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Holocene paleoclimate inferred from stable isotope (δ^{18} O and δ^{13} C) values in *Sphagnum* cellulose, Mohos peat bog, Romania

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Abstract We measured stable isotopes (δ^{18} O and δ^{13} C) in Sphagnum cellulose that was extracted from a long peat core drilled in the ombrotrophic Mohos peat bog, Ciomadul Mountain, Romania. The 10-m-long peat profile spans the period from 11,800 cal yr BP to present. The δ^{18} O and δ^{13} C data indicate there were several cooling events and warm periods in the area of the Mohos peat bog during the Holocene. The 8.2-ka cold event, however, was not detected using δ^{18} O and δ^{13} C values. Response of the peat bog to changing environmental conditions was inferred using data on organic matter accumulation, independent of the stable isotope results. All cool periods during the Holocene, whether of short or long duration, were identified as times of reduced organic matter accumulation rate. Similarly, dry periods were also correlated with reduced accumulation rates of organic matter.

Keywords Stable isotopes · Holocene · Paleoclimate · Cellulose · Peat bog · Romanian Carpathians

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Introduction

The stable carbon and oxygen isotope ratios (δ^{13} C and δ^{18} O) of plant organic matter provide valuable information that is frequently used in paleoenvironmental and paleoclimate research. Several studies of the oxygen isotope composition of plant cellulose have established that plant isotope ratios are well-correlated with multiple climate factors, in particular temperature, precipitation, moisture source and humidity (Aucour et al. 1996; Ménot-Combes et al. 2002; Wolfe et al. 2007; Moschen et al. 2009; Tillman et al. 2010; Bilali et al. 2013).

Paleoclimate information can be determined from the oxygen isotope composition of the water that is used in plant cellulose synthesis, if the plant remains are well-preserved. Continuously accumulating peat deposits can be useful archives of past climate information, especially in ombrotrophic peat bogs (Barber and Charman 2003), where peat accumulation may be undisturbed for thousands of years and the source water for the plants is derived entirely from precipitation.

Peat bogs play a large role in the global fixation and sequestration of carbon. In peat bogs, carbon accumulates when the amount of primary production in the environment exceeds the amount of organic matter decomposition. This makes peat bogs important ecosystems in the context of climate change, as fixed CO_2 is one of the main greenhouse gases, along with methane, and all wetlands, including peatlands, are

natural sources of methane (Nisbet et al. 2016; Harenda et al. 2018; Günther et al. 2020). Carbon dioxide, however, has a longer atmospheric residence time in the atmosphere (20–150 years) than does methane (10 years). Climate variables like temperature and humidity influence both the production and decomposition of *Sphagnum* (Breeuwer et al. 2008).

The oxygen isotope values in Sphagnum tissues reflect the oxygen isotope composition of the water taken up by the plant, as well as isotopic enrichment during evapotranspiration from the Sphagnum surface, and isotopic fractionation involved in the biochemical synthesis of cellulose in environmental water (Brenninkmeijer et al. 1982; Moschen et al. 2009; Granath et al. 2018). Therefore, the oxygen isotope composition of cellulose reflects environmental conditions that influence source waters in ombrotrophic bogs, mainly precipitation and evaporation (Moschen et al. 2009: Tillman et al. 2010; Daley et al. 2010). The δ^{18} O value of precipitation is influenced by temperature, relative humidity, precipitation events, air mass history, amount, circulation, altitude and latitude effects, the form of precipitation (snow, rainfall) and the moisture source region (Dansgaard 1964; Gat and Gonfiantini 1981; Rozanski et al. 1992; Tan 2014). Peat bogs are usually dominated by Sphagnum (Booth and Jackson 2003; Bilali et al. 2013), which is the most abundant peat-forming genus in the middle to high latitudes. Bulk peat and extracted cellulose have different oxygen isotope compositions, so separation of Sphagnum cellulose from the bulk peat is required. Sphagnum cellulose preserves the stable isotope composition during plant growth, and therefore provides important data for paleoclimate studies, necessitating extraction of the cellulose component from Sphagnum. Enrichment between source water and Sphagnum cellulose, which occurs during cellulose synthesis, has been described in many studies, and amounts to an excess of $27 \pm 3\%$ for the heavier isotope (¹⁸O) (DeNiro and Epstein 1981; Zanazzi and Mora 2005).

The stable carbon isotope ratio of *Sphagnum* cellulose has the potential to record changes in bog wetness, which can also be related to bog hydrology, and thus to climate variability (Ménot-Combes et al. 2004; Loader et al. 2007; Lamentowicz et al. 2008). The *Sphagnum* species do not have stomata or vascular tissues, and are therefore unable to control water uptake and loss. Hence, water uptake and loss is controlled only by environmental conditions, and the

mosses fix and lose water more rapidly than vascular plants. In addition, the stable carbon isotope composition of the cellulose extracted from Sphagnum is highly dependent on water availability. The chloroplasts are surrounded by so-called "hyaline cells" that function as water reservoirs. The concentration and isotopic composition of CO₂ in the chloroplast depend on isotopic discrimination during biochemical fixation of CO₂ (Ménot and Burns 2001; Loader et al. 2007). In wet environments, the hyaline cells are filled with water and CO₂ diffusion is relatively low, in which case the proportion of fixed ¹³C increases because diffusion of the CO₂ from the atmosphere is slower and the pool of CO₂ therefore takes longer to be replenished. In dry environments, CO₂ diffusion is relatively high and the proportion of fixed ¹³C decreases (Ménot and Burns 2001; Moschen et al. 2009; Granath et al. 2018). As a consequence, the δ^{13} C of the cellulose is more positive in wet environments, whereas it is less positive in drier conditions.

There are differences in oxygen isotope composition among different plant genera in peat bogs (Moschen et al. 2009), but some studies have shown that there are no significant differences in δ^{18} O among Sphagnum species (Daley et al. 2010; Bilali et al. 2013). In contrast, some studies indicate it is important to separate different Sphagnum species because they bond the ^{12,13}C and ^{16,18}O differently (Tillman et al. 2010; Granath et al. 2018). It has also been shown that there is a stable isotope offset between branches and stems (Tillman et al. 2010). The recommended approach for using the Sphagnum archive to infer paleoclimate involves separating the Sphagnum samples from bulk material, isolating stems and branches, and extracting the cellulose from the separated Sphagnum branch material.

