Natural and anthropogenic impacts reflected by paleoclimate proxy parameters in a lake-forest system in Bukovina, Romania

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Abstract

The research area is located in the Eastern Carpathians, Romania. This region is rich in various formations and indicates significant potential for paleo-environmental reconstruction. The present research was carried out on sediment cores collected at lake Bolătău-Feredeu, Feredeului Mountains (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 ^{210}Pb 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.

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

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Introduction

Research on paleoclimate and paleo-environmental 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, C. 1830). Over time, however, paleo-environmental research has become an increasingly complex and multidisciplinary scientific field supported by a wide range of methodologies and techniques for investi-

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gating 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, W.M. and Smol, J.P. 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, B.G. *et al.* 2001; Magyari, E.K. *et al.* 2009; Kłapyta, P. *et al.* 2016; Haliuc, A. *et al.* 2019). 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, I. *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, M. *et al.* 2013, 2016; Florescu, G. *et al.* 2017; Karlik, M. *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 (Meyers, P.A. 2003; Eglinton, T.I. and Eglinton, G. 2008; Karlik, M. *et al.* 2018). Elemental analysis is among fundamental methods employed in sedimentology, with XRF measurements becoming widespread in the last 50 years (Engstrom, D.R. and Wright, H.E. Jr. 1984; Couture, R.A. and Dymek, R.F. 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, B.K. and Haake, B.G. 2003; Jin, Z. *et al.* 2006).

Materials and methods

Study site

Lake Bolătău-Feredeu (47°37′20.74′′N, 25°25′54.43′′E) is located in the south-western sector of Feredeului Mountains (Eastern Carpathians, Romania), in the vicinity of Obcina Feredeului peak (1,364 m a.s.l.) and pertains to Sadova river catchment *(Figure 1).* Sadova stream is a tributary of River Moldova. The lake formed in the upper area of Sadova catchment, at ca. 1,137 m a.s.l., subsequent to a landslide event which dammed the deep, narrow valley head of Holohoșca stream (Mîndrescu, M. *et al.* 2013). The lake surface is only 0.3 ha with an average 2 m 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, M. *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.

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

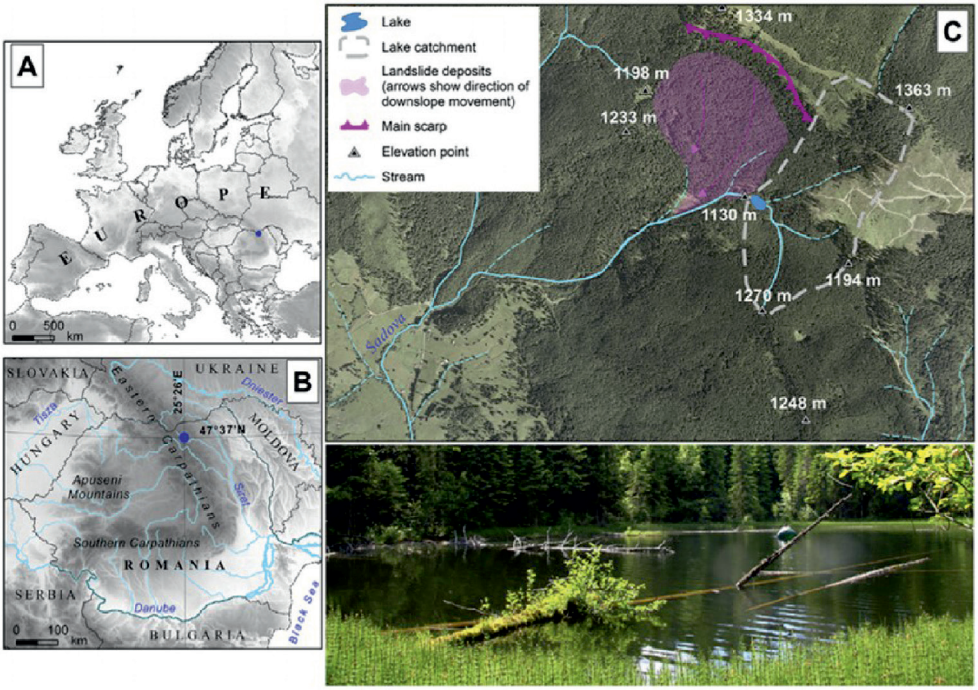

Fig. 1. Location of research area at continental scale (A); in the Eastern Carpathian region (B); and a closer view of Lake Bolătău-Feredeu (C). The grey dashed line shows the catchment boundary. A site photo is displayed below the map (Karlik, M. *et al.* 2018).

