, and their subsequent remobilisation between 15- and 20-cm depth (Och et al. 2012). The gravity corer used to retrieve the cores presented in this work is not adapted to sample the top 30 cm of sediments without disturbing the lithological layering. Furthermore, the pore water sampling resolution used in

the present study (1 sample every 20–30 cm) is too low to highlight the Mn and Fe cycling in the top 30 cm of the sediment column. Nevertheless, for the sake of completeness, we introduce these Mn- and Fe-related shallow biogeochemical processes in our discussion, taking the relevant geochemical trends from Och et al. (2012), Pogodaeva et al. (2007) and Pogodaeva et al. (2017). The discussion on Mn- and Fe-related shallow diagenesis is completed with the indications of additional shallow (≈ 0 –25-cm depth) and deeper (>25 cm) biogeochemical processes deduced based on the data presented in this work (Figs. 2, 3 and 4).

Figure 5a is a simplification of the main biogeochemical processes taking place in background Baikal sediments as deduced from Och et al. (2012), Pogodaeva et al. (2017; 2007) and the present work. The nomenclature of geochemical environments follows that proposed by Canfield and Thamdrup (2009). In the near absence of dissolved $SO_4^{2^-}$ (~50 µmol kg⁻¹) and with only minor concentrations of

Fig. 4 Pore water concentrations of HCO_3^- , Ca^{2+} , Mg^{2+} , Na^+ , $C\Gamma^-$, SO_4^{2-} and K^+ in cores 099G and 100G from the Krasniy Yar seepage area that show the typical geochemical signature of downflow of bottom Baikal

waters into the sediments. Note: the light brown shaded area represents the maximum depth of inflow of bottom waters in core 099G

 NO_3^- (< 10 µmol kg⁻¹) (see Table 2), organic matter diagenesis in Baikal sediments takes place mainly via oxidation with O_2 (reaction 1), Mn(IV) oxides (reaction 2), Fe(III) oxides (reaction 3) and via methanogenesis (reaction 4) which define the relevant organic matter respiration processes (Fig. 5a):

$$CH_2O + O_2 \Longrightarrow CO_2 + H_2O \tag{1}$$

$$CH_2O + 2MnO_2 + 3CO_2 + H_2O => 4HCO_3^- + 2Mn^{2+}$$
 (2)

$$CH_2O + 4FeOOH + 7CO_2 + H_2O => 8HCO_3^- + 4Fe^{2+}$$
 (3)

$$CH_2O => CO_2 + CH_4 \tag{4}$$

The chemical changes produced by these respiration processes give rise to the oxic, manganous, ferruginous and methanic geochemical zones (Canfield and Thamdrup 2009) (Fig. 5a). Note that since dissolved Mn^{2+} and Fe²⁺ are not consumed below the Mn and Fe crust in the considered sediment interval, the manganous and ferruginous geochemical zones coincide (Fig. 5a).

The HCO_3^- released by reactions 2 and 3 is converted to CO_2 when upwards diffusing Mn^{2+} and Fe^{2+} react with dissolved oxygen, precipitating as solid oxides and hydroxides in the upper portion of the Mn and Fe crust:

Solute Average seawater Average Lake Average Lake Baikal composition Baikal composition composition $(mol \ kg^{-1})^b$ $(mg L^{-1})$ $(\text{mol } \text{kg}^{-1})$ Cl 558×10^{-3} 11.7×10^{-6} 0.44^c 479×10^{-3} 151×10^{-6} Na⁺ 3.47^c Mg^{2+} 54.3×10^{-3} 126×10^{-6} 3.02° SO42- 28.9×10^{-3} 5.51^c 57.4×10^{-6} Ca²⁺ 403×10^{-6} 10.5×10^{-3} 16.1^c K^+ 10.4×10^{-3} 24.1×10^{-6} 0.94° DIC 2.05 66.79^{ac} 1.09×10^{-3a} 0.4×10^{-3} $10-300 \times 10^{-6}$ 12.8^d O_2 $< 40 \times 10^{-6}$ $4-10 \times 10^{-6}$ NO₃ $0.25 - 0.62^{d}$

 Table 2
 Comparison of the most abundant dissolved ions in seawater

 and in Lake Baikal waters
 Comparison of the most abundant dissolved ions in seawater

