Chapter 5

Identifying the imprint of Milankovitch cyclicity within early Paleocene lignites (Montana, USA) using high-resolution bulk δ\textsuperscript{13}C, δ\textsuperscript{15}N, and compound-specific δ\textsuperscript{13}C isotope records

ABSTRACT

Cyclicity along bulk geochemical and geophysical variables in coal zones has been linked to climatic and environmental changes driven by the Milankovitch cycles. It is hypothesized that orbital-forced climate changes might have caused cyclic drowning and drying of peat mire environments expressed, for example, in bulk nitrogen isotope records (δ\textsuperscript{15}N). Such cyclic responses of these environments, however, can be equally caused by autogenic compensational stacking. Further, peat mire drowning and drying can cause hiatuses in the sedimentary record that may span one or more orbital cycles. Bulk carbon isotope (δ\textsuperscript{13}C) variations in early Paleocene lignites of the lower Fort Union Formation (Montana, USA) are considered to primarily record changes in atmospheric pCO\textsubscript{2} and hence climate change. The validity of this hypothesis, however, but not yet been tested by additional compound-specific δ\textsuperscript{13}C analyses. Precession-induced climate change could potentially be recognized within these lignites because previous work in this area revealed a short-eccentricity regulated climate control over peat formation. To assess if the presence of Milankovitch cyclicity in these lignites can be identified using bulk δ\textsuperscript{13}C and δ\textsuperscript{15}N, we analyze five spatially separated coal zones in the lower Fort Union Formation of north-eastern Montana (USA). We present thermo-gravimetric (TGA), bulk δ\textsuperscript{13}C, bulk δ\textsuperscript{15}N, and compound-specific δ\textsuperscript{13}C high-resolution stratigraphic records of these coal zones. We find that Milankovitch cyclicity was not obvious in the bulk δ\textsuperscript{13}C, δ\textsuperscript{15}N and TGA records, likely due to most likely post-depositional diagenetic and vegetation-compositional influences. However, short-eccentricity-paced 1-2 ‰ δ\textsuperscript{13}C changes in atmospheric CO\textsubscript{2} could be identified in unaltered carbon isotopic records of well-preserved mid- and long-chain n-alkanes.
INTRODUCTION

Cyclostratigraphic analyses of geophysical and geochemical proxy records in coal zones, intercalated in fluviodeltaic siliciclastic sedimentary sequences, have yielded series of spectral analyses peak frequencies resembling the Milankovitch cycles (Jones et al., 1997; Large et al., 2003; Large et al., 2004; Wang et al., 2011). Correspondingly, these studies attribute the origin of the cyclicity to peat mire drowning and drying, i.e. peat-environmental changes, driven by orbital-forced climate change. However, drowning and drying may result in significant non-depositional hiatuses (Jerrett et al., 2011) that may span one or more orbital cycles. Additionally, peat mire drowning and drying can result from shifts in the groundwater table associated with the autogenic processes of river channel migration and avulsion (Van Asselen et al., 2009). The resulting stratigraphic record can, therefore, also record rhythmic alternations that are not the result of orbital climate forcing, but these can be comparable with the ratios of the Milankovitch parameters (Hajek and Straub, 2017). Autogenic controls can be disentangled from allogenic forcing (in this case orbital forcing) if a stratigraphic architecture is found that bears a clear imprint of orbital forcing superimposed on sedimentation caused by autogenic processes. Although, such recognition is scarce they have been previously identified in the Permian Bainmedart coal measures of Antarctica (Fielding and Webb, 1996) and recently in Paleocene coals of the lower Fort Union Formation in Montana, USA (Noorbergen et al., 2018). Both studies postulated that orbital forcing primary controlled peat formation since the fluvial successions display laterally extensive coal-clastic repetitions and lack evidence of the gradual lateral transition of overbank peat lithofacies into time-equivalent channel-belt lithofacies. These observations reveal that autogenic channel avulsion or lateral migration cannot be responsible for the coal-clastic alternations. Fielding & Webb (1996) detected ca 20-kyr precession cycles while Noorbergen et al. (2018) identified a 100-kyr short-eccentricity-scale climate control on sedimentation. In the conceptual stratigraphic model of Noorbergen et al. (2018, model 2), the eccentricity-modulated precession cycles are considered as the major actors of climate change, since variations in solar insolation due to eccentricity alone are expected to be too small to have a significant impact on climate change (Hilgen et al., 2015). However, the question remains, if individual precession cycle forcing can be disentangled from hiatuses and autogenic fluvial processes within coal zones.

