**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*

**PhD Thesis**

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# Chapter I.: Introduction

## I.1. Short history of climate and environment observations and research topic

Throughout history understanding weather and environmental change has been essential for human life. Already in the age of the Egyptian civilization, mankind documented the changes in the weather. Since the flooding of the Nile provided a fertile sediment for agricultural works, water level variations in the Nile Valley were regularly observed and recorded by the local population (Ryan & Pittman, 1999).

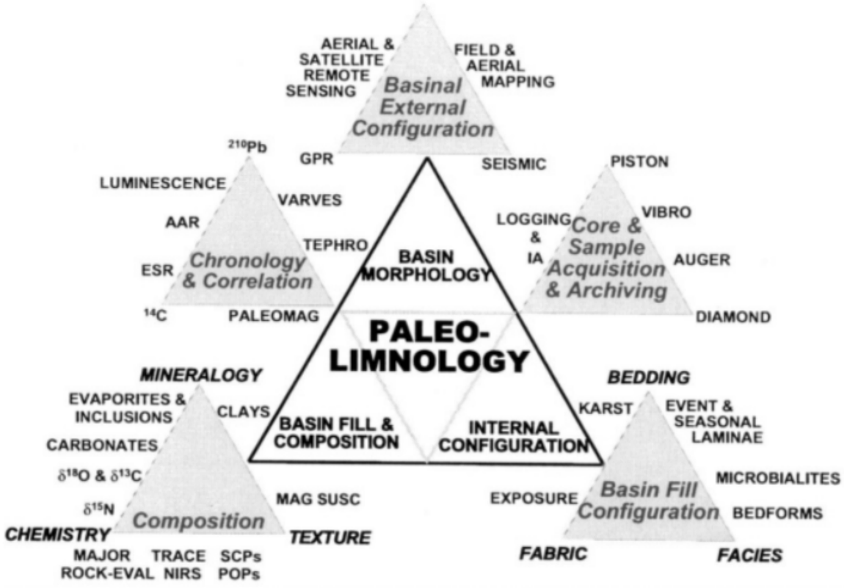
Initial observations have called for the explanation of climatic events and phenomena. In the early stages of human civilization, there were mainly religious and mythological explanations. However, it should be noted that important natural events can also be found in myths and religious writings (King and Goff 2010; Middleton 2012). As such, scientific understanding of observed environmental changes appeared earlier in ancient India, China, and the Persian Empire than in Europe.

The first researchers who studied the environment and its changes were travelers. Their primary focus was the accurate description of localities and their weather events (Fairbridge, 2009). The scientific topic of paleoclimate research was initiated by Robert Hooke (1635 –1703), who inferred the warmest climatic conditions in the history of the Earth based on the size and anomalies of turtle fossils (Schramm, 1963). With the development of technology, the emphasis shifted from the descriptive approach to the analytical one. In the 20th century, with the development of analytical methods, it became possible to study previously uninterpretable geological archives. One of the first groups of these materials is also the most well-known in the public mind. The ice cores investigation goes back almost 80 years (Langway, 2008). New geological and biological archives were discovered during paleoclimate research. The use of these groups of materials is still popular among researchers today. In particular, lake sediments (Zang, et al,. 2020; Naracic, et al. 2022), paleosoils (Bradák, 2022; Hou et al., 2022.), tree rings (Housett, 2018; Büntgen, 2022), corals (Delong, 2013; Rahaman et al., 2022), speleothems (Ronay, 2019; Demény, 2021) are actively studied.

## I.2. Lake sediments as a complex historical archive

Lake sediments are commonly applied in paleoclimate and paleoenvironmental research (Last & Smol, 2001). However, not all lake sediments are suitable for this purpose. Choosing a research site requires great care. The turbidity of lake sediments can make successful research difficult or impossible. Furthermore, the ideal lake should be located away from anthropogenic influences. It should have sufficient depth so that weather effects on the surface do not disturb the sediment. Currently, the group of lakes considered most suitable are upland lakes, which fulfil the ideal lake parameters.

During sedimentation, organic and inorganic components from the lake catchment are transported to the lake basin. Therefore, lake sediment can provide unique source of environmental and climatic information about changes in the watershed and its surroundings (Dearing, 1991). The study of lake sediments, i.e., paleolimnology, typically requires a multidisciplinary approach, the complexity of which is best illustrated in I. Figure 1. (Last & Smol, 2001) (I. Figure 1):



I. Figure 1.: Schematic diagram of techniques and disciplines used in the study of lake sediments (Last & Smol, 2001.)

Paleolimnology requires to understand the lake sediment in detail. The individual proxy information alone is often difficult to interpret or only provides partial information. The combined interpretation of data obtained from different analytical methods is necessary to make an accurate paleoclimate and paleoenvironmental reconstruction.

At the beginning of the research, it is important to understand the study area and the sediment itself. The petrological description can be prepared using optical microscopy and cathodoluminescence spectroscopy as the most widely used technology. (Götze, 2012; Braekmans, & Degryse, 2016) Detailed analysis of thin sections for petrological analysis provides an opportunity to identify processes in the sediment. The optical tools can be effectively used to complement the Fourier-transform infrared spectroscopy and Raman spectroscopy. These information can describe the mineral particles in the material, organic and chemical bonds of organic and inorganic substances. (Moody et. al., 2005.; Luo et. al., 2021.) Mineralogical overview by the X-ray diffraction of powder samples gives the main mineralogical characteristics of the composition of the material. The detection limit of this method is ~5 V/V%. There are a number of methods for elemental analysis of geological and lake sediment samples, the two most commonly used at present being Inductively coupled plasma - optical emission spectrometry/mass spectrometry and X-ray fluorescence spectroscopy. Based on elemental analytical data and mineralogical composition changes in weathering conditions and processes in the research area are easily determine. (Ekoa Bessa et al., 2018) Natural or anthropogenic changes in the catchment area can significantly affect the sedimentation processes. Thus sedimentation grain size distribution can be used to determine these events. (Yan et al., 2011.) The organic matter content of lake sediments provides important information on the paleoclimate and paleoenvironmental research. With gas chromatography measurements organic geochemical proxy information can be obtained (e.g. n-alkane ratios). Changes in these ratios can be used to understand the changes of vegetation in the catchment and in the water body. (Meyers. & Teranes 2002.) Results of stable isotope measurements and C% and N% measurements can refine the information from the n-alkane indices, and help to determine the origin of the organic matter. (Meyers, 2003.; Lamb et al. 2006). The analysis of pollen preserved in lake sediments is a common technique which can give information about the flora of the cacthment area. (Seppä & Bennett, 2003.) In the present study, the following large-scale analytical tools were used (I. Table 1.).

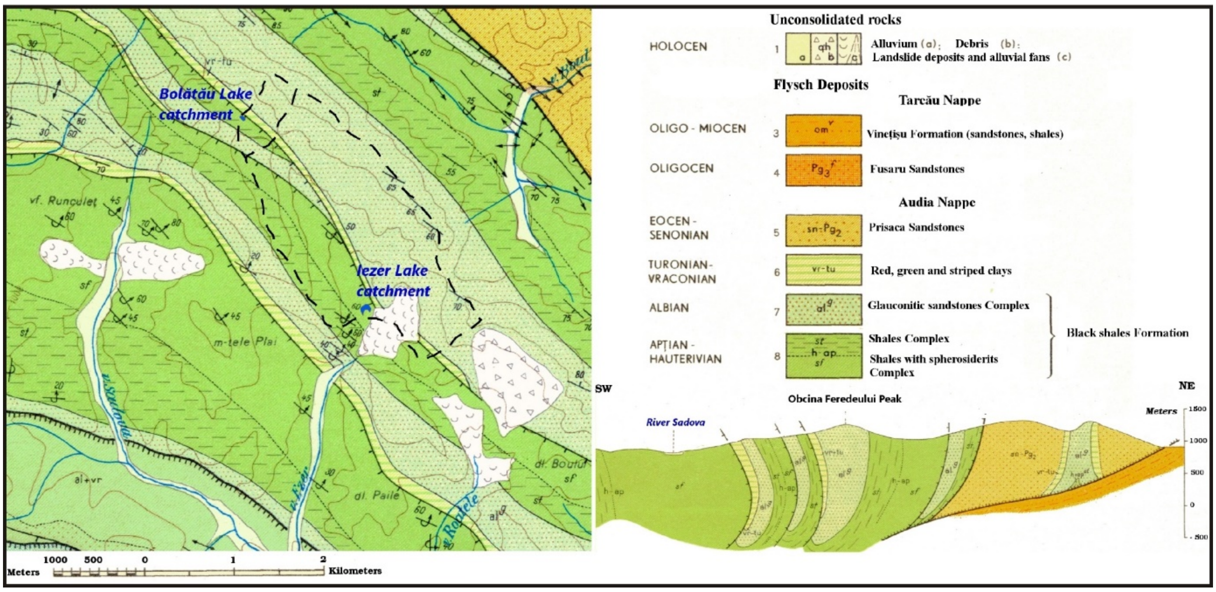
I. Table 1.: List of samples and methods

| Methods | Samples |
|---|---|
| Optical rock microscopy | 117 |
| Cathodoluminescence microscopy | 56 |
| Fourier-transform infrared spectroscopy | 139 |
| X-ray fluoreszcens spectrometry | 69 |
| X-ray powder diffraction | 69 |
| Raman spectroscopy | 80 |
| Gas chromatography | 12 |
| Stabile isotope measurem | ~400 |
| C% and N% measurements | ~400 |
| Particle size analysis | 69 |

## I. 3. Description of the research area – Bukovina, Romania

The Carpathians mountains are rich in paleolimnology research opportunities. Many small lakes have been developed in the area over time, many of which have not been explored due to their remote location. In many cases these lakes do not even appear on geological and geomorphological maps. However, they are excellent candidates for study due to their small surface area and considerable depth, allowing for fine stratification of the sediment.

In the last decade, several studies have been published about the Carpathian lakes (e.g. Vreca and Muri, 2006; Feurdean et al., 2015; Magyari et al., 2014; Hutchinson et al., 2016; Tóth et al., 2017). The present study area belongs to the westernmost subunit of the Audia Nappe, Bukovina, Romania (Black Palaeolithic Formation). Preliminary data indicate that the area of the aquifer contains sandstones of Cretaceous age. (I. Fig. 2.) The investigated Lake Bolătău - Feredeu ( 47° 37′ 20.74″ N, 25° 25′ 54.43″ E) is one of the three known lakes in Bukovina with potential annual stratigraphy. These lakes were named by their explorer as millennial lakes (Iezer lake, Pascanu lake, Bolătău - Feredeu lake) (Grădinaru et al., 2012; Mîndrescu et al., 2013) The study of these finely stratified (submilimeter) lakes provides a unique opportunity for high-resolution paleoclimate data analysis and paleoenvironmental reconstruction.



I. Figure 2.: Geological map of the the research area. (Pojorâta geological map, 1:50 000 scale - Geological Institute of Romania)

## I.4. Aims and structure of the dissertation

The finely stratified sediments of Lake Bolătău -Feredeu allow an accurate paleoenvironmental reconstruction for the period under study. Their thorough analysis requires the combined use and precise knowledge of several methodologies. The inherent research and analytical challenges of paleoclimate topic have fostered my interest in the subject.

The first objective of this research was to explore the real potential of the sediment archive of Lake Bolătău -Feredeu and to perform environmental reconstruction for the period under study. The main focus was to explore the different analytical possibilities, with particular emphasis on the applicability of organic geochemistry. The organic geochemistry approach is not commonly applied in paleolimnology research in the Carpathian region, nor it is typical in the international literature on young sediments. Using inorganic and organic geochemical methods as well as particle size data, my aim was to describe an accurate and precise environmental history over the past ~500 years with particular emphasis on anthropogenic and climatic influences. The extensive methodology has made it possible to explore the hitherto unknown relationships among the different paleoclimate proxy parameters. The data and findings of Lake Bolătău -Feredeu, reported here, will be used and compared with those of Millenium lakes (Iezer, Pascanu) to develop the high-resolution paleoenvironmental reconstruction in the region.

Chapter I is an introduction of the dissertation. Chapter II describes the mineralogy of the area, weathering processes and the description of the lake sediments. Knowledge and documentation of the weathering processes, the details of bed rock, soil, and lake sediments occurring in the catchment area, and the bed rock mineral composition compared with previous data are essential for a correct paleoenvironmental research. Chapter III presents in detail the results of the organic geochemical analyses complemented by stable isotope measurements. The applicability of n-alkanes for organic geochemical proxies in young sediments is also reported in the chapter. It contains the sediment age model, which was determined based on Pb-210 (published in Bihari et al, 2018) and radiocarbon dates. Pb-210 data indicates that the sediment was undisturbed. Thanks to the exceptionally good age data it was possible to perform high-resolution analyses for the first 500 years of the core. The results obtained are used to isolate several periods, with particular emphasis on vegetation change.

Inorganic parameters are one of the most common analytical tools in lake sediment analysis. Chapter IV includes the investigation of the particle size distribution and inorganic elemental composition parameters. It is essential to clarify the results of previous studies and to explore hitherto unknown relationships among proxy parameters, given that joint interpretation is uncommon in this region. Chapter IV also contains the temporary high-resolution paleoenvironmental reconstruction. Chapter V is the last one and reports the main conclusions and includes the thesis.

# Chapter II.: High resolution mineralogical characterization of sediments - lake Bolătău-Feredeu (Romania)

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## II. Abstract

The catchment (bedrock and soil) and sediments of lake Bolătău, Romania were studied by high resolution multi-methodological investigations to characterize paleoenvironmental and formation conditions. Particle size analyses, optical and cathodoluminescence microscopy, FTIR-ATR and Raman spectroscopy, X-ray powder diffraction, and XRF were applied for microtextural, chemical, micro-mineralogical and embedded organic material characterization and distribution of the sediments, especially concerning geochemical conditions, like pH and redox potential change. Our results support physical and chemical weathering in the process of soil formation with appearance of the new minerals appear (10Å sized phyllosilicates and clay minerals). Comparison of these studies offer possible differentiation of syn- and diagenetic mineralization, the clarification of debris contribution, microbial mediation and complex mineralization via decomposition of cell and extracellular polymeric substance. Based on the analyses on the abrasives, a suboxic environment prevailed in the depositional area and considerable microbial contribution is proposed via accumulation of lake sediments.

**Keywords**: lake sediment, high resolution analysis, mineralized biosignatures, biomineralization

## II.1 Introduction

The lake sediments are one of the most common popular study field in the paleoenvironmental topic because lakes are excellent indicators of environmental change (Battarbee, 2000). In the last fifty years, numerous studies have been performed on the methodology of paleolimnological research (Kummel & Raup, 1965; Berglund, 1986; Last & Smol, 2001). A number of approaches are used in this multidisciplinary field. Regarding the research topic, a number of organic and inorganic components were used in the paleoenvironmental research (e.g. Meyers & Teranes, 2002; Grygar et al., 2006; Eglinton & Eglinton, 2008; Bordon et al., 2009; Buczkó et al., 2009; Gąsiorowski & Sienkiewicz, 2010). The Romanian Carpathians have many lakes suitable for this type of research and, also, deserves special attention. In the past period several papers have been elaborated using organic and inorganic proxies (e.g. Magyari et al., 2009, Tóth et al., 2018). Detailed knowledge of the catchment was essential for the success of these researches.

To understand the process of sediments formation a detailed knowledge of the catchment area is required. The rock layer is the main starting material for inorganic components. The milling process is influenced by a number of parameters and knowledge of these processes facilitates subsequent analyzes (Wan et al., 2019). If more than one chemical composition is found in the catchment area, the direction of each element can be taken into account in the subsequent analysis of the sediment, for example in the event of precipitation events or changes in cover. Chemical and biological processes in the soil result in changes in the composition of the existing or new minerals. Vegetation from microbial levels to trees has a prominent role in such processes (Jackson et al., 1948; Sverdrup, 2009). The formation and composition of lake sediments depend on a number of parameters that greatly influence the results of subsequent organic and inorganic geochemical analyzes. Preliminary microscopic microtextural observations raised considerable microbial contribution to the sediment. Based on this, the aim of the study was the high resolution microtextural, micro-mineralogical and embedded organic material characterization and distribution of the sediment, especially concerning geochemical conditions, like pH and redox potential change. These studies offer possible differentiation of syn- and diagenetic mineralization, the clarification of debris contribution, microbial mediation and complex mineralization via decomposition of cell and extracellular polymeric substance (EPS) (Polgári et al., 2019).

## II.2. Geological background, catchment area, sampling

### II.2.1. Geological background

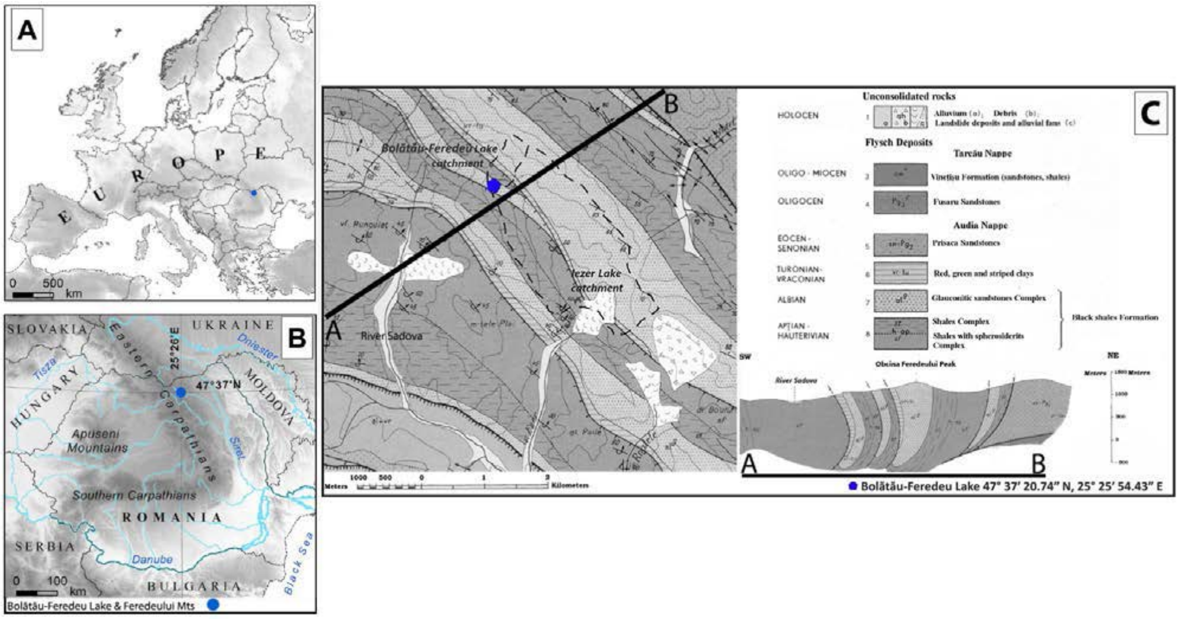
The study area was located in the East-Carpathian region near to the catchment of Sadova river, Romania. The geology of region where the locality is placed belongs to the westernmost sub-unit (Black Shales Formation) of the Audia Nappe (Fig. 1), comprising, mostly Cretaceous shales (Săndulescu, 1984). The catchment of the lake Bolătău is the eastern part of thementioned region. This small area consists of three different geological formations. The Cretaceous deposits are predominantly clayey, and the Palaeogene ones are mostly represented by uniform layers of sandstone, with small intercalations of clays and marly clays. The study catchments are situated within the westernmost sub-unit (Black Shales Formation) of the Audia Nappe comprising shales of Cretaceous age. These geological formations are highly susceptible to landsliding as they comprise alternations of black marly shales, glauconitic, siliceous or calcareous sandstones, red, green, striped, and grey clays (Fig. 1) (Ionesi, 1971; Mîndrescu et al., 2013).

### II.2.2. Location and main details of the lake Bolătău and the catchment area

Sadova stream is a tributary of river Moldova - Romania. The Bolătău lake (47° 37′ 20.74″ N, 25° 25′ 54.43″ E) means pond of puddle, which is a common name in the region (Grădinaru et al., 2012). The lake is near to Feredeului Mts., just below the Obcina Feredeului peak (1364 m asl) and in the neighborhood to the Lezer lake. A landslide event indicated the catchment and the lake current formation (Mîndrescu et al., 2013).

The lake maximum depth was 5.2 m and the surface 0.3 ha in 2010. The water quality was measured in 2010, the total phosphorus concentration in the lake was 0.014 mg/L (Mîndrescu et al., 2010), corresponding to mesotrophic class regarding the trophic status (OECD, 1982). The dissolved oxygen measurements were made in 2014. It was measured at four profiles. In the top of the lake the dissolved oxygen value was between 8-9 mg/L, which attenuate to 0.2 mg/L in the deepest section. Indeed, these redox conditions make the bottom water to become very methanogenic (Karlik et al., 2018).

The landslide, expanding over ca. 30 ha, affected mainly the right-side slope, as well as the valley head slope to a lesser extent (Mîndrescu et al., 2010). The catchment diameter is only 700 m but the elevation amplitude within the catchment is significant, amounting to ca. 227 m (1364 m a.s.l. to 1137 m a.s.l.) (Mîndrescu et al., 2013). The flora of the catchment is currently composite. 6 ha of the catchment is deforested and variants of herbs can be found. Currently the main species of the conifer forest (24 ha) are Norway spruce (Picea abies) and silver fir (Abies alba), goat's willow (Salix caprea), alder (Alnus incana), trembling aspen (Populus tremula), birch (Betula pendula) that can be found at the lake shore, and among water-loving herbaceous plants the rush (Bolbosschoenus sp.) occurs (Mîndrescu et al., 2010).



II. Figure 1. Location of Lake Bolătău-Feredeu A) at continental scale; B) in the Eastern Carpathian region, national scale; C) closer view of the research area (Pojorâta geological map, 1:50 000 scale - Geological Institute of Romania

### II.2.3. Sampling

The catchment area is small but the relief dates are varied. To correctly analyze the catchment material and identify the starting material in the sediments for comparison, the catchment soil and the bedrock were sampled during 2016 to 2020 years period. Sampling was performed at random in areas demarcated on the basis of environmental variations. The random samples from each territory were homogenized. After homogenization/mixture, three representative rock samples and three soil samples were compound.

In the catchment area three different regions of the bedrock and soil were located: “up side”; “right side” and “left side”. The soil samples were collected near to the bedrock deposits. Bulk samples of lake sediment, catchment soil samples (~5 sample/area) and homogenised to 1 sample/area, and bedrock samples from 3 area (~5-7 sample/area) and homogenized to 1 sample/area (bulk measurement) were analysed by XRD and XRF.

Lake sediments were analyzed with especially sonar. The reflection from the different sediment layers help to decide the most promising drilling points in the center of the lake. The sediment cores were collected during to April of 2013. At that time the lake surface was frozen. The sediments were drilled with two different type of corer instruments (Russian corer and a gravity corer).

