Doctoral School of Earth Sciences

The environmental change in the Lake Bolătău-Feredeu basin over the last 500 years

Bolătău-Feredeu tó vízgyűjtő területén bekövetkezett környezetváltozás az elmúlt 500 év folyamán

Thesis of PhD dissertation

Author:

Máté Karlik

Supervisor:

Gábor Bozsó PhD.

Senior lecturer

Department of Mineralogy, Geochemistry and Petrology

Faculty of Science and Informatics

University of Szeged

Szeged

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I. Introduction and Objectives

Research into the paleoclimate and the paleoenvironment is gaining more and more emphasis in the recent period, thus becoming one of the most popular areas of environment research which has emerged as essential for a broader understanding of climate change. Many geological archives are suitable for this type of research, including speleothems, various sediments etc. One of the major research areas is the study of lake sediments, which requires knowledge pertaining to several disciplines and a multidisciplinary approach (Last and Smol, 2001). Research on lake sediments related to the paleoenvironment was initiated as early as the 19th century (Lyell, 1830). The lake sediment retains traces of the environmental changes which have occurred in the lake-catchment system, with the preserved pollens providing information on a larger scale. Productivity in the lake and the catchment area constantly follows the changes in the environment and/or the disturbances caused by human influences. For a complete and accurate interpretation of lacustrine sediment data it is necessary to know the current state of the lake and of the catchment area, and to document the processes and conditions specific to it (Jackson et al., 1948; Sverdrup H., 2009; Wan et al., 2019).

Organic geochemical methods, especially n-alkanes, are excellent tracers of the changes in vegetation composition (Meyers, 2003; Eglinton and Eglinton, 2008). Large amounts of samples are required in order to use these methods (20 g lake sediment per sample for organic matter extraction). The time resolution of sample units for organic geochemical analysis varies greatly depending on the organic matter content within the core, considering that there was no previous experience on the extractable organic matter content and composition of young sediments, the goal was to ensure a sufficient sample quantity. The value of C% measured in points varies between 2.6 % and 8 % in the examined range The knowledge of mainly inorganic parameters (mineralogical analyzes, stable isotopes, weathering indices, elemental composition, particle size distribution) with low sample requirements also provides information for the reconstruction of the environment and paleoclimate. By examining these parameters, it is possible to detect changes in the catchment area (example: temperature, Rainfalls, human impact), especially those which modify the lake input conditions (Engstrom & Wright, 1984; Couture & Dymek, 1996). Many processes take place in the water body and lake sediments, which involve changes in pH and eH. Examples include the decomposition of organic matter, microbial activity, or the reduction of the dissolved oxygen content in the sediment, the formation of an anoxic environment. Examining the inorganic parameters of the sediment provides an opportunity to describe these processes and to learn about the environment formed as a result of these processes.

The Carpathians and the Carpathian Basin are rich in suitable paleoclimate and paleoenvironment research areas, especially in terms of the changing geological conditions. (example: Lakes, ice and stalactite caves), Several studies have already been published in the field of lake sediment research in this region many of which included paleoenvironmental reconstructions (e.g., Wohlfarth et al., 2001; Haliuc et al., 2009; Magyari et al., 2009; Kłapyta. et al., 2016). The selected research area is located in the Eastern Romanian Carpathians in the Bukovina region and overlies the catchment area of the river Sadova. Lake Bolătău-Feredeu is located at 1134 meters above sea level, adjacent to a Natura 2000 protected site. The lake is one of the three Millenial Lakes of Bukovina. The sediments of the lakes are stratified and provide information about the last 1000 years The catchment area is ~ 30 ha, whereas the surface of the lake is 0.3 ha. The water depth measured at the time of sampling was 5.2 m. (Mîndrescu M. et al., 2013 & 2016).

The aim of this research was to study the lake sediment and the catchment of Lake Bolătău-Feredeu with geological and geochemical aspect, mainly in terms of paleoenvironmental and paleoclimatic reconstruction. The final edge was to document a detailed paleoenvironmental story covering the entire analyzed time frame.

The subject of the study consisted in the elemental analytical and mineralogical examination of the bedrock, the comparison of the results with previous data. The examination of the mineralogical, chemical and grain size of the formed soil (and lake sediment), and the understanding of the weathering processes prevailing in the lake catchment.

The analysis of the lake sediment required careful high-resolution characterization and examination. In order to carry out a correct description of the examined lake sediment research, an accurate high-resolution age-depth model was necessary. The study focused on the application of a wide range of methodologies in the studied section, using both organic and inorganic methods. Within the organic geochemical approach, the aim of the study was to investigate the applicability of n-alkanes as proxy parameters in young sediments. Stable isotope measurements were performed using an IR-MS mass spectrometer. Due to the small sample requirement, sampling was performed directly from the drill cores using a micro drill.