Our study focused on a 10-m-long peat core from Mohos peat bog, Ciomadul Mountain, Romania, as a paleoclimate archive. We used a single peat core for cellulose extraction and isotope measurements, designed to draw reliable conclusions about the climate of the past. Organic matter accumulation in the Mohos peat bog over the past ~ 12,000 years was examined in conjunction with δ^{18} O- and δ^{13} C-inferred environmental variables, to better understand the response of the peat bog to changing environmental conditions. Descriptions of local and regional patterns of Late Pleistocene-Holocene climate oscillations in the Carpathian-Pannonian region have been presented in numerous papers (Schnitchen et al. 2006; Constantin et al. 2007; Magyari et al. 2009, 2013; Buczkó et al. 2013; Geanta et al. 2014; Haliuc et al. 2016; Longman et al. 2017; Hubay et al. 2018a). There are some disagreements among those studies with respect to paleoclimate interpretations in space and time, and about wet versus dry and cold versus warm periods in the past. These recent studies, which include several detailed local and regional reconstructions of Holocene climate oscillations, provided the motivation to undertake a comprehensive study of paleoclimate in the region, and moreover, to compare findings with environmental conditions on a global scale. We therefore undertook a high-resolution study of paleoenvironmental changes in the region of the Mohos peat bog, using multiple variables in peat deposits that had accumulated continuously over the past \sim 12,000 years, with a focus on the δ^{18} O and δ^{13} C of cellulose extracted from the accumulated Sphagnum samples.

Study site

The Mohos peat bog (46°08'3.60"N, 25°54'19.43"E, 1050 m altitude) is located in the Eastern Carpathians, in the Ciomadul Massif. The Ciomadul is a single dacitic volcano with two craters, the younger occupied by Lake Saint Ana (Lacul Sfânta Ana), and the older by the Mohos peat bog (Fig. 1). The Lake Saint Ana crater is the result of the last volcanic eruption, when ejected material settled in the area and filled the preexisting crater that contains the Mohos peat bog. The last eruption was dated to between 35 and 27.5 kyr BP (Harangi et al. 2015; Szakács et al. 2015; Karátson et al. 2017). The Mohos bog covers about 65 ha in a crater of approximately 285 ha. There is no water inflow into the bog, so the only water source is precipitation and runoff from the crater. In this sense, the Sphagnum-dominated wetland is classified as an ombrotrophic bog. It has one outflow, Veres spring. The climate is temperate, with 800-1000 mm annual precipitation (Karátson et al. 2013) and a current mean annual temperature of 15 °C.

Materials and methods

Core collection and sampling

An undisturbed 10-m-long peat core was taken in 2012 using a novel modified coring technique (Hubay et al. 2018b). Each core section was stored in a refrigerator and cut into 2-cm increments before laboratory analysis, except between 7.5 and 6.5 m, where it was sectioned at 1-cm increments to achieve higher temporal resolution in the interval of expected paleoclimate events.

Chronology

Sphagnum samples were taken every 30 cm along the 10-m-long peat core and were chemically prepared for ¹⁴C dating. Dry *Sphagnum* samples for AMS dating were prepared using the modified BABAB (base-acidbase-acid-bleaching) method (Nemec et al. 2010), with scaled-up amounts doubling the amount of reagents for peat cellulose preparation. The clean cellulose samples were combusted in sealed tubes and converted first to CO₂, and then graphite, after which they were measured on an EnvironMICADAS accelerator mass spectrometer (Molnár et al. 2013). Details of the sampling, radiocarbon dating and development of the core chronology are found in Hubay et al. (2018b). All ages were used in the BACON model, and no dates were excluded as outliers. The upper 930 cm of the Mohos peat bog core spans the age range from 11,770 cal yr BP to AD 2012. The agedepth model of the sequence is shown in Fig. 2 and the 95% confidence intervals range from 6 yr at 1 cm depth to 950 yr at 566 cm depth.

Sphagnum cellulose sample preparation and stable isotope analysis

To facilitate complete extraction for stable isotope analysis, bulk material must be first homogenized and sieved. To obtain a *Sphagnum* sample for stable isotope analysis, it is necessary to separate the *Sphagnum* component from the mixture of plant remains, and isolate *Sphagnum* branches from the bulk peat. A stacked sieve system was used for isolation, in which 1000-, 560-, 200- and 40-µm mesh sizes were employed and samples were wet-sieved using deionized water. Sieved material was observed under a



Fig. 1 Location of the Mohos peat bog with sampling point

microscope. Larger fragments of *Sphagnum* and other plant fragments were retained by the 1000- μ m sieve. Smaller branches, free leaves and stem sections were retained by the 560- μ m sieve. Remaining branch samples on the 200- μ m sieve were used for stable isotope analysis. Some mineral particles remained on the 40- μ m sieve.

The peat core shows a continuous record up to present, consisting of peat with different degrees of humification, which was analysed manually by microscope (all analysed slices) where the individual *Sphagnum* leaves and stems could be easily identified. Apparently, the peat core had been slightly affected by biological degradation. C/N ratios and δ^{15} N analysis of pure peat samples revealed more about the degree of humification.