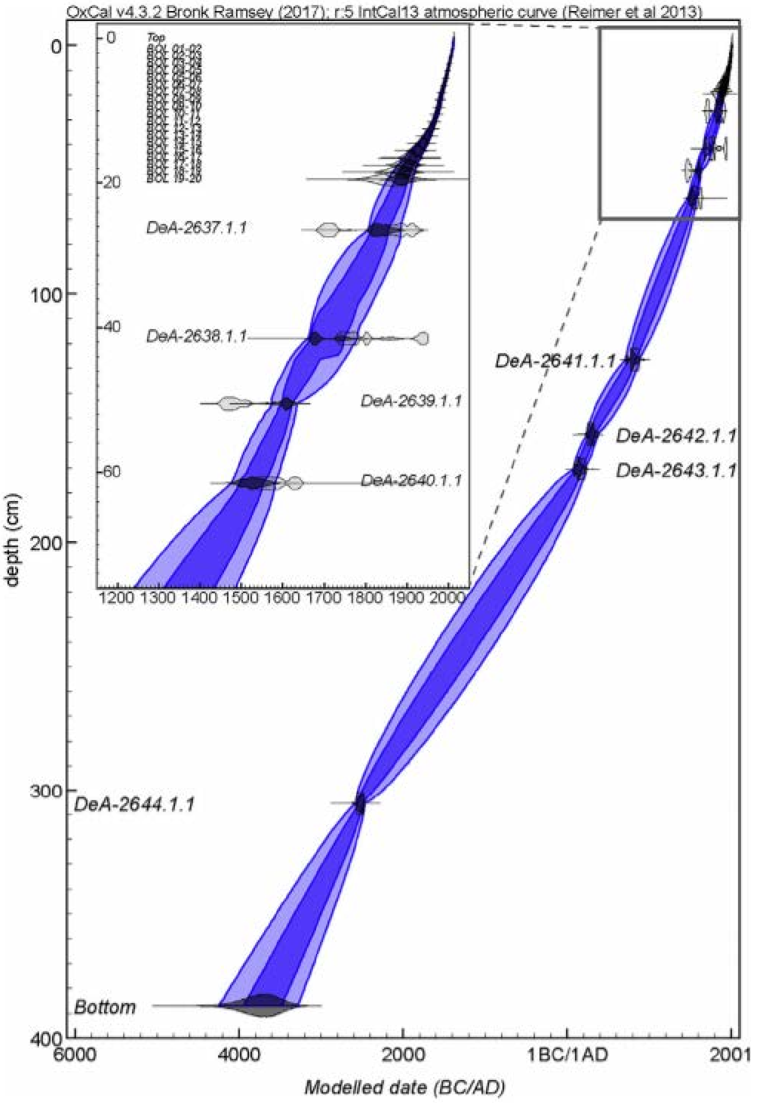
Due to the corers parameter which was similar (the d=6.5 +/-0.1 cm and the S= 33.2 ± 0,6 cm2), the sampling points were very close, (distance between the two sampling points is less than 1 m). The collected cores have between 66 cm and 400 cm length. The cores and the layers wet condition was documented, descripted and photographed. The overlapping region of the two cores fitted perfectly based on comparison of characteristic zones of the cores (Mîndrescu et al., 2016).

### II.2.4. Chronology of the sediment

In the multi proxy analyses one of the most important things is the correct dating and the perfect time model events or changes (Birks & Birks, 2006). The first detailed micro sedimentological and geochronological analyses proved the great potential of the Bolătău sediment archive for future high resolution paleolimnological investigations (Mîndrescu et al., 2016). To make a high-quality time model the sediment chronology model was based on two different isotopes methods: the chronology based on radiocarbon (Mîndrescu et al., 2016) and the another one, Pb-210 ages (Bihari et al., 2018).

Pb-210 (T1/2=22.23 yr) is one of the most used isotopes in the first 150 years sediment dating processes and used in lakes with similar conditions in Romania (Appleby, 2001 & 2008; Begy et al., 2009 & 2011). The Pb-210 chronology and the calculations were published in Bihari et al., (2018), where they used different accumulation models in the calculated Pbex-210 (Fig. 2).

Each model and measurement were validated with two Cs-137 fallout events (nuclear weapon test 1963 & Chernobyl NPP accident 1986). The final chronology was based on Pb-210 ages for the top 20 cm and 8 AMS 14C ages. The model built with P_Sequence function of the Oxcal v.4.2 (Bronk Ramsey, 2009) program. The same software was used for the calibration of 14C dates to calendar years in conjunction with the Northern Hemisphere IntCal13 (Reimer et al., 2013) dataset. The bottom of the lake sediments was ~6000 year old (Karlik et al., 2018).



II. Figure. 2 Sediment chronology of the Bolătău-Feredeu sequence. Light (dark) shading shows the 95% (68%) confidence range of the Bayesian model. Original and modelled probability density functions of the radiometric ages are plotted by light and dark grey, respectively. Uppermost 70 cm is enlarged offering a more detailed image (Karlik et al., 2018)

## II.3. Methods

In this study, bulk samples were investigated from the past 600 years. List of samples and the used methods are summarized in Table 1.

II. Table 1: List of samples and the used methods

| Sample ID | Description | Methods | | | | | |
|---|---|---|---|---|---|---|---|
| | | OM | CL | FTIR | Ram | XRD | XRF |
| 6 | microbialite | 49 | | 79 | 20 | | |
| 8 | microbialite | 37 (24) | 24 | 23 | 20 | | |
| 10 | microbialite | 45 (32) | 32 | 20 | 20 | | |
| 15 | microbialite | 46 | | 17 | 20 | | |
| Lake sediment bulk samples | | | | | | 63 | 63 |
| Catchment soil (~5 sample/area) and homogenised to 1 sample/area | | | | | | 3 | 3 |
| Bedrock sample from 3 area (~5-7 sample/area) and homogenized to 1 sample/area (bulk measurement) | | | | | | 3 | 3 |
| Total | | 177 | 56 | 139 | 80 | 69 | 69 |

Abbrev.: OM: optical rock microscopy; CL: cathodoluminescence microscopy; Ram: Raman spectroscopy; FTIR: infrared spectroscopy, XRD: X-ray powder diffraction, XRF: X-ray fluorescence spectroscopy.

Particle size distribution was determined by Fritsch Analysette 22 Microtech Plus laser diffraction particle size analyzer, which measures in the range of 0.08 µm - 2.0 mm. Samples were treated for carbonate and organic matter removal according to USDA (United States Department of Agriculture) NRCS method (Burt, 2004). Three particles/pieces (ca. 1 g) were taken from each treated sample. Five minutes of ultrasonic treatment and sodium-pyrophosphate (55 g l-1) was applied to allow a complete dispersion of the specimens. Refractive index and the imaginary part were assumed to be 1.54 and 0.01 (Eshel et al., 2004; Varga et al., 2015). The percentage of sand (2000–50 μm), silt (50–2 μm) and clay fractions (below 2 μm) were reported, according to a modified USDA texture classification scheme (Konert & Vandenberghe, 1997).

The mineral components were measured by Rigaku Miniflex600 power diffractometer. It has got a theta/2theta configuration with graphite monochromator. Instrument build in Rh-tube with Cu anode (used X-ray line is Cu KA1&KA2 (1,54060 KeV & 154443 KeV). Under themeasurement process generator setting was 50Kv/10mA and the goniometer speed was 2°/min with 0,5° step size. Diffractograms were measured by 2 to 70 degree. Sample preparation procedure: The representative samples were powered in agate mortal, then the main composite was measured with oriented sample preparation. The XRD system detection limit is ~5 V/V%.

The chemical composition of lake sediment samples were measured with RIGAKU Supermini wavelength dispersive X-Ray fluorescence spectrometer with Pd X-ray tube 50 kV excitation voltage and 40 anodes current. EZScan was the applied measuring method the time of measurements from Fluorine to uranium was 40 minutes. The catchment bedrock and the sediment samples were analyzed in Spectro xSort XRF & Docking station system. The used fundamental parameter calibration: Mining - FP (Mg to Uranium). The measurement time with two filter was 180 sec. The EZ-Scan and the Mining calibration reliability was tested with international lake sediment standards.

Petrographic structural-textural studies were made on ten representative thin sections taken from different depths in transmitted light by optical rock microscopy (NIKON SMZ800 microscope and NIKON ECLIPSE 600 rock microscope). 177 photos of representative sections were taken.

Cathodoluminescence (CL) petrography was carried out on 2 thin sections using a Reliotron cold cathode cathodoluminescence apparatus mounted on a BX-43 Olympus polarization microscope. Accelerating voltage was 7-7.7 keV during the analysis. Cathodoluminescence spectra were recorded by using an Ocean Optics USB2000+VIS-NIR spectrometer. Spectrometer specifications are 350-1000 nm wavelength range, and 1.5 nm (FWHM) optical resolution. For characterization of CL 56 photos were taken.

High resolution in situ micro-Raman spectroscopy was used for micro-mineralogy and organic matter identification and distribution. Raman spectra acquired along lines vertical to observed lamination of samples, where the distance between each point was 10 μm. A Thermo

Scientific DXR Raman Microscope was used with a 532 nm (green) diode pumped solid-state (DPSS) Nd-YAG laser using 3 mW laser power, 50x objective lens in confocal mode (confocal aperture 25 μm pinhole). Full acquisition time/measuring point was 1 min (acquisition time: 3 sec; number of exposures: 20 sec) and spectral resolution was ~2 cm-1 at each measurement. Diagrams were organized on peak height versus analytical spot number of each of the phases along the Raman scanned section (80 spectra were acquired). Intensities were normalized to the highest peak for each spectrum. The following Raman bands were used for normalization: anatase: ~144 cm-1; quartz: ~463 cm-1; K-feldspar: ~513 cm-1. Identification of minerals was made with the RRUFF Database (Database of Raman – spectroscopy, X-ray diffraction, and chemistry of minerals: http://rruff.info/). Contamination by epoxy glue was taken into consideration.

Fourier transform infrared spectrometer (FTIR) was used for in situ micro-mineralogy and organic material identification on five thin sections (139 spectra), using a Bruker FTIR VERTEX 70 equipped with a Bruker HYPERION 2000 microscope with a 20x ATR objective and MCT-A detector. During attenuated total reflectance Fourier transform infrared spectroscopy (ATR) analysis, the samples were contacted with a Ge crystal (0.5 micron) tip with 1 N pressure. The measurement was conducted for 32 seconds in the 600–4000 cm-1 range with 4 cm-1 resolution. Opus 5.5 software was used to evaluate the data. Contamination by epoxy glue, glass, wood stick, and dichloromethane were taken into consideration.

## II.4. Results

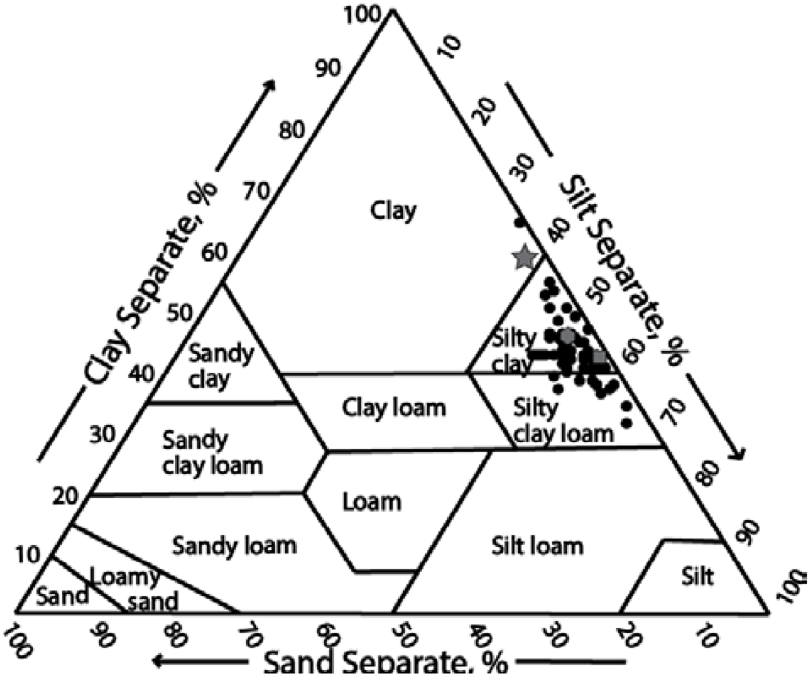
High resolution microtextural, particle size analyses and also in situ mineralogical and organic matter determination and distribution were made.

### II.4.1. Particle size analyses, mineralogy and chemistry

The values of the particle size analyses were distributed to four sections, colloid fraction <0.5 μm, clay fraction <8 μm, silt fraction from 8 μm to 50μm, and sand fraction from 50 μm to 2000 μm.

All of the soil samples gave similar result, the clay fraction was between 45 to 60 %, the silt fraction was between 38 to 47 %. The sand fraction was less than 10%. In the lake sediment samples colloid fraction have been the less fraction in this measurement, the maximum value was 2 % and the minimum 0.9 %. The average of the colloid fraction was 1.5 % with scatter of

0.4 %. The clay and silt fractions were the most dominant fractions in the lake sediment samples. The average of the clay fraction was 43.2 % with 5.4 % scatter and the silt fraction was 52.4%, with 5.2 % scatter. The dominant particle size of the material vary from 0.5 - 8 μm to 50 μm. The sand fraction was only 4 % with 2.2 % scatter. The classification was elaborated based on Konert & Vandenberghe's (1997) (II.Fig. 3). Most of the samples are located (placed) in the silty-clay class, 9 samples were in silty clay loam and only one in the full clay class. No sand fraction occurred.



II. Figure 3. Sediment classification based on Konert & Vandenberghe (1997). (Black – lake sediment; star – right side soil; circle – left side soil; square – upper side soil.

The bedrock is mixture of sandstone and shales complex. The XRD analyses of the three bedrock samples showed the same composition (quartz).

Soil samples were richer in minerals, same to the bedrock samples, the left and up side samples are also, the same, the two samples include: quartz, 10Å phyllosilicate, and clay minerals (near to the detection limit). The right side soil sample includes: quartz, 10Å phyllosilicate, plagioclase, chlorite, illite or smectite, and kaolinite. Mineral composition of the lake sediment is: quartz, 10Å phyllosilicate, plagioclase, clay minerals, and magnetite/maghemite. The lake sediment doesn’t include carbonates by XRD measurements.

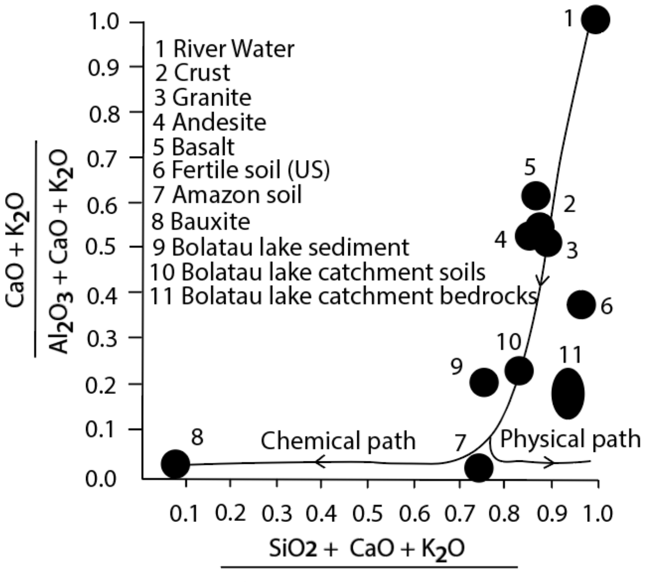
In the catchment three different regions of the bedrock and soil were located: “up side”; “right side” and “left side”. The element composition of the collected bedrock in the up side and left side was similar to each other the $SiO_2$ concentration is higher than ~90 % and the

$Al_2O_3$ concentration is near ~2.8%. The chemical composition of the bedrock of the third area was strongly different, the SiO2 concentration was ~70%, and the second dominant element fraction was the $Al_2O_3$ with ~16%. The soil samples were collected near from the bedrock deposits. The measured samples were richer in elements than the bedrock samples. The soil samples of the three area represent the same element composition. The first 65 cm represent time period between AD. 1400 - A.D. 2000. The 63 particles element composition data has been averaged to help the comparison with the bedrock and the soil data. (II. Table 2)

II. Table 2: Element composition data (1: Bedrock up side; 2: Bedrock left side; 3: Bedrock right side; 4: Soil up side 5: Soil left side; 6: Soil right side; 7: Lake sediment average; 8: Lake sediment relative deviation, nd: no data

| | MgO % | Al2O3 % | SiO2 % | SO3 ppm | K2O % | CaO % | TiO2 % | Fe2O3 % | Zn ppm | Rb ppm | Sr ppm | Y ppm | Zr ppm |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | <0.5 | 2.6 | 91.51 | 53 | 0.7 | 0.1 | 0.3 | 4.1 | 34 | 19 | 22 | 9 | 117 |
| 2 | <0.5 | 3.0 | 94 | <46 | 1.3 | 0.1 | 0.3 | 3.0 | 50 | 39 | 37 | 8 | 116 |
| 3 | 0.9 | 16.3 | 70.9 | 564 | 2.5 | 0.2 | 0.8 | 5.3 | 104 | 90 | 69 | 22 | 246 |
| 4 | <0.8 | 18.0 | 76.9 | 167 | 2.6 | 0.2 | 0.6 | 4.6 | 93 | 101 | 60 | 13 | 139 |
| 5 | <0.5 | 14.4 | 62.6 | 983 | 3.2 | 1.0 | 0.9 | 3.0 | 62 | 133 | 92 | 10 | 146 |
| 6 | <0.7 | 15.6 | 57.5 | <51 | 3.8 | 0.05 | 0.9 | 7.2 | 94 | 178 | 75 | 14 | 146 |
| 7 | 0.4 | 1,7 | 49,5 | 5275 | 3.3 | 0.9 | 0.8 | 5.2 | 183 | 222 | 101 | nd | nd |
| 8 | 16 | 13 | 3 | 34 | 6 | 8 | 10 | 9 | 14 | 12 | 15 | nd | nd |

Figure 4. shows the position of samples in weathering diagram, which help to understand the origin of the sediments. The calculation is based on Kronberg & Nesbitt (1981). The sodium content was under the detection limit in all samples.



II. Figure 4. Theoretical weathering curves of the Bolătău bedrock, soil, and lake samples

(based on Kronberg & Nesbitt, 1981)

### II.4.2. Optical rock microscopy

Optical microscopy in the thin sections (samples 6, 8, 10 and 15) represent variable microtextural features of mineralized microbialite. Panorama photos show fine lamination (Fig. 5). Brown, woven, organic matter-rich structures represent series of biomat-like and stromatolitic structures, which are common (mineralized biosignatures of microbial activity and mineralized biosignatures of putative Fe-oxidizing bacteria (FeOB). Rarely larger well-structured microfossils also occurred (Fig. 5). In very high resolution (100-1000x) the whole samples were densely woven by filamentous inner necklace-like microstructures or coccoid forms, aggregates and vermiform brain-like micro-textures (mineralized biosignatures). These filaments contain randomly disseminated 0.5-1 μm large mineral phases (II.Fig. 5).

CL photos showed very fine grained randomly disseminated particles, which showed scarce bright yellow luminescence (apatite) and dull blue luminescence (quartz). Along microbialite laminae segregated quartz occurred (II.Fig. 5).

The Raman spectroscopy measurements determined carbonaceous matter (CM) with low maturity, which occur at each measuring point along both sections. However, enrichment of CM related to lamination of the samples were not observable along the sections. Most probably quartz, feldspar and anatase grains occur in the sample (II.Fig. 5).

FTIR-ATR analyses were carried on four thin sections selected on observation by optical microscopy. Mineral composition is feldspar, apatite, quartz, montmorillonite, ferrihydrite and chlorite. Highly variable embedded organic matter occurred in all samples (C=N/CH-amid, graphite, O=C, dCH2, C-O). Details of two representative samples are presented in the tables (II. Table 3 and 4).