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, M. *et al.* 2016).

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 event) (Mîndrescu, M. *et al.* 2016). The sediment chronology of the top 24 cm has been significantly improved using by ^{210}Pb 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, C. 2009) software *(Figure 2).* The latter was also employed for the calibration of ^{14}C dates to calendar years in conjunction with the Northern Hemisphere IntCal13 (Reimer, P.J. *et al.* 2013; dataset: Karlik, M. *et al.* 2018).

Particle size distribution 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

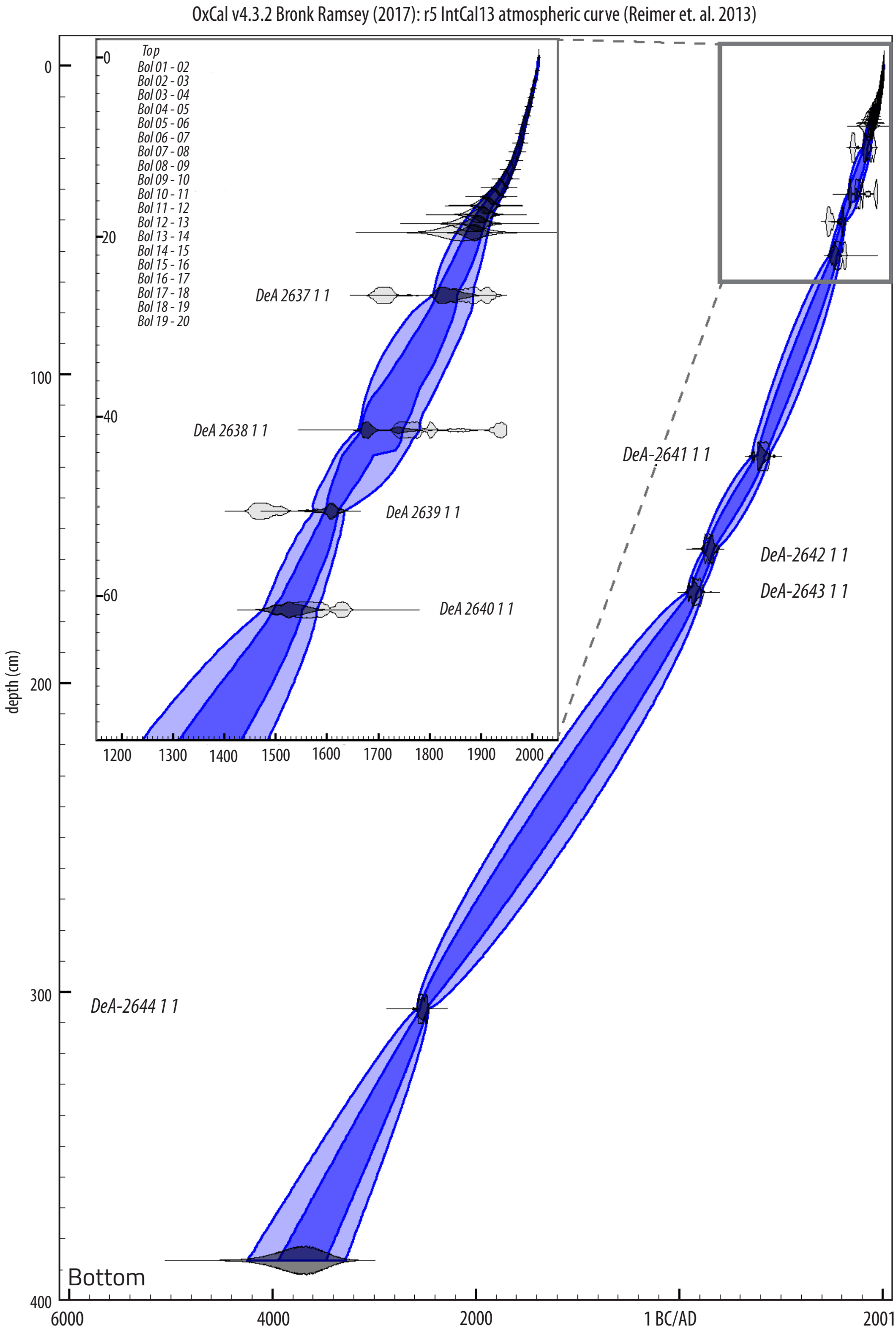

Fig. 2. Sediment chronology of the Bolătău-Feredeu sequence. Light (blue) shading shows the 95 percent (68%) confidence range of the Bayesian model. Original and modelled probability density functions of the radiometric ages are plotted by light and dark blue, respectively. The uppermost 70 cm is enlarged,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

