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ORIGINAL PAPER

Sediment lithology and stable isotope composition of organic matter in a core from a cirque in the Krkonoše Mountains, Czech Republic

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Abstract This study presents detailed lithostratigraphy and stable carbon and nitrogen isotopic variations in a 520-cm-long sediment core from a cirque basin in the Labský důl Valley, Krkonoše Mountains, Czech Republic. Detailed study of the core reveals five major periods of sedimentation during the last 7600 years: silt and sand deposition during ~7.6–5.1 ka cal BP, *Sphagnum* peat accumulation during ~5.1–4.0 ka cal BP, sandy silt and sand during ~4.0–2.8 ka cal BP, raised peat bog during ~2.8–2.0 ka cal BP (*Sphagnum* peat), and sedimentation of sandy silt since ~2.0 ka cal BP. The $\delta^{13}C$ values of the organic matter in the core vary in the range typical for C3 plants, from −24.35 to −27.68‰, whereas the $\delta^{15}N$ values vary from −2.65 to +4.35‰. Core sections having ash contents ≥70% have $\delta^{15}N > 1$‰ and $\delta^{13}C < -26$‰, whereas those having ≤70% ash content have $\delta^{15}N < 1$‰ and $\delta^{13}C > -26$‰. Strong linear correlations are observed between $\delta^{13}C$ and $\delta^{15}N$ values as well as between C:N ratios and $\delta^{15}N$ values in the horizons with ash content >10%, primarily for sand and silt horizons. On the other hand, poor correlations between $\delta^{13}C$ and C:N ratio, as well as $\delta^{15}N$ and C:N ratio, were observed in *Sphagnum* peat layers (45–125 and 185–265 cm). We conclude that the primary stable isotope variations are not preserved in the layers where significant correlation between $\delta^{15}N$ and C:N ratio is observed. The relatively small $\delta^{13}C$ variation in the uppermost *Sphagnum* peat layer suggests stable temperature during ~2.8–2.0 ka cal BP.

Keywords Carbon · Nitrogen · Stable isotope · Peat · Preservation · Holocene · Krkonoše

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Introduction

The Labský důl Valley in the Krkonoše Mountains is part of the Hercynian ranges in Central Europe and has a well-preserved sediment record rich in palaeoecological evidence. Sedimentation in mountain catchments is influenced to a large degree by local as well as regional climate. Owing to climate fluctuations during the Holocene, variation in precipitation and outflow in the Krkonoše Mountains was important in controlling sedimentation dynamics, including the dominant type of sediment in the area. Intense and frequent rainfall events influence fluvial processes that represent the primary process in landscape development during the Holocene. Generally, when outflow and erosion are very limited, plant organic matter is deposited in sedimentary basins, leading to peat formation (Ménot and Burns 2001).

The Holocene has been traditionally divided into the following climatic subperiods, with ages given as calibrated years BP according to Roberts (1998): Boreal (11.5–8.9 ka), Atlantic (8.9–5.7 ka), Sub-Boreal (5.7–2.6 ka), and Sub-Atlantic (since 2.6 ka). Holocene climate changes were, however, substantially different in different regions of Europe (Maisch 2000; Davis et al. 2003). The evidence from Central Europe suggests that the climate was warm and humid during the Middle Atlantic period (Ložek 1999), which may have played a key role in sedimentation in the Labský důl Valley. Because of a general warming trend, permafrost and relict local mountain glaciers thawed during this time in the Krkonoše Mountains (Braucher et al. 2006). Consequently, precipitation and the erosive power of rivers increased and coarser material was frequently transported to the foreland of the mountains (Chmal and Traczyk 1998). Substantial cooling was reported from the Krkonoše Mountains in the Subboreal period (Jankovská 2004), whereas the stable carbon isotope and pollen data from the nearby Jizerské hory Mountains suggest warm climate (Skrzypek et al. 2009). The Subboreal environment was characterized by reactivation of mass movements and sedimentation was facilitated by increased precipitation (Chmal and Traczyk 1998). The Subatlantic period experienced a cool and wet climate (Skrzypek et al. 2009). During the Subatlantic period, the rate of fluvial processes increased, forming the lowermost fluvial terraces in the valleys of larger rivers (Bieroński et al. 1992). Detailed study of the lithology and isotope systematics in sedimentary successions from the Krkonoše Mountains may reveal aspects of the Holocene climate variations.

Peatlands are areas where the rate of biomass production is greater than the rate of decomposition, leading to the accumulation of significant amounts of organic matter. Preservation of organic matter is enhanced in bog environments because of two dominant factors: (1) acidic conditions in bogs due to metabolism of the dominant plant species (*Sphagnum*), and (2) nitrogen (nutrient) deficiency (Malmer and Nihlgård 1980). Although good preservation of organic matter in bogs has been confirmed in numerous studies (Johnson and Damman 1993; Kuhry and Vitt 1996), only a few have focused on preservation of the stable carbon and nitrogen signatures in peat cores and their application in paleoenvironmental reconstructions (Jędrysek et al. 1995; Novák et al. 1999, 2009; Ménot and Burns 2001; Skrzypek and Jędrysek 2005; Asada et al. 2005; Lamentowicz et al. 2008). In particular, if the stable carbon and nitrogen isotopic composition of the parent organic matter can be shown to be preserved during peat formation (i.e., the isotopic composition is not significantly altered during decomposition), then the isotopic composition of peat cores can be used as a proxy for paleoclimate and paleoenvironment reconstruction.

The stable carbon isotopic composition ($\delta^{13}C$) of a plant is a function of complex environmental factors, but is determined predominantly by the metabolic pathway used (C3 or C4) in photosynthesis. Temperature, however, plays the primary role in fixing the $\delta^{13}C$ value for plants having the same metabolic pathway and growing in comparable ecosystems (i.e., under similar altitude, humidity and nutrient availability). Therefore, in such cases, slight variation in temperature of the growing season will result in different $\delta^{13}C$ values, even for plants that use the same metabolic pathway. Data from several sources (Smith et al. 1973; Whelan et al. 1973; Troughton and Card 1975; Lipp et al. 1991) suggest that the change in $\delta^{13}C$ of various C3 plants per degree change in temperature varies from −1.2 to +0.33‰/°C. Isotope data from peat-forming moss species obtained by Skrzypek et al. (2007a, b) along an altitudinal transect (500–1,400 m) in the Sudetes Mountains (Poland) show the $\delta^{13}C$ value of moss varies linearly with temperature of the growing season; the $\delta^{13}C$ value for *Sphagnum* decreases by

1.5‰ per 1°C increase in temperature. In addition, Skrzypek et al. (2007a) showed that δ^{13}C composition of both extracted cellulose and total organic matter of fresh mosses can be successfully used for environmental studies.

Several studies postulated that the carbon stable isotope composition in *Sphagnum* could be significantly affected by bog wetness, i.e., water table variation in a bog (Williams and Flanagan 1996; Ménot and Burns 2001; Moschen et al. 2009). Furthermore, since diffusivity of CO_2 is comparatively higher in air than in water, desiccation (a relatively dry bog surface) causes an increase in discrimination against $^{13}CO_2$ during photosynthesis (Williams and Flanagan 1996). Consequently, $\delta^{13}C_{cellulose}$ of *Sphagnum* mosses is relatively lower under dry conditions, compared to a wet bog surface (Moschen et al. 2009). Water stress may affect δ^{13}C of plants; however, in the case of *Sphagnum* mosses, a high ground water table is required to support photosynthesis (Farquhar et al. 1989; Williams and Flanagan, 1996). Mosses have an unusual ability to survive prolonged desiccation, but when water is significantly limited, very little organic matter is produced relative to wet conditions (Titus and Wagner 1984; Rydin 1985; Schipperges and Rydin 1998; Proctor 2000; McNeil and Waddington 2003). The amount of organic matter produced during prolonged desiccation represents only a small fraction of the total mass produced during periods of *Sphagnum* growth and deposition in normal, wet conditions. Therefore, the effect of desiccation on δ^{13}C of *Sphagnum* is negligible over the *Sphagnum* growth period.

