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Producers and oxidizers of methane in the bottom sediments of Lake Baikal and their potential role in the formation of anomalously ^{13}C-enriched authigenic carbonates

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Motivation and Aim: In the sediments of Lake Baikal, methanogenesis is the main terminal process in the chain of anaerobic organic matter (OM) degradation. Also at the bottom of the lake there are many zones of discharge of hydrocarbon-containing fluids, in which methane is not only of biogenic, but also of thermogenic origin. Therefore, the study of microorganisms involved in the methane cycle is necessary for understanding the biogeochemical processes occurring in Baikal sediments. One of these processes is the formation of anomalously ^{13}C-enriched authigenic carbonates ($\delta^{13}C \leq +36.3$ ‰ VPDB) in the discharge areas in contrast with almost complete absence of carbonates in the other sediments of the lake. If in marine cold seeps and mud volcanoes, carbonate formation is driven by sulfate-dependent AOM, in Lake Baikal, where SO_4^{2-} is 500-fold less abundant than in seawater, active methanogenic destruction of OM and silicate weathering was proposed as such a process [1]. Therefore, the purpose of this study was to reveal the features of the structure of microbial communities and the chemical composition of pore waters in sedimentary layers containing isotopically heavy carbonates, as well as to assess their compliance with the hypothesis of the formation of carbonates during the methanogenic destruction of OM.

Methods and Algorithms: We analysed the composition of microbial communities in the carbonate layers and normal bottom sediments of three mud volcanoes MV Malenky, MV Kukuy K-9 and MV Kedr-1. Sediment samples were collected using the bentos and gravity corers. Diversity of microorganisms was assessed via 16S rRNA gene diversity survey using high-throughput sequencing on Illumina MiSeq. The chemical composition of pore water was determined using liquid chromatography, atomic absorption and flame emissivity methods. The isotopic composition ($\delta^{13}C$ and $\delta^{18}O$) of carbonates and dissolve organic carbon (DIC) was measured with a Finnigan Delta plus XP masspectrometer. Scanning electron microscopy and spot analyses of Ca, Mg, Mn and Fe in carbonate samples were carried out using a Quanta 200 microscope with an energy-dispersive X-ray spectroscopy SDD Apollo 10 attachment.

Results: In sediments of MV Malenky and MV Kukuy K-9, authigenic siderites ($FeCO_3$) with moderately positive $\delta^{13}C$ values +7.24 and +7.77 ‰ VPDB were deposited in diatom ooze at depths 27–28 and 36–37 cmblf respectively. In MV Kedr-1, siderite nodules were located in clays and had extremely heavy isotopic $\delta^{13}C$ values: +32.25 ‰ VPDB (125–127 cmblf), +27.39 ‰ VPDB (127–130 cmblf) and +33.32 ‰ VPDB (150-152 cmblf. At the same time, $\delta^{13}C$-DIC values measured for the bottom sediments of

MV Kedr-1 were on average lower in sedimentary layers with carbonates (from +8 to +10.5‰ VPDB) than in carbonate-free interlayers (from +9.7 to +19.5‰ VPDB).

Analysis of the chemical composition of the pore water showed that the carbonate interlayers fall into the core intervals with elevated ammonium concentrations (0.56–2.88 mg/L). However, statistical analysis did not reveal significant differences between carbonate layers and the closest carbonate-free sediments.

The analysis of the composition and structure of microbial communities associated with siderites revealed that they had a very similar range of dominant taxa, the members of which can destruct organic matter (*Bathyarchaeia*, *Hadarchaeales*, *Cladatribacteriota*, *Chloroflexi*, *Caldisericota*) and produce methane (*Methanomassiliicoccales*, *Methanosaetaceae*, *Methanoregulaceae*). However, the significant proportion of methanotrophic microorganisms (*Methanoperedensaceae*) was also identified in the carbonate interlayers of MV Malenky and MV Kedr-1. We did not detect iron-reducing microorganisms of the genera *Shewanella, Geobacter, Geothrix*, and *Thermanoerobacter* typically associated with siderites in other ecosystems. Also, the communities of carbonate layers did not have significant differences from the microbial populations of the surrounding carbonate-free sediments.

Conclusion: The available data suggest that the activity of microbial communities probably is not the only factor leading to the crystallization of siderites in the sediments of Lake Baikal. The discharge activity and the composition of fluids that provide additional supply of DIC or CO_2 from deeper sediment intervals can also affect the formation of carbonates and their isotopic composition in mud volcanoes. In the sediments of MV Kedr-1, the discharge of secondary microbial gas characterized by the presence of CO_2 enriched in isotope ^{13}C ($\delta^{13}C \leq +30$ ‰ VPDB) was recorded [2], whereas in the sediments of MV Malenky and MV Kukuy K-9, gas have microbial or early mature thermogenic origins with the $\delta^{13}C$ values of $CO_2 \leq +4.3$ and $\leq +11.0$ ‰ VPD respectively [3; e.g. A. Hachikubo, unpublished]. Under the conditions of additional fluid influx, the deposition of carbonates can occur in the layers with locally elevated DIC concentrations/alkalinity generated during various biogenic processes, including methanogenic destruction of organic matter coupled with silicate weathering, and, possibly methane oxidation, which are insufficient under normal conditions to shift equilibrium towards the deposition of carbonate minerals. In this case, isotopic characteristics of DIC or CO_2 coming with the fluids will largely determine the $\delta^{13}C$ values of the formed carbonates that are differ between the study areas.

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References

1. Krylov A., Khlystov O., Zemskaya T., Minami H., Hachikubo A., Kida M. et al. First discovery and formation process of authigenic siderite from gas hydratebearing mud volcanoes in fresh water: Lake Baikal, Eastern Siberia. *Geophys Res Lett*. 2008;35:L05405.
2. Hachikubo A., Minami H., Yamashita S., Khabuev A., Krylov A., Kalmychkov G. et al. Characteristics of hydrate-bound gas retrieved at the Kedr mud volcano (southern Lake Baikal). *Sci Rep*. 2020;10:14747.
3. Krylov A.A., Khlystov O.M., Hachikubo A., Minami H., Nunokawa Yu., Shoji H. et al. Isotopic composition of dissolved inorganic carbon in the subsurface sediments of gas hydrate bearing mud volcanoes, Lake Baikal: Implications for methane and carbonate origin. *Geo-Mar Lett*. 2010;30:427-437.