Two hundred mg of sieved *Sphagnum* samples were used for cellulose extraction, with two replicates made

from each cellulose preparation. Every fourth sample was prepared for cellulose, except between 7.5 m and 5.5 m (where the 8.2-ka event was assumed to be), and between 9.3 and 9.0 m, where all samples were prepared for cellulose. Samples that returned outlier stable isotope ratios were re-run, with both the sample preparation and stable isotope measurement steps repeated. In the case of isotope-inferred climate events, measurements were carried out at higher temporal resolution. The extraction of resin was performed prior to the purification of cellulose from organic material using a 2:1 mixture of chloroform and ethanol, for approximately 6 h (Ménot-Combes et al. 2002). The next step was oxidation of lignin using an acidified sodium chlorite solution (Cullen and Grierson 2006; Daley et al. 2010) in an ultrasonic bath at 70 °C, followed by removal of hemicellulose in sodium hydroxide in an ultrasonic bath at 80 °C



Fig. 2 Bayesian age-depth model for Mohos peat bog core constructed with the age-depth modeling software BACON (Hubay et al. 2018b). The three plots in the upper panel show the MCMC (Marcov Chain Monte Carlo) iterations (left); the prior (green curves) and posterior (grey histograms) distributions for

(Tillman et al. 2010). As a final step, the samples were rinsed in deionized water (Daley et al. 2010) and subsequently freeze-dried. The term cellulose is used hereafter because α -cellulose is not a defined molecule, since it is not a chemical entity. It is simply a convenient measure of the 'true' cellulose, which is insoluble in sodium hydroxide in an ultrasonic bath at 80 °C. For that reason we use the term cellulose.

Oxygen and carbon stable isotope ratio measurements were carried out on the extracted cellulose samples. Cellulose $(0.30 \pm 0.02 \text{ mg})$ was weighed into silver capsules, and samples were prepared for oxygen isotope analysis using a Thermo Finnigan TC/ EA (temperature conversion elemental analyzer) equipped with a zero-blank autosampler (Kéri et al. 2015). Samples for carbon stable isotope measurements were prepared with a Fisons Instruments NA 1500 NCS elemental analyzer, with 0.65-0.70 mg of cellulose sample weighed into aluminum capsules and dropped into the autosampler of the elemental analyzer (Major et al. 2018). Both instruments were attached to a Thermo Finnigan Delta^{PLUS} XP continuous-flow isotope ratio mass spectrometer. Results are expressed in conventional delta notation, where the δ^{18} O and δ^{13} C values are relative to VSMOW and VPDB standards, respectively. We used cellulose reference materials for δ^{18} O from IAEA-C3 and Merck, + 32.14 and + 28.67‰, relative to VSMOW,

the accumulation rate (middle panel), and memory properties (right panel). Bottom panel shows the calibrated ¹⁴C dates (blue) and the age-depth model (grey line showing the 95% confidence intervals). The red line represents the model based on weighted mean age at each depth. (Color figure online)

respectively (Saurer et al. 1998; Kéri et al. 2015). For δ^{13} C, we used IAEA-C3 cellulose (-24.91%, VPDB) and an in-house sulfanilamide standard (-26.69%, VPDB). The δ is expressed as follows: δ (‰) = ($R_{\text{sam-ple}}/R_{\text{reference}} -1$) *1000, where R is the ¹⁸O/¹⁶O or ¹³C/¹²C ratio of the sample or reference standard. Every cellulose sample was measured at least twice for each stable isotope and standard deviations of individual δ^{13} C and δ^{18} O measurements were \pm 0.2 and \pm 0.3‰, respectively.

Organic matter concentrations and accumulation rates

To determine the accumulation rate of the organic material, loss on ignition (LOI) was performed on all samples from the 10-m peat core. In each case, 1 cm³ of bulk peat was dried for 24 h at 105 °C, weighed, then combusted at 550 °C for 4 h and weighed again (Heiri et al. 2001). The weight loss on ignition represents the organic matter content, which can be expressed as percent of dry mass or in terms of mg/cm³ wet peat. Using the age-depth chronology, the LOI was converted to organic matter accumulation rate.

Stable isotope analysis of recent precipitation and modern *Sphagnum* samples

A rainwater collector was installed on the saddle between the two Ciomadul craters (Santa Ana and Mohos) in September 2016 to collect monthly precipitation. Paraffin oil was added to the collecting bottles to prevent evaporation. Surface bog water from the Mohos peat bog was collected in May and September 2016, in July 2017 and in May 2018, and was used to compare isotope values in the water with those in recent Sphagnum samples. The collected precipitation and bog water samples were measured for $\delta^{18}O$ and δ^2 H using a laser absorption spectrometer (Los Gatos Research [LGR]). All water samples were measured in triplicate and measurement precision was better than $\pm 0.15\%$ for δ^{18} O, and $\pm 1.5\%$ for δ^{2} H. Recent Sphagnum samples were taken in May and September 2016, and in July 2017 from the exact place where the bog waters were taken.

We used meteorological data from Meteoblue in the area of Băile Tuşnad (Lat: 46°15′N, Long: 25°85′E, Alt: 845 m), the closest meteorological station to Mohos peat bog (distance: 5 km). Mean annual values for the time span 1985 to 2018 were used, with monthly temperature averages (°C) and monthly precipitation amounts (mm) applied as recent climatological variables. We also used meteorological data from the WMO Station, Miercurea Ciuc (Station identifier: 961, Lat: 46°22′N, Long: 25°44′E, Alt: 661 m), which is 26 km from Mohos peat bog. Mean annual values were calculated from records spanning 1960 to 2015.

Results

Recent climate variables at Ciomadul Crater

Oxygen isotope values for recent precipitation collected from the Ciomadul Volcano, and cellulose extracted from recent *Sphagnum* samples from the Mohos peat bog, were compared with average temperatures and precipitation amounts. Based on the meteorological data from Băile Tuşnad and Miercurea Ciuc, annual precipitation was about 650 mm. Monthly variation in precipitation throughout the year showed a maximum in June (Table 1). Eleven monthly precipitation samples were collected between October 2016 and August 2017 and measured for $\delta^{18}O$ (Table 2). The δ^{18} O values ranged from -19.1 to -2.1% (Fig. 3), with highest δ^{18} O values observed in summer and lowest values in winter months. The oxygen isotope ratios of recent precipitation were compared with monthly average temperatures for Băile Tuşnad and Miercurea Ciuc (Fig. 4). The lighter isotope values for precipitation can be attributed to colder climatic conditions, and heavier values occur during warmer climate conditions (Rozanski et al. 1992). There is a strong correlation between monthly temperatures at the Băile Tuşnad and Miercurea Ciuc stations, and those temperatures, in turn, show a strong correlation with δ^{18} O of collected precipitation (r = 0.82; r = 0.84, respectively). This strong relation can be used to develop a local calibration of the oxygen isotope thermometer for the Mohos peat bog, i.e. $\delta^{18}O = 0.566*T - 14.87$. A very similar connection is seen between monthly temperature averages of the two meteorology stations and δ^{18} O results from the collected precipitation (r = 0.81), with results showing a δ^{18} O increase of 0.55‰ per °C.