In general, bacterial decomposition of organic matter results in ^{13}C enrichment relative to the ^{12}C isotope (higher δ^{13}C value) of the remaining soil (Ehleringer et al. 2000; Wynn 2007). Novák et al. (1999, 2009) observed a downcore δ^{13}C gradient in bulk *Sphagnum* peat and related it to the progressive enrichment of the residual substrate in the heavier, ^{13}C isotope due to bacterial decomposition during early peat diagenesis. Similar trends have been reported by others (Jędrysek et al. 1995, 2003; Skrzypek and Jędrysek 2005; Skrzypek et al. 2008), however, these observations seem to be valid for very young peat only and have not been noted for older peat. Most likely, fractionation of stable carbon isotopes occurs only during the initial decomposition of organic matter, i.e., during transition from acrotelm, the upper layer of peat where decomposition of organic matter takes place under oxic conditions, to the catotelm, the peat that lies below the water table where further decomposition of organic matter is very limited due to anoxic conditions.

Recently, Loader et al. (2007) analyzed the stable carbon isotope composition of *Sphagnum* in peat and demonstrated that the δ^{13}C signal of growth increments of different individual *Sphagnum* remains is coherent through time. They reported a consistent offset (up to 1.5‰) in the δ^{13}C value of stems and branches, with branches having a higher δ^{13}C value. This offset was observed for both modern *Sphagnum* and *Sphagnum* remains extracted from a peat monolith. Moschen et al. (2009) also reported a similar offset (mean = 1.5‰) between the δ^{13}C values of stems and branches. Data from both Loader et al. (2007) and Moschen et al. (2009) show that δ^{13}C values of both stems and branches tend to shift in parallel. Consequently, the climate signal carried by the isotopic composition of stems and branches is similar (Loader et al. 2007). Furthermore, Loader et al. (2007) concluded that “on the scale of sampling of a peat core/monolith comprising multiple plants record environmental forcing in a similar manner.”

Moschen et al. (2009) concluded δ^{13}C of bulk peat changes downcore because the ratio of branches to stem sections also decreases downcore. Their study also shows that selected random pieces of branch or stem collected from peat samples reflect the environmental conditions in a particular growing season or a few seasons. Although deriving paleoclimate information solely from the isotopic composition of stem sections recovered from peat seems promising, Moschen et al. (2009) suggest that separating branches and stems is not necessary for data spanning long periods. In our opinion, for long-term data covering hundreds or thousands of years, it is better to use bulk peat, or to separate representative samples, such as a few grams of *Sphagnum* stems from each horizon. This will eliminate individual plant variations that can occur on shorter time scales. However, separating specific fractions is extremely time consuming, and difficult to accomplish in old peat. For paleoclimate studies, isolation of components from bulk peat has been proposed: cellulose (Jędrysek and Skrzypek 2005; Loader et al. 2007; Moschen et al. 2009) or lignin (Akagi et al. 2004) extraction, as well as *Sphagnum* species separation (Moschen et al. 2009), or separation of stems, branches and leaves (Loader et al. 2007;

Lamentowicz et al. 2008; Moschen et al. 2009). On the other hand, correlation of bulk peat δ^{13}C with other independent variables such as δ^{13}C of tree rings (Jędrysek et al. 2003), pollen percentages (Skrzypek et al. 2009), multiproxy models of temperature variations (Skrzypek and Jędrysek 2005), suggests that δ^{13}C of bulk peat is representative of environmental conditions. Lastly, despite the variability observed within individual co-existing plants, Loader et al. (2007) suggested that if isolation of a single component is not possible, environmental information can still be obtained from analyses of a homogeneous concentrate or mix of *Sphagnum* components. Therefore, the variation of carbon stable isotope composition of total organic matter of mosses seems to be sufficiently recorded in bulk peat, and faithfully reflects paleoclimate variations, even if the ratio between visible branches and stems varies in a core.

The nitrogen stable isotope composition (δ^{15}N) of plants is primarily related to the isotopic composition of nitrogen in the water source and nitrogen assimilation strategies (NO_3^-/NH_4^+/free amino acids) of individual plant species (Evans 2001; Dawson et al. 2002; Bragazza et al. 2005a, b; Asada et al. 2005; Krab et al. 2008). Generally, plants that take up nitrogen produced from the decay of earlier deposited organic matter are characterized by δ^{15}N values in the range −2 to −8‰, whereas those using nitrogen from symbiotic relationships with nitrogen-fixing organisms have δ^{15}N in the range −2 to +2‰, close to the δ^{15}N value of atmospheric nitrogen (Nadelhoffer and Fry 1994; Jonasson and Shaver 1999). In contrast to biogenic nitrogen, δ^{15}N values of anthropogenic NO_x could be significantly more positive (+5 to +13‰) for coal-fired power plant emissions, and about +4‰ for vehicle tailpipe emissions (Kendall et al. 2007). For instance, Elliott et al. (2007) and Kendall et al. (2007) reported $\delta^{15}N_{NO_x}$ values in rain between −1.3 and +0.6‰ for most polluted areas and between −7.5 and −5.5‰ for most pristine areas in the USA. Bragazza et al. (2004, 2005a, b) suggested that both the ratio of anthropogenic to natural N and the ratio of reduced to oxidized nitrogen (NH_x/NO_x) in depositional environments has an influence on the δ^{15}N values in rainfall. The δ^{15}N of live *Sphagnum* mosses, collected from ombrotrophic mires in 11 European countries ranged from about −8 to −3‰, which is related to the average δ^{15}N values in atmospheric deposition and to the total amount of atmospheric N deposition in the respective areas (Bragazza et al. 2006). Therefore, δ^{15}N of *Sphagnum* may be used as a proxy for the δ^{15}N signature of atmospheric precipitation and anthropogenic NO_x input.

Although the C:N elemental ratio and nitrogen deposition rates in *Sphagnum* (Bragazza et al. 2006; Gerdol et al. 2007; Phuyal et al. 2008) have been reported, preservation of δ^{15}N in peat has not been explored. In general, organic matter decomposition and nitrogen mineralization usually result in ^{15}N enrichment in soil (Nadelhoffer and Fry 1994; Amundson et al. 2005). Bacterial decomposition preferentially removes ^{14}N from the parent organic matter, so nitrates released to water become enriched in ^{14}N (lower δ^{15}N value) relative to the remaining organic matter that becomes enriched in ^{15}N (higher δ^{15}N value). Therefore, the δ^{15}N values for older, decomposed matter tend to be higher than that of the parent plant matter. Asada et al. (2005) reported significant increase in the δ^{15}N value, around 2–3‰ during the first 3 years, during the early stage of *Sphagnum* litter decomposition. They observed that *Sphagnum* litter decomposition in the oxic zone (acrotelm) leads to high mass loss and ^{15}N enrichment, resulting from interactions with soil microbes and preferential loss of ^{14}N. Litter in the anoxic zone, however, had smaller mass loss and ^{15}N enrichment.