^a The concentration of the bicarbonate ion is presented

^b Berner and Berner (1996)

^c Falkner et al. (1991)

^d Och et al. (2012)

 $2Mn^{2+} + O_2 + 4HCO_3^- => 2MnO_2 + 4CO_2 + 2H_2O (5)$ $4Fe^{2+} + O_2 + 8HCO_3^- + 2H_2O => Fe(OH)_3 + 8CO_2 (6)$

Dissolved HCO_3^- is also converted to CO_2 by reaction of solid Mn(IV) oxides with dissolved Fe^{2+} (Krylov et al. 2010):

 $MnO_2 + 2Fe^{2+} + 3HCO_3^{-} + 2H_2O => 2Fe(OH)_3 + Mn^{2+} + 4CO_2$ (7)

Upwards diffusing methane is possibly consumed anaerobically by reaction with manganese and iron oxides (Beal et al. 2009; Och et al. 2012):

$$CH_{4} + 4MnO_{2} + 7CO_{2} + 2H_{2}O =$$

$$> 8HCO_{3}^{-} + 4Mn^{2+}$$

$$CH_{4} + 8Fe(OH)_{3} + 15CO_{2} + 13H_{2}O =$$
(8)

$$> 16 \text{HCO}_3^- + 8 \text{Fe}^{2+}$$
 (9)

Reactions 1 to 9 explain the downwards changes in concentration of O_2 , Mn^{2+} and Fe^{2+} in the oxidised sediment layer, and the appearance of CH_4 at the boundary between the oxic and anoxic sediments (Fig. 5a).

The major dissolved ions that are analysed in the present work (HCO₃⁻, Ca²⁺, Na⁺, K⁺ and Mg²⁺) (Fig. 5b) are involved in biogeochemical processes in part different from the ones introduced above. Dissolved HCO₃⁻, Mg²⁺ and Ca²⁺ are consumed in the oxidised layer, while this layer is a source of Na⁺ and K⁺ (Fig. 5b). Net consumption of HCO₃⁻ in the oxidised layer can take place if reactions 1 to 9 are a net sink of HCO₃⁻. But the cation trends need to be explained too. Reverse weathering reactions (Michalopoulos and Aller 2004; Wallmann et al. 2008) could explain consumption of HCO₃⁻, Ca²⁺ and Mg²⁺. In this process, biogenic opal reacts with metal hydroxide, cations and HCO₃⁻ are taken up in the neo-formation of authigenic silicate phases and CO₂ is released:

Biogenic opal + metal hydroxides +
$$Ca^{2+} + Mg^{2+} + HCO_3^- =>$$
 authigenic silicates + CO_2 (10)

The availability of biogenic opal and iron hydroxides is critical for this process to take place. These constituents are abundant in surface Baikal sediments (Torres et al. 2014).

Cation absorption-desorption processes on the surface of clay minerals can complicate this picture. The charged surfaces of clay particles transported by rivers are occupied by Na⁺, Mg²⁺, Ca²⁺ and K⁺ ions (Charlet and Tornessat 2005; Sayles and Mangelsdorf 1977; Sayles and Mangelsdorf 1979; von Breymann et al. 1990). In sediments, the NH₄⁺ and H⁺ produced by organic matter degradation processes (reactions 1 to 4) may replace the cations adsorbed on the surface of clay minerals, resulting in their release to pore fluids (von Breymann et al. 1990; Wallmann et al. 2008). Note that although NH₄⁺ does not appear in the reactions above, it is produced by reactions 2 to 4, while H⁺ ions are produced by the release of the weak acid CO_2 via the relevant reactions cited above. Adsorption/desorption processes will compete with other processes in defining the concentration of dissolved cations. Therefore, the increase in dissolved Na⁺ and K⁺ could take place if desorption from the surface of clay minerals is faster than their consumption in reverse weathering processes like reaction 10. Deeper, in the anoxic sediments, the downcore increasing concentrations of Ca^{2+} , Mg^{2+} , Na⁺ and K⁺ could be due to adsorption/ desorption from the surface of clay minerals. The marked downcore increase in HCO_3^- , however, needs to be explained.

