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Long-chain alkenones in the lake sediments of North-Minusinsk Basin (South Siberia): implications for paleoclimate reconstructions

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ABSTRACT. The core-top calibration study of 22 lakes indicates that in salt lakes the total alkenones increase sharply at a salinity of about 20 g/L, while alkenones are absent in the sediments of freshwater lakes. For the first time, this study shows that the Uk40 and Uk40' unsaturation indices are positively correlated with salinity and thus can be used to reconstruct salinity. The C37/C38 ratio is negatively correlated with salinity, and therefore this parameter can be used as an indicator of salinity. Also, the %C37:4 indicator is not correlated with salinity. It was found that the average chain length of alkenones increases with salinity, but the correlation was weak. Analysis of the alkenone composition and 18S rRNA suggests that all lakes are inhabited by Group II haptophytes, except for one freshwater lake, where the Group I of LCA-producing haptophytes was found. The taxonomic composition of haptophyte algae and the alkenone composition in the lakes were comparable to those in the lakes of the Canadian Prairies, apparently due to the similarity of climatic factors and the ionic composition of lake water in the two regions.

Keywords: alkenones, salinity indicator, lake sediments, South Siberia, paleoclimatology

1. Introduction

Knowing how the climate has changed over the past 2000 years is essential to understanding the relationship between current global warming and natural climate fluctuations. (McKay and Kaufman, 2014). Nevertheless, the patterns of climate fluctuations in the higher latitudes of Asia, for example, in Siberia, have not been studied enough. The Minusinsk Hollow is one of the site of special interest for paleoclimate research. Reconstruction of the paleoclimate from lake sediments can help reveal patterns of climate variations. In regions with arid and semiarid climate, endorheic lakes are sensitive to fluctuations in the balance of precipitation and evaporation. They respond by changing the volume of water, and the change in water salinity is inversely proportional to the change in volume. Significant research efforts have recently been focused on the search for molecular markers of climatic variations, among which the most promising are long-chain alkenones (LCAs). LCAs are C35–C42 methyl and ethyl ketones with 2-4 unsaturated double bonds in the aliphatic chain (Araie et al., 2018). Based on the 18S rRNA gene analysis, all known alkenone-producing haptophytes were divided into three groups: Group I freshwater species; Group II the species inhabiting waters of a wide range of salinity levels and Group III marine species. The C37/C38 ratio has been shown to decrease with increasing salinity. A more recent study has shown that in some lakes the proportion of %C37 relative to total alkenones is negatively correlated to salinity. It has also been observed that the average length of alkenones positively correlates with salinity. Except for a few lakes on the vast territory of Siberia, alkenones and the species composition of alkenone producers have not been studied yet.

Thus, the purpose of the current study was to analyze the relationships between the distributions of alkenones, and taxonomic composition of their producers and external factors in the region of Minusinsk Hollow where such research had not been done before and assess potential for alkenone-based regional paleo-reconstructions.

2. Materials and methods

The sediments core samples were collected from 21 lakes situated in the North-Minusinsk Valley during the field studies on July 24–26, 2019 and May 15–17,

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2020. Additionally, samples from Lake Slabitelnoye-2 were collected on July 21, 2021. Sediment samples were collected using a corer sampler UWITEC (Austria) at positions located in the central parts of the lakes. Then, the top 1-cm sediment layers were placed into separate sealed plastic bags and stored at -20 °C. Before sample collection, vertical profiles of temperature, conductivity, oxygen, pH, and redox potential were measured using a YSI EXO2 multi-parameter water quality sonde. Water samples for analysis of haptophyte DNA were collected from several lakes where alkenones were detected using a 0.5-L bathometer.

At the Analytical Laboratory of the Institute of Biophysics SB RAS, wet sediment samples (5–10 g) were dried at 50 °C until completely dry. Then alkenones were extracted for 24 h using the chloroform–methanol mixture (7:3 v/v) supplemented with the internal standard. After that, saponification was performed. Non-saponifiable components were separated using a 7890/5975C GC-MS chromatograph (Agilent Technologies, U.S.A.) with a VF-200MS capillary column. Identification of LCAs was based on determining molecular weight, the ratio of the weight to the base peak charge, and comparison of mass spectra with those available in literature (Jaraula et al., 2010).