The peat bog water stable isotope results (Fig. 5) fall on the Local Meteoric Water Line (LMWL) calculated from the precipitation results (Ciomadul), which confirms the precipitation origin of the peat water, and there is apparently no isotopic enrichment from evaporation.

The δ^{18} O of cellulose from recent *Sphagnum* samples and bog water samples

Modern Sphagnum samples and bog water samples were collected from the Mohos peatbog at the same place, at three different times. The cellulose δ^{18} O values measured from modern Sphagnum samples and the bog water samples are presented in Table 3. Bog water δ^{18} O values (Table 3) represent the source water that the Sphagnum takes up for cellulose synthesis. There is a direct correlation between the oxygen isotope composition of cellulose and the source water, where the enrichment factor, ε , is given as $27 \pm 3\%$ (DeNiro and Epstein 1981; Sternberg et al. 1986). The enrichment factor is an indication of the degree of isotopic fractionation between the parent and intermediate compound during a specific synthesis reaction, and it is derived from the fractionation factor α , through the relationship $\varepsilon = 1000 \ (\alpha - 1)$, where α reflects the ratio of the rate constants for the

Months	Precipitation (mm) Miercurea Ciuc	Temperature (°C) Miercurea Ciuc	Precipitation (mm) Băile Tuşnad	Temperature (°C) Băile Tuşnad
January	29	-7	33	-3
February	26	-5	30	-3
March	27	0	37	1
April	43	7	46	8
May	71	12	57	13
June	91	15	60	16
July	83	17	54	18
August	66	16	39	18
September	40	12	44	13
October	33	6	32	9
November	28	1	31	3
December	29	-5	38	-2

Table 1 Mean monthly precipitation (mm) and temperature (°C) for Miercurea Ciuc (1961–2015) and Băile Tuşnad (1985–2018)

Table 2 The δ^{18} O values
of precipitation and
monthly precipitation
amount (mm) at Ciomadul

Monthly precipitation at Ciomadul	δ ¹⁸ O _{precipitation} (‰, VSMOW)	Precipitation amount (mm)	
2016 October	-14.5	115.9	
2016 November	-13.3	67.5	
2016 December	-19.2	24.8	
2017 January	-15.2	0.6	
2017 February	-13.3	41.4	
2017 March	-14.8	38.9	
2017 April	-11.4	54.8	
2017 May	-2.1	14.0	
2017 June	-6.4	121.7	
2017 July	-4.3	44.6	
2017 August	-8.5	98.1	

heavy/light isotopes. In other words, the different rates at which these species react reflects the extent of changes expected in the isotopic composition of a particular compound during its reaction. In this case, this means: $\delta^{18}O_{source water} = (\delta^{18}O_{cellulose} - 27.4) \times$ 1.274. Thus, the oxygen isotope composition of the cellulose apparently reflects that of the source water and we can calculate the isotopic composition of the source water, using the known enrichment factor. These recent values are useful for validating our subsequent paleoclimate reconstruction. The calculated $\delta^{18}O$ values of source water from $\delta^{18}O_{cellulose}$ overlap the $\delta^{18}O_{bog water}$ values of September 2016 and of July 2017, which might indicate that (1) the δ^{18} O values of bog water and *Sphagnum* cellulose in ombrotrophic bogs are directly correlated (correcting for the enrichment factor), and hence (2) the oxygen isotope composition of cellulose is suitable for inferring environmental variables. In one case in May 2016, when $\delta^{18}O_{bog water}$ and $\delta^{18}O_{calculated}$ did not match, the isotope composition of the cellulose appears to reflect the value in earlier precipitation, perhaps mixed with older bog water. The $\delta^{18}O_{cellulose}$ sampled in May 2016 did not reflect the isotopic composition of the same time, which could indicate that the plant had



Fig. 3 a δ^{18} O of collected precipitation (Ciomadul) with the precipitation amounts in mm. b δ^{18} O of collected precipitation (Ciomadul) with the mean monthly temperatures. Error bars

incorporated water into its cellulose from an earlier time, before sampling.

 δ^{18} O and δ^{13} C records from Mohos peat bog

Examination of the stable oxygen and carbon isotope variability in the peat core indicates the potential for paleoclimate reconstructions over the past $\sim 12,000$ years (Fig. 6, Electronic Supplementary Material [ESM) Table S1, Table 4). The deepest and oldest peat in the core where *Sphagnum* can be found has an age of 11,800 cal yr BP. There are deposits in the core older than 11,800 cal yr BP, but they contain only

based on the standard deviation of data from meteorological stations Miercurea Ciuc and Băile Tuşnad

clastic sediments. The deepest *Sphagnum* sample (950 cm; 11,750 cal yr BP) in the Mohos peat core has low δ^{18} O and δ^{13} C values (+ 12.2‰ [VSMOW] and -29.8‰ [VPDB], respectively), which correspond to a cold and dry climate period that can be correlated with the timing of the Younger Dryas. After 11,800 cal yr BP there is a period of continuous, rapid warming and wetter climate up to 11,300 cal yr BP, (Dansgaard et al. 1993; Grootes and Stuiver 1997; Alley 2000; Rasmussen et al. 2006). This period is characterized by more positive δ^{18} O values, between + 24.2 and + 25.7‰, and δ^{13} C values between -25.5 and -24.5‰. These results suggest



Fig. 4 δ^{18} O of collected precipitation (Ciomadul) versus monthly temperature average of Miercurea Ciuc and Băile Tuşnad, with the 95% confidence interval. Error bars based on the standard deviation of meteorological station data



Fig. 5 Local meteoric water line (LMWL) based on the collected precipitation (Ciomadul) with plotted peat bog water (Mohos peat bog), GMWL—global meteoric water line (Craig 1961)

that the Holocene Epoch began with rapid warming in this region.