During the transition between acrotelm and catotelm in the initial stage of decomposition, the carbon and nitrogen isotope compositions of the parent organic matter could be well-preserved, if peat formation takes place in an anaerobic and acidic environment characterized by a stable water table that inhibits decomposition (Coulson et al. 2005; Skrzypek et al. 2008). Postdiagenetic changes in catotelm are limited and probably have little influence on the δ^{13}C and δ^{15}N values of organic matter. Therefore, peat may serve as a geochemical archive of paleoenvironmental changes (Brenninkmeijer et al. 1982; Aucour et al. 1996; Jędrysek et al. 2003; Akagi et al. 2004; Skrzypek and Jędrysek 2005; Skrzypek et al. 2009). The conditions in a bog setting may vary over time, from steady accumulation to extensive erosion. Water table fluctuations may lead to changes in sedimentation conditions, from anaerobic to highly oxidizing. Previously well-preserved organic matter may also undergo decomposition during low-water-table conditions, and redeposition or flushing events that lead to highly oxidizing conditions (Caseldine et al. 2000). If decomposition affects the isotopic composition, then using this information for climate reconstruction would lead to erroneous interpretations. The state of decomposition can be useful for preliminary inferences about paleoclimate variations (von Post 1946). Since bacterial decay affects both $\delta^{13}C$ and $\delta^{15}N$ (as well as the C:N elemental ratio) in a similar way, causing ^{13}C and ^{15}N enrichment, linear correlation between these isotopes would be expected if organic matter undergoes extensive decomposition during peat formation or post-sedimentation (Blackford and Chambers 1993; Wynn 2007). The isotope signatures of carbon and nitrogen sources for plants, as well as the assimilation mechanisms for these two elements are independent, i.e., unrelated. Therefore, a linear correlation between $\delta^{15}N$ and $\delta^{13}C$ (and C:N ratio) is not expected in well-preserved peat.

In this study, we collected a 520-cm-long sediment core from our study area in the Labský důl Valley in the Krkonoše Mountains, Czech Republic. The geochemical signatures in the profile were used to reveal a record of sedimentation and environmental change. The primary objectives of this study were to: (1) measure stable carbon and nitrogen isotope values in sediments accumulating in a mountain catchment and ascertain whether the original isotope composition of organic matter is preserved in the profile, and (2) study the sedimentary environment and sedimentation dynamics during the past 7.6 ka.

Sampling location

A simplified geomorphological map of the study area is shown in Fig. 1 along with the peat bog sampling site, located at the bottom of a cirque at 1,039 m above sea level (asl). This peat bog developed on the surface of fluvial and limnic sediments. It forms a slightly inclined surface (slope 1–3°) in the centre and a convex-up profile towards the eastern margin of the cirque. The cirque floor is about 200 m long, 50 m wide, and has up to 15 m of sediments including 2.5 m of peat. Currently, the surface of the bog is covered mainly with a carpet of *Sphagnum girgensohnii*, *Polytrichum commune*, *Eriophorum vaginatum* and *Juncus filiformis* (Jankovská 2004). *Pinus mugo* and *Sorbus sudetica* are present in the transitional area between the bog and the cirque

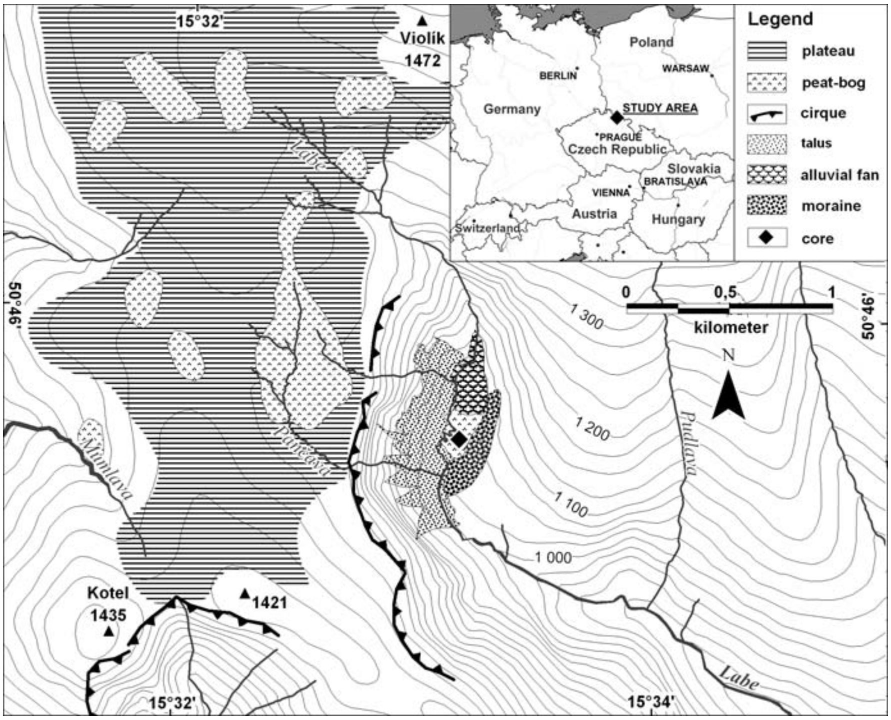

Fig. 1 Simplified geomorphological map showing mire locations in the Labský důl Valley (Krkonoše Mountains, Czech Republic). The *solid diamond* in the central portion of the map (N 50°45′46.6″, E 15°33′8.2″) represents the sampling location

headwall, whereas the southern margin is covered by *Picea abies* forest.

The leeward position of the cirque affects the topoclimatic conditions at the sampling site. Predominantly W-E winds remove snow from the summit plateaus and it accumulates in the cirque (Jeník 1961). Data collected at Labská bouda weather station (1,310 m asl) from 1961 to 2000 suggest that the mean annual temperature in the study area is ~2.0°C and the mean annual precipitation is ~1,459 mm year^{-1} (Metelka et al. 2007). Once every few years or decades, heavy precipitation events occur, with >100 mm of rainfall per day. As the maximum water retention capacity of the soil profile in the Labe river headwater is about 70–90 mm, intense precipitation events result in higher outflow from the headwater area into the cirque (Tesař et al. 2000). Therefore, the cirque floor is inundated during such precipitation events.

The sampling location is devoid of carbonate rocks. Two types of granite of early Carboniferous age predominate in the catchment area. Therefore, it is unlikely that inorganic carbon-bearing sediments are added during rock erosion and subsequent sediment transport to the bottom of the cirque. Furthermore, there is very limited input of allochthonous inorganic and organic material from atmospheric deposition that can be traced to the winter snow cover (Spusta et al. 2003).

Materials and methods

A core was drilled at the deepest point in the cirque basin (50°45′46.6″ N, 15°33′8.2″E; WGS 84), located about 200 m to the NE of the confluence of the Labe and Pančava Rivers (Fig. 1). A 520-cm-long core was sampled using an Eijkelkamp peat sampler, collected as uncompressed cores in 50-cm-long sections. The upper 20 cm of the core contained fresh plant material and was sampled with a knife. The whole core was divided into 5-cm slices. The slices were homogenized and dried for stable isotope analysis (~1.0 mg sample powder), ash-content analysis (1 g) and particle-size analysis (3 g). Thirteen samples were selected for radiocarbon dating: macroremains of *Sphagnum* (10 samples from the 50–354 cm core section) and plant tissue (3 samples from 395, 465 to 500 cm depth).