In the anoxic zone of marine sediments, detrital silicate minerals can be altered, converting methanogenic CO_2 to HCO_3^- , releasing cations and resulting in the formation of secondary silicate minerals:

Cation-rich silicate + $CO_2 =$ cation-depleted silicates + $HCO_3^- + Ca^{2+} + Mg^{2+} + Na^+ + K^+$ (11)

Thisprocessisknowntotakeplaceinthemethanogeniczone of marine sediments where the rates of organic matter productionarehigh(Scholzetal.2013;Solomonetal.2014;Wallmann etal.2008). In the marine environment(Wallmannetal.2008), silicate weathering processes dominate over absorption/ desorptionprocesses in the production of cations in the methanic zone of sediments. The existence of this process in lakes was first proposed by (Mizandrontsev 1981). Pogodaeva et al. (2007) proposed that this process is taking place in the reduced sediments of Lake Baikal.

The HCO_3^- and cation trends in the top few meters of the anoxic zone of Baikal sediments are coherent with submarine weathering processes taking place in deeper sediments. Indeed, submarine weathering of silicates takes place over sediment depths of tens to hundreds of meters and the geochemical pore water signature of this process is transported to shallower sediment depths by molecular diffusion (Wallmann et al. 2008). Indeed, the downcore linear trends in the concentration of HCO_3^- and of the major dissolved cations (Fig. 2) suggest transport from deeper sediment intervals rather than production in the top few meters of the Baikal sediment section.

The downcore gradient of dissolved HCO_3^- in Baikal sediments can be compared to the downcore gradient in total alkalinity (TA) in the methanogenic zone of sediments of the Sakhalin slope (Sea of Okhotsk) where silicate weathering is currently taking place. HCO_3^- is the major contributor to TA accounting for approximatively 75% of TA in seawater (Zeebe and Wolf-Gladrow 2001). In the methanogenic sediments of the Sakhalin slope, the submarine weathering of detrital silicates currently results in an increase of 3 mmol kg⁻¹ of TA per meter of depth. In the methanogenic zone of Baikal sediments, the increase in HCO_3^- is roughly half this amount (Fig. 2), suggesting that detrital silicate weathering is an important process also in the sediments of Lake Baikal. More work is necessary in the Baikal sediments to fully characterise the weathering of detrital silicates which, according to the HCO_3^- and major cation trends discussed here, is a process likely to take place in methanogenic sediments.

Geochemical evidence for a hydrogologically active cold seep system at Krasniy Yar

We interpret the convex upwards pore water profiles in core 095G (Fig. 3) as indicative of active seepage of fluids to bottom waters. The presence of gas hydrates near the seafloor and the steep geochemical gradients in the top 10 cm of sediments suggest that upwards seepage of fluids is currently active or very recent. By assuming that dissolved HCO_3^- and Ca^{2+} behave conservatively in their transit through the top 56 cm of sediments, their pore

water profiles can be used to estimate the rate of fluid advection by applying the following transport equation:

$$\phi \cdot \frac{dC_i(x)}{dx} = \phi \cdot D_i^{\text{eff}} \cdot \frac{d^2 C_i(x)}{dx^2} - \phi \cdot w \cdot \frac{dC_i(x)}{dx}$$
(12)

where C_i (in µmol cm⁻³) is the concentration of solute *i* (HCO₃⁻ or Ca²⁺); D^{eff} (in cm² year⁻¹) is the effective molecular diffusion coefficient of solute *i*, calculated from the free solution molecular coefficient (*D*, in cm² year⁻¹) as a function of temperature and salinity using equations given in Boudreau (1997) and applying Archie's law to consider the effects of tortuosity on diffusion. The applied coefficient (*m* = 2 in Archie's law) results in the following:

$$D^{\rm eff} = \phi \times D \tag{13}$$

where ϕ (-) is the porosity and w (in cm year⁻¹) is the upwards fluid advection rate. Porosity is set constant and equal to 0.7, to account of the fact that gas hydrates in the core decrease the porosity that is equal to 0.8-0.9 in surface Baikal sediments (Och et al. 2012). By imposing upper and lower boundaries equal to the measured concentrations and a sediment column length equal to the length of the core (58 cm), Eq. 12 is integrated in time from linear initial conditions until steady state is attained. The rate of upwards advection of fluids (w) was varied in successive model runs until the best fit of the HCO_3^- and Ca²⁺ model profiles to the measured concentration was obtained for and advection rate of 15 cm year⁻¹ (Fig. 3). To our knowledge, this is the first estimate of fluid advection rates at cold seeps in the Baikal basin. This advection rate is in the range of typical fluid advection rates at oceanic colds seeps (Luff and Wallmann 2003).