Therefore, high-resolution stratigraphic bulk δ13C, bulk δ15N, and compound-specific δ13C proxy records have been established for various of these Paleocene coal zones of the lower Fort Union Formation. Orbital-forced climate changes might have caused cyclic drowning and drying of peat mire environments, which can be documented in bulk nitrogen isotope records (δ15N) (Storme et al., 2012). Additionally, the carbon isotopic (δ13C) variations of the bulk fraction in the Fort Union coals are considered to record the δ13C of the atmosphere, which varies due to changes in atmospheric pCO2 (Arens et al., 2000; Arens and Jahren, 2000; Jerrett et al., 2015). A more novel development is the δ13C analysis of compound-specific leaf-waxes, which might provide reliable proxy records for the hydrological conditions of the peat-mire (Ficken et al., 2000) as well as atmospheric δ13C (Pancost and Boot, 2004).

Bulk isotopic data require additional investigation of other factors such as diagenesis and plant-specific fractionation (e.g. Jones et al., 1997) which can be accomplished by complementary analysis the δ13C composition of plant leaf waxes, such as long chain n-alkanes (Eglinton and Hamilton, 1967). The compounds are relatively resistant to degradation, so that variations in their δ13C value throughout a sedimentary archive can be directly linked to past changes in the δ13C composition of atmospheric pCO2 (e.g. Kuypers et al., 1999, Pancost and Boot, 2004). Deviations in the trends
of bulk δ¹³C and compound-specific δ¹³C values, can then be indicative of, for example, early-stage diagenetic processes of kinetic fractionation during plant/peat litter decomposition (Esmeijer-Liu et al., 2012).

The lower Paleocene Fort Union Formation in the Williston Basin (north-eastern Montana, USA, Fig. 5.1) comprises the so-called ZY- and X- coal zones (Collier & Knechtel, 1939; Figs. 5.1B and 5.2), which could serve as provide potential archives to identify intra-coal Milankovitch cyclicity because (1) precession-related cyclicity can be expected based on the regional recognition of superimposed eccentricity-paced coal-clastic cycles (Noorbergen et al., 2018; Chapter 4) and (2) changes in atmospheric pCO₂ may be the major contributor to bulk coal δ¹³C (Arens and Jahren, 2000). In this study, high-resolution bulk stable carbon and nitrogen isotope (δ¹³C and δ¹⁵N) proxy records were established in five spatially separated coal sections, as well as one high-resolution compound-specific n-alkane δ¹³C record of the ZY-coal-section (Figs. 5.1 and 5.2). Additionally,

**Figure 5.1.** A: Map of the study area showing the location of the five early Paleocene coal sections (yellow circles) and the location of the photograph taken that is shown in panel B (blue circle). B: Photograph of the lower Fort Union Formation at Hell Hollow, Garfield County (Montana, USA). The ZY- and X-coals are indicated.
loss-on-ignition (LOI) measurements were performed in order to determine the total organic content of the samples and the proportion of the combustible fraction. By critically evaluating the factors contributing to each of the geochemical variables we aim to decipher if orbital-forced climate signals, including precession, can be present in one or more of the proxy records, and if orbital forcing may exerted control on drowning and drying of humic peat environments in fluvial systems.

**MATERIAL**

**Sample localities**

The coals of the lower Paleocene Fort Union Formation are well-exposed in the north-eastern Montana (USA) badlands that were incised by the Missouri River and its tributaries. The targeted ZY- and X-coals overly strata with impact spherules and an Iridium (Ir) anomaly corresponding to the Cretaceous-Paleogene Boundary (KPB) impact. The KPB has been widely documented across the study area and serves as a key stratigraphic marker. An Ir anomaly (0.57 ppb) has been found at the base of the Hell Creek Road (HCR-) Z- and IrZ-coals (Baadsgaard et al., 1988), whereas the Snow Creek Road (SCR-) ZY-coal is situated 13 meters above the ~20 cm thick IrZ-coal (Swisher III et al., 1993). At the base of IrZ-coal the micro-tektite- spherule layer of the KPB with Ir anomalies