Analytical methods

The peat samples collected in the field for stable isotope analyses were frozen (−20°C) within a few hours to prevent bacterial activity. After thawing the samples in the laboratory, pieces of wood and roots were removed. The samples were rinsed with 4% HCl to remove carbonate, vacuum-dried, and powdered. The HCl treatment does not affect isotope composition of organic matter (Kolasinski et al. 2008). Sample preparation was carried out in the Laboratory of Isotope Geology and Geoecology, the University of Wrocław, Poland. Stable isotope and C:N elemental ratio analyses of bulk organic matter were performed at the Laboratory for Stable Isotope Geochemistry at the University of Texas at San Antonio, USA. Analysis was carried out using an Elemental Analyzer (Costech CHNS EA 1020) coupled online with a Thermo-Finnigan Delta$^{\text{Plus}}$ XP Stable Isotope Ratio Mass Spectrometer. Isotopic compositions are reported in the standard δ notation. We used the “multiple-point” normalization technique (Paul et al. 2007) to normalize all raw isotopic data to isotope reference scales; δ^{13}C values are reported using the VPDB scale (Vienna PeeDee Belemnite) and δ^{15}N values relative to AIR. The following International Atomic Energy Agency (IAEA) reference standards were analyzed with each set of samples and utilized for normalization: NBS22, USGS24 and IAEA-600 for δ^{13}C; IAEA-N1, N2, N3 and IAEA-600 for δ^{15}N. The uncertainties associated with stable isotope analyses (1σ standard deviation) were 0.10‰ for δ^{13}C and 0.15‰ for δ^{15}N.

Thirteen selected samples from the profile were dated using Accelerator Mass Spectrometry (AMS) at the Radiocarbon Laboratory of Erlangen, the University of Erlangen, Germany. Sample material was prepared with the AAA (acid-alkali-acid) method, using HCl and NaOH. In addition to these standard preparation procedures, samples were centrifuged with a $ZnCl_2$ solution. Conventional ^{14}C ages were corrected for sample isotopic fractionation to a normalized value of $\delta^{13}C = -25$‰ and calibrated using OxCal 4.4/IntCal04 (Reimer et al. 2004). All radiocarbon dates are given as corrected and calibrated ages in thousands of years (ka) before present (BP).

Particle size was measured using a combined sieving and laser diffraction method at the Department of Geological Science, the Masaryk University in Brno, Czech Republic. A Retch AS 200 sieving machine was used for coarser grain fractions (4–0.063 mm) and a Cilas 1064 laser diffraction granulometer was used for the finer fractions (0.0004–0.5 mm). Ash content was measured in the Laboratory of the Geological Institute, Charles University, Prague. Following the procedure of Gale and Hoare (1991), samples were dried at 105°C and combusted in an oven at 550°C for 8 h. Results are expressed as percent of dry weight, assuming that organic matter + ash content = 100 wt%.

Least squares regression was used to describe relations between variables. The r^2 and probability (*P*-value) associated with the *F*-test were calculated for each relationship. Outliers were identified using Studentized Residuals, with values >3.0 considered critical to determine outliers. The r^2 coefficient of determination is the correlation between the response and predicted values of the model. Where the text refers to a strong correlation, then a strong correlation between the response and the linear model predictions is intended.

Results

Lithostratigraphy

Detailed lithological description of sediment succession in the Labský důl core is presented in Fig. 2. While organic-rich material and peat dominate in the section above 265 cm, mineral/clastic sediments prevail in the lower part of the core. The clastic sediments are characterized as poorly sorted sand to silt. The uppermost section down to 45 cm depth (~0–2.0 ka cal BP) consists of both peat and sandy silt; the lower limit is sharp. The first peat section (H3–H4 according to the von Post classification) lies between 45 and 125 cm (~2.0–2.8 ka cal BP) where organic matter content exceeds 80%. Mineral content increases gradually in the lower part of this red (2.5YR4/6) peat layer and prevails down to 185 cm, in a section dominated by sandy silts (~2.8–4.0 ka cal BP). The second distinct peat section (185–265 cm, ~4.0–5.1 ka cal BP) is comprised of decomposed peat (H7–H8 according to the von Post classification). This section contains very dusky red (2.5YR2.5/2) organic material with more fragmented remains of *Eriophorum vaginatum* and has higher ash content than the upper peat section.

Sediments from 265 to 520 cm depth (~5.1–7.6 ka cal BP) differ significantly from the rest of the core samples. The organic content in this layer is very low and declines rapidly downwards. Organic content of the lowermost section (515–520 cm) is less than 3%. There is a greater variability in grain size characteristics from 265 to 520 cm depth, which is caused by the occurrence of several sandy layers in this section. These layers are 0.4–13 cm thick, discrete, and associated with an influx of sand-size sediment (up to 65%). They consist of predominantly rounded to sub-rounded clasts, which are poorly sorted compared with the overlying and underlying silt.

Thirteen calibrated radiocarbon dates are presented in Table 1. The calibrated ages are given for the 95.4% confidence interval. Calibrated and corrected ages based on the median of the probability distributions are also presented in Table 1 and are used in our discussion. The depth-age model presented in Fig. 3 was prepared using a Bayesian model for deposition implemented in the OxCal software. The approximate deposition rates (Table 1) were calculated using the calibrated age and depth of adjacent sample pairs.

Variation in $\delta^{13}C$ and $\delta^{15}N$ values, C:N ratio and ash content

The $\delta^{13}C$ and $\delta^{15}N$ values of organic matter in the core vary from −24.35 to −27.68‰ (mean −26.02‰) and from −2.65 to +4.35‰ (mean 0.91‰), respectively (Fig. 4). The ash content (wt%) varies widely depending on the type of sediment; 1.8% in pure raised *Sphagnum* peat to 97.2% in sand layers (Fig. 4). Higher values of ash content correspond to lower percentages of organic carbon content and higher contents of sand and clay. In the whole core, C:N ratio varies from 16 to 85 (mean = 32). The highest values (>30) of C:N ratio coincide with well-preserved pure *Sphagnum* peat, whereas the lowest values (~20) with high-ash layers. The $\delta^{13}C$ and $\delta^{15}N$ values for the cube of plants cut from the current bog surface (0–5 cm) are −28.19 and −4.36‰, respectively, more negative than for peat; the C:N ratio (29) of the same is close to the average value in the core.