II. Table 3. FTIR dataset of sample No. 6

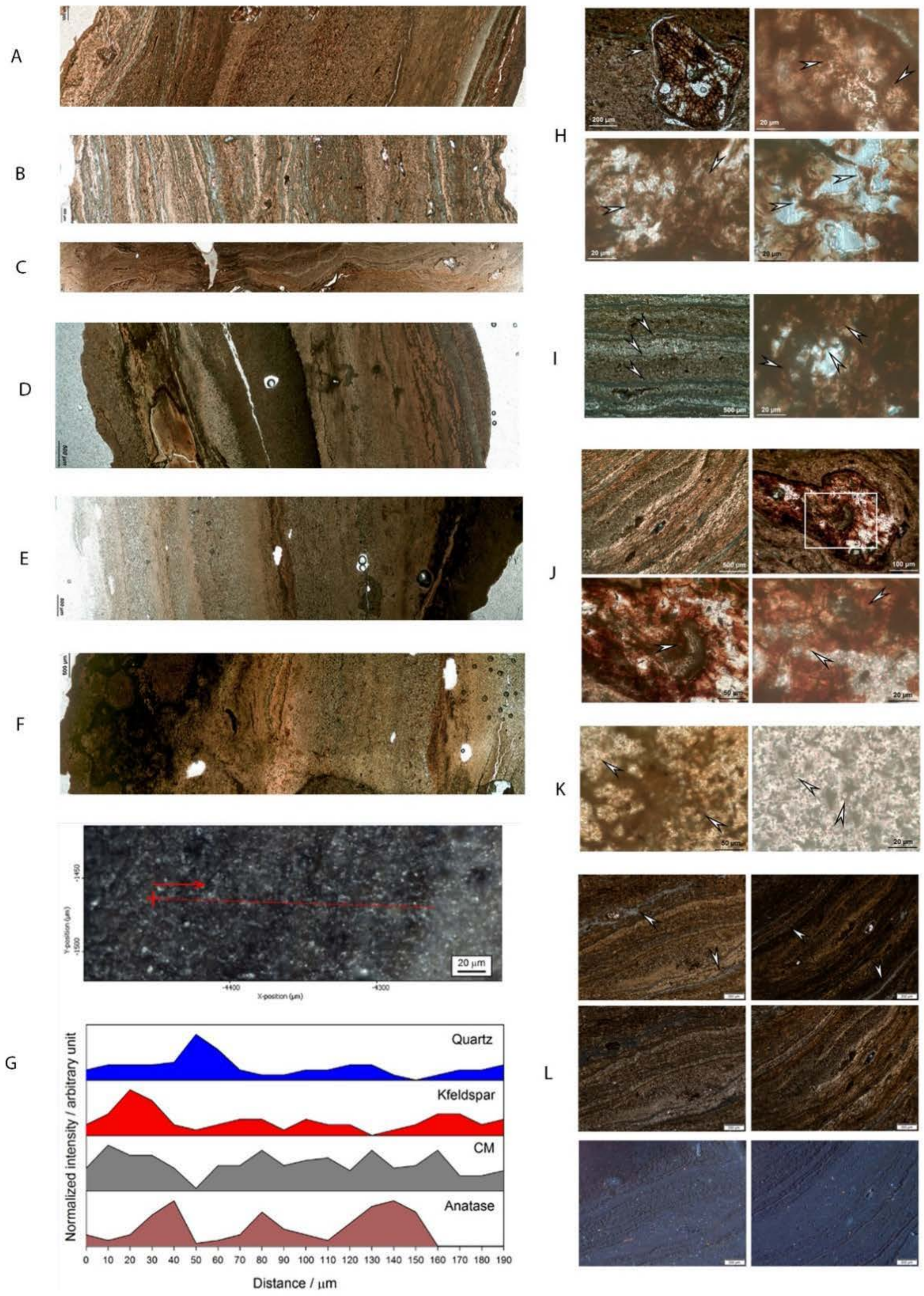
| **No. 6** | | **Measuring area** | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Wavelength (cm$^{-1}$)** | **Type Wavelength (cm$^{-1}$)** | **1 n: 5*** | **2 n: 6** | **3 n: 9** | **4 n: 7** | **5 n: 10** | **6 n: 8** | **7 n: 4** | **8 n: 6** | **9 n: 15** | **10 n: 9** | **Ref.** |
| **Organic matter** | | | | | | | | | | | | |
| 1170 | v C-O | x | x | x | x | x | x | x | x | x | x | 1 |
| 1360-1450 | vs CO | x | x | x | x | x | x | x | x | x | x | 1 |
| 1454-1482 | d CH2 | x | x | x | x | x | x | x | x | x | x | 1 |
| 1526 | C-N, CH deformation | x | x | x | x | x | x | x | x | x | x | 1 |
| 1540-1550 | C-N N-H amide II | | x | | | | | | | | | 1 |
| 1598 | C=C asym. Stretch | | x | | | x | x | x | | | x | 1 |
| 1632-1652 | amide I C=O, C-N, N_H | | | | | | | | | | | 1 |
| 1720-29 | v as COOH | | | | | | | | | | | 1 |
| 1799 | C-O | | | | | | | | | | | 1 |
| 2343 | CO | x | x | x | x | x | x | x | x | x | | 2 |
| 2365 | CO | x | x | x | x | x | x | x | x | x | | 2 |
| 2853 | C-H sym. Stretch CH2 | | | | | | | | | x | | 1 |
| 2926 | C-H asym. Stretch CH2 | | | | | | | | | x | | 1 |
| **Mineralogy** | | | | | | | | | | | | |
| **feldspar** | 798, 950, 1000 | x | x | x | x | x | x | x | x | x | x | 2 |
| **quartz** | 685, 773, 808, 1055, 1083 | | | x | x | | | | | x | x | 2 |
| **apatite** | 790, 1012, 1093 | | x | | | | | | | | x | 3 |
| **montmorillonite** | 988, 779, 1000, 1615, 3600 | | | | | | | x | | | | 4 |
| **ferrihydrite** | Fe-O, 692, 830, 930 | | x | | | | | | | | x | 5 |

Legend: * n: number of acquired spectra; References: 1: Parikh & Chorover (2006), 2: Müller et al. (2014), 3: Beasley et al. (2014), 4: Madejová & Komádel (2001), 5: Glotch & Rossmann (2009)

II. Table 4. FTIR dataset of sample No. 10

| **No. 10** | | **Measuring area** | | | | |
|---|---|---|---|---|---|---|
| | | | | | | |
| **Wavelength (cm$^{-1}$)** | **Type Wavelength (cm$^{-1}$)** | **1 n: 5*** | **2 n: 6** | **3 n: 5** | **4 n: 4** | **Ref.** |
| **Organic matter** | | | | | | |
| 1170 | v C-O | x | x | x | x | 1 |
| 1360-1450 | vs CO | x | x | x | x | 1 |
| 1454-1482 | d CH2 | x | x | x | x | 1 |
| 1526 | C-N, CH deformation | x | x | x | x | 1 |
| 1540-1550 | C-N N-H amide II | | x | | | 1 |
| 1598 | C=C asym. Stretch | x | x | | | 1 |
| 1632-1652 | amide I C=O, C-N, N_H | | | | | 1 |
| 1720-29 | v as COOH | | | | | 1 |
| 1799 | C-O | | | | | 1 |
| 2343 | CO | x | | | x | 2 |
| 2365 | CO | x | | | x | 2 |
| 2853 | C-H sym. Stretch CH2 | | | | | 1 |
| 2926 | C-H asym. Stretch CH2 | | | | | 1 |
| **Mineralogy** | | | | | | |
| **feldspar** | 798, 950, 1000 | x | x | x | x | 2 |
| **apatite** | 790, 1012, 1093 | | | | | 3 |
| **montmorillonite** | 988, 779, 1000, 1615, 3600 | | | | | 4 |
| **chlorite** | 980, 3400 | | | | x | 6 |
| **ferrihydrite** | Fe-O, 692, 830, 930 | | | | | 5 |

Legend: * n: number of acquired spectra; References: 1: Parikh & Chorover (2006), 2: Müller et al. (2014), 3: Beasley et al. (2014), 4: Madejová & Komádel (2001), 5: Glotch & Rossmann (2009), 6: Udvardi et al. (2014)



II. Figure 5. Panorama figures of thin section profiles (optical rock microscopy, transmitted light, 1N, photo composition (A: Section 6; B: Section 8; C: Section 10; D: Section 15A; E: Section:15B; F: Section 15B); High resolution in situ micro-Raman spectroscopy (G); Mineralized microbialite microtextural features (H: Section 6; I: Section 8; J: Section 10; K: Section 15); Cathodoluminescence microscopy (L) Arrows show segregated quartz. On the CL images very small minerals show cathodoluminescence: bright yellow-apatite, blue-quartz.

## II.5. Discussion

Source area of these sediments is in direct connection with the geological unit where Lake Bolătău is placed. The bedrock XRF and XRD analyses confirm the findings has sense of the find the objects of Ionesi (1971) and Mîndrescu et al. (2013) concerning mineralogy and chemistry.

In the catchment area two, a little bit different bedrocks are located, one is mostly sandstone (samples from the upside and left side) with high $SiO_2$ content (more than 90%). The mineralogy of the second bedrock type is also sandstone with clay mineral content (samples from the right side) and it has got a high aluminum content in addition to silicon ($SiO_2$:~70% $Al_2O_3$:~16%) – II. Table 2. Because the catchment area is closed by mountains, this material has been the primary source of the soil and lake sediment in the last 6000 years. The bedrock surface is transformed to soil material by physical weathering.

The chemical parameters give us information on the weathering processes. Compared with the bedrock chemical composition, two types of weathering processes were realized (Fig. 4). Physical and chemical weathering resulted the final form of the soil. The sand size faction was less than 10%, in the future studies this information can be used to understanding the environmental signals in the sediment (precipitation events, or high impact energy effects (deforestation, etc.). The right side area soil classification was “Clay” type, another two area soils were “Silty clay” type. In the classification diagram right side soil sample position was near to the border line of “Silty clay”. The mineral composition of soils is same: quartz, 10Å phyllosilicate and clay minerals, and in the right side sample extra further mineral, plagioclase occur. Based on dataset of the soil samples around the lake, it is not necessary to take into account the possible preferred directions of leaching when examining the lake sediment.

The two most dominant lake sediment particle sizes were clay and silt fraction (43.2 ±5.4% and 52.4 ±5.2%). The sand fraction is only 4 ±2%. The significant changes are the result of high intensity environmental changes. The Loss-on-Ignition (LOI) value is around 20% in each sample, because the sediment is carbonate free it come from the organic material. The S component had the biggest changes with 34%. The S signal significantly come from the organic material. The organic material refers to paleoenvironmental information about the catchment (Karlik el at., 2018), namely the change of n-alkanes refers to deforestation event.

Optical rock microscopy (1N and xN) transmitted light photos do not support debris contribution on considerable level. XRD mineralogy and Raman spectroscopy determined quartz, 10Å phyllosilicate, plagioclase, clay minerals, magnetite/maghemite as main constituents, and also apatite, and feldspar. These fit with the FTIR results, but FTIR is more sensitive. FTIR identified variable organic matter as main constituent, and mineral assemblage of apatite, feldspar, poorly crystallized segregated quartz (wide peaks), rarely ferrihydrite and montmorillonite. The size of minerals is very small, 0.5-1 µm, which disseminate in the network of the organic matter in the extracellular polymeric substance (here after EPS). Size distribution study also resulted 30-40% of grains below 8 µm. These grains do not follow the lamination of microbialite and their small size, and also their CL features (no luminescence) support complex early diagenetic mineralization based on microbial mediation and cell and EPS decomposition rather than debris material contribution. It is also supported by the mineral assemblage (apatite, feldspar, poorly crystallized segregated quartz (wide peaks), rarely ferrihydrite and montmorillonite) which is typical for these processes. Based on these results this basin is a starving one in sense of debris contribution. Details on complex mineralization on the pool of microbially mediated elements fit well with the results of Polgári et al. (2019). Concerning the formation conditions of minerals support suboxic, slightly alkaline conditions, which turned locally to anoxic, represented by pyrite formation.

## II.6. Conclusion

The bedrock measurements confirm the findings of Ionesi (1971) and Mîndrescu et al. (2013) concerning mineralogy and chemistry. But the chemical differences between the bedrock types element composition much higher than the expectation. The mineral composition in the two average sample were similar: quartz, and one is different: quartz and clay minerals. It was confirmed by the chemical analysis. The sandstone was fragmented during physical weathering to the soil primary material.

Physical and chemical weathering in the soil took place in parallel. The weathering processes were modified by the chemical and mineral composition. The chemical and mineral composition of the soil samples is not highly different. Some new minerals were detected by XRD: quartz, 10Å phyllosilicate, plagioclase, chlorite, illite or smectite, and kaolinite. The differences observed in the bedrock samples, do not appear predominantly in the soil samples. Sediment size classification based on Konert & Vandenberghe (1997) were “Clay” and “Silty clay”.

The most dominant size of lake sediment fractions were clay and silt. Their distribution changed with depth. The chemical composition ranged over a wide interval. It was likely that the inorganic parameters of the lake sediment provide an opportunity for paleoenvironmental reconstruction. The interpretation of the data may be aided by previous organic geochemical results included in Karlik et al (2018). Based on the analyses on the abrasives, a suboxic environment prevailed in the sediment and considerable microbial contribution is proposed via accumulation of lake sediment.

## II. Acknowledgement

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# Chapter III.: Natural and anthropogenic changes in a lake-forest system in Bukovina (Romania) since 1340 AD documented by sedimentary organic geochemistry (C, N and n-alkanes)

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## III. Abstract

Lake Bolătău-Feredeu is a small (surface: 0.3 ha; catchment area: 31 ha) landslide-dammed lake in Bukovina (Eastern Carpathians, Romania). Elemental concentration, stable isotope composition of carbon and nitrogen, and n-alkane composition of the saturated hydrocarbon fraction of the organic material were analyzed along the sediment profile from Lake Bolătău-Feredeu covering the past ∼700 years. The ranges of $\delta^{13}C$ values (−30.5 to −26.6‰) and C/N atomic ratios (10.5 and 15.4) placed the organic material of the recent Bolătău-Feredeu sediment between the C3 Land Plants and the lacustrine algae. The n-alkane proxies provide better distinction between organic matter inputs. Detected major shifts in the n-alkane composition and the C and N concentrations along with the stable isotope compositions pointed towards three distinct stages in the environmental history of the lake-catchment system. The proxy information indicate a substantial landscape change characterized by deforestation and an increase in open pastureland with herbaceous vegetation from ∼1820. The C/N, $\delta^{15}N$, and $\delta^{13}C$ values showed the highest variability probably linked to a variable lacustrine environment and decreased productivity in the catchment between ∼1640 A.D and 1760 A.D. It can be assumed that the extended periods of lake ice cover during the cold decades experienced at the turn of the 17th-18th centuries resulted in diminished biological productivity both in the lake and its catchment. Finally, afforestation and the decline in lake productivity have been reconstructed for the period of ∼1470 A.D.–1560 A.D.

Keywords: n-alkanes; Lacustrine organic matter; Lake sediment; Eastern Carpathians; Deforestation;

## III. 1.Introduction

The biological productivity in the lake environment responds to present or past conditions of the lake environment and their changes. Thus, lakes are excellent sensors of environmental change, and to that effect lake sediments can provide high resolution records of past environmental changes on various time scales (Battarbee, 2000).

Paleoclimatological and paleoenvironmental studies on lacustrine sequences have proliferated in the Carpathian-Balkan region during the last decades, with time frames ranging from the recent past (e.g. Ivanić et al., 2017; Vreca and Muri, 2006; Feurdean et al., 2015; Hutchinson et al., 2016; Gąsiorowski and Sienkiewicz, 2010), to the Late Glacial (e.g. Bordon et al., 2009; Tonkov et al., 2011; Magyari et al., 2014; Tóth et al., 2017), to as early as the middle Pleistocene (e.g., Lacey et al., 2016).

A promising new target region for regional paleolimnological efforts consists of the landslide-dammed basins of the so-called Triangle of Bukovinian Millennial Lakes. These lakes were only recently acknowledged and came to the attention of paleolimnological research (Mîndrescu et al., 2013; Florescu et al., 2017). Recent studies determined exceptionally fast accumulation in these lake basins (Mîndrescu et al., 2016; Florescu et al., 2017), thus providing a good opportunity to achieve high-resolution multi-proxy records for complex interpretation of the landscape evolution and environmental history.

Although various paleobiological, geochemical, and paleomagnetic parameters have been studied rather frequently in lacustrine sequences in the Carpathian-Balkan Region (for details see Buczkó et al., 2009, Kłapyta et al., 2016, Mîndrescu et al., 2017), few if any study investigated organic biomarkers in their recent sediments, despite the great potential of the organic geochemical proxies to detect the natural and the anthropogenic changes of the lakes and the surrounding areas (Meyers, 2003). In particular, geochemical studies of sedimentary longchain n-alkanes in recent sediments are completely missing as yet, although lipid biomarkers are well preserved in many geological archives and are increasingly used for paleoclimate and paleoenvironmental reconstructions (Eglinton and Eglinton, 2008).

The stable carbon and nitrogen isotope composition and C/N ratio are widely used to trace sources of particulate organic matter of the lake sediments (Herczeg et al., 2001; Noble et al., 2016). However, the interpretation of these proxies is often complicated since bulk material consists of mixtures from several sources and selective early diagenesis can substantially alter nitrogen isotope composition.

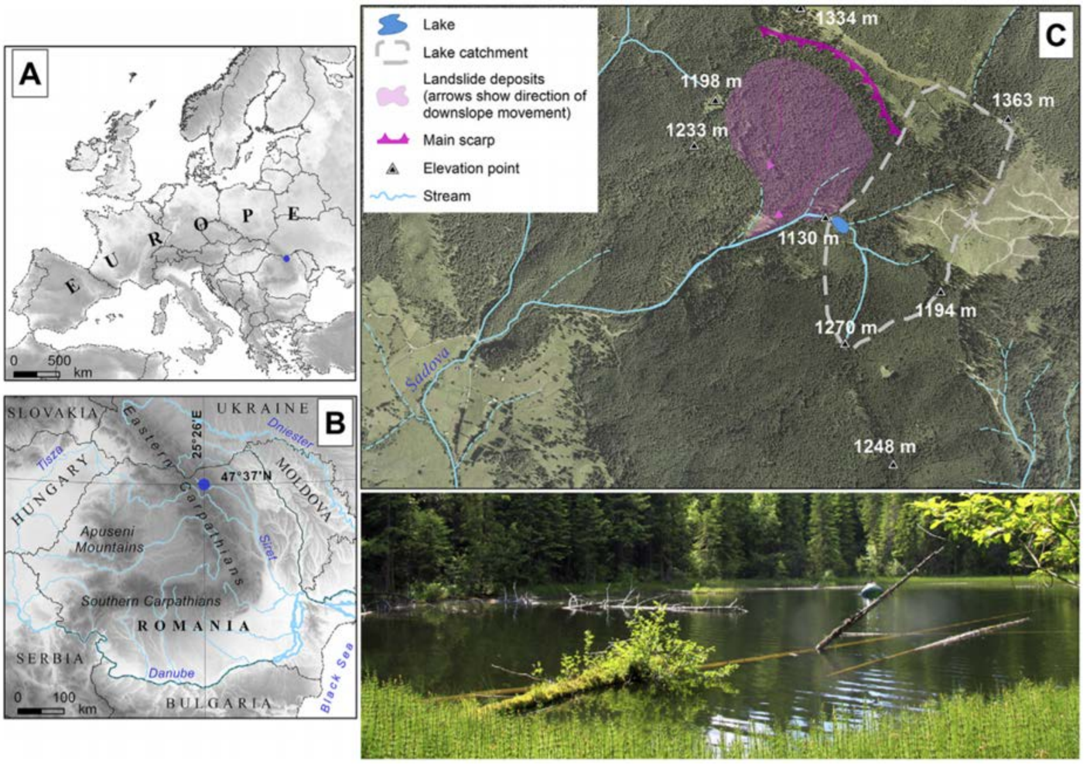
Long-chain n-alkanes (> C25), for example, are essential constituents of epicuticular leaf waxes and thus serve as specific biomarkers for higher terrestrial plants (Eglinton and Hamilton, 1967). Long-chain n-alkanes (C27–C35) are typically the dominant component of epicuticular waxes in higher plants, while mid-chain n-alkanes (C23–C25) originate mainly from aquatic macrophytes, and short-chain n-alkanes (C17–C21) are produced by aquatic algae and bacteria (Eglinton and Hamilton, 1967; Cranwell et al., 1987). Long-chain and mid-chain n-alkanes are relatively resistant to degradation, and can therefore be well preserved in sediments.

The aim of this study is to perform the first assessment of alkane geochemistry of a young lacustrine sequence in the Carpathian-Balkan region. The alkane data will be combined with stable carbon and nitrogen isotope information.

The selected site is from Bukovina region, Romania, where historical records documented substantial landscape changes throughout the past centuries, such as deforestation (Barbu et al., 2016), providing a promising site to evaluate the preservation of the imprint of historical landscape changes on the lacustrine organic geochemical record. Additional motivation is that a study on paleobotanical data (pollens and macrofossils), paleomagnetic and elemental geochemistry records form a lacustrine sequence from the neighboring watershed demonstrated the preservation of deforestation within those parameters (Florescu et al., 2017), thus indicating that Lake Bolătău-Feredeu is likely a good candidate to host such a pilot study.

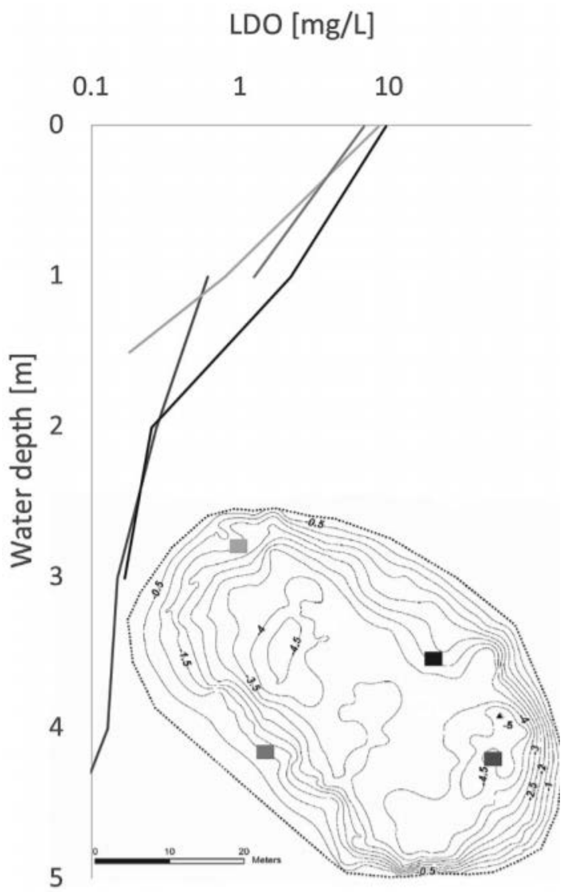
## III. 2. Study site and core collection

Lake Bolătău-Feredeu (47° 37′ 20.74″ N, 25° 25′ 54.43″ E) is located in the southwestern sector of Feredeului Mts just below Obcina Feredeului peak (1364 m asl) and pertains to Sadova catchment (Fig. 1). Sadova stream is a tributary of river Moldova. The lake formed in the upper catchment, at ca. 1137 m asl, as the result of a landslide which dammed the deep, narrow-shaped valley head of Holohoșca stream (Mîndrescu et al., 2013). The landslide, expanding over ca. 23 ha, affected mainly the right-side slope, as well as the valley head slope to a lesser extent (III. Fig. 1c).



III. Figure. 1. Location of research area a) at continental scale; b), in the Eastern Carpathian region; c) a closer view of the Lake Bolătău-Feredeu. The grey dashed line shows the catchment boundary. A site photo displayed below the map.

The landslide event led to the formation of a small-sized (0.30 ha) yet deep (maximum depth was 5.2 m in 2010) lake (Mîndrescu et al., 2010). An ad hoc water quality measurement in March 2010 reported total phosphorus concentration as 0.014 mg/L (Mîndrescu et al., 2010) corresponding to mesotrophic class regarding the trophic status (OECD, 1982). Dissolved oxygen has been measured at four profiles at late February 2014 (Fig. 2). Observations suggest that redox conditions vary by depth. Oxidation is high at the surface (∼8–9 mg/L) and decrease very fast dropping to ∼1 mg/L and < 0.2 mg/L, by 1 m and 3 m, respectively (Fig. 2). Indeed, these redox conditions makes the bottom water to become very methanogenic. While the lake catchment extends over no more than 31 ha, the elevation amplitude within the catchment is significant, amounting to ca. 227 m (1364 m asl to 1137 m asl) compared to a horizontal distance of just 700 m. The catchment is situated within the westernmost sub-unit (Black Shales Formation) of the Audia Nappe comprising Cretaceous shales (Ionesi, 1971). The catchment has been completely covered by spruce forest until two decades ago when approx. 19% of its area (6 ha) were deforested.



III. Figure. 2. Luminescent Dissolved Oxygen (LDO) plotted against depth from Lake Bolătău-Feredeu measured along four profiles at February 2014. Profile locations (squares) are shown on the isobathymetric map in the lower right corner. Corresponding locations and curves are marked with the same grey saturation.