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**Figure 5.2.** A: Chrono- and regional stratigraphic context of the early Paleocene coal sections within the Wheeler diagram (Fig. 4.3) of the Garfield-McCone correlation panel (Fig. 4.2) of Chapter 4. White dashed-line rectangle refers to Fig. 5.7. Durations of magnetochrons are based on B12 (Batenburg et al., 2012) and D14 (Dinarès-Turell et al., 2014) (see Chapter 4 for more details). Bold numerically labelled coal seams 1-6 are after Noorbergen et al. (2018). B: O Orbital short (red) and long (black) eccentricity curves (Laskar et al., 2011) and the bulk marine sediment δ13C record of ODP site 1262 (green) (Kroon et al., 2007). For details see Chapter 4 and Fig. 4.3.

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up to 2.22 ppb (Alvarez, 1983) and 11.7 ppb (Smit and van der Kaars, 1984) are found at sites in the vicinity of SCR. Magnetostratigraphy across the HCR-Z-coal (Lerbekmo et al., 1996; Sprain et al., 2018) and across the SCR-ZY-coal (Chapter 4) yields reversed polarities corresponding to chron C29r (Fig. 5.2). Magnetostratigraphy across the Garbani Hill (GH-) X-coal (Sprain et al., 2018), Flat Creek (FC-) X-coal (Chapter 4), and the Bug Creek (BC-) X-coal (Noorbergen et al., 2018) reveals the transition from reversed (C29r) to normal polarities (C29n) just below or in the lower part of the X-coal (Fig. 5.2).

Sampling
A total of 34 samples, with average spacing (as) of 5 cm, over a stratigraphic interval (si) of 169 cm were taken from the Z-coal at Hell Creek Road (HCR), 42 (as=6; si=244) from the ZY-coal at Snow Creek Road (SCR), 39 (AS=6; si=222) from the X-coal at Garbani Hill (GH), 27 (AS=5; si=135) from the X-coal at Flat Creek (FC), and 26 (AS=3; si=87) from the X-coal at Bug Creek (BC). In the field (Fig. 5.1), suitable coal exposures were selected at steep hill slopes to avoid effects of deep surface weathering and slumped surfaces. The coal beds were trenched at least 1 meter deep to remove the weathered surface. Samples were pre-cleaned by removing outer crusts in the field and wrapped in aluminum foil for transport.

ANALYTICAL METHODS
Thermo-gravimetric analysis (TGA) and bulk δ¹³C and δ¹⁵N stable isotope analyses were performed at the Vrije Universiteit Amsterdam (the Netherlands) and the n-alkane-specific δ¹³C stable isotope analyses were done at Utrecht University (the Netherlands).

TGA analysis
The samples were dried overnight at 50°C, then powdered, and subsequently dried again at 50°C. The samples were placed in a Thermo-gravimetric analyzer (TGA-601, Leco Corporation) and combusted under pure O₂ immediately after the last drying cycle to remove absorbed moisture, in order to determine the weight percentages of organic fractions in the samples. Weight loss was measured stepwise with temperature trajectory up to 1000°C. The percentages of loss of on ignition (LOI), i.e. mostly organic material, were displayed as contour-maps in combination with the residue percentages. The measured total organic content of the samples was used to determine the optimal sample amount for bulk stable isotope analysis.

Bulk δ¹³C and δ¹⁵N stable isotope analysis
The bulk δ¹³C and δ¹⁵N stable isotopes were measured on Finnigan Delta+ XP Mass Spectrometer (irMS) coupled to an elemental analyzer (Flash 1112 EA) via a ConFlo ll device. Optimal analyses require 50 μg of carbon (C) and nitrogen (N). Considering a typical chemical composition of 64 wt.% C and 1 wt.% N for lignite-rank coals in the Fort Union Formation (Collier and Knechtel, 1939, Vassilev et al., 2010), the required amount of coal sample material was calculated for each sample. For the samples from siliciclastic partings and volcanic ash intervals, the percentage of total organic material obtained by the TGA analyses was also taken into account to determine the required sample amount. Untreated samples for δ¹⁵N analysis were folded in tin foil cups, whereas δ¹³C samples were treated with 37% hydrochloric acid to remove coexisting CaCO₃ prior to folding in silver foil cups. Before tightly closing the cup, samples were dried overnight at 50°C. During
analysis, the Flash oxidation reactor was set to 1020°C and the reduction reactor was at 650°C. The stable isotopes of the released CO₂ and N₂ gases were analyzed on the irMS and calculated against the CO₂ and N₂ monitoring gasses. After analysis, the international standards USGS40 and USGS41 were used to calibrate the δ¹³C and δ¹⁵N values, which are expressed against V-PDB and Nair, respectively. The isotope standards cover the whole δ¹³C and δ¹⁵N ranges of the samples. The analytical uncertainty of these control standards was < 0.2‰ (s1).