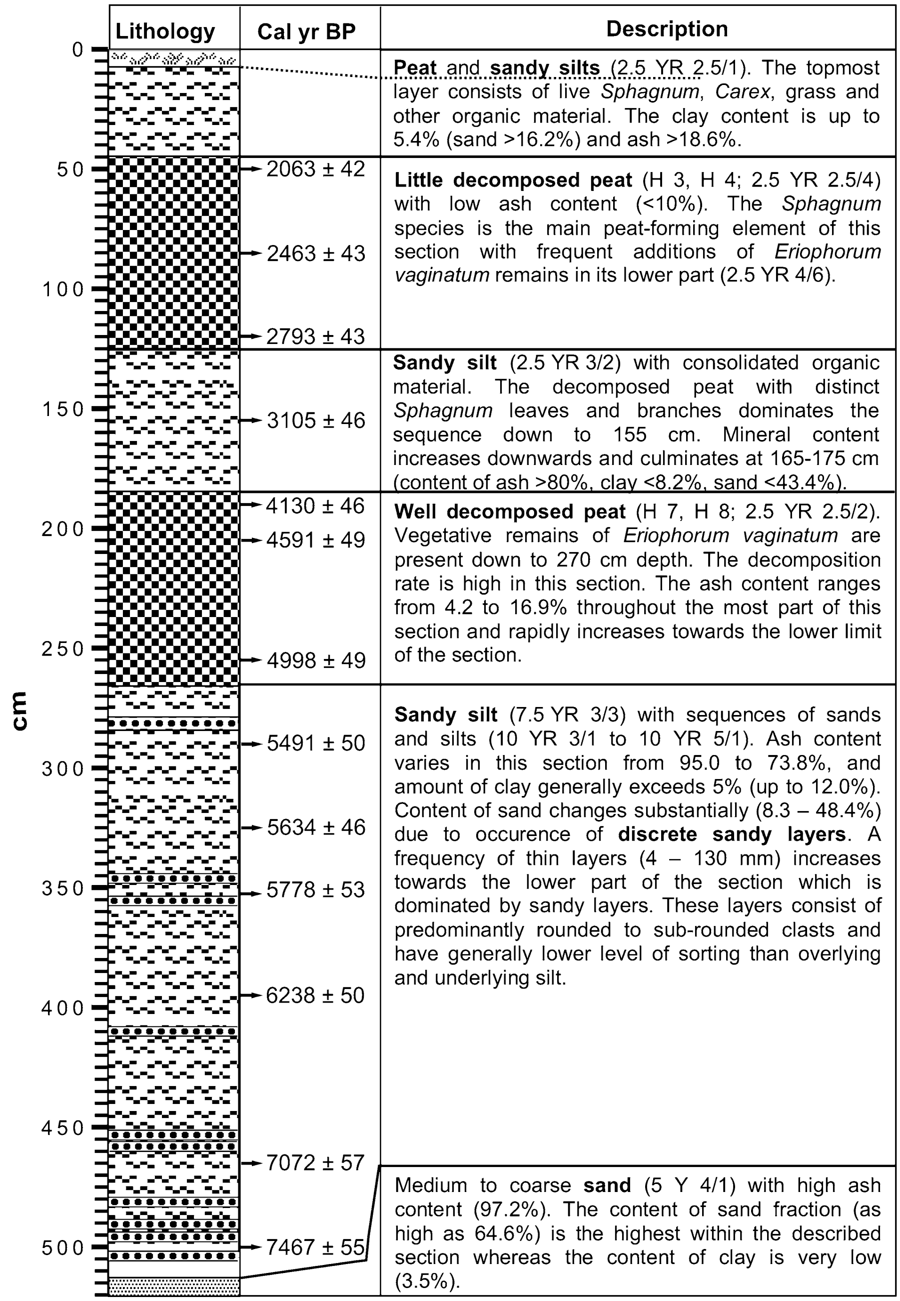

Fig. 2 Lithostratigraphy of sediment core from the Labský důl (Krkonoše Mountains)

In the $\delta^{13}C$ vs. $\delta^{15}N$ plot, all samples fall into two distinct clusters (Fig. 5). The sediment samples (such as silty peat, sandy silt, and sand with organic matter) having $\delta^{13}C < -26‰$ and $\delta^{15}N > 1‰$ are characterized by ash content >70%. On the other hand, peat samples from the two distinct peat horizons in Fig. 2 are characterized by $\delta^{13}C > -26‰$ and $\delta^{15}N < 1‰$ and ash content <70% (for pure peat the ash content is <10%). Figure 6 shows the relationships between $\delta^{15}N$ and C:N, and $\delta^{15}N$ and $\delta^{13}C$ for two separate groups of matter: pure peat (45–125 and 185–265 cm) has <10% ash content, whereas other sediments (125–185 cm and 265–345 cm) have >10% ash content. The C:N ratio of samples with low ash content (pure peat) varies over a wide range, in contrast to a restricted range for sediments having

Table 1 The radiocarbon ages and calculated deposition rates for the core in the Labský důl Valley, the Krkonoše Mountains

Depth (cm)	Radiocarbon lab code	Calibrated age[a] (cal. years BP)	Calibrated age[b] (cal. years BP)	Deposition rate[c] (mm $year^{-1}$)
50	Erl-10098	2,291–1,948	2,063 ± 42	0.9
85	Erl-10099	2,701–2,348	2,463 ± 43	1.1
120	Erl-10100	2,864–2,744	2,793 ± 43	1.1
155	Erl-10101	3,250–2,958	3,105 ± 46	0.3
190	Erl-10102	4,288–3,981	4,130 ± 46	0.3
205	Erl-6295	4,815–4,435	4,591 ± 49	1.2
255	Erl-10103	5,279–4,859	4,998 ± 49	0.7
290	Erl-10104	5,589–5,325	5,491 ± 50	2.4
325	Erl-10105	5,739–5,488	5,634 ± 46	2.0
355	Erl-6318	5,904–5,653	5,778 ± 53	0.9
395	Erl-10106	6,386–6,023	6,238 ± 50	0.8
465	Erl-10107	7,247–6,934	7,072 ± 57	0.9
500	Erl-10108	7,571–7,332	7,467 ± 55	–

[a] Corrected and calibrated ages for the 95.4% confidence interval. Calibration with OxCal 4.4 using IntCal04 (Reimer et al. 2004)

[b] Calibrated and corrected age based on the median of the probability distribution

[c] Deposition rate calculated on the basis of calibrated age and depth of adjacent samples pairs

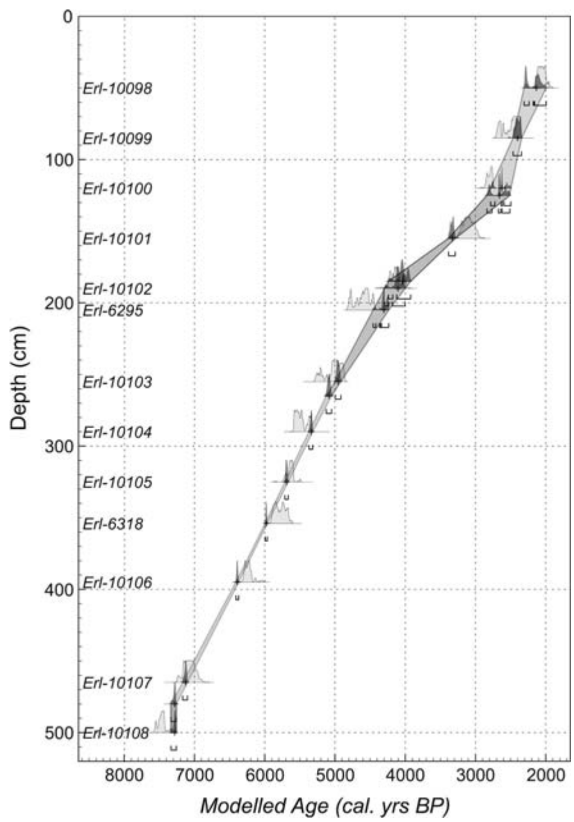

Fig. 3 Depth-age model for the core using Poisson mediated deposition model in OxCal

high ash content. Figure 7 shows the relationship between $\delta^{15}N$ and $\delta^{13}C$ versus ash content. Although there is a good correlation between the isotopic compositions and ash content ($r^2 = 0.82$ for $\delta^{13}C$, $r^2 = 0.72$ for $\delta^{15}N$, $P < 0.001$), the plot reveals two separate clusters, similar to Fig. 5. Samples with low ash content are characterized by a narrow range of carbon isotopic composition and low $\delta^{15}N$ values compared with the samples with high ash content (wide range in $\delta^{13}C$ and higher $\delta^{15}N$ values).