For DNA analysis, water samples (40-300 ml each) were filtered through Advantec 0.2-μm cellulose acetate membrane filters and after that sample filters were stored at -20 °C. Total DNA was extracted using DNeasy PowerSoil Kit (Qiagen) according to the manufacturer's instructions. DNA was amplified using micro-eukaryote-specific primers V4F and V4RB containing adapter sequences (Illumina), linker, and barcode. Sequencing was performed at the SB RAS Genomics Core Facility (ICBFM SB RAS, Novosibirsk) using a MiSeq DNA sequencer (Illumina) with Reagent Kit v3 (2×300, Illumina). Phylogenetic analysis was based on the obtained operational taxonomic units (OTUs). Closest relatives were identified with the GenBank database (NCBI) using BLASTn. Multiple alignment of 18S rRNA gene sequences of all selected organisms was performed using the Muscle algorithm in MEGA X. The phylogenetic tree was constructed based on the Neighbor-Joining algorithm. Tree branch support was evaluated using the Bootstrap method with 1000 iterations.

Multivariate analysis by the RDA (redundancy analysis) method was performed in the R software environment using the vegan package. All data were previously (log + 1) transformed and standardized in the same package.

3. Results and discussion

Study lakes differed substantially in their characteristics. Salinity varied between 0.02 and 44 g/L and depth between 0.9 and 44 m. Anion SO_4^{2-} prevailed in most lakes, but in some brackish lakes (with salinity of 0.5 - 3 g/L) and freshwater ones (salinity below 0.5 g/L), the dominant anion was HCO_3^-. The dominant cation in all lakes except Lake Fyrkal was Na^+ followed by Mg_2^+. In freshwater Lake Fyrkal, Mg_2^+ prevailed over Na^+.

The total content of alkenones in the sediments varied widely, between 4 and 7400 μg/g dry sediment, with the exception of four freshwater lakes where alkenones were not found. Alkenone concentrations showed a strongly nonlinear salinity dependence: they were low in lakes with salinity up to 20 g/L, increasing dramatically, by two orders of magnitude, at salinity above 20 g/L. In the salinity range between 20 and 30 g/L, there were alkenone concentrations above 1000 μg/g dry sediment, and at salinity above 30 g/L, alkenone concentrations decreased.

C37–C39 alkenones were detected in all lakes. In the lakes with the total alkenone concentrations >100 μg/g, there were also C40 alkenones, but their proportion was the lowest in the total alkenone content. C37 and C39 alkenones were represented by methyl isomers, and C38 and C40 by ethyl isomers. Unlike other lakes, the isomers C37:3b and C38:3b were detected in Lake Matarak. The C37/C38 ratio varied between 1.11 and 3.54. A significant anti-correlation was revealed between the C37/C38 ratio and salinity (-0.5, $n=18$, $p<0.05$). There was practically no correlation between %C37:4 and salinity. A significant correlation was found between salinity and indices Uk40 ($r = 0.72$, $n = 11$, $p<0.05$) and Uk40' ($r = 0.86$, $n=11$, $p<0.05$)

Only 10 OTUs were identified as *Haptophyta*, and four of these were of the order *Isochrysidales*. *Isochrysidales*, which have been so far regarded as the only producers of alkenones, were detected in all alkenone-containing lakes except Lake Shunet, where they were not found. In Lake Krasnenkoye (at the village of Borets), where no alkenones were detected, no *Isochrysidales* OTUs were identified as well. Alkenone-producers of the Group II were found in all other studied lakes, except for Lake Matarak where OTU 878 showed 100% similarity of the sequences with phylotypes of Group I typical for freshwater lakes. OTU 6 from Lake Uchum showed 100% similarity with *Isochrysidales* sp. phylotype MK092737.1 from Canadian lakes; it was assigned to Group II of alkenone producers.

The RDA (redundancy analysis) method showed that Total alkenones (TotAlk) had a stronger correlation with salinity than with any other parameter. The lakes formed several distinct groups. Group I included freshwater lakes, in which there were no alkenones: Kiprino, Itkul, Fyrkal, and Krasnenkoye (close to the village of Borets). Group II comprised saline and brackish lakes containing alkenones

4. Conclusions

For the first time, the potential of alkenones for reconstructing salinity in the semiarid steppe region in South Siberia was studied, and it was found that alkenone properties and their relationship with external factors are generally similar to those previously established for other regions. Total alkenones in sediments can increase dramatically at salinity above 20 g/L; hence, alkenone peaks in sediment cores can indicate an increase in salinity and the exceeding of the threshold of 20 g/L caused by the drying of the closed lakes. In addition, new indices of unsaturation of C40 alkenones were used and their correlation with salinity was shown; however, the data are not sufficient to definitely them as salinity indicators. Studies have shown that the species composition of alkenone producers and the range of alkenones are similar to those in North America regions with the same climatic conditions.

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Conflict of interest

The authors declare no conflict of interest.

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