The sediment cores were retrieved in April 2013 using both a Russian corer (core code: LB-R-01) and a gravity corer (core code: LB-G01) from the frozen surface of the lake. Two additional gravity cores (core codes: LB-G-02 and LB-G-03) were extracted using a floating platform in November 2013. The cores extracted in April were visually inspected on site, described, photographed and sectioned at 1 cm intervals into pre-labelled plastic bags (Mîndrescu et al., 2016). The undisturbed gravity cores extracted in November were transported to the Institute for Geological and Geochemical Research, Research Centre for Astronomy and Earth Sciences, MTA, for sedimentological and geochemical analyses within 2 days after retrieval. The topmost part of the LB-G-03 core has turned out to be affected by a prograding delta facies (Németh et al., 2014) therefore the current study focused on the LB-G01 and LB-G-02 cores.

## III.3. Methods

### III.3.1. Stable carbon and nitrogen isotope ratios and element percentage

Stable carbon and nitrogen isotope ratios and element percentages were measured on bulk sediment samples at the Institute for Geological and Geochemical Research, Research Centre for Astronomy and Earth Sciences, MTA. Macroscopic vegetal remains were removed from the sediment samples to avoid bias in the element concentration and stable isotope analysis.

#### III.3.1.1. Carbon and nitrogen element percentage

Duplicate aliquots of 20–25 mg of the sediment samples were weighed and packed into Sn capsules (IVA Analysetechnik e.K. Meerbusch, Germany) for the analysis of C and N elemental percentage. The element specific peak area was detected by the internal TCD detector of the Flash 2000 Elemental Analyzer (Thermo Scientific, Rhodano, Italy). The element percentage was calculated according to Hedges and Stern (1984) as:

$$\mathrm{X\%} = \frac{(A_{spl}^{X} - A_{blk}^{X})/K}{W_{spl}} * 100$$

where X stands for C or N, Aspl and Ablk stand for the peak area of the sample and the blank, respectively, and K is the average K-Factor determined by a 6-point calibration curve fitted with the K-factor function in the mass range of 1–2.5 mg. Applied standard material was N-phenylacetamide (Acetanilide, Thermo Scientific, Cambridge, UK). Reproducibility of the measurements is estimated by the standard deviation of the Acetanilide standards (n = 12) which was 0.4% and 2% for C% and N%, respectively. C/N weight ratio has been calculated simply as the ratio of the corresponding C% and N% values for each sample. Weight ratio was converted into an atomic ratio multiplying by 1.167 to account for the different atomic mass of carbon and nitrogen (Meyers and Teranes, 2001).

#### III.3.1.2. Stable carbon and nitrogen isotope analysis

The LB-G-01 core was sub-sampled in uniform at 1 cm. This gapless sampling protocol provided continuous information, so it can reflect trend-like changes more reliably. Analyzed material from LB-G-02 core was extracted from 0.5 cm thick layers at 57 horizons with uneven spacing along the profile. This sampling protocol offered a finer time resolution; however, certain short events might be missed due to the discontinuous sampling. Thus, the two records provided complementary information.

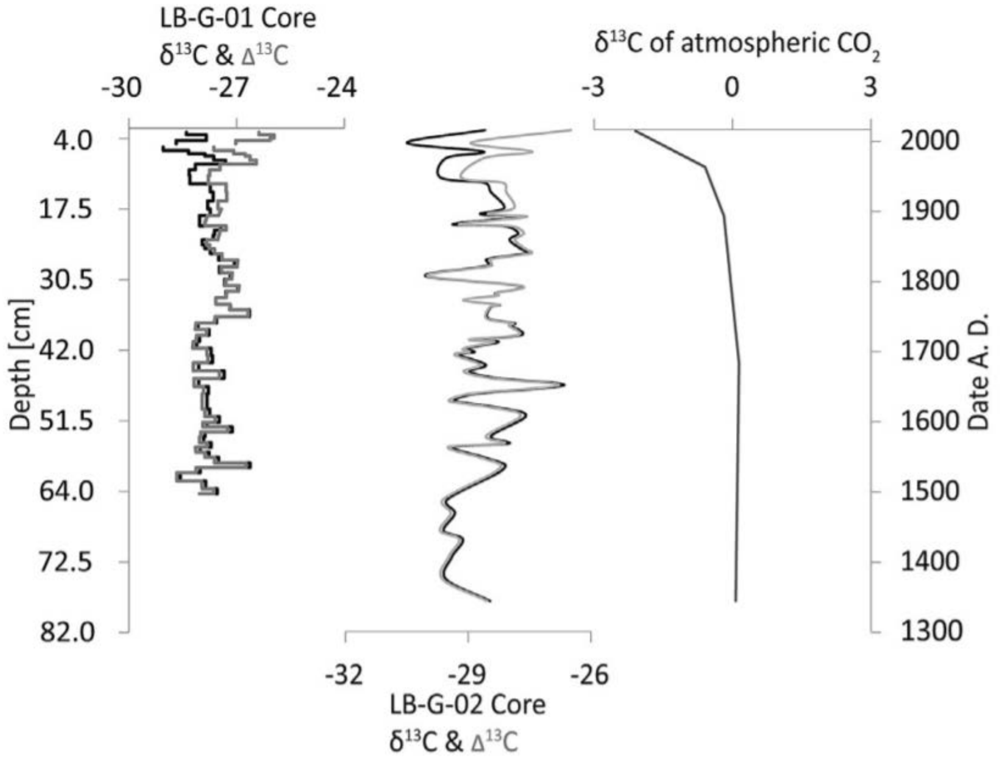
Aliquots of 0.6–0.7 mg and 10–15 mg of the sediment samples were weighed and packed into Sn capsules (IVA Analysetechnik e.K. Meerbusch, Germany) for stable carbon and nitrogen isotope analysis, respectively. Samples were combusted using a Ficken et al., 2000 Organic Elemental Analyzer (Thermo Scientific, Rhodano, Italy). Operational details were as follows: combustion reactor 1000 °C, reduction reactor 640 °C, GC temperature 75 °C. Yielded gases were transferred via a Conflo III into an isotope ratio mass spectrometer (Delta V Advantage, Thermo Finnigan, Bremen, Germany) operating in continuous flow mode with a carrier gas (He + O2, Messer 4.6) flow speed of 90–95 ml/min. Carbon and nitrogen stable isotope ratios of the combusted organic material were measured and reported in per mil (‰), using the δ notation (McKinney et al., 1950). Modified single-point normalization technique and two-point linear normalization was applied for $\delta^{13}C$ and $\delta^{15}N$, respectively, to recalculate raw isotope values to the internationally recognized VPDB or AIR scales (Paul et al., 2007; Skrzypek, 2013). The reference standard (IAEA-CH-7, $\delta^{13}C$: −32.51‰) (Coplen et al., 2006) was used for calibration for carbon and two laboratory standards (carbamide and gelatine) were used for nitrogen. Carbamide and gelatine were calibrated independently to isotopic reference materials IAEA-N-1 ($\delta^{15}N$: +0.4‰) and IAEA-N-2 ($\delta^{15}N$: +20.3‰) (Böhlke and Coplen, 1995). Standard deviation of the reference standards analyzed at every 6th place were < 0.08‰ and < 0.2‰, for $\delta^{13}C$ (n = 114) and $\delta^{15}N$ (n = 36), respectively, indicating the reproducibility of the measurements. Actual sample errors of the sediment samples may be greater than these due to sample inhomogeneity so replications ( × 3 for $\delta^{13}C$; 2 × for $\delta^{15}N$) were measured to get a better picture on the actual analytical uncertainty.

A preliminary random sampling found no traces of carbonate along the entire 6 m long lacustrine sediment profile (Mîndrescu et al., 2016). However, all samples from these short gravity cores with $\delta^{13}C > -27‰$ were sent for X-ray diffraction (XRD) analysis. Since $\delta^{13}C$ of the inorganic carbonate is ~20‰ higher compared to organic matter (Leng et al., 2006), if no carbonate can be detected in these relatively less depleted samples then all the samples are very likely carbonate-free and the C concentration and their isotopic signal measured in the bulk sediment can be considered to be equivalent to the lacustrine organic matter from a practical point of view.

Oriented samples were prepared and analyzed by a Rigaku Miniflex 600 powder X-ray diffractometer with graphite monochromator, and Cu anode tube (1.54 Å Cu Kα). In the measurement the tube setting was: 40 kV and 15 mA, the recorded range in 2theta between: 2–70, with acquisition step size 0.5° and 2°/min goniometer speed.

#### III.3.1.3. Correction of the raw isotopic values

Both LB-G-01 and LB-G-02 profiles showed an obvious declining trend from ~20 cm up to the sediment top in the $\delta^{13}C$ values of the organic material (III. Fig. 4). The estimated beginning of the declining trend was in the 19th century in both cores, corresponding well to the historic depletion of $\delta^{13}C$ in atmospheric $CO_2$ due to fossil fuel burning (Francey et al., 1999). Measured values for $\delta^{13}C$ of the organic sediment are expected to be related to the historic isotopic signatures of atmospheric $CO_2$ since dissolved $CO_2$ serves as input signal to the photosynthetically fixed organic carbon. To test a correction for the changes in the $\delta^{13}C$ of the atmospheric $CO_2$ reconstructed data based on a compilation of $\delta^{13}C$ of $CO_2$ measured from air inclusions of ice cores (Leuenberger, 2007) was used.



III. Figure. 4. The measured ($\delta^{13}C$) and the corrected ($\Delta^{13}C$) stable carbon isotope composition of sedimentary organic matter from LB-G-01 and LB-G-02 cores from Lake Bolătău-Feredeu. In the right panel long-term changes of δ13C of the atmospheric $CO_2$ reconstructed based on a compilation of $\delta^{13}C$ of $CO_2$ measured from air inclusions of ice cores (Leuenberger, 2007) are shown. $\Delta^{13}C$ records were calculated as the difference between the $\delta^{13}C$ of the sedimentary organic material and the $\delta^{13}C$ of the atmospheric $CO_2$.

Early diagenetic processes occurring after sedimentation can systematically alter the primary isotopic signal recorded in sedimentary organic matter and must be accounted for in order to detect changes in the $\delta^{15}N$ of nitrogen inputs to the sediment surface. In order to account for the diagenetic effect a quantitative mechanistic model was applied (Brahney et al., 2014). The model was fitted to the bulk $\delta^{15}N$ record by minimizing the root mean squared error (RMSE).

### III.3.2. Gas chromatography

The ~78 cm long LB-G-02 core was cut into 12 non-uniform samples. Non-uniform sampling steps were decided because pilot sampling suggested variable organic content. Samples were dried at 40 °C, then ground, and ~20 g was filled into stainless steel cells. Extraction was carried out in an Accelerated Solvent Extractor (ASE350) at 75 °C and 100 bar, using 5:2 chloroform-methanol as solvent. The samples were run twice to ensure sufficient extraction. The extract was fractionated via column chromatography into saturated hydrocarbon (HC), aromatic HC, and resin fraction. The dominant fraction was resin of the extracted organics. Saturated HC fraction ranged from 1.1% to 5.3% of the extracted total organics.

The entire saturated HC fraction was analyzed by gas-chromatography using a Fisons 8000 GC with Flame Ionisation Detector using the following parameters: injector temperature: 310 °C, split: 1:10, DB-TPH 30 × 0.32 × 0.25 column, detector temperature: 310 °C. The oven was kept at 60 °C for 1 min, then heated up to 150 °C (20 °C/min), then up to 330 °C (6 °C/min) for 5 min.

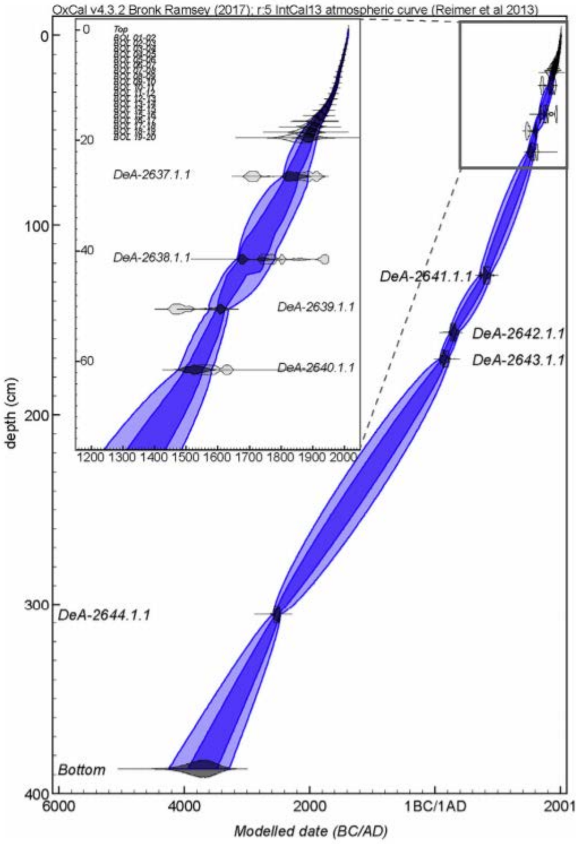
To avoid the potential bias due to the variable amount of saturated HC subsamples, the changes in the alkane composition will be evaluated using well-known indices calculated as ratio between summed peak areas of certain alkane groups (III. Table 1).

III. Table 1. Summary of the indices and their calculations used in this study to describe the changes in the alkane composition of the Bolătău-Feredeu sediment profile.

| Index | Calculation | Reference |
|---|---|---|
| $TAR_{HC}$ | $(C_{27}+C_{29}+C_{31})/(C_{15}+C_{17}+C_{19})$ | Silliman et al (1996); Meyers (2003) |
| CPI (Carbon Preference Index) | $[(C_{25} + C_{27} + \cdots + C_{33})/(C_{24} + C_{26} + \cdots + C_{32}) + (C_{25} + C_{27} + \cdots + C_{33})/(C_{26} + C_{28} + \cdots + C_{34})]/2$ | Bray and Evans (1961) |
| Paq | $(C_{23} + C_{25})/(C_{23} + C_{25} + C_{29} + C_{31})$ | Ficken et al. (2000) |
| Pwax | $(C_{27}+C_{29}+C_{31})/(C_{23}+C_{25}+C_{27}+C_{29}+C_{31})$ | Zhu et al. (2008) |
| Phw | $2*C_{31}/(C_{27}+C_{29})$ | Zhu et al. (2008) |

### III.3.3. Sediment chronology

An initial sediment chronology was established for the Bolătău-Feredeu sequence based on 8 AMS radiocarbon dates from terrestrial macrofossils and validated for the recent section by the double peaks of the $^{137}$Cs flux (i.e. mid-1960s: global fallout maximum; 1986: Chernobyl accident) (Mîndrescu et al., 2016). Four of the dated remains (one from LB-G-01 and 3 from LB-R-01) were collected from the upper 80 cm of the sediment which constitute the focus of the current study. Further on the sediment chronology of the topmost 24 cm has been significantly improved based on $^{210}$Pb geochronology of the LB-G-01 core (Bihari et al., 2018). $^{210}$Pb ages for the top 20 cm, until the accompanied uncertainty was below the 30% of the estimated age, and all $^{14}$C dates were included in this Bayesian age-depth model using the P_Sequence function of the OxCal v.4.2 (Bronk Ramsey, 2009) program (III. Figure 3). The same software was used for the calibration of $^{14}$C dates to calendar years in conjunction with the Northern Hemisphere IntCal13 (Reimer et al., 2013) dataset.



III. Figure. 3. Sediment chronology of the Bolătău-Feredeu sequence. Light (dark) shading shows the 95% (68%) confidence range of the Bayesian model. Original and modeled probability density functions of the radiometric ages are plotted by light and dark grey, respectively. Uppermost 70 cm is enlarged offering a more detailed view on the section being in the focus of the current study

## III. 4. Results

### III. 4.1. Carbon and nitrogen elemental concentrations

The bulk sediment XRD analysis has not determined any trace of carbonate in the sediment samples, therefore C concentration results represent the total organic carbon percent and stable carbon isotope ratios represent the $\delta^{13}$C of the organic material.

The range of C% is between 8.8% and 2.6% with a median of 5.4%. The average time resolution of the elemental concentration records can be estimated to ~10 years. The data have a decreasing trend from 78 cm to 40.2 cm with relative high variability followed by the minimum value. At the topmost 20 cm the variability increased again.

The C/N weight ratio median is 11.5 and the data ranged from 8.9 to 13.2. The minimum was found at 40.2 cm and the maximum at 47 cm. A decreasing trend can be observed towards the core top. The variability of the data remarkably decreased for the top ~35 cm.

### III. 4.2. Stable carbon isotope ratios

The $\delta^{13}C$ values of LB-G-01 ranged from −29.0‰ to−26.6‰, with a median value of −27.7‰. The average time resolution is ~8 years. From the deepest point onwards the data indicate a marked change within a short timeframe, with a minimum value of−28.5‰ ensued by the maximum value of −26.6‰. Between 57 cm and 43 cm the $\delta^{13}C$ stabilized around −27.9‰, whereas from 43 cm to 27 cm the plot reached a local maximum and stabilized subsequently. Above 27 cm the $\delta^{13}C$ values showed a decreasing trend and reached the lowest value at 6.5 cm.

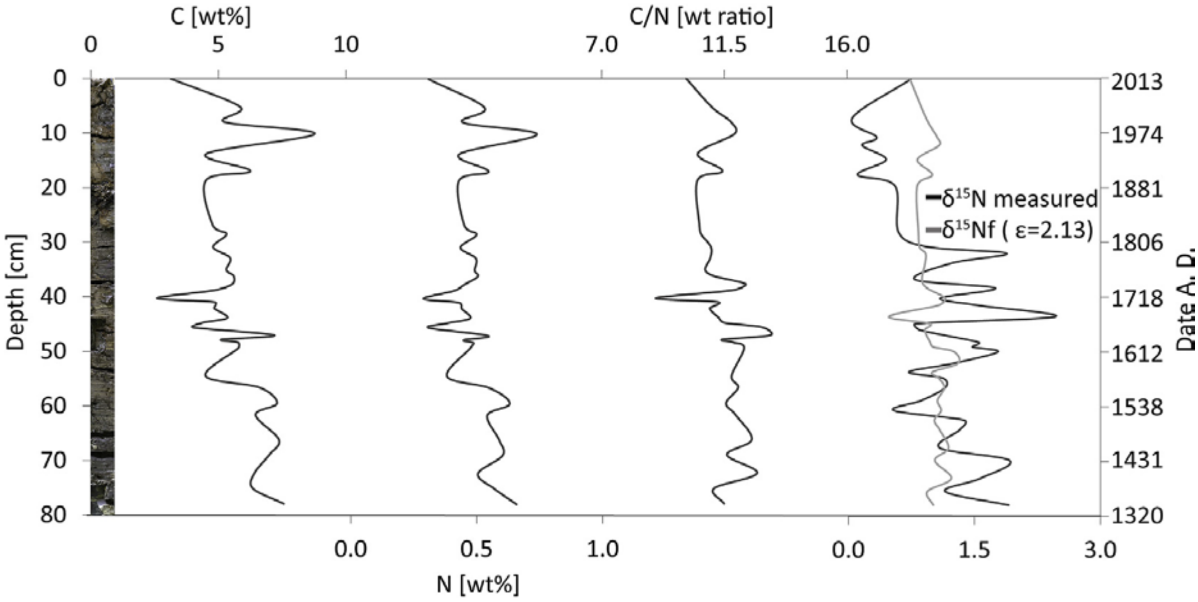
The $\delta^{13}C$ values of LB-G-02 ranged between−30.5‰ and−26.7‰, with a median of −28.6‰. From the deepest point to 65 cm δ13C fluctuated close to −29.3‰. The average time resolution of this record corresponds to ~6 years. From 65 cm upwards the $\delta^{13}C$ values increased by ~1.5‰, which corresponds to a similar pattern in LB-G-01. The second timeframe exhibiting an interesting behavior starts at 48 cm up to 31 cm, where the $\delta^{13}C$ shows extreme fluctuation throughout the core within a short period. A declining trend can be observed in the top 27 cm of the core.

Although recent decline in the $\delta^{13}C$ of the atmospheric $CO_2$ very likely contributes to the declining trend of $\delta^{13}C$ of the organic material in the recent sediment of Bolătău-Feredeu tested correction resulted in extreme effect which would result in unrealistically elevated values at the top section (III. Fig. 4). The simple subtraction of the atmospheric trend would likely result in over-correction. The reason could be a delay in transferring of the atmospheric input signal into the sedimentary organic material. Therefore, in this case, the environmental signal was evaluated based on the raw $\delta^{13}C$ record

### III. 4.3. Stable nitrogen isotope ratios

The median value of the $\delta^{15}N$ parameter is 1.1‰ with a relatively high scatter (0.6). The measured data ranged from 0.02‰to 2.5‰. The peak was detected at the depth of 40.2 cm. The largest variability was observed between 56 cm and 27 cm where the fluctuations exceeded one per mill within a centimeter. The $\delta^{15}N$ showed remarkably suppressed variability over the top 26 cm and reached the lowest value near the recent end of the profile.

The δ15N record showed a pronounced enrichment trend downward along the profile (Fig. 5). The variations in C% suggest that the organic content fluctuated along the profile. The N and C concentrations followed very similar vertical distributions, thus suggesting that N% variations reflect the changes in the organic content, which can overprint the diagenetic changes of the N-bearing compounds. However, the C/N ratios increased with depth in line with the expected trend of diagenetic changes, therefore the model employing the C/N weight ratio was used estimating the diagenetic trend (Brahney et al., 2014) of the Bolătău-Feredeu sediment profile. The best fit model (RMSE=0.61) was obtained with ε=2.13 (Fig. 5). This epsilon value fits to the expected range (Brahney et al., 2014). The best-fit model with low RMSE showed no correlation to the actual $\delta^{15}$N series (r=0.01), thus indicating a weak diagenetic control on lake sediment $\delta^{15}$N variation. The raw δ15N record has been corrected for the modeled diagenetic effect and the environmental signal was evaluated based on the corrected record.



III. Figure. 5. Elemental concentrations of C, N, and C/N weight ratio and the comparison of the measured $\delta^{15}$N values and the modeled diagenetic trend. Estimated diagenetic trend (thick grey line) was calculated from C/N (Brahney et al., 2014). Sediment photo of LB-G-02 displayed near to the depth scale at the left. Note here: the black stripes in the log are drying cracks occurred after sampling.

### III.4.4. Variations in the lipid fraction

The $C_{13}$-$C_{35}$ alkanes were detected in the sediment samples in Lake Bolătău-Feredeu, while the coarsest time resolution of ~54 years was obtained for the n-alkane record.