Less positive δ^{18} O values (+ 22.6 to + 23.5‰,) in the Early Holocene suggest three cool periods (11,250–11,000, 10,950–10,450, and 10,200–9750 cal yr BP). Although the intensity of the cold periods declined through time, their duration increased. During those periods, continuous, but weakening dry–wet climate fluctuations can be inferred from fluctuations in the δ^{13} C values.

Sampling	$\delta^{18}O_{cellulose}$ (‰, VSMOW)	$\delta^{18}O_{bog water}$ (‰, VSMOW)	$\delta^{18}O_{source water calculated}$ (‰, VSMOW)
2016 May	20.1	-10.2	-7.5
2016 September	18.9	-8.7	-8.7
2017 July	18.3	-9.2	-9.3

Table 3 The δ^{18} O values of cellulose from modern *Sphagnum* samples, along with measured and calculated δ^{18} O values of bog water

The time between 9000 and 5500 cal yr BP was relatively stable, with δ^{18} O values between + 23.7 and + 26.3‰. Minor colder and drier periods are recognized between 7200 and 6700 cal yr BP, when δ^{18} O was + 23.2‰ and δ^{13} C was between -26.6 and -23.0‰. This more arid period in the peat bog lasted until 5500 cal yr BP.

Fluctuating but decreasing temperatures are observed in the less positive δ^{18} O values (+ 23.3 to + 25.8‰) between 4500 and 2600 cal yr BP. This period was interrupted by short, but strong dry periods between 3100 and 2900 cal yr BP, inferred from more negative δ^{13} C (-26.2‰) and less positive δ^{18} O values (+ 23.0‰) of the peat.

Between 2500 and 1600 cal yr BP, a warmer period is evident in the relatively stable and more positive δ^{18} O values (+ 24.5 to + 25.9‰). Continuously decreasing δ^{13} C values (-23.2 to -28.0‰) until 1850 cal yr BP, indicate an increasingly dry climate.

A short cooling period is observed between 1600 and 1200 cal yr BP (AD 350–750) from the less positive δ^{18} O values (+ 21.8‰). Between 1000 and 700 cal yr BP (AD 950–1250), there appears to have been slight warming. Between 600 and 150 cal yr BP (AD 1350–1800), a period of slight cooling can be observed by the decline in δ^{18} O values from + 25.8 to + 23.3‰.

Organic matter accumulation during the Holocene

The 12,000-year record of organic matter accumulation rate in the Mohos peat bog can be examined in parallel with the δ^{18} O- and δ^{13} C-inferred environmental variables to determine the response of the peat bog to changing environmental conditions (Fig. 6; Table 4). The accumulation rate of organic matter was highest (48 mg/cm²/yr) at the end of Younger Dryas, between 11,800 and 11,600 cal yr BP, which represents a transitional phase from a lake to a peat bog (Fig. 6). After 11,600 cal yr BP, the accumulation rate of organic matter decreased continuously to a low of 0.5 mg/cm²/yr, ca. 11,100 cal yr BP, after which a short period of higher (8–12 mg/cm²/yr) accumulation rate occurred until 9800 cal yr BP, at which time the bog reached a steady-state phase when the organic matter accumulation rate was fairly constant (7–10 mg/cm²/yr) until ca. 7200 cal yr BP. The cellulose stable isotope (δ^{18} O, δ^{13} C) values display a pattern that tracks the organic matter accumulation rate, but the isotope values increased markedly after 11,800 cal yr BP, fluctuated somewhat until about 9600 cal yr BP, then also reached a rather steady phase until about 7200 cal yr BP.

After 7200 cal yr BP the organic matter rate decreased (0.8 mg/cm²/yr), but then between 6800 and 5500 cal yr BP, increased again (8–10 mg/cm²/yr). After 5500 cal yr BP, a minor decrease (6 mg/cm²/yr) occurred until 4700 cal yr BP, and again the δ^{13} C values followed this trend.

Between 4750 and 3700 cal yr BP, a continuous decrease of organic matter accumulation rate (to 3 mg/ cm²/yr) was observed, a time during which there were fluctuating, but decreasing stable isotope ($\delta^{18}O, \delta^{13}C$) values (4600-3700 cal yr BP), which were associated with drier and somewhat colder climate in the area. From 3700 to 3200 cal yr BP, a continuous increase in peat accumulation rate occurred (22 mg/cm²/yr). A brief peak (40 mg/cm²/yr) in organic matter accumulation rate occurred between 1850 and 1450 cal yr BP (AD 100-550), overlapping in part with more negative δ^{18} O and δ^{13} C values between 1650 and 1200 cal yr BP, which can also be associated with a short cooler and drier period. There was a brief period of high organic matter accumulation rate $(47 \text{ mg/cm}^2/\text{yr})$ about 600 cal year BP (AD 1350), after which values decreased continuously to about 8 mg/cm²/yr by ca. 150 cal year BP (AD 1800).



Fig. 6 Organic matter accumulation rate, and δ^{18} O and δ^{13} C values for *Sphagnum* cellulose samples from the Mohos peat core, compared to the δ^{18} O of GRIP (Grootes and Stuiver 1997).

Periods of dominant climate cycles

To further explore the inferred climate fluctuations of the past, the stable isotope (δ^{18} O, δ^{13} C) values and organic matter accumulation rate records were subjected to wavelet analysis in which the 95%

Grey bands represent colder periods inferred from the peat core stable oxygen isotope results from the Mohos peat core

confidence level (alpha level 5%) was calculated by Monte Carlo iteration (areas outlined in black in Fig. 7).