Figure 5.3. Thermogravimetric (TGA), bulk carbon isotopic (δ¹³C), and bulk nitrogen isotopic (δ¹⁵N) record of the five coal sections.
Up to four \( \delta^{13}C \) and up to three \( \delta^{15}N \) measurements repeated on the same sample generally show reproducible carbon and nitrogen bulk isotope values within < 0.2‰ (Fig. 5.3). Repeated measurements providing deviations larger than 0.5‰ were omitted (n = 12 for \( \delta^{13}C \), n = 78 for \( \delta^{15}N \)) from the total dataset of 379 \( \delta^{13}C \) and 331 \( \delta^{15}N \) measurements. Bulk stable carbon isotope records (\( \delta^{13}C \)) of the HCR-Z-coal and from the top of the SCR-ZY-coal down to the KPB (base IrZ-coal) have been previously sampled by Arens and Jahren (2000).

**n-Alkane distributions and compound-specific \( \delta^{13}C \) analysis**

Plant wax \( n \)-alkanes are found within the upper epicuticular wax layer and have an odd over even predominance (Eglinton and Hamilton, 1967). These straight chain molecules are relatively resistant against degradation and therefore \( n \)-alkanes are generally well-preserved in sedimentary record (Eglinton and Logan, 1991). Odd numbered short-chain \( n \)-alkanes (C\(_{15}\), C\(_{17}\) and C\(_{19}\)) are mainly produced by algae, whereas mid-chain \( n \)-alkanes (C\(_{21}\), C\(_{23}\), C\(_{25}\)) are produced by aquatic flora (macrophytes), and long-chain \( n \)-alkanes (C\(_{27}\), C\(_{29}\), C\(_{31}\)) by higher terrestrial plants such as trees (e.g. Eglinton and Hamilton, 1967; Ficken et al., 2000; Diefendorf et al., 2015). The relative abundance of mid- to long-chain \( n \)-alkanes can be used as a proxy for aquatic macrophyte input versus higher terrestrial plant input to lake sediment, quantified as \( P_{aq} = \frac{(C_{23} + C_{25})}{(C_{23} + C_{25} + C_{27} + C_{29})} \) (Ficken et al., 2000). According to Ficken et al. (2000), \( P_{aq} = 0.4 - 1 \) corresponds to submerged/ floating macrophytes, 0.1 - 0.4 to emergent macrophytes, and < 0.1 to higher terrestrial plants. The stable carbon isotopic compositions of plant-wax \( n \)-alkanes originating from C3 plants in the early Paleocene primarily reflect atmospheric \( pCO_2 \) (Pancost and Boot, 2004).

Based on 25 pilot samples (5 for each coal), only samples from the SCR-ZY coal contained sufficient amounts of \( n \)-alkanes for compound-specific \( \delta^{13}C \) analysis. The samples from this section were freeze-dried, after which 2.5 - 5.5 g of each sample was homogenized using mortar and pestle. Lipids were Soxhlet extracted with dichloromethane (DCM)/methanol (MeOH) 7.5:1 (v/v) for approximately 24 hours, after which the total lipid extracts were dried using rotary evaporation under near vacuum. The extracts were separated into non-polar and polar fractions using an activated Al\(_2\)O\(_3\) column and elution with hexane:DCM 9:1 (v/v) and DCM:MeOH 1:1 (v/v), respectively. The non-polar fractions, containing plant alkanes, were analyzed on a Hewlett Packard 6890 series gas
chromatograph (GC) coupled to a flame ionization detector and a flame photometric detector (GC-FID-FPD), equipped with a fused silica capillary column (30mx0.32mm) coated with CP Sil-5 CB (film thickness 0.10 μm), using helium as a carrier gas. Samples were injected on-column at 70°C. The oven was programmed to 130°C at 20°C/min, and then at 4°C/min to 320°C, at which it was held isothermal for 20 min. In cases where elemental sulfur was present, this was removed by reacting with activated Cu overnight. Samples selected for compound specific δ¹³C measurements were injected on a Hewlett Packard 6890N GC combustion coupled to a Thermo Fisher Delta Plus XP isotope ratio mass spectrometer (GC-C-irMS) with similar column properties and following the same oven program as the GC analysis. GC-C-irMS performance was checked daily by injecting a Schimmelmann B standard. The δ¹³C values are reported in ‰ against VPDB and average values are calculated based on duplicate analysis.