II. Methods

During the research, the methods used play a key role due to the reproducibility of the research and measurements. The methods used are presented in this chapter. In order to make it easier to understand, the division of the chapter is based on the examined materials. A joint overview of the analysis carried out on individual groups of materials (e.g., bedrock, soil, lake sediment) helps to understand the research results

II.1 Summary of methods used for bedrock and soil materials

Sampling from the bedrock was carried out based on the preliminary data (geological map; Ionesi, L (1971.) and field observations at the same time as the soil sampling. During the field observations, the topographical conditions and plant cover were clearly distinguished. Local researchers (Marcel Mindrescu and Ionea Gradinaru) who have decades of experience in the geological and botanical investigation of the Carpathians assisted in the selection of the sampling points and during the sampling.

I made an average sample of the rock samples. I braked the rock samples than I powdered the same amount of samples. The subsamples were taken into examinations after dusting and homogenizing. An X-ray powder diffractometer was used for mineralogical determination, which was supplemented with X-ray fluorescence analysis, and the obtained values were used to calculate weathering indices.

In the case of soil samples, no separation of individual soil horizons was performed due to the fact that stratification was not observed. The samples were taken on a same place than the rock samples. the samples were homogenized before transport. To perform the tests, subsamples were formed from the samples. Quantitative analysis of the particle size distribution was performed using laser diffraction particle size distribution analysis. The samples were pulverized and prepared for further analysis. Similar to the petrological studies, X-ray powder diffraction measurements were performed to separate the mineral phases, while X-ray fluorescence analysis was used to calculate the chemical composition. The weathering indices were calculated based on the data obtained from these analyses.

II.2. Summary of methods used for lake sediment samples

Extensive analytical options were available for the study of lake sediment. Thin sections were made from the cores, based on which the mineral composition and organic contents were measured, and the stationary processes were determined. This phase of the research employed the following methods: Optical microscopy, cathodoluminescence microscopy, infrared spectroscopy (FTIR-ATR), micro-raman spectroscopy.

Stable isotope measurements were also performed on two sediment cores and were used to synchronize the cores thus, the individual depths of the drill cores can be matched to each other. The two drilling points under the water were located at a distance of about 50 cm from each other. These measurements were carried out using an IR-MS mass spectrometer ($\delta^{13}C$; $\delta^{15}C$; C%; N%; C/O atomic ratio). The obtained data were used to determine the source of the organic matter and as an indicator of productivity. IR-MS measurements were performed on 1-cm average samples on both cores (LB-G-01 and LB-G-02) with high-resolution (mm scale) sampling directly from the drill core.

Furthermore, in the case of LB-G-02, the measured C% value was used to delimit the samples to be measured for n-alkane. The n-alkane measurements were performed by gas chromatography. Index calculations were carried out based on the peak intensities (TAR_{HC}; P_{aq}; P_{wax}; P_{hw}).

In addition to organic geochemistry and stable isotope measurements, the methods used on the LB-G-01 core subsamples, which had previously been age-determined. The 1-cm average samples were analyzed for: stable isotope measurements using IR-MS spectrometer. Mineralogical composition was determined from a powder sample with a diffractometer (XRD). Elemental analysis was carried out with X-ray fluorescence spectrometry (WD-XRF) on pastilled samples. I interpreted the obtained data independently and as calculated weathering indices during the definition of processes and events. The particle size distribution of samples was determined by laser diffraction particle size distribution analysis. The particle size distribution data is primarily one of the main indicators of the change in application conditions.

III. New scientific results

The research presented in the dissertation resulted in the following novel scientific results:

1. I established that there are two main bedrocks (sandstones) in the catchment area based on the elemental composition (XRF) and mineralogical (XRD) analysis, The two rock types differ only in aluminum and silicon content (SiO_2 ~90%, Al_2O_3 ~2.8%; SiO_2 ~70%, Al_2O_3 ~16%), they cannot be distinguished from a mineralogical point of view. The latter contradicts previous research results: according to Ionesi (1971), several types of mineral constituents can be found in the rock (e.g. glauconite), however,

during my research, I did not detect any other minerals only quartz. From the XRF and XRD analyses, I also established that the heterogeneity of the initial bedrock does not appear in the case of the soil samples. It follows from this that, although the topography of the catchment is segmented, the direction of the material entering the lake does not affect the inorganic composition of the incoming material.