Discussion

Sedimentation in the Labský důl Valley catchment

The section of the core between 520 and 355 cm (~7.6–5.8 ka cal BP) represents a period of declining lacustrine sedimentation in the Labský důl Valley. Initial signs of a diminishing lake appear in the section from 520 to 470 cm (~7.6–7.1 ka cal BP) where the organic matter content rapidly increases from 3 to 17%. Silty sediments prevail in the section, but an increase of the sandy fraction suggests that the area of accumulation in the cirque floor gradually decreased. Frequent occurrence of

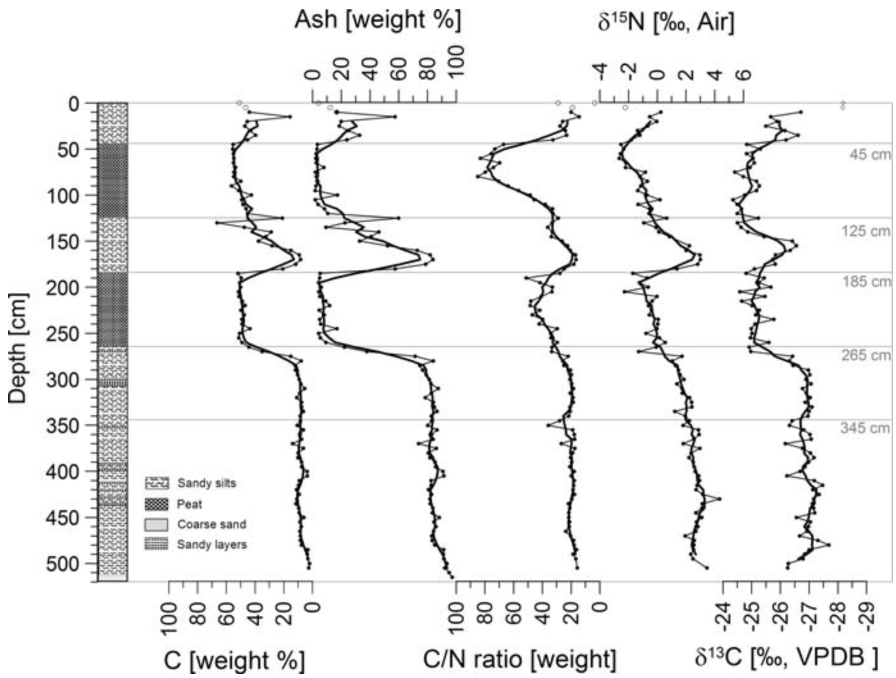

Fig. 4 Variation in $\delta^{13}C$, $\delta^{15}N$, C:N and ash contents in the core. *Thick solid curves* represent 5-point running averages. Note that *Y*-axes for $\delta^{15}N$ and ash content (shown on *right* hand side) are reversed in order to show the similarity amongst the observed trend *lines*. Two top *open symbols* represent fresh plant material from bog surface and plant litter in very early stages of decomposition; these data were excluded from regression calculations

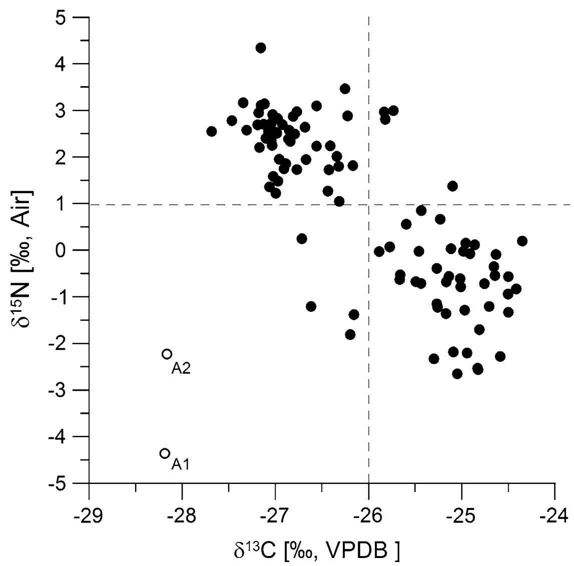

Fig. 5 Correlation between $\delta^{13}C$ and $\delta^{15}N$ of organic matter in the core. Most data are located in two quadrants. *Open symbols* represent fresh plant material from the bog surface (*A1*) and plant litter in a very early stage of decomposition (*A2*)

distinct sandy layers in this sequence suggests that clastic sediment delivery from the surrounding terrain was rapid and most likely happened during intense precipitation events. These layers differ from deposits above and below in terms of grain size distribution, particle morphology and organic matter content. Jankovská (2004) reported increasing deposition of *Sphagnum* spores in the core between 460 and 350 cm, and interpreted it as declining lacustrine conditions during the Early Atlantic period (~5500–4000 BC). Almost constant values of sediment accumulation (0.8–0.9 mm year^{-1}) in the lower part of the section (up to 355 cm, i.e., until 5.8 ka cal BP) suggest uniform sedimentation conditions and regional climate. The conditions correspond to the phase of limited sedimentation found in the Łomnica Valley on the northern side of the Krkonoše Mountains (Chmal and Traczyk 1998).

The section from 355 to 265 cm (~5.8–5.1 ka cal BP) reflects a period of rapid environmental changes. Sediment yields were highest at the beginning of this period compared with the entire 7.6-ka history (Table 1). During this time, a remarkable input of coarser material associated with increased fluvial runoff, was frequently delivered to the cirque floor from adjacent areas. The lower part of the section, up to 290 cm (~5.5 ka cal BP), reveals a high rate of sedimentation (~2.4 mm year^{-1}), which then decreases to around 0.7 mm year^{-1}. A high rate of sedimentation (1.7 mm year^{-1}), facilitated by increased precipitation during the early Subboreal period, was also reported from the Łomnica Valley by Chmal and