The $TAR_{HC}$ index ranges from 12.2 to 162.6, with a median of 23.29. The higher values of $TAR_{HC}$ represent an increased terrestrial contribution to the sedimentary n-alkane composition relative to the insitu lacustrine production (Silliman et al., 1996; Meyers, 2003). The plotted data show three periods of increased terrestrial n-alkane input: between 66 and 56 cm, where the $TAR_{HC}$ doubled compared to the background level, while larger amplitude fluctuations can be observed in the upper sediment section; between 35 and 28 cm, where $TAR_{HC}$ increases from

35.1 to 105.6, and subsequent to this maximum the lowest $TAR_{HC}$ index (12.2) is recorded; finally, in the topmost sample, i.e. the 0–13 cm section, where $TAR_{HC}$ jumps to 162.6.

$P_{aq}$ in the Bolătău-Feredeu sediment sequence accounting for the past 700 years ranges from 0.3 to 0.51 with a 0.42 median value (Fig. 7). The higher values of $P_{aq}$ indicate increased contribution of the aquatic biota to the sedimentary n-alkane composition (Ficken et al., 2000; Ortiz et al., 2016). If $P_{aq} < 0.1$ it corresponds to terrestrial plants; if the value is in the 0.1–0.4 range, it points towards inputs from emergent macrophytes, while the values ranging from 0.4 to 1 indicate inputs from submerged/floating macrophytes (Ficken et al., 2000). The natural background of $P_{aq}$ can be characterized by the 0.39 value detected at the deepest point of the core. Minor fluctuations characterize $P_{aq}$ up to 47.83 cm depth, where it reaches the maximum. From then on, the index values show a monotonic decrease up to the core top, suggesting a persistent decline in the relative contribution of the aquatic organic matter compared to the terrestrial sources during the recent past.

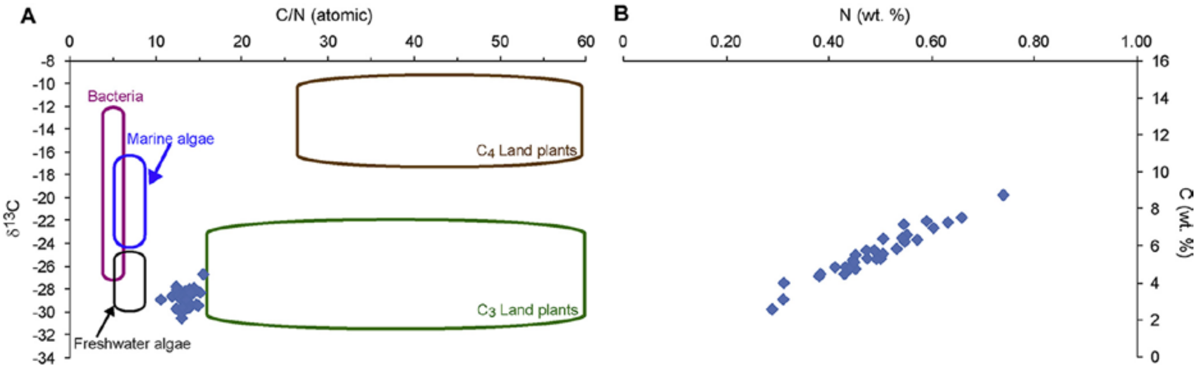
The $P_{wax}$ index value ranges between 0.68 and 0.80 with a 0.73 median. $P_{wax}$ reflects the relative proportion of waxy hydrocarbons derived from emergent macrophytes and terrestrial plants to total hydrocarbons (Zheng et al., 2007). Therefore, higher $P_{wax}$ values suggest a larger input from vascular plants. The inferred terrestrial contribution fluctuates along the Bolătău-Feredeu sediment sequence. The $P_{wax}$ amounts to 0.73 in the deepest sample and exhibits some small amplitude fluctuations upwards, dropping to its lowest value at 47.83 cm. Lower values were also recorded in the two upper samples, therefore suggesting a diminished terrestrial contribution to the sedimentary organic material during a prolonged period of time. The $P_{wax}$ index recovered at the depth of 35.09 cm and gradually increased upward, reaching the maximum value in the topmost sample.

The $P_{hw}$ index ranges between 0.23 and 0.84 with a 0.47 median. This index can be used to distinguish the relative abundance of woody and herbaceous plants in long chain alkanes (Zhu et al., 2008). The higher values of $P_{hw}$ indicate an increased contribution of herbaceous plants to the sedimentary n-alkane composition compared to woody plants. $P_{hw}$ showed a decreasing trend from 78 cm to ~61.5 cm, ensued by relatively higher values peaking at 0.61. Subsequent to the peak, $P_{hw}$ dropped to the lowest recorded level (0.23) between 47.83 and 43.83 cm, and then it stabilized around 0.47. A remarkable shift can be observed at 28.5 cm, where $P_{hw}$ increased by a factor of ~1.7. Less elevated values (0.72) were determined for the most recent sediments; however, these are still well above the values obtained for the sediment below 28 cm.

## III. 5. Discussion

### III. 5.1. Major sources of the organic material in Bolătău -Feredeu sediment

The C/N ratio and δ$^{13}$C have been widely employed to distinguish the sources of sedimentary organic matter in aquatic environments (Meyers, 2003; Lamb et al., 2006). The C/N ratio of terrigenous organic matter is always greater than 15, while typical algal organic matter has C/N ratios between 4 and 10, and the bacterial contribution can be characterized by a rather narrow range, between 4 and 6 (Meyers, 1994; Tyson, 1995). δ$^{13}$C values of C3 plants are scattered around an average value of about −27‰ (range: −32 to −21‰), C4 plants have δ$^{13}$C values of around −13‰ (range: −17‰ to −9‰) (Deines, 1980; Tyson, 1995; Meyers, 1997). Thus, the ranges of δ$^{13}$C values (−30.5 to −26.6‰) and C/N atomic ratios (10.5–15.4) placed the organic material of the recent Bolătău-Feredeu sediment between the C3 Land Plants and the lacustrine algae (III. Fig. 6a). This finding was expected and is in agreement with the geographical situation of the lake, as the terrestrial vegetation in the study area is dominated by C3 plants (Mîndrescu et al., 2010). In turn, this correspondence verifies the reliability of the obtained organic geochemical data. The C-N scatter plot (III. Fig. 6b) showed that the composition of the organic material is distributed along a single mixing line. Major changes in the characteristic sources of organic matter could result in multiple mixing lines in the C-N scatter plots (see e.g., Noble et al., 2016; Ivanić et al., 2017). The geochemical data suggest that the relative contribution of the above mentioned two major sources (C3 land plants and the lacustrine algae) played the dominant role in the changes of the organic matter in the sediments of Lake Bolătău-Feredeu throughout the period accounted for by the studied section. Consequently, increasing terrestrial inputs into the lake under conditions of intensified surface runoff from the catchment would elevate the relative share of terrestrial organic matter in the lake sediments, resulting in a shift in the δ$_{13}$C values of the sedimentary organic matter towards those indicative of terrestrial C3 plants (see Fan et al., 2017).



III. Figure. 6. Major sources of the organic material in sediments of Lake Bolătău-Feredeu. A: $\delta^{13}C$ and C/N atomic ratios of organic matter sources of the lake sediment (blue markers). Reference fields redrawn based on Meyers (2003) and Lamb et al. (2006). B: Biplot of carbon and nitrogen concentrations of the lake sediment.

The Carbon Preference Index (CPI) has been utilized to explore the maturity of hydrocarbons in sediments (Bray and Evans, 1961). The mean CPI of Lake Bolătău-Feredeu sediment sequence is 8.34, which fits into the range (i.e. ~5 to 30) usually reported for epicuticular waxes derived from terrestrial plants (e.g., Eglinton and Hamilton, 1963; Mazurek and Simoneit, 1984; Vane et al., 2014), while marine- and petroleum-derived n-alkanes can be characterized by CPI=~1 (Simoneit, 1984). This indicates that the dominant source contributing to the recent Lake Bolătău-Feredeu sediment consists of slightly to nondegraded terrestrial organic matter. Hence, multidecadal variations seen in the characteristics of the sedimentary organic matter (n-alkane composition, elemental and isotopic parameters) carry meaningful information for the temporal variations in the organic input to the sedimentary sequence.

### III. 5.2. Reconstructed changes at Lake Bolătău-Feredeu and their correspondence to regional records

Past changes in the studied organic carbon and nitrogen proxies ($\delta^{13}C$, $\delta^{15}N$, C/N) and changes in the n-alkane assemblage can potentially be used to reconstruct the history of environmental variations of the lake-forest system. Three periods have been assigned based on concurrent changes in the sedimentary organic geochemical proxies indicating major changes in the studied catchment in South Bukovina throughout the past ~700 years.

### III.5.2.1. Environmental changes at Lake Bolătău-Feredeu since ~1340 AD

#### III.5.2.1.1. Modern landscape change (~1820–2013).

Multiple evidence in the organic geochemical record indicated substantial changes in the lake-catchment system from the early 19th century. As noted above, a marked decline in $\delta^{13}C$ can partially reflect the secular changes in the atmospheric isotopic signal of the $CO_2$ (see also Vreca and Muri, 2006), complicating its interpretation over this section. Diagenesis corrected $\delta^{15}N$ records shifted towards depleted compositions, suggesting that the sources of dissolved inorganic nitrogen have most likely changed. Extremities were detected also in the alkane composition since $P_{wax}$, and $P_{hw}$ reached their maximum values, while $TAR_{HC}$ displayed both the highest and the lowest index values in this period. The continuous increase in $P_{wax}$ suggests increasing terrestrial organic input since the beginning of the period, while the elevated values determined in the $P_{hw}$ record argue for the largest contribution of herbs and grasses throughout the entire timespan. In turn, the $P_{aq}$ is continuously decreasing; however, this might be only a statistical artefact assuming a quasi-constant aquatic production and a tremendously exaggerated supply of terrestrial organic matter.

All these proxy data point to a substantial landscape change triggered by deforestation and expanding of open pastures/grasslands with herbaceous plants. In addition, the deforestation event is strongly confirmed by the stratigraphic evidence of a ~3 cm thick accumulation of leaves, needles, and fine branches.

The shrinking forest cover could have increased the erodibility at the catchment scale. The input of soil nitrogen into the lake from the catchment mobilized a nitrogen pool depleted in $\delta^{15}N$ because soil nitrogen comes initially from atmospheric nitrogen through the fixation of nitrogen-fixing bacteria, atmospherically deposited N and terrestrial plant residues, and has a $\delta^{15}N$ value much lower than that of the dissolved inorganic nitrogen pool of the lake (Meyers, 1997, 2003; Talbot, 2001). Therefore, depleted diagenesis corrected $\delta^{15}N$ values support this explanation.

The sedimentary organic geochemical record supported by stratigraphical evidence clearly reflected the historical landscape changes documented by cartographical evidence for the 19th century in the Bukovina region (Barbu et al., 2016).

This experience encourages i) the interpretation of the variations in the organic geochemical proxies of the deeper sections of the Bolătău- Feredeu lacustrine sequence, in order to infer peleoenvironmental reconstructions for the lake-catchment system, and ii) the consideration of the organic geochemical parameters (including lipid biomarkers) for multi-proxy paleolimnological studies in the Carpathian-Balkan region.

#### III.5.2.1.2. Variable lacustrine environment decreased productivity in the catchment (~1640–1760).

The evidence obtained from organic geochemistry analyses refer to environmental changes in the lakecatchment system during the coldest decades of the last Millennium. In this period, the $\delta^{15}N$ and $\delta^{13}C$ values showed the highest variability. $P_{aq}$ reached the peak level in this timeframe, while both $P_{wax}$ and the $P_{hw}$ dropped to the lowest levels recorded in the ~700-year time range covered by the sediment sequence. Moreover, during the first part of this period, the C concentration drastically declined similar to the C/N ratio (III.Fig. 5).

Interestingly, this section coincides with a well-known cold period in Central Europe (Dobrovolny et al., 2010) thought to have been triggered by diminished solar irradiance during the so-called Maunder Minimum (Vaquero and Trigo, 2015). Historical evidence showed that recurring cold winter seasons (Rácz, 1994; Luterbacher, 2001) and, occasionally, extremely cold early springs characterized the turn of the 17th and 18th centuries in this region (Rácz, 1999), which very likely resulted in delayed break-up of the lake ice cover in Lake Bolătău-Feredeu. A variable lake environment corresponding to extended periods of lake ice cover can be assumed during the cold climate. Consequently, the shorter vegetation period and the prolonged ice cover of the lake logically translated to diminished biological productivity within the lake and its catchment.

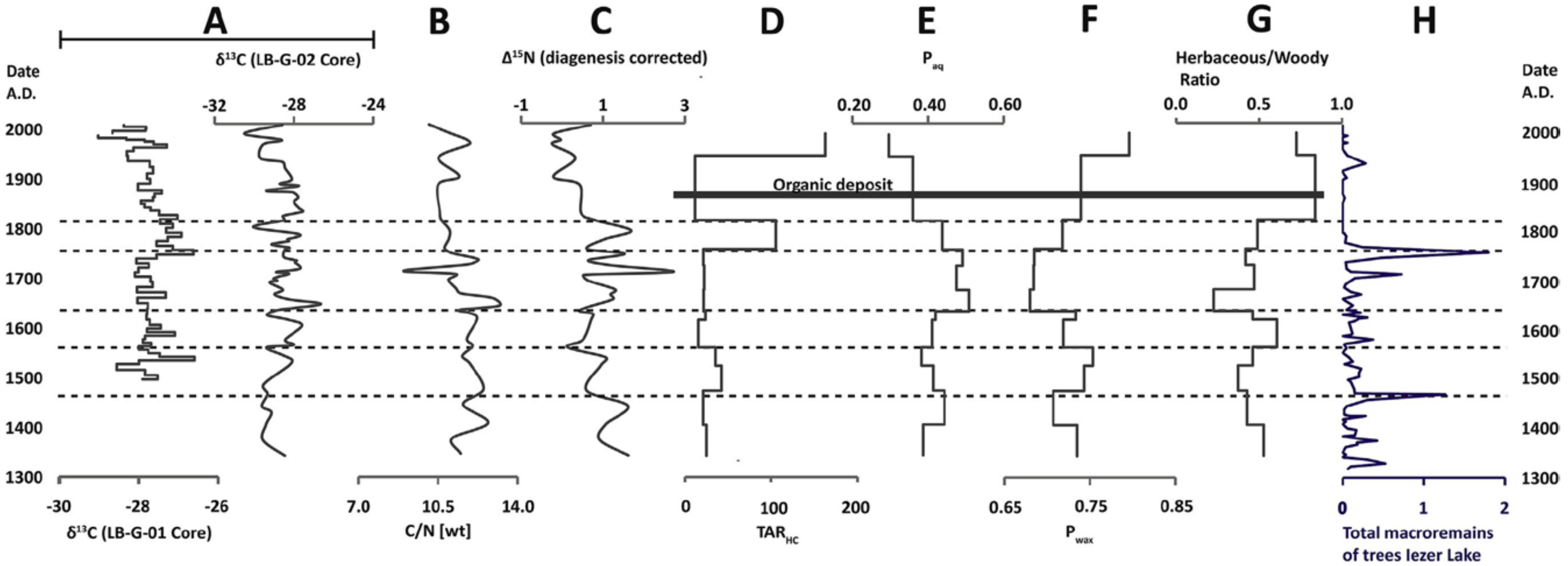
#### III.5.2.1.3. Afforestation and decline in lake productivity (~1470–1560).

Isotopic, such as $\delta^{13}C$ and $\delta^{15}N$, and C% data reached peaking values, albeit the C/N ratio diminished, suggesting increased lacustrine contribution, and consequently elevated productivity in the lake. The $TAR_{HC}$ index presented a small peak indicating increased terrestrial contribution to the organic fraction of the sediment. $P_{wax}$ also increased to a higher level, thus pointing to a boost in the terrestrial input, while the $P_{hw}$ index dropped to lower values, which likely imply a diminished contribution of herbs and grasses to the terrestrial proportion. Overall, these changes can be interpreted as a result of expanding forest cover and shrinking grasslands in the Bolătău-Feredeu catchment.

### III.5.2.2. Comparison with regional records

A complex study combining magnetic and elemental geochemistry record with palynological data and plant macrofossils from a sediment sequence obtained from the nearby Lake Iezer (Florescu et al., 2017) also argued for large scale deforestation in South Bukovina during the first half of the 19th century. Therefore, the corresponding deforestation signals detected in both Lake Bolătău-Feredeu and Lake Iezer record most likely document a deforestation activity in South Bukovina (III.Figure. 7). The timing of the deforestation event inferred from the nearby sedimentary record suggests a ~65 years delay at the Bolătău-Feredeu catchment compared to Lake Iezer (III: Figure. 7). This discrepancy might indicate the advancement of the historical forest exploitation activity. A high-resolution and accurately dated pollen record at ~75 km to the west (Tăul Muced, Rodnei Mts) showed little evidence of pollen types indicative of human activity before 1900 A.D. (Feurdean et al., 2015), suggesting a lack of regional scale deforestation before the 20th century in the Eastern Carpathians.

The changes in the proxy records derived from the lacustrine deposit from South Bukovina argue for coherent changes in the vegetation in the respective catchments due to the climate deterioration assigned to the Maunder Minimum period. During the cold period this study documented a drop in terrestrial productivity, when the herbaceous contribution probably also diminished (III. Fig. 7). The corresponding decline in the $P_{wax}$ and $P_{hw}$ indices can be interpreted as evidence for the decrease in the terrestrial contribution around Bolătău-Feredeu. Similarly, a relative decline in herbs compared to the increase in arboreal pollen contribution can be inferred from the relative changes in the pollen records of Iezer lake (III. Fig. 7).



III. :Figure. 7. Summary plot of the organic geochemical parameters derived from the Bolătău-Feredeu sedimentary sequence for the past ~700 years. (A) $\delta^{13}C$; (B) C/N [wt]; $\Delta^{15}N$ (diagenesis corrected); and n-alkane derived indices: (D) $TAR_{HC}$; (E) $P_{aq}$; (F) $P_{wax}$; (G) Herbaceous/Woody Ratio. The last plot (H) shows the tree macroremains record of the nearby Iezer Lake (Florescu et al., 2017).

## III.6. Conclusions

This study verifies that the lipid biomarkers of young, unconsolidated lake sediments can be utilized as powerful indicators for major changes in land cover, such as forest vs grassland, or for inferring the changing contributions of the sedimentary organic fractions from terrestrial and aquatic sources. Thus, the results of this investigation are encouraging for further studies following similar multi-proxy methodologies aimed at tracing environmental changes in the recent past of the Carpathian – Balkan region.

The organic fraction of the sediment of Lake Bolătău-Feredeu originated from two sources (C3 land plants and freshwater algae). Detected major shifts in the n-alkane composition and the C and N concentrations, together with the stable isotope compositions, pointed out three distinct stages in the environmental history of the lake catchment system.

- Modern landscape change (~1820 A.D.–2013 A.D.): The proxy information point towards a substantial landscape change triggered by deforestation and expanding open pastures with herbaceous plants. The episode of deforestation at Bolătău-Feredeu catchment appears to be delayed by ~65 yrs compared to a similar event reconstructed for a neighboring, lower lying catchment from Obcina Feredeului.

- Variable lacustrine environment decreased productivity in the catchment (~1640 A.D.–1760 A.D.): The C/N, $\delta^{15}$N, and $\delta^{13}$C values exhibited the highest variability, thus leading to the assumption that the cold decades experienced at the turn of the 17th-18th centuries translated to diminished biological productivity both in the lake (due to extended periods of lake ice cover) and its catchment.

- Afforestation and decline in lake productivity (~1470 A.D.–1560 A.D.): While $\delta^{13}$C, $\delta^{15}$N, and C% reached peaking values, the C/N ratio decreased, suggesting elevated lacustrine contribution. In the n-alkane proxies, $TAR_{HC}$ rose to a small peak during this period, indicating higher terrestrial input, whereas $P_{wax}$ increased and $P_{hw}$ reached a lower level, indicating an afforestation process occurring in historical times in this region.

## Acknowledgements

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# Chapter IV.: Natural and anthropogenic impacts reflected by paleoclimate proxy parameters in a lake-forest system in Bukovina (Romania)

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## IV. Abstract

The research area is located in the Eastern Carpathians, Romania. This region is rich in various formations and indicates significant potential for paleoenvironmental reconstruction. The present research was carried out on sediment cores collected at lake Bolătău-Feredeu, Feredeului Mts (Eastern Carpathians, Romania). Preliminary examination of the sediment confirmed the possibility for data analysis with high temporal resolution. The aim of the research was to clarify and supplement the findings of previous research at this site, to explore the relationships between proxy parameters and to elucidate the cause for the changes. Core dating was carried out using Pb-210 and radiocarbon isotopes and indicated that sediment cores span the past 500 years. The research uses a wide range of methodologies, including organic geochemistry with calculated n-alkane indices ($P_{hw}$ and $P_{wax}$). Based on these proxies, the changes of woody and herbaceous coverage in the catchment can be estimated. Moreover, element concentration, weathering indices and particle size distribution assist to detect climate changes in the catchment area. The data and conclusions yielded by the analysis were compared with the regional modelled temperature profile, based on which five periods were separated. In addition to natural and anthropogenic events, the main factor among the natural processes is the change in annual temperature. Based on the obtained data, several parameters were found to be suitable for monitoring past temperature changes.

key words: deforestation, landscape change, weathering index, n-alkanes, temperature reconstruction, paleoclimate

## IV.1.Introduction

Research on paleoclimate and paleoenvironmental changes ranks among the most hotly debated topics due to the fast pace at which environmental conditions are currently changing. The earliest scientific approach to use lake sediment as an environmental archive dates back to the early 19th century (e.g., Lyell, 1830). Over time, however, paleoenvironmental research has become an increasingly complex and multidisciplinary scientific field supported by a wide range of methodologies and techniques for investigating lake sediments. Numerous tools connected to various fields of science (such as physics, geology, climatology, mathematics, botany and others) have become available for lake sediment research (Last &. Smol  2001.)