(Burt, R. 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 (2,000–50 μm), silt (50–2 μm) and clay fractions (below 2 μm) were reported according to a modified United States Department of Agriculture (USDA) texture classification scheme (Konert, M. and Vandenberghe, J. 1997).

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 *(Table 1).*

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 percent of the extracted total organics (Karlik, M. *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 30 x 0.32 x 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 were evaluated using well-known indices calculated as the ratio between summed peak areas of certain alkane groups (Karlik, M. *et al.* 2018) *(Table 2).*

Results

Weathering indices curves (CIA, CIW, PIA, V) show similarity to each other throughout the entire examined time interval *(Figure 3).* 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.

The uppermost 52 cm (~500 years) yielded enough material for particle size analysis. Three fractions have been inferred based on particle size distribution: clay fraction < 2 μm,

Table 1. Calculations of the weathering indices

Index	Calculation	Reference
CIA	$[Al_2O_3/(Al_2O_3 + CaO^* + Na_2O + K_2O)] \times 100$	Nesbitt, H.W. and Young, G.M. 1982
CIW	$[Al_2O_3/(Al_2O_3 + CaO^* + Na_2O)] \times 100$	Harnois, L.1988
PIA	$[(Al_2O_3 – K_2O)/(Al_2O + CaO^* + Na_2O – K_2O)] \times 100$	Fedo, C.M. *et al.* 1995
V	$(Al_2O_3 + K_2O)/(MgO + CaO + Na_2O)$	Vogt, T. 1927

Notes: 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 Index of Alteration is used to monitor the plagioclase weathering.; V = Vogt's Residual Index reflect the degradation of clay minerals.

Table 2. Calculations of the n-alkane indices

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

Notes: P_{wax} = reflects the relative proportion of waxy n-alkanes; $P_{hw:}$ = reflect the herbaceous proportion in the total terraneous plants.

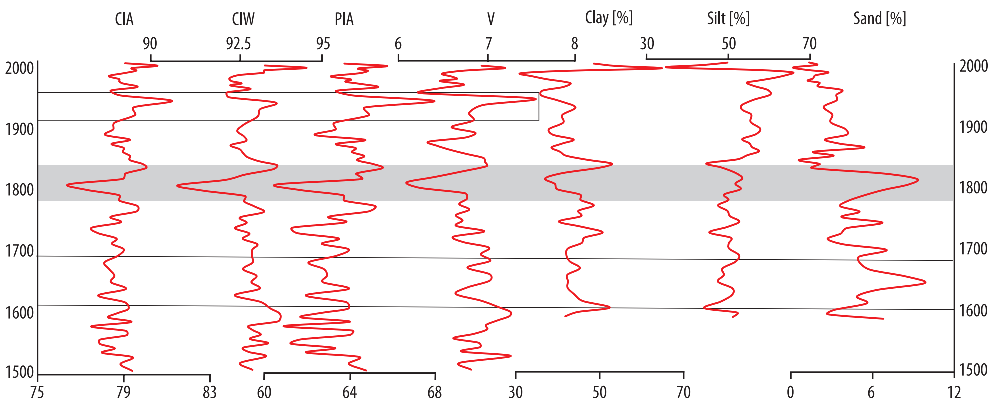

Fig. 3. Weathering indices and particle size distribution data. CIA = Chemical Index of Alteration; CIW = Chemical Index of Weathering; PIA = Plagioclase Index of Alteration; V = Vogt's Residual Index.

silt fraction from 2 to 50 µm, and sand fraction from 50 to 2,000 µm. The clay and the silt fractions accounted for more than 90 percent of the composition (see *Figure 3*).

The proportion of the clay fraction ranged between a maximum of 65.4 percent and a minimum value of 31.5 percent, thus, covering a wide range of approximately 34 percent. 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 percent, with a standard deviation of 3 percent. 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 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 (see *Figure 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 percent with a standard deviation of 2 percent. 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 (see *Figure 3*).