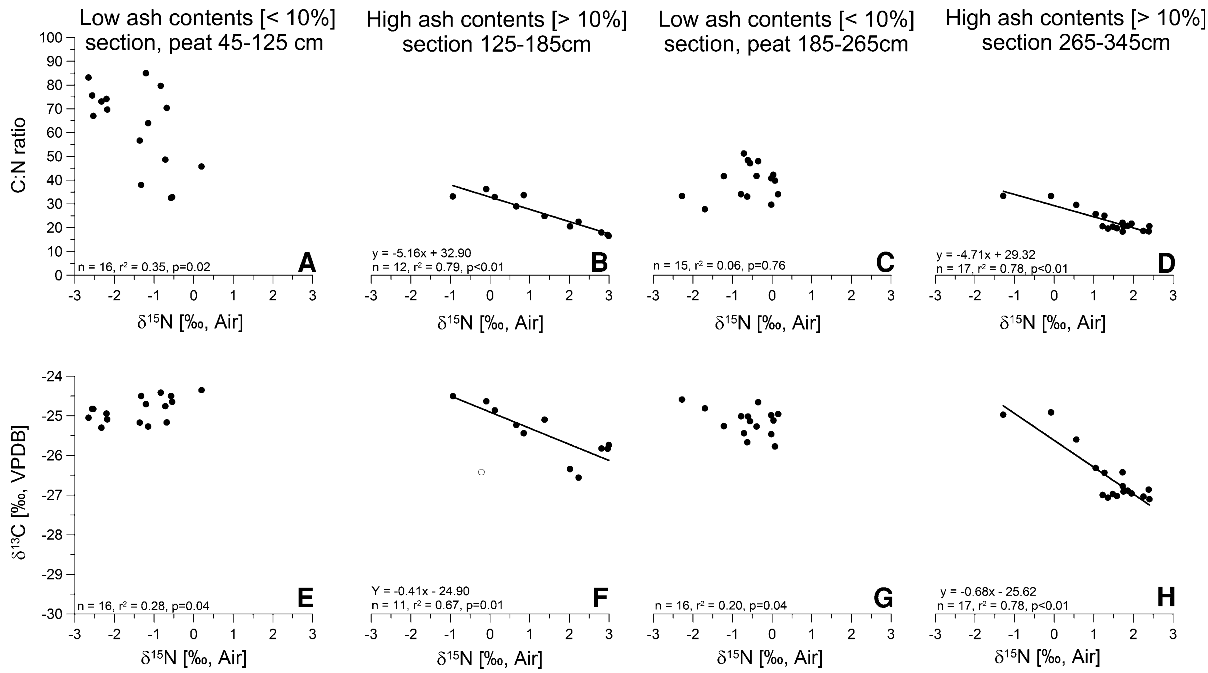

Fig. 6 Poor linear correlations are observed between δ^{15}N and C:N ratio (plot **a**, **c**) and between δ^{15}N and δ^{13}C (plot **e**, **g**) for peat sections from 45–125 to 185–265 cm depth, and with low ash content. In contrast, strong correlations are observed for sections confined to 125–185 cm and 265–345 cm depth and with >10% ash content (plot **b**, **d**, **f** and **h**, respectively). *Open symbol* in *F* represents one outlier point (at 137.5 cm) excluded from the regression (Studentized residual for this point is 3.6, which is higher than the critical value for outliers)

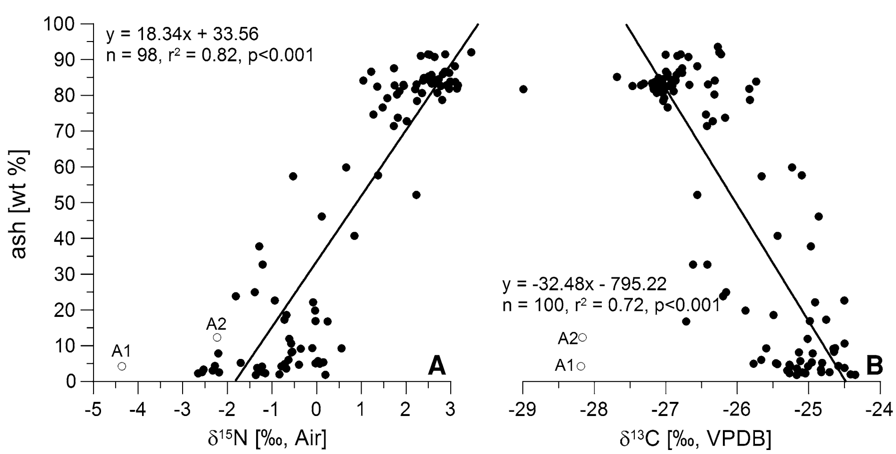

Fig. 7 Relationship between ash content (wt%) and δ^{15}N (**a**) and δ^{13}C (**b**) for all samples. Isotopic composition in the pure peat layer (ash content <10%) varies within a wide range compared with the samples of other sediments having ash content >10%. *Open symbols* represent fresh plant material from the bog surface (*A1*) and plant litter in a very early stage of decomposition (*A2*), both excluded from regression calculations

Traczyk (1998). Formation of the peat layer between 265 and 185 cm ($\sim$5.1–4.0 ka cal BP) followed the period of lake sedimentation (Fig. 2). During the transition phase from lake to bog conditions, the δ^{13}C of organic matter rapidly increased from −26.42 to −24.97‰, whereas δ^{15}N decreased from +1.72 to −

1.29‰ (Fig. 4). According to Lamentowicz et al. (2008), more negative $\delta^{13}C$ values may suggest higher contributions from organic matter of aquatic origin. We infer that, after 5.1 ka, the sedimentary environment as well as the nature of the organic matter source changed rapidly from limnic/algae to bog/*Sphagnum*. The rate of sedimentation varied in the range of 0.3–1.2 mm $year^{-1}$ during peat formation, with $\delta^{13}C$ in the range between −25.67 and −24.59‰ and $\delta^{15}N$ from −2.28 to 0.56‰. Since the ash content in this section of the core varies in the range 4.2–11.9% (Fig. 4), we infer minor inputs of clastic sediments during this period.

The deposition of clay and sand along with minor organic components between 185 and 125 cm (~4.0–2.8 ka cal BP) was characterized by variable sedimentation conditions (sedimentation rate from 0.3 to 1.1 mm $year^{-1}$). Predominantly clastic sediments were transported from the catchment by fluvial and slope processes. These sediments are characterized by a rapid decrease in $\delta^{13}C$ (down to −26.56‰) and an increase in $\delta^{15}N$ (up to 2.99‰), and an increase in ash content up to 83.8% (Fig. 4).

Deposition of the peat layer between 125 and 45 cm (~2.8–2.0 ka cal BP) was controlled by the growth of the peat bog, which has prevailed within the last 2800 years. The ash content in this peat layer varies in the range 1.8–10.6%, $\delta^{13}C$ between −25.30 and −24.35‰, and $\delta^{15}N$ between −2.65 and 0.19‰. Occasionally, clastic material was supplied to the bog, but only during seasonal flood events or avalanches. The calculated accumulation rate of peat was around 1 mm $year^{-1}$. Sedimentation of sandy silts supplemented peat accumulation in the upper 45 cm (last 2000 years).

Carbon and nitrogen stable isotope signatures of organic matter

The $\delta^{13}C$ value of organic matter in the core varies in the range typical for C3 plants. A similar range is also reported for mosses and peat from Central Europe (Novák et al. 2001; Ménot and Burns 2001; Skrzypek and Jędrysek 2005). The $\delta^{15}N$ values of organic matter in our core (−2.65 to +4.35‰) show a restricted range compared to that in *Sphagnum* peat reported by Asada et al. (2005) ($\delta^{15}N$ from −11 to +3‰) and Bragazza et al. (2005b) ($\delta^{15}N$ from −8 to −3‰). Our core does not consist exclusively of in situ-deposited *Sphagnum*. The $\delta^{15}N$ value of the portion of the core with only *Sphagnum* peat varied between −2.65 and +0.56‰. The δ values of fresh plants ($\delta^{13}C = -28.19$‰ and $\delta^{15}N = -4.36$‰) from the bog surface are more negative than in the peat.

High-altitude catchments like our sampling site are nitrogen-poor environments. The rapid outflow of rainwater and low circulation in granite debris cause low mineral content in water available to plants in the subalpine location of the Krkonoše Mountains (Marszałek 2007). Three major factors may contribute to the final isotope composition of nitrogen dissolved in surface waters available for plants: (1) presence of symbiotic bacteria such as *Burkholderia*, which could be the primary nitrogen fixer (Belova et al. 2006; Opelt et al. 2007); (2) decomposition of previously deposited organic matter; and (3) isotope composition of rain. The last two factors may be sensitive to anthropogenic pollution. The stable isotope composition of peat also depends on the isotope composition of peat-forming plants and post-diagenetic changes in the peat. Gerdol et al. (2007) argued that *Sphagnum* growth and rates of *Sphagnum* litter decomposition can vary because of climate change, as both processes are controlled by climate factors. Based on the C and N content of *Sphagnum* and other plants collected from four bogs from various locations in Europe, Breeuwer et al. (2008) concluded that mass loss of *Sphagnum* is much more limited than that of vascular plants, therefore *Sphagnum* organic matter in bogs is more likely to be preserved than organic matter from vascular plants. Breeuwer et al. (2008, 2009) also suggested that increasing rates of atmospheric nitrogen deposition may reduce growth and accelerate decomposition of *Sphagnum* mosses in bogs. The Krkonoše Mountains area was heavily polluted during the 1980s and 1990s. The mass of peat produced during the past 25 years was negligible, as observed in the upper 5-cm horizon, which records a very low rate of peat growth (Jędrysek et al. 2003). Currently in the Krkonoše Mountains, the annual mean NO_2 concentration in air at 1,490 m asl is very low, ~4 μg/m³ (6 μg/m³ for winter and 2 μg/m³ for summer) (State Inspectorate of Environmental Protection 2004–2008, http://air.wroclaw.pios.gov.pl). Our results show that live *Sphagnum* mosses have more negative $\delta^{15}N$ (−4.36‰) compared to the peat in the core. Bragazza et al. (2005b) also reported similar values ($\delta^{15}N \sim -3.5‰$) for *Sphagnum* mosses collected from the Czech Republic. Because pristine areas have more negative $\delta^{15}N$ values than polluted areas (Elliott et al. 2007; Kendall et al. 2007), our data suggest a relatively low contribution of air pollution to the total pool of NO_x available for plants at present.