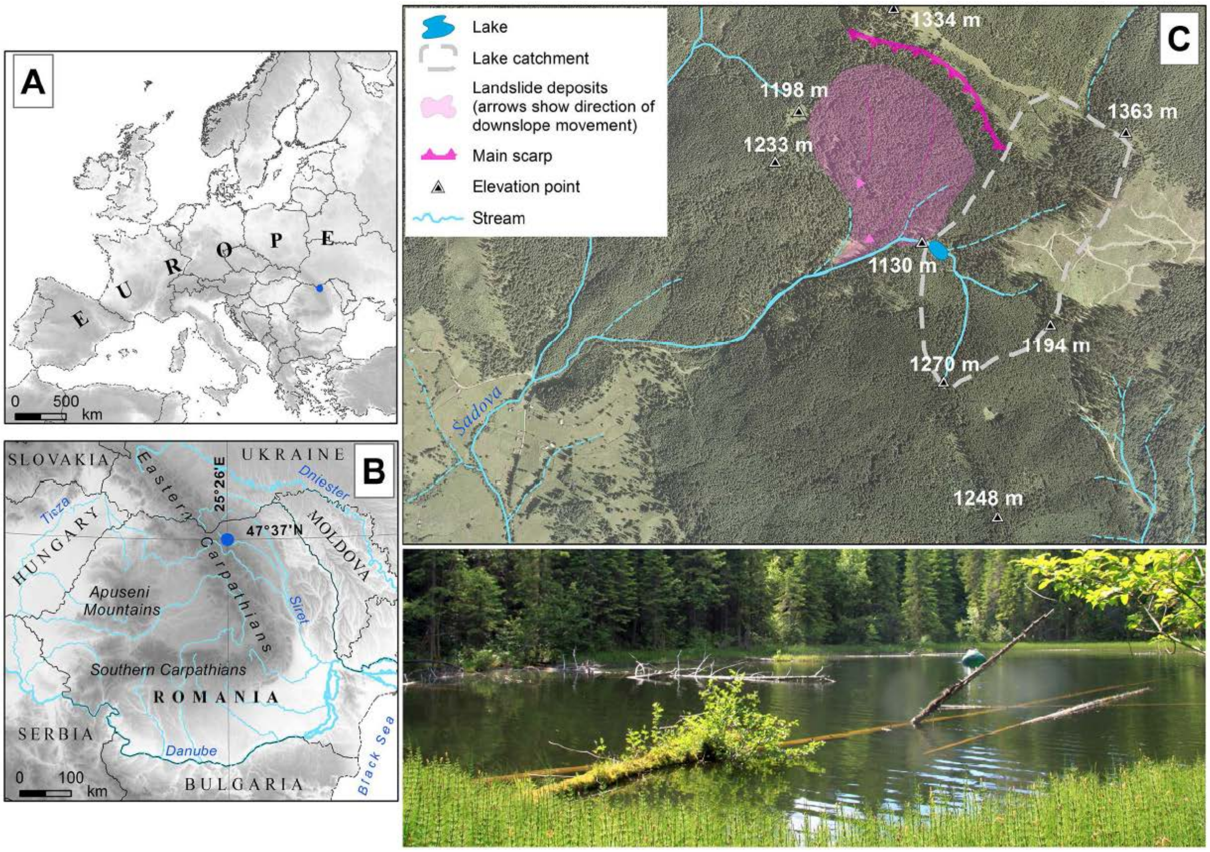
The Romanian Carpathians seemingly abound in areas with significant potential for paleoenvironmental research, therefore several studies based on lake sediments have been carried out to date (e.g., Wohlfarth. et al., 2001; Haliuc. et al. 2009; Magyari et al. 2009; Kłapyta et al. 2016). The study site selected for this analysis is located in Bukovina region, Romania, where historical records documented substantial landscape changes throughout the past centuries, including mainly deforestation and subsequent land cover / land use shifts (Barbu et al. 2016). Lake Bolătău-Feredeu is regarded as one of the Bukovinian Millenial lakes and is suitable for high-resolution analysis, based on the findings of previous studies at this site and in the neighbouring area (Mîndrescu et al. 2013 & 2016, Florescu et al. 2017; Karlik et al. 2018 & 2021).

The aim of this work is to analyse the geochemical and particle size parameters of lacustrine sediments and interpret the data in relation to/as a response to climatic and vegetation changes. We focus on correlations between each parameter with special regard to temperature-induced changes. The lipid biomarker distribution, especially long-chain n-alkanes, in recent sediments is a useful tool to detect natural and anthropogenic changes in the vegetation of lakes and catchment areas (Meyer 2003; Eglinton and Eglinton 2008; Karlik et al. 2018). Elemental analysis is among fundamental methods employed in sedimentology, with XRF measurements becoming widespread in the last 50 years (Engstrom and Wright 1984.; Couture and Dymek 1996). Elemental composition data reflect the organic, vegetation, inorganic and/or climate changes occurring in the lake-catchment system, whereas particle size distribution data are essential for interpreting elemental analytical data. This type of complex data analysis creates an opportunity to explore hitherto undiscovered processes, relationships and help to detect high impact effects (Das and Haake 2003.; Jin et al. 2006).

## IV.2.Material and methods

### IV.2.1 Study side

Lake Bolătău-Feredeu (47°37’20.74’’ N, 25°25’54.43’’ E) is located in the south-western sector of Feredeului Mts (Eastern Carpathians, Romania), in the vicinity of Obcina Feredeului peak (1364 m a.s.l.) and pertains to Sadova river catchment (IV. Fig. 1). Sadova stream is a tributary of River Moldova. The lake formed in the upper area of Sadova catchment, at ca. 1137 m a.s.l., subsequent to a landslide event which dammed the deep, narrow valley head of Holohoșca stream (Mindrescu et al. 2013). The lake surface is only 0.3 ha with an average 2 metre depth in 2010, while the catchment area is ~30 ha. The vegetation cover of the catchment is composed of various plant species, among which herbaceous associations account for 6 ha and Picea abies-dominated forests for 24 ha) (Mîndrescu et al. 2010.) The bedrock consists predominantly of sandstone, and the soil profile depth increases towards the lake. The slope gradients within the catchment range between ~18° (eastward), ~24° (northward) and ~25° (southward), whereas the outflow of Lake Bolătău-Feredeu flows to the west.



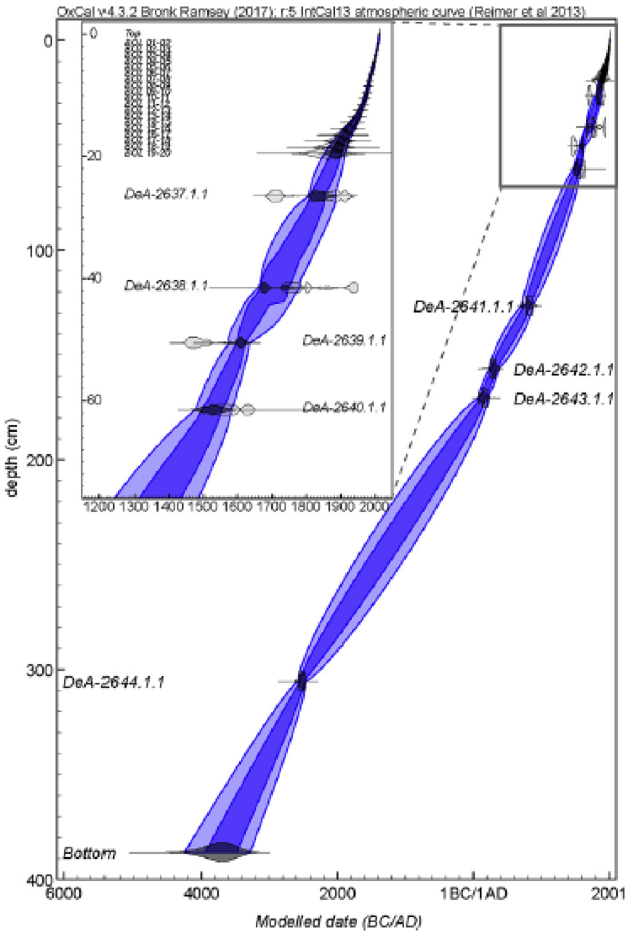
IV. Figure 1. Location of research area a) at continental scale; b) in the Eastern Carpathian region; c) a closer view of Lake Bolătău-Feredeu. The grey dashed line shows the catchment boundary. A site photo is displayed below the map (Karlik et al 2018).

### IV.2.2. Core collection

The sediment cores were retrieved in April 2013 using both a Russian corer (core code: LB-R-01) and a gravity corer (core code: LB-G-01) from the frozen surface of the lake. The corer parameters were identical (d=6,5+/-0,1 cm; S=33,2+/-0,6 cm$^2$). Two additional gravity cores (core codes: LB-G-02 and LB-G-03) were extracted using a floating platform in November 2013. The cores extracted in April were visually inspected on-site, described, photographed and sectioned at 1 cm intervals into pre-labelled plastic bags (Mîndrescu et al. 2016).

### IV.2.3. Chronology

An initial sediment chronology was established for the Bolătău-Feredeu sequence based on 8 AMS radiocarbon dates from terrestrial macrofossils and validated for the recent section by the double peaks of the 137Cs flux (i.e. mid-1960s: global fallout maximum; 1986: Chernobyl event) (Mîndrescu et al. 2016). The sediment chronology of the top 24 cm has been significantly improved using by 210Pb chronology (Bihari Á. et al. 2018). The $^{210}$Pb ages for the top 20 cm (with an uncertainty of the estimated ages below 30%) and all $^{14}$C dates were included in the Bayesian age-depth model using the P_Sequence function of the OxCal v.4.2 (Bronk Ramsey 2009) software (VI. Fig. 2). The latter was also employed for the calibration of $^{14}$C dates to calendar years in conjunction with the Northern Hemisphere IntCal13 (Reimer et al. 2013; dataset: Karlik et al. 2018).



IV. Figure 2.: Sediment chronology of the Bolătău-Feredeu sequence. Light (blue) shading shows the 95% (68%) confidence range of the Bayesian model. Original and modelled probability density functions of the radiometric ages are plotted by light and dark blue, respectively. Uppermost 70 cm is enlarged offering a more detailed view on the section on which the current study is focused (Karlik et al. 2018).

## IV.2.4. Methods

### IV.2.4.1 Particle size analysis

Particle size distribution was determined using a Fritsch Analysette 22 Microtech Plus laser diffraction particle size analyser, which measures in the range of 0.08 µm - 2.0 mm. Samples were treated for carbonate and organic matter removal according to USDA NRCS method (Burt, 2004). Three aliquots (ca. 1 g) were taken from each treated sample. Five minutes of ultrasonic treatment and sodium-pyrophosphate (50 g/l) were applied to the samples in order to allow a complete dispersion of the specimens. Refractive index and the imaginary part were assumed to be 1.54 and 0.01 (Eshel G. et al. 2004; Varga Gy. et al. 2019). The percentages of sand (2000–50 µm), silt (50 µm -2 µm) and clay fractions (below 2 µm) were reported according to a modified United States Department of Agriculture (USDA) texture classification scheme (Konert and Vandenberghe 1997).

### IV.2.4.2. Geochemical analysis

XRF is widely regarded as a very versatile and fairly accurate method for elemental analysis. This method is able to detect elements in the mass range from fluorine to uranium in solid and liquid samples. The types of XRF equipment are very diversified and the detection limits and any other measured parameters highly depend on the accepted excitation voltage, measuring time, detection settings etc. XRF is generally used for soil and sediments analyses and is a widespread technique in earth and environmental analytics (Schramm R. 2012).

The samples were measured using a RIGAKU Supermini wavelength dispersive X-Ray fluorescence spectrometer with Pd X-ray tube 50 kV excitation voltage and 40 anodes current. The EZScan measuring method was applied for 40 minutes on each sample to determine elements from fluorine to uranium.

VI. Table 1. Calculations of the weathering indices (CIA: Chemical index of alteration is interpreted as a measure of the extent of conversion of feldspars to clays; CIW: Chemical Index of Weathering is identical to the CIA, except that it eliminates K content from the equation; PIA: Plagioclase lndex of Alteration is used to monitor the plagioclase weathering.; V: Vogt's Residual lndex reflect the degradation of clay minerals)

| Index | Calculation | Reference |
|---|---|---|
| CIA | $[Al_2O_3/(Al_2O_3+CaO^*+Na_2O+K_2O)] \times 100$ | Nesbitt and Young ,1982 |
| CIW | $[Al_2O_3/(Al_2O_3+CaO^*+Na_2O)] \times 100$ | Harnois ,1988 |
| PIA | $[(Al_2O_3-K_2O)/(Al_2O_3+CaO^*+Na_2O-K_2O)] \times 100$ | Fedo et al., 1995 |
| V | $(Al_2O_3+K_2O)/(MgO+CaO+Na_2O)$ | Vogt, 1927 |

### IV.2.4.3. Organic geochemical analysis

The ~78 cm long LB-G-02 core was cut into 12 non-uniform samples. Non-uniform sampling steps were decided based on the pilot sampling, which suggested variable organic content. Samples were dried at 40°C and subsequently ground, and ~20 g samples were filled into stainless steel cells. Extraction was carried out in an Accelerated Solvent Extractor (ASE350) at 75°C and 100 bar, using 5:2 chloroform: methanol as solvent. The samples were run twice to ensure sufficient extraction. The extract was fractionated via column chromatography into saturated hydrocarbon (HC), aromatic HC, and resin fraction. The dominant fraction was resin. Saturated HC fraction ranged from 1.1% to 5.3% of the extracted total organics (Karlik et al. 2018).

The entire saturated HC fraction was analysed by gas-chromatography using a Fisons 8000 GC with Flame Ionisation Detector using the following parameters: injector temperature: 310°C split: 1:10, DB-TPH 30x0.32x0.25 column, detector temperature: 310°C. The oven was kept at 60°C for 1 min, then heated up to 150°C (20°C/min), then up to 330°C (6°C/min) for 5 min. To avoid the potential bias due to the variable amount of saturated HC subsamples, the changes in the alkane composition were evaluated using well-known indices calculated as the ratio between summed peak areas of certain alkane groups (Karlik et al. 2018).

VI. Table 2. Calculations of the n-Alkane indices ($P_{wax}$: reflects the relative proportion of waxy n-alkanes; $P_{hw}$: reflect the herbaceous proportion in the total terraneous plants)

| Index | Calculation | Reference |
|---|---|---|
| $P_{wax}$ | $(C_{27}+C_{29}+C_{31})/(C_{23}+C_{25}+C_{27}+C_{29}+C_{31})$ | Zeng et al., 2007 |
| $P_{hw}$ | $2*C_{31}/(C_{27}+C_{29})$ | Zhu et al., 2008 |

## IV.3 Results

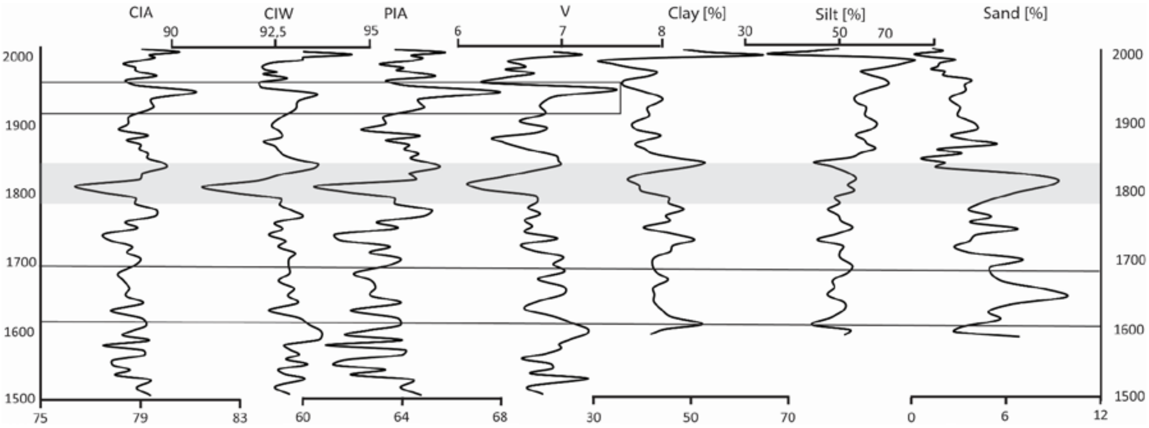
Weathering indices curves (CIA: Chemical index of alteration; CIW: Chemical Index of Weathering; PIA: Plagioclase lndex of Alteration; V: Vogt's Residual lndex) show similarity to each other throughout the entire examined time interval. From 1500 A.D. to 1776 A.D. the weathering index values fluctuated around the same level. The stable period is interrupted by a negative peak around 1820 A.D. The second time frame (between 1845 A.D. and 2010 A.D.) starts with a positive peak. After a short stable period (~55 years), a significant positive peak can be observed in all charts (1902 A.D. - 1948 A.D.) followed by a rapid decline upwards. In the last 55 years the values have been increasing. (VI. Fig. 3.)

The uppermost 52cm (~500 years) yielded enough material for particle size analysis. Three fractions have been inferred based on particle size distribution: clay fraction <2 µm, silt fraction from 2 µm to 50µm, and sand fraction from 50 µm to 2000 µm. The clay and the silt fractions accounted for more than 90% of the composition. (IV. Fig. 3.)

The proportion of the clay fraction ranged between a maximum of 65.4% and a minimum value of 31,5 %, thus covering a wide range of approximately 34%. The data set can be divided into three main intervals. The first interval (from 1592 A.D. to 1802 A.D.) is characterised by a fluctuation around ~45%, with a standard deviation of 3%. The dominant trend is not visible in this period, whereas four peaks can be observed in 1607 A.D., 1676 A.D. (small), 1731 A.D. and 1776 A.D. Between 1607 A.D. and 1730 A.D. the values are relatively low. The second interval spans from 1802 A.D. to 1845 A.D. Within this short period, both a negative and a positive peak have been detected. The third interval starts in 1854 A.D. and lasts until 2010 A.D. Between 1984 A.D. and 1994 A.D. the values show a declining trend with four peaks. (1985 A.D., 1912 A.D., 1938 A.D. and 1977 A.D.). The end of the period (from 1994 A.D. to 2010 A.D.) indicates a significant signal of current changes. (IV. Fig. 3.)

Silt fraction values commonly vary inversely compared to clay fraction values. In the first interval (from 1592 A.D. to 1802 A.D.) values fluctuate around ~50% with a standard deviation of 2%. A dominant trend has not been detected. However, six significant peaks can be separated (1592 A.D., 1629 A.D., 1694 A.D., 1749 A.D., 1802 A.D. and 1820 A.D.). In the second time frame (from 1802 A.D. to 1845 A.D.) the silt fraction decreases continuously. The third interval spans from 1854 A.D. to 2010 A.D. Between 1984 A.D. and 1994 A.D. the values show an increasing trend, whereas the uppermost part (from 1994 A.D. to 2010 A.D.) has been disturbed as previously mentioned. (IV. Fig. 3.)

The percentage of the sand fraction is generally less than 10% throughout the entire sediment sequence under investigation. The data set can be divided into two main parts. Between 1592 A.D. and 1820 A.D. the sand fraction values show high variability. From 1592 A.D. onwards, after a short decreasing period, three peaks have been determined at 1618 A.D., 1650 A.D. (the highest) and 1705 A.D., followed by ca. 70 yrs. Of relatively low stable values. The ensuing period covering ~62 years started in 1775 A.D with a 3.7% sand fraction value, showed an increase up to a maximum value of 9.3% in 1820 A.D, and ended in 1883 A.D. at 1.6%. The last time frame lasted between 1883 A.D. and 2010 A.D. After a 20-year increase, a declining trend followed without major fluctuations. (VI. Fig. 3.)



IV. Figure 3.: Weathering indices (CIA: Chemical index of alteration; CIW: Chemical Index of Weathering; PIA: Plagioclase lndex of Alteration; V: Vogt's Residual lndex) and particle size distribution data.

LOI (Loss-on-Ignition) values range between 16% and 27% in the core. From 1500 A.D. to 1767 A.D., the values have not shown any significant changes. Following this stable period, the largest shift can be observed from 16.5% (1776 A.D.) to 26.7% (1811 A.D.), ensued by a subsequent drop to 16.3% (1838 A.D.). An increasing trend has been detected up to 1902 A.D., followed by a stabilisation at around the previous level (1500 A.D. to 1776 A.D.). (IV. Fig. 4.)

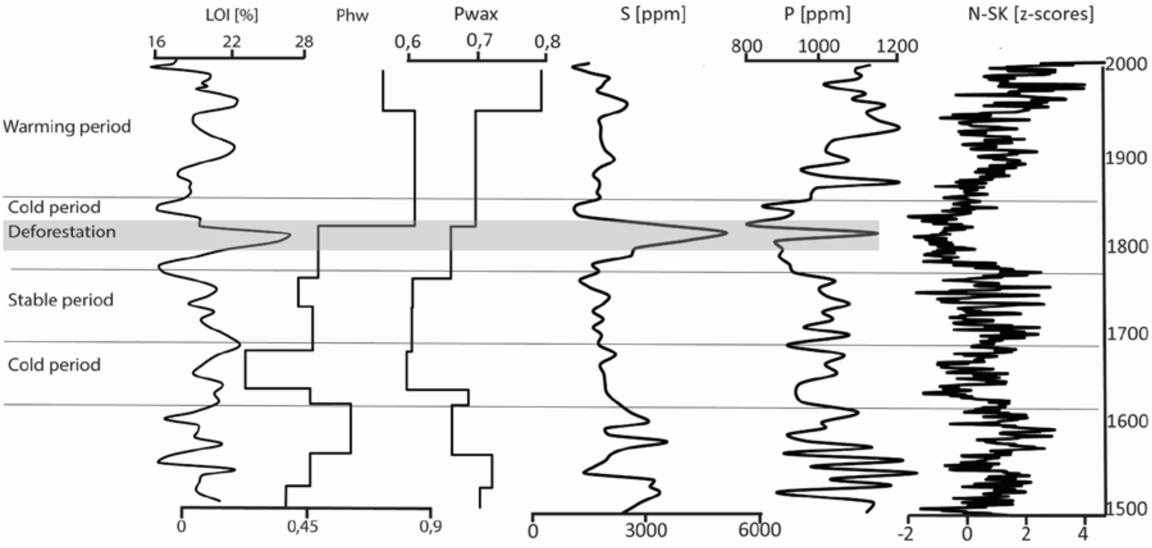
The $P_{hw}$ index ranges from 0.23 to 0.84 with a median of 0.47. This index can be used to study the relative abundance of woody (versus herbaceous) plants reflected by long-chain alkanes (Zhu L. et al. 2008). The high values of $P_{hw}$ indicate an increased contribution of herbaceous plants to the sedimentary n-alkane composition compared to woody plants. $P_{hw}$ shows an increasing trend from 1500 A.D. to 1662 A.D. ensued by relatively higher values peaking at 0.61 (from 1562 A.D. to 1618 A.D.). Subsequent to the peak, $P_{hw}$ drops to the lowest recorded level (0.23) between 1635 A.D. and 1679 A.D. and then it is stabilised around 0.47. A remarkable shift can be observed at 1820 A.D., where Phw is increased by a factor of ~1.7. Less elevated values (0.72) were determined for the most recent sediments; however, these are still well above the values obtained for the sediment below 1820 A.D. (Karlik el al 2018). (IV. Fig. 4.)

The $P_{wax}$ index ranges between 0.68 and 0.80 with a 0.73 median. $P_{wax}$ reflects the relative proportion of waxy hydrocarbons derived from emergent macrophytes and terrestrial plants to total hydrocarbons (Zeng et al. 2007). Therefore, higher $P_{wax}$ values suggest a larger input from vascular plants. The inferred terrestrial contribution fluctuates along the Bolătău-Feredeu sediment sequence. The $P_{wax}$ is 0.73 in the lowermost sample and exhibits some small fluctuations upwards, dropping to its lowest value at 1635 A.D. Low values were also recorded in the two upper samples, therefore suggesting a diminished terrestrial contribution to the sedimentary organic material during a prolonged period of time. The $P_{wax}$ index recovers at the depth of 1761 A.D. and gradually increases upwards, reaching the maximum value in the topmost sample (Karlik et al. 2018) (IV. Fig. 4.)