Next to core 095G where fluids are advected upwards to bottom waters (Fig. 3), cores 099G and 100G contain pore waters in the top 150 cm that have a chemical composition equal to that of bottom waters (Fig. 4). Vertically constant pore water concentrations in the top sediment layer can only be maintained if bottom waters are actively mixed in the sediment to counter the effect of molecular diffusion that tends to produce a vertically linear concentration profile (supposing a constant porosity with depth). Mixing of bottom waters into the sediment is a common process at cold seeps where it is driven by downwards entrainment of bottom waters into the sediment as a response to bubble streams rising in the sediment (Haeckel et al. 2007). Gas flares in echosounder records have been observed above the Krasniy Yar seepage area (Makarov et al. 2016a) indicating that bubble streams rising in the sediments are present at Krasniy Yar. In the cold seeps of the Sakhalin Slope (Sea of Okhotsk), rising bubble streams in the sediment result in inflow of bottom waters into the sediment down to a depth of 0.5–3 m (Haeckel et al. 2007), a range which includes the thickness of the sediment interval bearing pore waters with a chemical composition equal to that of Baikal bottom waters (sites 099G and 100G) (Fig. 4). Together with the evidence for active expulsion of warm fluids at site 095G, the indications for convection of bottom waters in the sediment imply a hydrologically active cold seep system at Krasniy Yar.

Convection of bottom waters into the sediment and mixing with fluids advected upwards from deeper sediment intervals explains a peculiarity of the geochemical signature of the fluids expelled at site 095G, while the concave upwards shape of the HCO_3^- and Ca^{2+} pore water profiles clearly indicates upwards advection of fluids; the concentrations of these components at the base of the 60cm core are lower than at 300-cm depth in the pore waters of normal Baikal sediments (Fig. 2). If upwards advection of fluids alone is responsible for the geochemical signature of pore fluids at site 095G, one would expect HCO₃⁻ and Ca²⁺ concentrations equal, or higher, than those at the base of cores from background Baikal sediments (Fig. 2). This can be expected because weathering of detrital silicates (Eq. 11) will continue in the methanic zone of sediments below the cores depth of 350 cm (Fig. 2), producing further increasing the concentration of HCO₃⁻, Ca²⁺, Mg²⁺, Na⁺ and K⁺. The relatively HCO₃⁻-rich and cation-poor character of fluids at the base of core 095G, therefore, suggests that the upwards advecting fluids at the base of core 095G have mixed with Baikal bottom waters convecting in the sediment, with the result that deep fluids are diluted. This mixing-and-dilution process is a typical consequence of shallow convection at cold seeps (Aloisi et al. 2004b; Haeckel et al. 2007) and confirms the hydrologically active nature of the Krasniy Yar cold seep system.

The potential oxidants (electron acceptors) for methane oxidation in aquatic environments are as follows: O_2 (Hanson and Hanson 1996), NO_3^- (Haroon et al. 2013), Mn(IV) and Fe(III) oxides (Beal et al. 2009) and SO_4^{2-} (Boetius et al. 2000). In Lake Baikal sediments, anaerobic oxidation of methane with NO_3^- and SO_4^{2-} (reaction 18) can only have a limited importance due to the low concentration of these electron acceptors in Baikal bottom waters (Table 2). The obvious electron acceptor in Lake Baikal sediments is O_2 :

$$CH_4 + O_2 => CO_2 + 2H_2O$$
 (14)

In addition, there are indications that anaerobic oxidation with Mn(IV) and Fe(III) oxides (reactions 8 and 9) (Beal et al. 2009) might take place at seep sediments of lake Baikal (Pimenov et al. 2014). These authors have measured methane concentrations and methane oxidation rates (both aerobic and anaerobic) at methane seeps in southern and central Baikal; they show that the rates of aerobic (9–3485 μ mol m⁻² day⁻¹) and anaerobic (24–4125 μ mol m⁻² day⁻¹) oxidation of methane are comparable. Although the electron acceptor for the anaerobic oxidation process has not been determined, based on the low concentrations of NO₃⁻ and SO₄²⁻ in Lake Baikal waters, it leaves only Mn(IV) and Fe(III) oxides as electron acceptors. Mn(IV) and Fe(III) oxides are indeed very abundant in the upper centimetres of the sedimentary section of Lake Baikal (Granina et al. 2004; Och et al. 2012).