2. I created an age model based on Pb-210 and radiocarbon data for the investigated time period. One of the key results of the model is that it provides high-resolution data analysis in time. The obtained Pb-210 activity data come from the upper 24 centimeters of the sediment layer with a resolution of cm. Radiocarbon data indicate the age of plant remains (pieces of branches) found in the sediment. The decay of radioactive isotopes is a process whose rate is specific to the isotope and cannot be influenced. Another important outcome of the model is hat the lake sediment was not disturbed or mixed. This was confirmed by the observation that there were no outliers between the data/activities during the creation of the age model. The good age model is an essential criterion for environmental reconstruction. Even at the deepest point of the examined section, the age model only contains an error of ~+/-10 years.

3. Based on the results of organic and isotope geochemical analysis of the lake sediment, I established that its organic matter content comes from two sources: C3 plants and freshwater algae. I found that there were no new sources of organic matter entered to the lake-forest system during the examined period (~500 years) based on the cross-

diagram of N% and C%. During my research, I also calculated n-alkane indices (TAR_{HC}, CPI, P_{aq}, P_{wax}, P_{hw}) from the peak intensity of the measured chromatograms, which are widely used tools for environmental reconstruction on mature organic materials. In my research, I proved that, in addition to aged organic matter, these indices are also suitable for young, immature organic materials. To validate the usage of n-alkane proxy information I compared them with the available historical records from the area. The effect of deforestation known from military maps and historical documents is clearly visible in the n-alkane indices. For example, the P_{hw} index which expresses the ratio of n-alkanes from herbaceous/woody plants, changed from 0.47 to 0.8. Using n-alkane data and stable isotope measurement results, I separated three main periods, which are as follows:

i. - Deforestation and the decline of the lake's biological productivity: ~1470 A.D. - 1560 A.D.
ii. -Changing of lake environment, decreasing productivity in the catchment area: ~1640 A.D. - 1760 A.D
iii. -Modern landscape change: ~ 1820 A.D.-2013 A.D.

4. I found that the degree of productivity and the direction of the natural biological processes taking place in the area depend mainly on the temperature. In cold periods, the productivity shows a decrease, and the herbaceous vegetation was the first to react to the changing conditions, based on the P_{hw} n-alkane index the herbaceous content decreased. The comparison of the proxy parameters with the available rainfall and storm event data for the region did not yield any evaluable results.

5. I found that the change in the phosphorus content of the sediment follows the change in the ambient temperature. The maximum and minimum periods of the N-SK temperature proxy parameter and the measured phosphorus content show good agreement.

   The phosphorus content of the sediments studied comes from two sources: inorganic components (e.g. minerals) and organic components. Given that phosphorus is a secondary biogenic element and the sediment has a significant organic matter content (C% 2.6-8.8), the change in phosphorus is definitely related to the change in the flora in the area. In my opinion, the phosphorus content can also be used to characterize the temperature changes.

6. Based on the parameters examined in the sediment (n-alkane indices, stable isotope data, particle size data, elemental analytical data, weather indices), I documented the detailed environmental history of the area and I clarified previous information with my own findings. I determined the following time periods:

   i. 1500 A.D. – 1620 A.D. – Distribution of herbaceous plants in the catchment area: Based on the data, the herbaceous vegetation appeared scattered in the previously closed forest vegetation.

   ii. 1620 A.D. – 1700 A.D. – Cold period in the catchment area: Productivity decreases in the area due to drop in temperature. As the herbaceous vegetation diminished, the filtering effect on the lake shore also decreased. Therefore, larger particle sized materials reached the lake more easily.

iii. 1700 A.D. – 1780 A.D. Nearly stable period: Only short-term events occur in the catchment area which generate no significant differences.

iv. 1780 A.D. – 1860 A.D. – Cold period and deforestation in the catchment area: During this cold period, deforestation occurred as an anthropogenic effect. I established the date of the deforestation event in the Bolătău-Feredeu catchment area based on the measured parameters (n-alkane indices, weathering indices, etc.). I compared my results with published data from the neighboring catchment area (Florescu et al 2017). Based on the published Lake Iezer macrofossil dataset and results of my thesis, I found that the deforestation occurred primarily in the Lake Iezer catchment area, and only reached the Lake Bolătău-Feredeu catchment area 65 years later, around 1811 A.D. After the deforestation event, new vegetation began to form in the catchment area.

v. 1860 A.D. – 2010 A.D. – Modern landscape change in the catchment area: As a result of previous deforestation, the proportion of woody vegetation has decreased in favor of herbaceous plants. In addition, the anthropogenic disturbance of the area continued, especially during World War II.

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