The C:N ratio of the peat sections in our core is different from the ratio in other sediments of the core. The C:N ratio of the upper pure peat horizon (45–80 cm) varies in the range of 67–85 and then gradually decreases to 33 at 120 cm, and decreases similarly from 50 to 30 in the lower peat horizon (190–260 cm). High values of C:N ratio (21–85) in our peat sections are typical for pure, well-preserved *Sphagnum* peat, which is in agreement with Kuhry and Vitt (1996). The lowest values of C:N ratio in high-ash layers are characteristic of well-decomposed organic matter (Diefendorf et al. 2008). In general, carbon is removed from organic material faster than nitrogen, so a lower C:N ratio is usually observed for more decomposed material (Staffa and Berg 1982). The C:N ratio of surface plant material (cut block of acrotelm) in our study area is ~29. The C:N ratio for separated, live *Sphagnum* mosses harvested at several altitudes in the Krkonoše Mountains varies in the range 35–49 (unpublished data from G. Skrzypek). In our study, the C:N ratios are lower for live mosses and plant cubes than for peat. A similar finding was reported by Diefendorf et al. (2008).

As discussed earlier, a strong correlation between $\delta^{13}C$ and $\delta^{15}N$, or between the isotopic composition and C:N ratio of sediment samples in a profile would suggest that the samples had undergone significant decomposition. In the core sections with high ash content, a significant correlation is observed between $\delta^{15}N$ and C:N (r^2 0.79, $P < 0.01$, and 0.78, $P < 0.01$; Fig. 6 b, d), and between $\delta^{15}N$ and $\delta^{13}C$ (r^2 0.67, $P = 0.01$, and 0.78, $P < 0.01$; Fig. 6 f, h). In contrast, poor correlations (r^2 0.35 and 0.06, 0.28 and 0.20 in Fig. 6 a, c, e, g, respectively) are observed for pure *Sphagnum* peat (ash < 10%). We observed that C:N decreases simultaneously with an increase in $\delta^{15}N$. The progressive decrease of C:N ratio is considered to be an indicator of progressive decay (Gerdol et al. 2007; Breeuwer et al. 2008). Hence, we argue that weak correlations for peat sections (low ash contents) and strong correlations for other sediments (high ash content) suggest that pure peat has experienced relatively low decomposition, and therefore, has undergone little isotopic fractionation. Because sections with high ash content have experienced significant decomposition and isotopic fractionation, the organic matter in these sections is not considered to be well-preserved. We conclude that the isotope composition of the parent organic matter is well-preserved in the peat layers.

To demonstrate that $\delta^{13}C$ of well-preserved organic matter can be used for paleoclimate interpretation, we used $\delta^{13}C$ variations in the peat core section (45–125 cm) to estimate relative variations in temperature of the growing season. This peat section includes the commonly accepted (worldwide) "transition period" at about 2.6 ka, which is recognized at the continental/global scale as the Subatlantic/Subboreal boundary (Birks and Birks 1980). The observed $\delta^{13}C$ variations in the peat (Fig. 8) are relatively small, which suggests stable environmental conditions for the growing season between ~2.8 and 2.0 ka. A distinguishable decreasing trend in $\delta^{13}C$, reaching a minimum value around 2.5 ka, is observed in samples from the depth range 105–90 cm. Following the calibration for *Sphagnum* mosses by Skrzypek et al. (2007b), this rapid decrease in $\delta^{13}C$ (0.92‰) is interpreted as a short-term warming episode at the end of the Subboreal. Occurrence of a short-term warming episode around 2.5 ka cal BP can be corroborated in future studies on $\delta^{13}C$ variations in other peat cores from Central Europe that show a minimum $\delta^{13}C$ signature during this time.

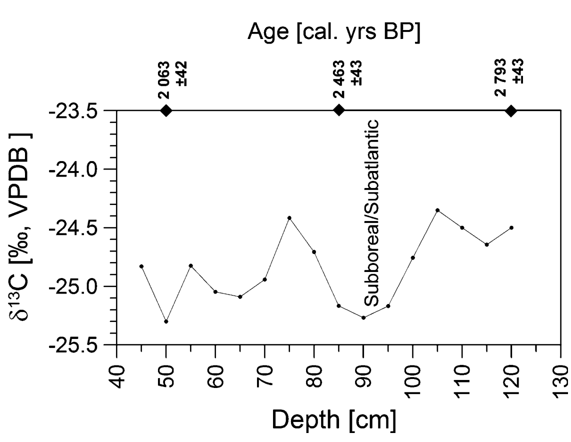

Fig. 8 Variation in $\delta^{13}C$ in the pure *Sphagnum* peat layer (45–125 cm, ~2.0–2.8 ka cal BP). The minimum $\delta^{13}C$ value during the Subboreal/Subatlantic transition period reflects short-term warming (see text for "Discussion")

Conclusions

Lithostratigraphy and geochemical signatures of a 520-cm-long sediment core obtained from the Labský důl Valley indicate that sedimentation conditions at Labský důl varied significantly during the last 7.6 ka due to substantial climate change (temperature and precipitation). Lithostratigraphy reveals five major periods of sedimentation: sedimentation of silt in a lacustrine environment, interrupted by occasional deposition of sand during flood events (520–265 cm, ~7.6–5.1 ka cal BP), accumulation of peat (265–185 cm, ~5.1–4.0 ka cal BP), sedimentation of sandy silt and sand (185–125 cm, ~4.0–2.8 ka cal BP), accumulation of raised peat (125–45 cm, ~2.8–2.0 ka cal BP), and sedimentation of sandy silt (45–20 cm, ~2.0–1.7 ka cal BP).

Our results show significant correlation between $\delta^{13}C$–$\delta^{15}N$ and $\delta^{15}N$–C:N ratio for the core horizons that typically contain clastic sediments, i.e., have ash content >10%. This suggests that the stable isotopic composition of organic matter in these horizons is affected by significant isotope fractionation due to decomposition during the burial process or redeposition. On the other hand, poor correlations between $\delta^{13}C$–$\delta^{15}N$ and $\delta^{15}N$–C:N ratios of the organic matter in *Sphagnum* peat (45–125 cm and 185–265 cm sections) suggest that relative variations in the stable isotope composition of parent organic matter are well-preserved in peat. The small $\delta^{13}C$ variation in the peat section (45–125 cm) suggests relatively stable paleoenvironmental conditions between 2.8 and 2.0 ka cal BP (125–45 cm). A distinguishable, decreasing trend in $\delta^{13}C$ around 2600 cal BP indicates a substantial short-term climate change, i.e., a warming episode at the end of the Subboreal period.

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