Comparison with biogeochemical processes in oceanic continental slope sediments

In this section, we will outline the main differences in the biogeochemical processes taking place in Baikal cold seep sediments and their background sediments of the Selenga delta slope, compared to those taking place in oceanic cold seep and continental slope sediments. Although biogeochemical processes in background Baikal sediments are relatively homogeneous throughout the lake (Pogodaeva et al. 2017), biogeochemical processes in oceanic sediments vary widely, mainly reflecting differences in the concentration of organic matter and the composition of the solid phase of sediments (Berner 1980). In the present comparison, our "oceanic sediment" reference broadly represents sediments of continental margins with organic matter contents comparable to those of Baikal sediments (1.5-2.5 wt%) (Och et al. 2012). In particular, we will consider biogeochemical processes in the sediments of the Sakhalin slope (Sea of Okhotsk) (Wallmann et al. 2006a) where silicate weathering processes such as those we propose for Baikal sediments have been observed (Wallmann et al. 2008).

Baikal water vs oceanic water composition

Sedimentary biogeochemical processes are much affected by the composition of bottom waters, which both defines the upper boundary of the biogeochemical system and is the source of pore waters trapped in the sediment during the accumulation of the solid particles. We therefore start by comparing the chemical composition of Lake Baikal water with that of ocean water. This comparison is summarised in Table 2. The salinity of Lake Baikal water (salinity = 100 mg L⁻¹) is two orders of magnitude smaller than that of ocean water (salinity = 35 g L⁻¹). The most abundant dissolved ions in Lake Baikal are HCO₃⁻ (1.09 mM) and Ca²⁺ (0.4 mM) (compared to 1.7 mM and 10.5 mM in seawater, respectively). With regard to cold seep biogeochemical processes, the most important difference with seawater is the very small concentration of dissolved $SO_4^{2^-}$ in lake Baikal waters (57.4 µM), compared to seawater (28.9 mM). As we will see further on, the lack of dissolved $SO_4^{2^-}$ in Baikal water decreases the microbial filter resulting in enhanced methane fluxes to bottom waters compared to methane seeps in oceanic settings. All other ions that form the largest part of the dissolved salts in seawater (Cl⁻, Na⁺, Mg²⁺ and K⁺) are present in Lake Baikal waters in only very small concentrations (\leq 150 µM).

Biogeochemistry of background Baikal slope sediments vs ocean sediments

The nearly total absence of SO_4^{2-} and NO_3^{-} in Lake Baikal waters (Table 2) has the effect that, compared to oceanic sediments, in Baikal sediments the nitrogenous and sulfidic geochemical zones are relatively less important than the other geochemical zones (Fig. 5a and c). This has important consequences for the alkalinity balance in sediments and the formation of authigenic mineral phases. In fact, due to the scarcity of electron acceptors SO_4^{2-} and NO_3^{-} , a greater portion of the DIC produced by organic matter degradation (reactions 1 to 4) and subsequent redox reactions is in the form of CO₂ rather than HCO₃⁻. The first source of missing HCO₃⁻ in Lake Baikal is that produced by the oxidation of organic matter with dissolved SO_4^{2-} , which, in the ocean, is a major pathway of organic matter degradation (Bowles et al. 2014):

$$C(H_2O) + 0.5SO_4^{2-} => 0.5HS^- + 0.5CO_2 + 0.5 HCO_3^- + 0.5H_2O$$
(15)

Therefore, also missing, or extremely limited, is the HCO₃⁻-producing redox processes that rely on HS⁻ produced by reaction 15 as a reducing agent:

$$2Fe(OH)_{3} + HS^{-} + 5CO_{2} =$$

> Fe²⁺ + S[°] + 5**HCO**₃⁻ + H₂O (16)

$$MnO_{2} + HS^{-} + 3CO_{2} + H_{2}O =$$

> Mn²⁺ + S° + 3HCO₃⁻ (17)

as well as the anaerobic oxidation of $\rm CH_4$ with dissolved $\rm SO_4^{\ 2^-}$ that is an important source of $\rm HCO_3^-$ in

marine sediments (Boetius et al. 2000; Egger et al. 2018):

$$CH_4 + SO_4^{2-} => HCO_3^- + HS^- + H_2O$$
 (18)