Sulfur is regarded as one of the most significant all-round proxies for lacustrine sediments and varies throughout the sediment sequence between ~1110 ppm and ~5080 ppm, reflecting the bacterial productivity and pyrite formation (Gransch, 1974; Raiswell and Berner 1985), as well as the organic matter content (Werne et al. 2003). From 1500 A.D. to 1620 A.D. the sulfur content of the sediment changed considerably, whereas, during the following 150 years, the concentration of sulfur remains stable at around 1800 ppm. The highest peak was recorded between 1785 A.D. and 1838 A.D. showing an increase by three orders of magnitude. Subsequently, the sulfur content dropped to the previous level until present day (IV. Fig. 4.)

The phosphorus content originates in the organic matter of the sediment (Lu et al. 2005) and is involved in many biological processes, reflecting various factors such as lake productivity and terrestrial organic input (Engstrom and Wright 1984). The phosphorus content varies between ~820 ppm and ~1250 ppm during the analysed time frame of ~500 yrs. From 1500 A.D. to 1620 A.D., the values drop reaching a minimum of 920 ppm in 1592 A.D. In the following four decades, the decreasing trend is interrupted by a local peak. After 1618 A.D. a sudden decline in phosphorus content has been determined ensued by a short minimum period (~20 yrs.), subsequent to which the P concentration remains at lower levels compared to the previous period. From 1761 A.D. the value decreases; however, at 1820 A.D. a remarkable peak has been detected, whereas at 1829 A.D. the P concentration is the lowest recorded in the core. The phosphorus content shows an upward trend up to 1938 A.D. ensued by a downward trend until 2010 A.D. (IV. Fig. 4.)

N-SK [z-score] data set is a high resolution modelled paleotemperature proxy to the Carpathian region published by Büntgen et al. (2013). From 1500 A.D. to 1620 A.D., the values show a non-continuous increasing trend and a relapse dated around 1560 A.D. Subsequent to 1620 A.D. the value drops to a minimum between 1630 A.D. and 1650 A.D. From 1680 A.D. to 1760 A.D. the standard deviation of the data is higher than before, with values varying greatly. The ensuing main period starts with a rapid decline from 1760 A.D. to 1800 A.D., whereas during the following 200 yrs. an increasing trend can be observed. (IV. Fig. 4.).



IV. Figure 4.: Temperature and potential organic material proxies: LOI; $P_{hw}$ (published in: Karlik M. et al. 2018); $P_{wax}$ (published in: Karlik M. et al. 2018); S; P; N-SK [z-score temperature proxy] (Büntgen et al. 2013)

## IV.4 Discussion

### IV.4.1 Weathering processes in the catchment of lake Bolătău-Feredeu

Changes in the weathering conditions have been studied using four different weathering indices and particle size distribution data (VI. Fig. 3.). From 1500 A.D. to 1776 A.D. the inferred weathering conditions were relatively constant based on the particle size values of clay and silt fractions. The sand fraction peak detected around 1550 A.D. has not been explained according to the classical interpretation, which would point to a shift in weathering conditions due to rainfall effect etc. In this case, the weathering indices calculated based on element concentrations do not show a signal that would confirm the weathering condition changes theory.

From 1776 A.D. to 1838 A.D. all weathering indexes and particle size fractions showed rapid and significant changes. This effect is concentrated within a relatively short time frame with a sudden decline occurring in just 20 years, indicating a significant shift in the lake-catchment area system, which has been explained by the findings of Karlik et al. (2018) regarding extensive deforestation in the region.

From 1838 A.D. to the present the weathering index values are more scattered compared to the earliest period (1500 A.D. to 1776 A.D.), thus suggesting that the catchment-lake system was more disturbed likely due to greater anthropogenic impact. The time frame spanning from 1925 A.D to 1948 A.D. deserves special attention as it overlaps with World War II.

### IV.4.2 Environment changes in the lake-catchment system

The modelled temperature dataset of the east Carpathian region (Büntgen et al. 2013) was compared to the organic and inorganic proxies, which resulted in the following reconstruction of environmental changes in the lake-catchment system.

Spread of herbaceous species in the catchment (~1500 A.D. to 1620 A.D.)

This period is characterised by large variations in values. The most informative indices were the n-alkane proxy parameters ($P_{hw}$ and $P_{wax}$). The phosphorus content recorded a high fluctuation, whereas the LOI% and the S content show similar shapes. $P_{hw}$ increased from 0.4 to 0.61, while $P_{wax}$ decreased from 0.75 to 0.7. Unfortunately, particle size distribution data are not available for this period. Low fluctuations in sulfur content and LOI% suggest the lack of high impact events, which would have significantly altered the geographical structure of the catchment. However, the values indicate a change in the vegetation of the catchment as the n-alkane proxy parameters suggest that the closed forest of the area receded and herbaceous vegetation settled in the vacant spots. The phosphorus content shows a disturbed signal and has a similar shape to the N-SK record with a 30-year slip. This parameter is linked to lake water temperature (Kim et al. 2003.) and biological productivity (Wildung 1977), therefore the connection between P content and the N-SK record is plausible in this source.

### The effect of a cold period on the lake-catchment system (1620 A.D. to 1700 A.D.)

This section of the sediment sequence coincides with a well-documented cold period in Central Europe (Dobrovolny et al. 2010). The N-SK temperature proxy indicates the interval with the lowest temperature at around 1639 A.D. The low phosphorus concentration corresponding to this time period correlates well with the minimum N-SK index, whereas $P_{hw}$ and $P_{wax}$ drop to their minimum values. Moreover, the contribution of the sand fraction recorded one of its highest peaks at 1650 A.D. However, the weathering indices have not changed to a significant extent, therefore related processes are negligible. The change in temperature is responsible for the shift of the primary biosphere in the catchment area, with herbaceous species responding more sensitively to the environmental condition changes compared to woody species. The variations detected in the n-alkane proxies and the phosphorus content (with the latter at a significantly higher resolution) indicate a fast cooling period in the area of Bolătău-Feredeu lake catchment. The shape of the P content signal is very similar to the shape of the modelled temperature during the time frame when the minimum temperature was recorded in the catchment (from 1629 A.D. to 1650 A.D.). Herbaceous species, and especially the grass vegetation greatly influence the particle size distribution of the terrestrial input. From the proportion of the sand fraction, it can be deduced that the herbaceous cover had declined between 1620 A.D. and 1650 A.D.

### A seemingly stable period in the lake catchment system (1700 A.D. to 1780 A.D.)

This time frame spanning ca. 70 years marks a period of relative stability in the 18th century. Based on the available data, the apparent stability could be attributed in part to the sampling frequency. However, a more probable explanation is the slow response of this complex system to rapid, short-term shifts lacking any explicit trend. Whereas the modelled temperature shows significant changes, among the weathering indices only PIA (which is bound to the clay and silt fraction) reflects these variations. The sulfur content and, to a greater degree, the organic matter content (LOI%) both show a decrease. The phosphorus content follows the trend of the N-SK temperature proxy, albeit the resolution of the P curve is higher than N-SK. Phw drops to a minimum level in the second part of the period.

### Anthropogenic impact on the lake-catchment system during a cold period (1780 A.D. to 1860 A.D.)

Deforestation has been documented in Bukovina (Florescu et al. 2017) in the area where the catchment area is located (Karlik et al. 2018). The multi-proxy analysis supports a better understanding of the historical evolution of anthropogenic impact in this catchment and allows for comparisons with other areas. According to the N-SK temperature proxy this period was especially cold. The phosphorus content shows a similar trend with the exception of a peak detected between 1811 A.D. – 1829 A.D. During this period, all proxies displayed well marked trends. The maximum P value was reached in the 1820s. The highest LOI% value is recorded during this period, suggesting high organic material input in the lake catchment system. Moreover, a large sulfur peak (pointing to an anoxic zone) was detected, thus indicating high organic content. All weathering indices recorded unprecedented minimum values, with the clay fraction peak conforming to the trend of the weathering indices. Conversely, the sand and silt fractions show marked peaks. The n-alkane proxy parameters ($P_{hw}$ and $P_{wax}$) indicate significant changes; however, as the sample at this depth covers a large time interval, only the change itself was considered. Based on the examination of all parameters the deforestation started around ~1811 A.D. and went on for a decade. The effect of forest removal coupled with the major disturbance undergone by the soil modified the total lake – catchment system. The high organic input to the lake originating in the catchment most likely destabilised the lake balance. Subsequent to 1829 A.D. a new vegetation composition began to form.

### Modern landscape changes in the catchment (1860 A.D. to 2010 A.D.)

The deforestation documented during the early 19th century marked the onset of change in the Bolătău-Feredeu lake-catchment system. Some of the parameters recorded unprecedented levels or were evolved according to new trends. The silt and clay fraction balance was constantly shifting in the direction of the silt, with the exception of the last 20 years when high fluctuation became prevalent, whereas the sand fraction stabilised at a lower level. Based on these data, it can be asserted that continuous transformation is taking place in the catchment.

The fluctuation of the weathering indices was not consistent, which could be linked at least in part to human activity. The human impact was confirmed by the peaks recorded by weathering indices during World War II. LOI% and the sulfur content showed systemic repetition with coinciding peaks of these two parameters. The phosphorus content is comparable to the temperature model throughout this period, with the exception of the last 50 years when the P content trend deviates from N-SK. Thus, it can be argued that P content can be used to monitor the temperature. Although during this time frame the n-alkanes proxies were measured only in two samples, they are still effective parameters, suggesting that organic productivity in the catchment is much higher than before. In the first sample covering the period subsequent to deforestation in the catchment the herbaceous contribution is much higher than the woody content, which is a typical finding. However, the second sample which represents the end of the 20th century, shows the next step in afforestation, a decrease in herbaceous plants and an increase in woody vegetation.

## IV.5. Conclusions

In this study, a multi-proxy analysis was carried out, comprising both organic and non-organic proxies, in order to highlight the importance as well as the disadvantages of n-alkane biomarkers, and the connections between proxies and temperature. Based on the data, we have concluded that the phosphorus concentration and the $P_{hw}$ n-alkane proxy are the most promising temperature proxies at this study site and should be further studied in terms of their potential for past temperature reconstruction. Analysis of indices from multiple sources is essential for avoiding misinterpretation of data and allows for a more in-depth understanding of the paleoenvironment as a biological and inorganic system. Our study provided sufficient solid data to reconstruct the paleoclimate and vegetation changes in the catchment area.

The data interpretation suggests that between ~1500 A.D. and 1620 A.D. herbaceous species replaced the closed forest vegetation in the catchment area based on n-alkane distribution, corroborated by LOI, sulfur and phosphorus variations.

The effect of the well-documented cold period between 1620 A.D. and 1700 A.D. can be detected in the Bolătău-Feredeu lake-catchment system. Based on $P_{hw}$ and $P_{wax}$, we inferred that bio-production in the catchment area decreased drastically, which is further reflected by the sand fraction peak and low phosphorous content. Phosphorous data suggests that the coldest period occurred between ~1629 A.D. and 1650 A.D.

An apparent stable period was documented between1700 A.D. and 1780 A.D. with only a slight decrease of herbaceous contribution, presumably caused by the undisturbed growth of the woody species. However, rapid changes may influence herbaceous vegetation without significantly impacting woody plants, thus resulting in decreasing herbaceous contribution.

The signal of the cold period (1780 A.D. to 1860 A.D.) can be observed in the N-SK data and the phosphorus content. Earlier studies documented an anthropogenic deforestation event in the area (Karlik et al. 2018) based on organic proxies, albeit the exact date has not been determined. The non-organic datasets, especially the phosphorus and sulfur contents, the sand fraction distribution and the calculated weathering indices, helped to accurately understand the course of the event. Therefore, during this cold period the forest removal started around 1811 A.D. and finished around 1820 A.D. In this short period a large amount of organic matter was delivered into the lake from the catchment area. This significant deforestation was further reflected in the changing weathering conditions.

The time period spanning from 1860 A.D. to 2010 A.D. differs from the earlier periods in that human activity in the area has become an additional factor in the lake-catchment system. However, the human impact in the area is somewhat limited, as the Bolătău-Feredeu catchment is located in a relatively remote area, nearly entirely forested, under conservation status (NATURA 2000 framework). The anthropogenic effect was confirmed by several parameters, such as LOI%, the S content and the weathering indices. The vegetation showed various stages of natural forestation during this period: first, the herbaceous contribution increased in the catchment area, then it was displaced by woody vegetation.

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# Chapter V.: Conclusions

## V.1 Summary of the results

In the introductory part of the dissertation **(Chapter I)** I provide a brief historical overview of the history of paleoenvironmental and paleoclimate research. Following this, the problem of lake sediment research as a complex approach across disciplines and methods will be described. A multidisciplinary vision is essential to conduct research and provide correct interpretation. The objectives of the research were described in this section.

In **Chapter II** the main direction was to explore the inorganic source material of the lake sediment and to determine the processes occurring in the catchment, based on the analysis of the lake sediment component using high resolution systems. The data regarding the catchment originated in an old regional survey (i.e., information on the bedrocks has been acquired mainly based on interpolated data). Thus, the first task was to survey the bedrock in the study area, to which purpose XRD & XRF measurements were performed on the bedrock samples. The mineralogical results obtained during this analysis were in agreement with the previous information, showing that the bedrock consists of a mixture of sandstone and shale complex, while the main detectable component with powder XRD is quartz (detection limit ~ 5[V/V%]). During the survey the catchment was originally divided into three areas.  The lake is located on the edge of the catchment area. The area above the lake is the "upper side" and the area on the left is the "left side" and the area on the right is the "right side". The results of the elemental analytical measurement (which were derived from the average sample of these areas) showed a larger difference then the the XRD results. The elemental composition of two areas (upper side & left side) was approximately the same ($SiO_2$ ~ 90%; $Al_2O_3$ ~ 2.8%), whereas the third area (right side) showed a significant difference ($SiO_2$ ~ 70%; $Al_2O_3$ ~ 16%).

The primary objective of the soil studies was to investigate whether the differences in the bedrock significantly affect the properties of the soil formed on it. Based on these data, it can be assumed that the constituents (inorganic and organic components) entering to the lake depend on the direction. XRD and XRF measurements were supplemented with particle size analysis. Soil samples were richer in minerals, similar to the bedrock samples; the samples corresponding to the left side and the upper side are also similar, and include: quartz, 10Å phyllosilicate, and clay minerals (near the detection limit). The soil sample collected on the right side includes: quartz, 10Å phyllosilicate, plagioclase, chlorite, illite or smectite, and kaolinite. Using Konert & Vandenberghe’s (1997) classification system (based on data yielded by particle size analysis) of bedrock properties, the right side area ranks as clay, whereas the other two are silty clay. Based on the elemental analysis of the soil, no such difference was reflected in the soil samples (example: mineral composition, particle size data ect). Therefore, the directionality of the materials entering the lake sediment cannot be significant, because the differences in the bedrock were not inherited into the soil.

In the lake sediment samples (64 items), XRD; XRF and particle size analyses were performed. Using powder diffraction, it was determined that lake sediment consists of the following minerals: quartz, 10Å phyllosilicate, plagioclase, clay minerals, and magnetite/maghemite. Carbonate content could not be detected by XRD or by hydrochloric acid test, so the lake sediment not include carbonates. Anoxic conditions prevail at the bottom of the lake and in the sediment. Based on the particle size data, the lake sediment samples show an extremely large standard deviation. In terms of classification, the samples are: clay, silty clay and silty clay loam. The two most dominant lake sediment particle sizes were clay and silt fraction (43.2 ± 5.4% and 52.4 ± 5.2%). The sand fraction is only 4 ± 2%. This high degree of variability predicts the usefulness of the data in paleoenvironmental reconstruction. Elemental analytical studies on lake sediments show similar variability as the particle size values, suggesting that substantial changes can be detected using these data. Following the methodology of Kronberg & Nesbitt (1981), weathering processes can be determined using elemental composition data from the area and lake sediment. The first step was the physical weathering and fragmentation of the bedrock area. Our results show that physical and chemical weathering also take place in the soil, which contain mineral constituents that were not determined in the bedrock samples. Based on Kronberg & Nesbitt (1981) publication and the measured element composition, chemical weathering occurs within the lake sediment, new minerals were formed in the lake sediment which justifies a detailed examination of the sediment samples.

For the in-depth examination of the sediment, thin sections were made from the drill core. Several methods were used for the thin section analysis, including optical microscopy with cathode luminescence, infrared spectroscopy and micro-raman spectroscopy.

Using FTIR measurement and microscopy, a number of mineral constituents were identified such as apatite, feldspar, ferrihydrite and montmorillonite complex grains, and poorly crystallized quartz. In addition to the inorganic constituents, large amounts of organic matter were detected. Most of the mineral components range in size from 0.5 to 1 μm according to the thin section. The particles are contained in an organic extracellular polymeric material. Based on the obtained FTIR, cathodoluminescence microscopy, and optical microscopy results (Polgári et al. 2019), there is a significant mineral contribution formed on site which is of microbiological origin (example: Ferrihydrite).

**Chapter III** uses organic and isotope geochemical methods to study the lacustrine sediment. The use of organic n-alkane indices in the Carpathian Basin on such young sediments has not been seen before. There is no available publication dealing with n-alkane study on young lake sediments in the Carpathians. The n-alkane analysis are also usually used on samples which more than 1000 years old (99% of international publications). The primary goal was to prove the usability of these proxies. The research also synchronized the drill cores based on the $\delta^{13}C$ values due to the high volume required for n-alkane analysis. Radiocarbon and Pb-210 age data were pooled and validated during the process. Within the framework of the chapter, the age-depth model of the lake sediment was presented, which was used throughout the dissertation.

To characterize the sources of organic matter two different methods were used. The C% and N% cross-diagrams reflect the changes in the source of organic matter and are particularly good indicators of the emergence of new sources. The data points were located along a line, therefore the quality of the input mixture material does not change significantly over the last 700 years, so a new external source, of anthropogenic nature, can be ruled out. The types of organic matter sources in the lake sediment can be determined using a cross-sectional diagram of the $\delta^{13}C$ and C / N atomic ratios. Based on the publication by Meyers (2003), the two main sources of organic matter are $C_3$ plants and freshwater algae. The Carbon Preference Index (CPI) has been utilized to explore the maturity of hydrocarbons in sediments (Bray and Evans, 1961). The CPI of the Lake Bolătău-Feredeu sediment sequence is 8.34, which fits into the range (i.e., ~5 to 30) usually reported for epicuticular waxes derived from terrestrial plants. This indicates that the dominant source contributing to the recent Lake Bolătău-Feredeu sediment consists of slightly degraded to nondegraded terrestrial organic matter.

Changes in the organic carbon and nitrogen proxies studied ($\delta^{13}C$, $\delta^{15}N$, C / N atomic ratio) and n-alkane were used to detect changes in the environment over the past 700 years.

Based on the data, three main periods were identified:

Afforestation and the decline in lake productivity (~1470 A.D.–1560 A.D.) – Isotopic (i.e., $\delta^{13}C$ and $\delta^{15}N$) and C% data reached peaking values, albeit the C/N ratio diminished, suggesting increased lacustrine contribution, and consequently elevated productivity in the lake. The $TAR_{HC}$ index presented a small peak indicating increased terrestrial contribution to the organic fraction of the sediment. $P_{wax}$ also increased to a higher level, thus pointing to a boost in the terrestrial input, while the $P_{hw}$ index dropped to lower values, which likely imply a diminished contribution of herbs and grasses to the terrestrial proportion. Overall, these changes can be interpreted as a result of the expanding forest cover and shrinking grasslands in the Bolătău-Feredeu catchment.

Variable lacustrine environment, decreased productivity in the catchment (~1640 A.D.–1760 A.D.) – This period coincides with the well-known cold period documented throughout the Central European area (Dobrovolny et al., 2010). According to previous research results, the winter period has lengthened, which may have had an effect on the lake ice cover (Rácz, 1994; Luterbacher, 2001). $\delta^{15}N$ and $\delta^{13}C$ measurement results show the highest variability. $P_{aq}$ reached the peak level in this timeframe, while both $P_{wax}$ and the $P_{hw}$ dropped to the lowest levels recorded in the ~700-year time range covered by the sediment sequence. In conclusion, productivity in the catchment area has declined, presumably due to changing climatic conditions.

Modern landscape change (~1820 A.D.–2013 A.D.) – During this period, the value of $\delta^{13}C$ clearly shows the change in the value of d $\delta^{13}C$ in atmospheric $CO_2$, which was corrected to facilitate interpretation. Based on the n-alkane proxy information, it can be stated that the range of herbaceous plants has strengthened, which probably reflects the new plant cover resulting from deforestation. This theory is confirmed by the several cm layer of organic matter observed at the beginning of the period, which contains well-recognizable branches. Comparing the findings with the pollen data published in Florescu et al. (2017), it is likely that deforestation has taken place gradually in the area.

**Chapter IV** presents the inorganic parameters and their interpretation, with particular reference to the weathering indices and some of the preferred elements. They are compared with previous research results, data sets with special regard to n-alkanes. Based on the obtained data, the research results yielded so far will be clarified, and hitherto unknown processes will be explored.

The weathering indices (CIA, CIW, PIA, V) were calculated based on element concentrations The particle size data, obtained from measurements using laser diffraction particle size analyzer, greatly contribute to the interpretation of the weathering indices.

From 1500 A.D. to 1776 A.D. the weathering conditions were relatively constant in the lake catchment system. The sand fraction peak detected around 1650 A.D. has not been explained according to the classical interpretation, which would point to a shift in weathering conditions due to rainfall effect etc. The calculation of weathering indices based on elemental analytical studies does not confirm this classical interpretation, given that no displacement is observed. Relative deviation of weather indices between 1600 A.D.-1700 A.D. (where the peak is in the sand fraction dataset) were: CIA : 0,6 CIW: 0,3 ; PIA: 1,2; V=2,3

From 1776 A.D. to 1838 A.D. all weathering indices and particle size fractions showed rapid and significant changes. The change is concentrated within a short period of time of ~ 20 years. This shift indicates a significant change in the catchment area, which has been explained by the findings of Karlik, et al. (2018) regarding extensive deforestation in the region.

From 1838 A.D. to the present the standard deviation of the weathering index values is the largest determined during the examined time scale, especially compared with the calm period documented between 1500 A.D. to 1776 A.D., thus suggesting that the catchment-lake system was more likely to be disrupted by the increasing anthropogenic impact. The time frame between 1925 and 1948 should be granted special attention as it overlaps the Second World War period. At the same time as World War II, the weather indices show a clearly visible contiguous peak. Further investigations are needed to identify the root causes, but it suggests a military presence based on periodic coincidence and surviving local memories.