The δ^{18} O values have no apparent cyclicity longer than 500 years. The last 2000–3000 years, however, show significant periods with a 450–500 year cycle in δ^{18} O values, indicating ~ 500-year quasi-periodic cold-warm fluctuations. The δ^{13} C values show no significant cyclicity longer than 450 years. A 50–450-year cycle was established by about 2000 cal yr BP, which could be related to dry-humid climate fluctuations, as lower solar activity characterized that time (Lüdecke et al. 2015). The apparent fluctuations may, however, also reflect background noise that cannot be totally excluded.

Fig. 7 Wavelet analysis of: **a** $\delta^{18}O_{cellulose}$; **b** $\delta^{13}C_{cellulose}$; **b** $\delta^{13}C_{cel$

Between 6000 and 3000 cal yr BP, accumulation (OM) was characterized by strong power spectral density, which indicates 1000-year periodicity

Table 4 Climate proxy variables (δ^{18} O, δ^{13} C, OM accumulation rate) during specified time intervals, along with inferred climate conditions, lake/bog successional stage and vegetation abundance

Age (cal yr BP)	δ ¹⁸ O (‰ [VSMOW])	δ ¹³ C (‰ [VPDB])	OM (mg/cm ² / yr)	Cold/ warm	Wet/ dry	Lake-bog succession/ abundance of vegetation
11,750	+ 12.2	-29.8	48	Cold	Dry	Transitional phase from a lake to a pear bog
11,600–11,100			Decrease to 0.5			Transitional phase from a lake to a pear bog
11,300	+ 24.2 to + 25.7	-25.5 to -24.5	0.5	Warm	Wet	Declining vegetation
11,250–11,000	+ 22.6 to + 23.5	-27.8 to -26.2	0.8	Cold	Dry	Declining vegetation
11,100–9800			8 to 12			A steady-state phase
10,950–10,450	+ 22.6 to + 23.5		8 to 12	Cold		A steady-state phase
10,200–9750	+ 22.6 to + 23.5	-24.4 to -23.76	8 to 12	Cold	Dry	A steady-state phase
9800–7200			7 to 10			A steady-state phase
9000–5500	+ 23.7 to + 26.3			Warm		
7200–6700	+ 23.2	-26.6 to -23.0	0.8	Cold	Dry	Declining vegetation
6700–5500	+ 24.6 to + 26.3	-26.6 to -25.0	8 to 10	Warm	Dry	A steady-state phase
5500-4700			6			Somewhat declining vegetation
4500-2600	+ 23.3 to + 25.8			Warm		
3700-3200			22			Abundance of vegetation
3100-2900	+ 23.0	-26.2		Cold	Dry	Short cooler and drier period
2500-1600	+ 24.5 to + 25.9	-23.2 to -28.0		Warm	Dry	
1850–1450			40			Abundant vegetation
1600-1200	+ 21.8			Cold		
1000-700	+ 25.3			Warm		
600			47 (short peak)			Abundant vegetation
600–150	+ 25.8 to + 23.3		8	Cold		A steady-state phase



(Fig. 7c). The last 3000 years of OM were also characterized by a significant millennial cycle (1000 years). A similar millennial cycle was detected with respect to dust deposits in the Mohos peat bog (Longman et al. 2017), which the authors connected to fluctuations in local-regional dust sources related to the North Atlantic Oscillation (NAO), associated with the end of the African Humid Period. This millennial cycle might also be present in the stable isotope (δ^{18} O, δ^{13} C) records, but such cycles are not significant because of the low number of samples. The millennial cycle in δ^{13} C values between 6000 and 0 cal yr BP are similar to the cyclicity observed in the accumulation rate, indicating a strong connection between the $\delta^{13}C$ record and organic matter accumulation rate. Therefore, we infer that the peat growth and accumulation were strongly connected to humidity in the Mohos peat bog. This millennial cycle is also seen in the δ^{18} O values by the area of power spectral density, which is not significant, but occurs in the last ~ 3500 years of the Holocene. Changing environmental conditions, e.g. temperature or humidity, appear to have influenced the production or decomposition of Sphagnum (Breeuwer et al. 2008). In the case of the Mohos peat bog, fluctuations observed in the stable isotope values can be connected to cold/warm or dry/wet climate periods of the past, and could reflect the effects of solar dynamics, particularly as they affected North Atlantic circulation.

Discussion

Local and regional Holocene climate history inferred from peat cellulose isotope records

The continuous record derived from the 10-m core recovered from the Mohos peat bog can be compared to other evidence for climatie variability during the last 12 millennia. The deepest part of the core is older than 11,800 cal yr BP, when accumulation of clastic sediments occurred, reflecting a transition between a lake and a bog at the end of the Pleistocene Epoch. This period encompasses the last sharp decline in temperature and marks the end of the Pleistocene (Dansgaard et al. 1993; Alley 2000; Rasmussen et al. 2006). We compared our carbon and oxygen stable isotope data from cellulose in the Mohos peat bog to δ^{18} O values from the Greenland Ice Core Project (GRIP).

We found weak positive correlations between $\delta^{18}O$ and $\delta^{13}C$ in the peat record and $\delta^{18}O$ in the Greenland ice, r = 0.43 and r = 0.44, respectively. The correlations are much stronger for specified intervals, e.g. when the period between 11,700 and 8500 cal yr BP is considered (r = 0.64 and r = 0.81, respectively), and even stronger for the shorter interval, from 11,700 to 9000 cal yr BP (r = 0.69 and r = 0.89, respectively). Overall, comparison of the $\delta^{18}O$ and $\delta^{13}C$ records from Mohos bog cellulose and the GRIP $\delta^{18}O$ records (Fig. 6) suggests that the climate records from the two sites can be correlated since the end of the Younger Dryas (Dansgaard et al. 1993; Grootes and Stuiver 1997; Alley 2000; Rasmussen et al. 2006).

The greatest depth in the peat core where *Sphagnum* was found dated to 11,800 cal yr BP, which correlates with the onset of the Holocene. Increased temperature and precipitation ca. 11,700 cal yr BP were documented by stable isotope analysis of Romanian speleothems (Tămaş et al. 2005; Constantin et al. 2007). Coeval changes in other climate proxy records (pollen, diatoms, chironomids, and geochemical composition) were detected in lake sediments from the Southern Carpathians (Pál et al. 2018).