Thus, compared to ocean sediments, Baikal sediments (i) contain only limited amounts of dissolved sulfide and (ii) can be expected to produce relatively more CO₂ than HCO₃⁻, leading to diagenetic environments characterised by a lower pH (Mizandrontsev 1975). The absence of H₂S and the low pH have important consequences on the fate of the solid phase of sediments: (1) sulfide minerals such a pyrite (FeS₂) are less abundant in Baikal sediments than in oceanic sediments, (2) authigenic carbonate minerals are less likely to form in Baikal sediments than in oceanic sediments and (3) the low pH will stimulate both adsorption/desorption processes on the surface of clay minerals (Charlet and Tornessat 2005; Sayles and Mangelsdorf 1977; Sayles and Mangelsdorf 1979; von Breymann et al. 1990) and the weathering of detrital silicate minerals (Wallmann et al. 2008). The scarcity of authigenic carbonate and sulfide minerals in Baikal sediments, which are a sink or Mn^{2+} and Fe^{2+} , has the effect that dissolved Fe²⁺ and Mn²⁺ concentrations remain relatively important in the methanic zone of sediments, such that in Baikal sediments there is not net separation of the manganous, ferruginous and methanic geochemical zones (Fig. 5a), which is a characteristic of oceanic sediments (Fig. 5c).

Biogeochemistry of Baikal cold seeps vs oceanic cold seeps

The most evident difference between cold seep biogeochemical processes in Lake Baikal, compared to those of the oceanic realm, is the negligible role of sulfate in Lake Baikal sediments as an electron acceptor for the anaerobic oxidation of methane (reaction 18). In oceanic cold seeps, the anaerobic oxidation of methane with sulfate is a very effective benthic filter for methane advecting from deeper sedimentary intervals. Luff and Wallmann (2003) show that up to fluid advection rates of 50 cm year⁻¹, 99% of the deep methane flux is consumed by reaction with sulfate. Only at advection rates greater than about 100 cm year⁻¹ is a significant methane flux to bottom waters produced. At the cold seeps of Lake Baikal, where only O2 and possibly Mn(IV) and Fe(II) oxides are used as elector acceptors, it is likely that a larger percentage of the deep methane flux passes to bottom waters: the microbial filter in Lake Baikal is less effective than in the ocean. Note that the anaerobic oxidation of methane with sulfate might be taking place locally in the sedimentary succession—independent of water column chemistry where $SO_4^{2^-}$ -rich fluids of hydrothermal origin migrate through the sediments (e.g. Matveeva et al. 2003; Pogodaeva et al. 2007) (Fig. 6).

The negligible importance of methane oxidation with sulfate has the consequence that carbonate mineral precipitation is very limited in Lake Baikal cold seep sediments. At oceanic cold seeps, the large HCO_3^{-} flux produced by the oxidation of methane with sulfate (reaction 18) triggers the widespread precipitation of authigenic carbonates in the form of nodules in the sediments and carbonate crust pavements on the seafloor (Aloisi et al. 2000; Bohrmann et al. 1998; Luff et al. 2004). These wellrecognisable methane-related carbonates are absent in Baikal cold seep sediments, where only a very limited amount of authigenic siderite and rhodocrosite have been observed (Krylov et al. 2018; Krylov et al. 2008). Of the other methane sinks discussed above, the aerobic oxidation of methane (reaction 14) produces CO₂, a weak acid that inhibits carbonate mineral precipitation. The oxidation of methane with Mn(IV) and Fe(III) oxides (reactions 8 and 9), instead, produces HCO_3^{-} , but the lack of authigenic carbonates suggests that the rates of these processes are not high enough to significantly shift dissolved inorganic carbon equilibrium in favour of carbonate mineral precipitation. Finally, limited carbonate mineral precipitation in Lake Baikal cold seep sediments is also due to a concentration of dissolved calcium 20 times lower than that of the ocean (Table 2). No extensive carbonate pavements have been observed during MIR submersible dives on Baikal cold seeps in 2008-2010 (O. Khlystov, personal communication).