The percentage of the sand fraction is generally less than 10 percent 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 years. Of relatively low stable values. The ensuing period covering ~62 years started in 1775 A.D. with a 3.7 percent sand fraction value, showed an increase up to a maximum value of 9.3 percent in 1820 A.D., and ended in 1883 A.D. at 1.6 percent. 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 (see *Figure 3*).

LOI (Loss-on-Ignition) values range between 16 and 27 percent 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 percent (1776 A.D.) to 26.7 percent (1811 A.D.), ensued by a subsequent drop to 16.3 percent (1838 A.D.). An increasing trend has been detected up to 1902 A.D., followed by a stabilisation at around the previous level (from 1500 A.D. to 1776 A.D.) *(Figure 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

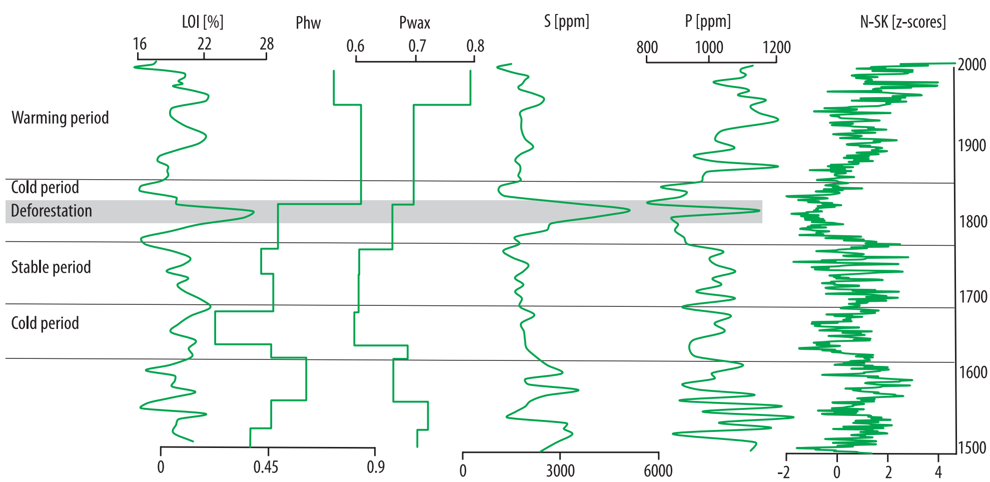

Fig. 4. Temperature and potential organic material proxies: LOI, P_{hw}, P_{wax} (published in: Karlik, M. *et al.* 2018); S, P, N-SK [z-score temperature proxy] (Büntgen, U. *et al.* 2013).

(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 P_{hw} 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, M. *el al.* 2018). (see *Figure 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 (Zheng, Y. *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, M. *et al.* 2018) (see *Figure 4*).

Sulfur is regarded as one of the most significant all-round proxies for lacustrine sediments and varies throughout the sediment sequence between ~1,110 ppm and ~5,080 ppm, reflecting the bacterial productivity and pyrite formation (Gransch, J.A. and Postuma, J. 1974; Raiswell, R. and Berner, R.A. 1985), as well as the organic matter content (Werne, J.P. *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 1,800 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 (see *Figure 4*).

The phosphorus content originates in the organic matter of the sediment (Lu, J.J. *et al.* 2005) and is involved in many biological processes, reflecting various factors such as lake productivity and terrestrial organic input (Engstrom, D.R. and Wright, H.E. Jr. 1984). The phosphorus content varies between ~820 ppm and ~1,250 ppm during the analysed time frame of ~500 years. 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 years), 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. (see *Figure* 4).

N-SK [z-score] data set is a high resolution modelled paleotemperature proxy to the Carpathian region published by Büntgen, U. *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 years. an increasing trend can be observed (see *Figure 4*).

Discussion

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 (see *Figure 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, M. *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.

Environmental changes in the lake-catchment system

The modelled temperature dataset of the east Carpathian region (Büntgen, U. *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, L.H. *et al.* 2003.) and biological productivity (Wildung, R.E. *et al.* 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, P. *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. P_{hw} drops to a minimum level in the second part of the period.

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

Deforestation has been documented in Bukovina (Florescu, G. *et al.* 2017) in the area where the catchment area is located (Karlik, M. *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. and 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.

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, M. *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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