Although it has been shown that a much warmer period began after the Younger Dryas, there were also climate shifts during the Holocene, but of smaller amplitude (Mayewski et al. 2004; Wanner et al. 2011). Shortly after the Late Glacial-Holocene transition, evidence of intense, short-term climate fluctuations is preserved in lake sediments and speleothems. In general, these short periods span 100-300 years, but their durations and characterization are affected by the accuracy of different age-depth models. Therefore, it is difficult to identify local and regional differences in climate from this period. Hence, it is important to identify paleoclimate events from many different areas using as many climate proxies as possible. Changes detected in stable isotope records are of similar scale, and changes are also observed in many other proxy climate records, e.g. in pollen, chironomid, diatom and geochemical stratigraphies (Buczkó et al. 2012; Magyari, 2013; Braun et al. 2013; Tóth et al. 2018).

Based on the stable isotope results from the Mohos peat bog, there were three cool periods (11,250–11,000, 10,950–10,450 and 10,200–9750 cal yr BP) during the early Holocene, when continuous, but weakening dry–wet climate fluctuations occurred. The first colder period is linked to the Preboreal Oscillation (PBO, 11,300-11,150 yr BP (Bjorck et al. 1996)), with maximum cooling at 11,250 yr BP (Fisher et al. 2002; Magny 2007). The PBO has been identified in many Central European lake records, which display evidence for higher lake levels between 11,250 and 11,050 yr BP (Magny 2004, 2007). Numerous studies, however, indicate that these cold events did not occur simultaneously in different areas. A significant decline was detected in the Greenland ice core δ^{18} O records around 11,400 yr BP (Rasmussen et al. 2006, 2007, 2014). According to the Poleva Cave (Romania) oxygen isotope record, cooling occurred earlier, between 11,400 and 11,200 yr BP (Constantin et al. 2007). Also, in the Southern Carpathian Mountains (Retezat Mts.), vegetation changes began slightly earlier, between 11,500 and 11,300 on the southern slope, and from 11,400 to 11,100 yr BP on the northern slope of this mountain range (Pál et al. 2018). Lower diatom productivity indicates the PBO occurred between 11,500 and 11,300 yr BP in the Retezat Mts. (Buczkó et al. 2018). In addition, a chironomid-based mean July temperature reconstruction from the Retezat Mts. showed that mean temperature declined between 11,480 and 11,390 cal yr BP, at 10,200 cal yr BP, and again between 9800 and 9700 cal yr BP (Tóth et al. 2012, 2015). At Lake Suchar Wielki (Poland), the first cooling occurred ca. 11,300-11,150 cal yr BP based on palynological records, and inferred water level suggests colder and wetter conditions at the time in this area (Filoc et al. 2018).

We inferred a second cooling event from our stable isotope records, between 10,950 and 10,450 cal yr BP. Slightly later ecosystem changes were described from the Southern Carpathians, ca. 10,500 and 10,300 cal yr BP (Pál et al. 2018), and δ^{18} O in speleothems from northwest Romania recorded similar cooling periods from 11,000 to 10,700, and from 10,500 to 10,200 cal yr BP (Tămaş et al. 2005). A cooling event at 10,300 cal yr BP was also recorded in Poleva cave (Constantin et al. 2007).

After ca. 9000 cal yr BP, stable isotope records indicate rather stable warm conditions, which coincide with the Holocene Climatic Optimum, roughly 9000–5500 yr BP (Andersen et al. 2004). A dramatic cooling event described from many areas at 8200 cal yr BP is the most widely detected climate event of the Holocene Epoch (Alley et al. 1997;

Thomas et al. 2007). The event appears as a significant decrease in δ^{18} O values in the Greenland ice cores (Rasmussen et al. 2014). The 8.2-ka cold event (Alley et al. 1997; Thomas et al. 2007), however, is not observed in Mohos peat core δ^{18} O and δ^{13} C results. Strongest evidence for this Early Holocene event comes from the North Atlantic region. Whereas the disruption in climate appears clearly in the Greenland ice cores, as well as sediment and other records from the temperate and tropical North Atlantic, it is less evident in this region. Few climate modeling experiments have addressed the 8.2-ka event, and most studies of proxy records across this event lack the time resolution to fully characterize the anomalies (Constantin et al. 2007; Magyari et al. 2009; Dragusin et al. 2014). Lack of evidence in the Mohos peat bog for this abrupt decrease in global temperature at 8.2 ka means that this event had little impact at this particular location. Longman et al. (2017) described an \sim 8200-BP event in the Eastern Carpathians based on testate amoebae and a dust record that indicates Saharan desertification. At nearby Lake Santa Ana, there is evidence for a decrease in water depth ca. 9000 cal yr BP and poor diatom preservation beginning ca. 8600 cal yr BP (Magyari et al. 2009). Surprisingly, this apparently global climate event is not detectable in many speleothem $\delta^{18}O$ records from the Carpathians (Onac et al. 2002; Tămaş et al. 2005; Constantin et al. 2007; Dragusin et al. 2014), despite the fact that pollen (Feurdean et al. 2007) and other climate proxies suggest climate changes during this period.

After 7200 cal yr BP, the peat accumulation rate in the Mohos bog declines, but increased again between 6800 and 5500 cal yr BP coincident with the Holocene Climatic Optimum (Andersen et al. 2004). The stable isotope ($\delta^{18}O$, $\delta^{13}C$) values indicate a somewhat colder and drier period between 7200 and 6700 cal yr BP, however the dry conditions persisted longer, until 5500 cal yr BP, i.e. the end of the Holocene Climatic Optimum (Kalis et al. 2003). This dry period coincided with reduced peat accumulation in the Mohos peat bog between 7300 and 6000 cal year BP, as discussed by Hubay et al. (2018a, b). From the same peat bog, Longman et al. (2017) reported a very dry period between 7400 and 6600 cal yr BP, based on testate amoebae. Furthermore, a dry phase was detected in mire surface conditions between 7550 and 4500 cal yr BP (Cristea et al. 2014).