In support of the above arguments, the rate of fluid flow $(15 \text{ cm year}^{-1})$ constrained at site 095G with the transport model ("Geochemical evidence for a hydrogologically active cold seep system at Krasniy Yar") is in the range of fluid flows that results in the widespread formation of authigenic carbonate crusts at cold seeps (Luff et al. 2004). However, we have found no macroscopic evidence of authigenic carbonate in core 095G. This confirms that the lack of AOM in Baikal seep sediments radically changes the TA/DIC balance near the benthic boundary. By extension, the TA/DIC balance of the fluids emitted at cold seeps will also be different in Baikal seep compared to the ocean, with Baikal seeps emitting fluids with a lower TA/DIC ratio that oceanic cold seeps where AOM dominates. In conclusion, in comparison with oceanic methane seeps, biogeochemical processes at methane seeps in Lake Baikal (1) have a reduced capacity to decrease the deep methane flux, likely resulting in larger benthic methane fluxes for a given fluid advection rate; (2) result in a larger CO_2/HCO_3^- ratio when methane is oxidised and (3) result in very limited carbonate mineral precipitation.

Directions for future research on Baikal cold seep biogeochemistry

The investigation of cold seep biogeochemical processes in Lake Baikal sediments is in its infancy. As geophysical and geological investigations are showing that cold seepage is widespread in the Baikal basin (Khlystov et al. 2013; Khlystov et al. 2014), geochemical and microbiological investigations suggest that, biogeochemically, Lake Baikal cold seeps are distinct from their oceanic counterpart. Based on the results of the present study, and of the work by Pogodaeva et al. (2007), Pogodaeva et al. (2017) and Och et al. (2012), we propose the following directions for future research to better understand the biogeochemical processes active at Lake Baikal cold seeps:

- A full set of pore water geochemical measurements that include dissolved O₂, CH₄ and TA concentrations, but also measurements of sedimentation rate and porosity, will enable to apply more sophisticated transport-reaction models (Luff and Wallmann 2003) to estimate the rates of methane consumption in the sediment and evaluate the efficiency of the benthic microbial filter in mitigating methane fluxes to Lake Baikal bottom waters;
- Microbial experiments to investigate the anaerobic oxidation of methane using Mn(IV) and Fe(II) oxides as electron acceptors will mechanistically inform on the existence of these processes in Lake Baikal cold seep sediments. The abundance of Mn(IV) and Fe(II) oxides in the very shallow sediments of Lake Baikal, together with the very low sulfate concentration, makes this a particularly promising setting to investigate these processes;
- Finally, spatially resolved video-observations, benthic flux measurements and bottom sampling operations with video-guided devices will make it possible to associate specific geochemical signatures (upwards advection vs convection, for example) to lake bed manifestations such as bubble streams and benthic methane fluxes—an essential step to extend investigations from process-oriented to the estimate of local and regional geochemical methane budgets.

Conclusion

The new pore water geochemical profiles obtained from the Krasniy Yar seepage of Lake Baikal, together with published data on biogeochemical processes in Lake Baikal slope sediments not affected by cold seepage, allow to draw the following conclusions with regard to the differences with biogeochemical processes at oceanic cold seeps: (1) the very different chemical composition of Lake Baikal water mass and the oceanic water mass has an important impact on biogeochemical processes; (2) in sediments not affected by seepage low bottom water, SO_4^{2-} and NO_3^{-} concentrations result in a low relative importance of the nitrogenous and sulfidic geochemical zones in Baikal compared to the ocean; (3) processes involving silicate minerals (shallow reverse weathering and deeper, detrital silicate weathering), instead, seem to act in a similar way in Lake Baikal and oceanic sediments and (4) in Lake Baikal cold seep sediments, the deep methane flux is mitigated by reaction with O₂, and possibly Mn(IV) and Fe(III) oxides, whereas in oceanic sediments the main methaneconsuming process is the anaerobic oxidation of methane with sulfate. As a consequence, Lake Baikal cold seep sediments experiencing advection rates similar to ocean seeps are nearly devoid of authigenic carbonate minerals, while extensive carbonate crust pavements cover large portions of the seafloor in oceanic cold seep systems.

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