In addition to the proxy information presented, organic and inorganic geochemical data was used to carry out a paleoenvironmental reconstruction by comparing the measured results and proxies with the model temperature dataset (Büntgen et al., published in 2013) for the Carpathian region, based on which the following phases were determined:

Spread of herbaceous species in the catchment (~1500 A.D. to 1620 A.D.):
In the characterization of the period, the n-alkane proxy information is the most informative given that the primary indicators of vegetation change are the $P_{hw}$ value increases, even if the $P_{wax}$ value diminishes, which indicates a decrease in woody vegetation. Based on the LOI% and the low volatility of the sulfur content, short-term intensive limitation / transformation in the area is unlikely. The value of phosphorus content shows a similar shape to the value of N-SK, albeit with a time shift of approximately 30 years. Based on this information, it can be assumed that a relationship between productivity and

temperature is likely, which is consistent with previous research (Kim, et al. 2003; Wildung, et al. 1977).

The effect of a cold period on the lake-catchment system (1620 A.D. to 1700 A.D.):
During this period the n-alkane indices ($P_{hw}$ and $P_{wax}$) assume minimum values. The particle size data and inorganic parameters (with better time resolution compared to the n-alkane indices), showed signal in 1650 A.D., at that time  the shows highest peak of the sand fraction was detected.. By relating this data to the N-SK temperature data series, the results indicate that the coldest period occurred around 1639 A.D. The shape of the phosphorus content is very similar to the N-SK temperature data set from 1629 A.D. to 1650 A.D. However, no such change was observed in the evolution of the weathering indices. The history of the emerging environment for the period coincides with the modeled temperature. As the temperature changes, the productivity of the catchment area decreases. Herbaceous species, especially grasses, greatly influence the particle size of the material entering the lake. Given that no change was documented in the weathering conditions, it can be concluded that the change in temperature is responsible for the variability in the sediment. Paralleling the phosphorus and the temperature datasets indicates that, due to the special environmental conditions, the change in the phosphorus values are a good indicator of the temperature shifts.

A seemingly stable period in the lake-catchment system (1700 A.D. to 1780 A.D.):
No significant fluctuations were detected in the analytical results, with the exception of the PIA and sand fraction, which showed some appreciable changes. The modeled temperature (N-SK) data during this time frame shows strong fluctuations within very short periods. However, the sediment sampling unit did not allow for such sudden changes to be tracked. Therefore, based on the data, it can be regarded as a stable period, during which no significant changes were documented in the natural vegetation and the lake.

Anthropogenic impact on the lake-catchment system during a cold period (1780 A.D. to 1860 A.D.):
During this period, for which the most information is available, the measured and calculated parameters show the greatest degree of change. Previous research (Florescu et al. 2017; Karlik et al. 2018) has confirmed that deforestation occurred in the broader vicinity of Lake Bolătău-Feredeu. This period is regarded as a particularly cold one based on the modeled temperature (N-SK). Most of the measured parameters clearly show the traces of

deforestation. Phosphorus and sulfur contents show clear peaks reaching maximum values around 1820 A.D., while the weathering indices confirm a significant degree of disturbance in the soil. Based on the parameters of the catchment area, deforestation began in 1811 A.D. and lasted for about 10 years. The n-alkane indices indicate that a new vegetation composition began to form subsequently.

Modern landscape changes in the catchment (1860 A.D. to 2010 A.D.):

As a result of deforestation, the vegetation and composition of the catchment have undergone a drastic transformation. The parameters examined showed unprecedented fluctuations and changes. Particle size data stabilized at a new level after these fluctuations, suggesting that the vegetation developed differently compared to previous centuries. The n-alkane indices ($P_{hw}$ & $P_{wax}$) show the process of afforestation, where the area is first dominated by herbaceous species, and later on by the growth of woody vegetation. The ever-present human influence is illustrated by the fluctuating weathering indices which clearly indicate the period of World War II.

# Summary

## 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, 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 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 places 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 that I determined that the lake sediment was not disturbed or mixed. This was confirmed by the fact 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 AD – 1860 AD – 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 Iezer lake macrofossil dataset and results of my thesis, I found that the deforestation occurred primarily in the Iezer lake catchment area, and only reached the Bolătău-Feredeu lake 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.

# Összefoglalás

## I. Bevezetés és célok

A paleoklímával és a paleokörnyezettel kapcsolatos kutatások egyre nagyobb hangsúlyt kapnak napjainkban. Ez jelenleg az egyik legnépszerűbb környezeti kutatási terület, mely a klímaváltozás szélesebb körű ismerete előtt is már megjelent. Az ilyen típusú kutatások végzéséhez számos geológiai rezervoár alkalmas. pl.: cseppkövek, különböző üledékek stb. Ezek közül is az egyik legsokoldalúbb lehetőség a tavi üledékek vizsgálata, mely több tudományterület ismeretét és multidiszciplináris látásmódalkalmazását igényli (Last, és Smol, 2001). A tavi üledékek paleokörnyezettel kapcsolatos kutatása a 19.-dik században kezdődött (Lyell, 1830). A tavi üledék ideális körülmények között megőrzi a környezetváltozás nyomait, mely a tóban és annak vízgyűjtő területén megy végbe, a vízgyűjtőnél nagyobb térbeli területről adhat információt az üledékben mért (szervetlen, és szerves, pl. pollen) adatok elemzése. Az élővilág (flóra) produktivitása és összetétele a tóban és a vízgyűjtő területén folyamatosan követi a környezet változását, elsődleges indikátora az emberi hatásoknak. Ezek teljes körű és pontos értelmezéséhez, elengedhetetlen a vízgyűjtő terület és a tó jelenlegi állapotának ismerete, rajta végbemenő folyamatok, állapotok dokumentálása (Jackson et al., 1948; Sverdrup, 2009; Wan et al., 2019). A szerves geokémiai módszerek (különös tekintettel az n-alkánok mérése) kiváló nyomjelzői a vegetációban bekövetkező változásoknak (Meyers, 2003; Eglinton és Eglinton, 2008). Ezen módszerek alkalmazásához nagy mennyiségű minta szükséges, jelen vizsgálatok során átlagosan 20 gramm tavi üledék került feldolgozásra mintánként a szervesanyag extrahálása során. A szerves geokémiai vizsgálatra szánt mintaegységek időfelbontása egy furaton belül szervesanyagtartalom függvényében változó, tekintettel ara, hogy nem volt korábbi tapasztalat fiatal üledékek extrahálható szervesanyag tartalmáról és összetételétől, a cél elegendő mintamennyiség biztosítása volt. Az pontokban mért C% értéke 2,6 és 8 % között mozog a vizsgált tartományon. A környezet és paleoklíma rekonstrukció során ugyancsak információval szolgál a kis mintaigényű főként szervetlen paraméterek (ásványtani elemzések, stabil izotópok, mállási indexek, elemi összetétel, szemcseméret eloszlás) mérése. Ez utóbbi paraméterek vizsgálatával lehetőség nyílik a vízgyűjtő területén végbemenő környezeti változások detektálására (pl.: hőmérséklet, csapadék, különleges események, emberi hatásos), különös tekintettel azokra, amelyek a behordási viszonyokat tükrözik (Engstrom

& Wright. 1984.; Couture & Dymek. 1996) A víztestben és a tavi üledékben számos folyamat zajlik le, mely pH és eH változással járnak. Ilyen például a szerves anyag bomlása, mikrobiális aktivitás, vagy az üledékben az oldott oxigéntartalom lecsökkenése, anoxikus környezet kialakulása. Az üledék szervetlen paramétereinek vizsgálata lehetőséget ad ezen folyamatok leírására, a folyamatok eredményeként kialakult környezet megismerésére.

A Kárpátok és a Kárpát-medence területe bővelkedik paleoklíma és palekokörnyezet kutatásra alkalmas egységekben, különös tekintettel a változó geológiai adottságokra (pl. tavak, jég és cseppkőbarlangok). A tavi üledékek kutatása területén is számos paleokörnyezet rekonstrukcióval foglalkozó publikáció jelent meg, melyek során elsődlegesen egy adott tudományterület oldaláról végezték a vizsgálatokat, (pl.: Wohlfarth et al., 2001; Haliuc et al. 2009; Magyari et al 2009; Kłapyt. et al. 2016). A választott kutatási terület Románia – Bukovina régiójában Keleti-Kárpátokban található, Sadova-folyó vízgyűjtő területén. A Bolătău -Feredeu tó 1134 méteres tengerszint feletti magasságban található, közvetlenül egy Natura 2000 terület mellett. A tó, egyike a Bukovinai Milleniumi tavaknak, melyek üledéke rétegzett és az elmúlt 1000 év eseményeiről szolgáltathatnak információt. A vízgyűjtő területe ~30 ha. A tó felszíne 0,3 ha, vízmélysége mintavételkor 5,2 m volt (Mîndrescu et al. 2013 & 2016).

A kutatás célkitűzése a Bolătău-Feredeu tó tavi üledékének és vízgyűjtőjének komplex geológiai és geokémiai megközelítésű vizsgálata volt, elsősorban paleokörnyezet és paleoklíma rekonstrukció céljából. A végső cél a vizsgált időszakot lefedő részletes paleokörnyezet-változás történetének leírása volt.

A vízgyűjtő területén vizsgálat tárgyát képezte az ágyazati kőzet elem analitikai és ásványtani vizsgálata, az eredmények összevetése korábbi rendelkezésre álló adatokkal. További cél volt a vízgyűjtő területén található talaj (és üledék) -ásványtani, kémiai és szemcseméret dokumentálása és értelmezése. Ezen adatok szolgáltak alapul a vízgyűjtő területén és a tavi üledékben végbemenő folyamatok átalakulásainak leírásához.

A tavi üledék furatanyagának vizsgálata során cél volt annak geológiai jellemzése, nagy felbontású vizsgálata (stabil izotópok mérése, mikroszkópia, FTIR,) és egypontos kormodell felállítása elsődlegesen környezetrekonstrukciós céllal. A vizsgált szakaszon az elérhető eszközparkkal széleskörű módszertan alkalmazása történtszerves és szervetlen módszerekkel egyaránt, melyet II. Alkalmazott módszerek fejezetben mutatok be. A szerves geokémiai megközelítésen belül a vizsgálat célja volt az n-alkánok mint proxy paraméterek alkalmazhatóságának vizsgálata fiatal üledéken, új, eddig ismeretlen kapcsolatok feltárása az egyes proxi paraméterek között.

## II. Alkalmazott módszerek

A vizsgálatok során az alkalmazott módszerek kulcsfontosságú szerepet töltenek be a kutatás és a mérések reprodukálhatósága miatt. Az alkalmazott módszerek bemutatása jelen fejezetben történik. A könnyebb áttekinthetőség érdekében, a fejezet tagolása a vizsgált anyagok alapján valósul meg. Az egyes anyagcsoportokon (pl. alapkőzet, talaj, tavi üledék) történt vizsgálatok együttes áttekintése segíti a kutatási eredmények megértését.

### II.1 Alapkőzet és talajtani vizsgálatok összefoglalása

Az alapkőzetből történt mintavétel során a mintavételi helyek kijelölése előzetes adatok (földtani térkép; Ionesi, L. (Ed.), 1971.) és terepi megfigyelések alapján valósult meg. A terepi megfigyelések során jól elkülönültek az egyes domborzati viszonyok és a növényi borítottság. A mintavételi pontok kijelölésében és a mintavétel során helyi kutatók (Marcel Mindrescu és Ionea Gradinaru) segédkeztek, akik évtizedes múltál rendelkeznek a Kárpátok ezen szakaszának geológiai és botanikai vizsgálatában. Az ágyazati kőzetestből való mintavétel egyidejűleg a talajtani mintavétellel történt.

A kőzetmintákból reprezentatív átlagmintát készítettem. Egy adott terület több pontjáról vett tömbi kőzetmintát megtörtem, majd azonos mennyiségeket porítottam az egyes tömbi mintákból. Az így kapott porított almintákat homogenizáltam. A minták ásványtani összetételének meghatározásához röntgen pordiffraktométert használtunk, mely kiegészült röntgenfluoreszcencia analízissel. A kapott értékeket mállási indexek számításhoz használtam fel.

Talajminták esetén nem történt meg az egyes talajszintek elkülönítése tekintettel arra, hogy a profilban rétegzettség nem volt megfigyelhető. A kőzetmintákkal azonos pontokon történt a mintavételezés, a minták szállítás elött homogenizálásra kerültek. A vizsgálatok elvégzéséhez a mintákból almintákat képeztünk. A szemcseméret eloszlásának kvantitatív elemzése lézerdiffrakciós szemcseméret eloszlás vizsgálattal történt. A további vizsgálatokhoz a minták porítása és mintaelőkészítése valósult meg. A kőzettani vizsgálatokhoz hasonlóan itt is röntgen pordiffrakciós mérések történtek az ásvány fázisok elkülönítésére, és röntgenfluoreszcens analízis pedig a kémiai összetétel vizsgálata céljából.

## II.2. Tavi üledéken végzett vizsgálatok

A tavi üledékek vizsgálata során széleskörű elemzési lehetőségek álltak rendelkezésre. A furatokból készültek vékonycsiszolatok, melyeken az ásványalkotók, szerves alkotók és a végbement helyhez kötött folyamatok vizsgálata történt meg. Ezen vizsgálatok során a következő módszereket alkalmaztam: Optikai mikroszkópia, katódlumineszcens mikroszkópia, Fourier-transzformációs infravörös spektroszkópia (FTIR-ATR), mikro-raman spektroszkópia.

Stabil izotóp mérések két furaton is történtek, mely segítségével a furatok szinkronizálása is megtörtént, így a furatok egyes mélységei megfeleltethetőek egymásnak. A fúrómagok ~50 cm-es távolságra helyezkedtek el egymástól a tó üledékében. A mérések IR-MS tömegspektrométeren történtek ($\delta^{13}C$; $\delta^{15}C$; C%; N%; C/N arány). A kapott adatokat a szerves anyag forrásának meghatározására és a produktivitás indikátoraként alkalmaztam.  Az LB-G-01 es furaton 1-cm es átlagmintákból történtek a IR-MS mérések, LB-G-02-es furaton pedig milliméteres nagy felbontású mintavételezéssel közvetlenül a fúrómagból.  Az LB-G-02 esetén a mért C% érték került felhasználásra az n-alkán mérésre szánt minták lehatárolásakor. Az n-alkán mérések gázkromatográfia módszerével történtek. A mért n-alkán csúcsintenzitások alapján index számításokat készítettem ($TAR_{HC}$; $P_{aq}$; $P_{wax}$; $P_{hw}$).

Az szervesgeokémiai és stabilizotóp mérésen kívül, a kutatás során alkalmazott módszerek az LB-G-01-es furatanyagokon valósultak meg, melyen korábban megtörtént a kormeghatározás is. Az 1 cm-es átlagmintákból, a már említett stabil izotóp méréseken kívül, vizsgálat tárgyát képezte:

Ásványtani összetétel meghatározás pormintából diffraktométerrel (XRD) történt. Elemanalítikai vizsgálatok röntgen fluoreszcens spektometriával (WD-XRF) valósult meg, pasztillázott mintákon. A kapott adatokat önállóan és számított mállási indexekként is értelmeztem a folyamatok, események meghatározása során. Minták szemcseméret eloszlásának meghatározását lézerdiffrakciós szemcseméret eloszlás vizsgálattal végeztem. A szemcseméret eloszlás adatok elsősorban a behordási viszonyok változásának egyik fő nyomjelzői.

## III. Új tudományos eredmények

A dolgozatban bemutatott kutatás során az alábbi új tudományos eredményeket határoztam meg:

1. Elemösszetétel (XRF) és ásványtani (XRD) vizsgálatok segítségével megállapítottam, hogy a vízgyűjtő területen két elemösszetétel szempontjából eltérő alapkőzet található. A két kőzettípus csak alumínium-, és szilícium-tartalomban ($SiO_2$ ~90% Al2O3 ~2.8%; $SiO_2$ ~70%, $Al_2O_3$ ~16%) tér el egymástól, ásványtani szempontból nem különböztethetek meg. Ez utóbbi ellentmond a korábbi kutatási eredményeknek: Ionesi (1971) szerint többféle ásvány alkotó is megtalálható a kőzetben (pl.: glaukonit), azonban kutatásom során, a kvarcon kívül nem sikerült más ásványt kimutatnom. A területen kőzettanilag homokkő található eltérő alumínium tartalommal. Az XRF és XRD elemzésekből megállapítottam továbbá, hogy a kezdeti alapkőzet heterogenitása nem jelenik meg a talajminták esetén. Ebből az következik, hogy bár a vízgyűjtő domborzata tagolt, a tóba érkező anyag iránya nem befolyásolja a beérkező anyag szervetlen összetételét.

2. Létrehoztam a vizsgált időszakra egy Pb-210 és radiokarbon alapú kormodellt. A kormodell lehetővé teszi az időben nagy felbontású adatelemzést. A kapott Pb-210 aktivitás adatok az üledékréteg felső 24 centiméteréből származnak cm-es felbontással. A radiokarbon adatok az üledékben talált növényi maradványok (ág darabok) korát adják meg. A radioaktív izotópok bomlása olyan folyamat, mely sebessége izotópra jellemző és nem befolyásolható. Tekintettel arra, hogy a kormodell létrejött és a felhasznált adatok/aktivitások között nem volt kiugró eredmény, megállapítottam, hogy az üledék nem bolygatott, keveredése nem történt. A rétegzettség megléte alapvető feltétele a környezetrekonstrukció elvégzéséhez. A kormodell a vizsgált szakasz legmélyebb pontján is csupán ~+/-10 év hibát tartalma.

3. A tavi üledék szerves és izotópgeokémiai elemzése során megállapítottam, hogy annak szerves anyag tartalma két forrásból (C3-as növényekből és édesvízi algából) származik. A N% és C% keresztdiagrammja alapján a vizsgált időszakban (~500 év) a rendszerbe új szervesanyag forrás a fentebb leírtakon kívül nem lépett be. Munkám során a mért kromatogrammok csúcsintenzitásából n-alkán indexeket is számoltam ($TAR_{HC}$, CPI, $P_{aq}$, $P_{wax}$, $P_{hw}$), melyek az érett szerves anyagokon történő környezetrekonstrukció széleskörben alkalmazott eszközei. Kutatásomban bizonyítottam, hogy ezek az indexek

a fentiek mellett alkalmasak a még érettlen fiatal szerves anyagokon történő alkalmazásra is. A katonai felmérésekből és történeti dokumentumokból ismert erdőirtás hatása egyértelműen megjelenik az n-alkán indexekben pl.: $P_{hw}$ 0,47.ről 0,8.-as értekre változik, mely lágyszárú/fásszárú növényekből származó n-alkánok arányát a lágyszárú növényzet előtörését fejezi ki. N-alkán adatok és stabil izotóp mérési eredmények segítségével három fő időszakot különítettem el, melyek a következők:

   i. -Erdősülés és a tó biológiai produktivitásának csökkenése (Kr.u. ~1470. - Kr.u. 1560.)
   ii. -Változó tavi környezet, csökkenő produktivitás a vízgyűjtő területén (~Kr.u. 1640.- Kr.u. 1760.)
   iii. -Modern tájváltozás (~Kr.u. 1820 - Kr.u. 2013)

4. Megállapítottam, hogy a produktivitás mértéke és a területen végbemenő természetes biológiai folyamatok iránya főként a hőmérséklettől függ. Hideg időszakokban a produktivitás csökkenést mutat, a lágyszárú vegetáció elsőként reagált a változó körülményekre ($P_{hw}$ n-alkán index alapján), aránya csökkent. A térségről rendelkezésre álló csapadék és viharesemények adataival való alapján nem mutatkozik érdemi összefüggés ezen paraméterek, illetve a vizsgált szervesanyag-mutatók között.

5. Megállapítottam, hogy az üledék foszfor tartalmának változása követi a környezeti hőmérséklet változását. Az N-SK hőmérséklet proxy paraméter és a mért foszfor tartalom maximum – minimum időszakai, jó egyezést mutatnak.

   A kutatás során vizsgált üledékek foszfortartalma két forrásból származik: a szervetlen behordott alkotókból (pl ásványok) és a szerves alkotóelemekből. Tekintettel arra, hogy a foszfor másodlagos biogén elem és az üledék jelentős szerves anyag tartalommal rendelkezik (C% 2.6-8.8), a foszfor változása mindenképpen összefügg a területen található flóra változásával. Meglátásom szerint a foszfor tartalom alkalmazható a hőmérséklet-változás jellemzésére is.

6. Az üledéken vizsgált paraméterek alapján (n-alkán indexek, stabil izotóp adatok, szemcseméret adatok, elem analitikai adatok, mállási indexek) leírtam a terület részletes környezet történetét, pontosítottam a korábbi információkat és saját megállapításaimat mely alapján a következő szakaszokat határoltam el:

   i. Kr.u. ~1500 - Kr.u. 1620 – Lágyszárúak elterjedése a vízgyűjtőn: Az adatok alapján a korábban zárt erdős vegetációban, elszórva jelent meg a lágyszárú vegetáció.

ii. Kr.u. 1620 - Kr.u. 1700 – Hideg időszak a vízgyűjtő területén: A vízgyűjtő területén a hőmérséklet csökkenés hatására csökkent a produktivitás. A lágyszárú vegetáció csökkenésével, csökkent a szűrő hatás a tó partján is, melynek következtében nagyobb szemcsés anyagok könnyebben bejutottam a víztestbe.

iii. Kr.u. 1700 - Kr.u. 1780 – Közel stabil periódus: A vízgyűjtő területén csupán rövid ideig tartó események zajlottak, melyek szignifikáns eltérést nem okoznak.

iv. Kr.u. 1780 - Kr.u. 1860– Hideg időszak és erdőírtás a vízgyűjtő területén: A területen uralkodó hideg időszak alatt, megjelent az erdőírtás mint antropogén hatás. Az erdőírtás időpontját a mért paraméterek (n-alkán indexek, mállási indexek ect.) alapján ~Kr. u. 1811-re esik. Az eredményeimet összehasonlítottam a szomszéd vízgyűjtő területéről publikált adatokkal. Publikált makrofosszilia adatsor alapján Florescu et al 2017). az erdőírtás elsősorban a Iezer tó vízgyűjtő területén következett be, és csak 65 évvel később érte el a Bolătău-Feredeu tó vízgyűjtőjét. A területen új vegetáció kialakulása kezdődött meg.

v. Kr.u. 1860 - Kr.u. 2010 – Modern kori táj változás a vízgyűjtő területén: A korábbi erdőírtás hatására a fás szárú vegetáció aránya csökkent a lágyszárúak javára. A terület antropogén zavarása nem szűnt meg, különös tekintettel a II. Világháború időszakára.

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