From 5500 to 4500 cal yr BP, climate displayed little variation, and there were no significant environmental changes in the area. An increase in water level at nearby Saint Ana Lake, ca. 5350 cal yr BP, however, was inferred from pollen, but both of these observations are in contrast with NW Romanian records (Feurdean et al. 2008), which indicated warmer and possibly drier conditions between 5500 and 3200 cal yr BP.

Fluctuating, but decreasing temperature was inferred from less positive δ^{18} O values between 4500 and 2600 cal yr BP. The interval is marked by a short, but strong dry and cold period between 3100 and 2850 yr BP, which corresponded to the Neoglacial (3300-2500 cal yr BP (Wang et al. 2012). That interval is widely recognized as the period of the Bronze Age in Europe (Wanner et al. 2011). Longman et al. (2017) recorded the Bronze Age through dust events in Mohos peat record. A cold period at 4200 cal yr BP was also detected in a stalagmite from Poleva Cave (Constantin et al. 2007). This period can be characterized as having an overall wet climate in this area (Magyari et al. 2001). Many studies from the Northern Hemisphere describe this period as cold and dry. Nevertheless, pollen spectra and stalagmites from Romanian records suggest the climate was cool and humid (Magyari et al. 2001; Constantin et al. 2007; Dragusin et al. 2014).

During the Roman Warm Period, between 2500 and 1600 cal yr BP (Wang et al. 2012), δ^{18} O values inferred from the Mohos record were more or less stable, and an increasingly dry climate can be inferred from the δ^{13} C values. Other European and North Atlantic records suggest this period was unusually warm (Desprat et al. 2003; Cristea et al. 2014).

A period of lower-magnitude cooling and drying occurred between 1600 and 1200 cal yr BP, revealed by more negative stable isotope values. A similar dry period occurred ca. 1430 cal yr BP in the Maramures Mountains (Cristea et al. 2014). Between 1000 and 700 cal yr BP (AD 950 to 1250), relatively higher δ^{18} O values in the Mohos record led to an inference for slight warming, which was associated with the Medieval Warm Period (Mann et al. 2009), which was also recognized by Longman et al. (2017), using the dust record in the Mohos peat bog.

Between 600 and 150 cal yr BP (AD 1350–1800), a period of cooling after the Medieval Warm Period can be inferred, and can be correlated with the Little Ice

Age (LIA) (Mann et al. 2009). Evidence for this colder period has been found at many sites across Romania, in the form of tree-ring (Popa and Kern 2009) and pollen records (Fârcaş et al. 2013; Geanta et al. 2014). The LIA is well documented in sediment from Tatra Mountain Lake Toporowy Staw Niżni, Southern Poland (Gasiorowski and Sienkiewicz 2010).

A rapid increase in organic matter accumulation rate was detected about 600 cal year BP (AD 1350), which thereafter decreased continuously to 150 cal yr BP (AD 1800), marking a period of slight cooling that can also be linked to the Little Ice Age (Mann et al. 2009). A decline in stable isotope values during that time reflects the somewhat colder and dryer climate.

In summary, stable isotope values in cellulose from the Mohos bog displayed smaller-amplitude fluctuations during the Holocene Epoch, compared to the terminal Pleistocene, but nevertheless indicate that climate was not uniformly warm and stable throughout the Holocene, as has been proposed. Results from the Mohos area display correlations with Holocene paleoclimate changes inferred from other studies in the Carpathian region. The assumed global 8.2-ka event, however, was not observed in the Mohos peat core δ^{18} O and δ^{13} C values. This does not mean that it did not occur in the area. It may simply be that our core sampling resolution was not high enough to capture what may have been a relatively short-lived climate event.

Conclusions

A 10-m core from the ombrotrophic Mohos peat bog was analyzed for stable isotopes (δ^{13} C and δ^{18} O) in *Sphagnum* cellulose and organic matter accumulation rate. The core spans the last 12,000 years and thus provided a record of changes between warm-cold and dry-wet conditions, from the late Pleistocene to present.

After 11,800 cal yr BP, which corresponds to the end of the cold Younger Dryas, there was a rapid transition into the warmer Holocene. Whereas the Holocene was not characterized by large-magnitude shifts in climate conditions, there were some climate fluctuations that correspond to oscillations identified in Europe and elsewhere around the globe. Several cool (11,250–11,000; 10,950–10,450; 10,200–9750; 7200–6700; 3100–2900; 1600–1200; 600–150 cal yr

BP) and warm intervals (9000–5500; 4500–2600; 2500–1600; 1000–700 cal yr BP) were inferred from the Mohos record. A notable exception is that the important 8.2-ka event did not appear in the Mohos peat core δ^{18} O and δ^{13} C results.

Organic matter accumulation in the Mohos peat bog was examined in conjunction with $\delta^{18}O$ and $\delta^{13}C$ values in Sphagnum cellulose to elucidate the response of the peat bog to changing environmental conditions. Cyclicity within the proxy records was investigated using wavelet analysis, and a 1000-year cycle was detected in the organic matter accumulation rate data and in the δ^{13} C record of the last 6000 years. Overall, all short or long cooling periods in the Holocene Epoch are correlated with short periods of lower organic matter accumulation in the Mohos peat bog. Similarly, drier periods were also linked to lower peat accumulation rate. Presumably, warmer and wetter environmental conditions favor Sphagnum growth. There is a strong positive correlation between peat accumulation rate and the δ^{13} C and the δ^{18} O values, indicating that isotope ratios in the sphagnum are controlled by the same climate factors (humid-dry and cold-warm) that influence the growth of peat. We treat the timing of climate changes cautiously, as it is very difficult to achieve sufficient resolution to identify climate events of < 100-yr duration.

In the context of ongoing anthropogenic climate change, peat bogs are important environmental sinks for fixed (organic) carbon (Harenda et al. 2018). Climate change in the future may have large consequences for peat bog carbon storage, as climate variables like temperature and humidity influence both the production and decomposition of *Sphagnum* (Breeuwer et al. 2008).

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