The δ¹³C of each plant-wax category (e.g. short-chains, long-chains) was calculated based on the weighed mean of the relative abundance of the associated n-alkanes derived from the GC-analysis.

RESULTS

Lithology, bulk δ¹³C, and bulk δ¹⁵N
Fluvial sediments (clay-, mud-, and sandstones) and tephras contain ~20% of combustible solid fraction, which LOI occurred primarily at ca 330°C. The coals show 50-100 % combustible solid fraction, where the LOI occurred dominantly at ca 550 °C (25-40 %) and to a lesser extent at ca 330 °C (10-25 %). The δ¹³C and δ¹⁵N values generally range between -26.5 to -23.5 ‰ and 2 to 5 ‰, respectively. Co-variances between bulk δ¹⁵N and bulk δ¹³C along the five records are virtually absent: 0.05 (SCR), 0.01 (HCR), -0.02 (BC), -0.21 (GH), and 0.03 (FC). The coal beds consistently show more enriched δ¹⁵N values (3.5-5 ‰) than fluvial sediments (2-3.5 ‰) for all five sections, while the δ¹³C values do not display a clear differentiation between these lithologies (Fig. 5.4). Additionally, samples derived from tephras intercalated within coal tend to occur in the enriched δ¹⁵N zone of coal lithologies.

n-Alkane occurrence, distribution, and compound-specific δ¹³C
Throughout the SCR-ZY coal section, C₁₉, C₂₁, C₂₃, C₂₅, C₂₇, C₂₉, and C₃₁ n-alkanes are present in varying distributions. Most abundant n-alkanes are C₂₃, C₂₅, and C₂₇. The Pₐq varies from 0.4 and 1 indicating the presence of submerged/ floating macrophytes (Ficken et al., 2000). The compound-specific δ¹³C varies from -31.6 to -27.6 ‰ (n-C₂₁), -30.8 to -26.9 ‰ (n-C₂₃), -30 to -27.6 ‰ (n-C₂₅), -31.7 to -28.3 ‰ (n-C₂₇), and -32.8 to -27.5 ‰ (n-C₂₉). The abundance weighed mean δ¹³C of the C₂₁, C₂₃, and C₂₅ n-alkanes, representative of aquatic (macrophytic) plants, ranges from -30.4 to -27.4 ‰. The SCR-ZY n-C₂₁-2₅ macrophyte carbon stable isotope (δ¹³Cₘₐₜ) record shows three negative excursions of 1 to 2 ‰ decrease at ca 40, 100, and 160 cm, coinciding with the coal intervals. Superimposed, the δ¹³Cₘₐₜ record shows a ca 2 ‰ negative-upward trend superimposed. At three coal-carbonaceous shale lithological boundaries the δ¹³Cₘₐₜ record merges with the n-C₃₉ higher plant carbon stable isotope (δ¹³Cₜ₉) record, while within the coals and shales the δ¹³Cₜ₉ consistently diverges with up to ~3 ‰ lighter values than δ¹³Cₘₜ. The divergent 60-cm-scale negative δ¹³Cₘₜ excursions are mostly accompanied by a Pₐq > 0.7. The lower convergence of δ¹³Cₘₜ/ δ¹³Cₜ₉ at 20 cm height is accompanied by a Pₐq of 1, the middle at 0.65 cm by 0.4, and the upper at 160 cm by 0.7 (Fig. 5.5).
DISCUSSION

Influences on bulk δ\(^{13}\)C and δ\(^{15}\)N

The lack of correlation between the bulk carbon and nitrogen isotope records (covariances range from 0.05 to -0.21) may be due to different underlying processes contributing to the total signal.

Bulk δ\(^{13}\)C

Major factors contributing to the bulk δ\(^{13}\)C signal of coal are: the in situ past peat mire environment (i.e. vegetation-compositional), atmospheric \(pCO_2\), and diagenesis (Jones et al., 1997; Lücke et al., 1999; Bechtel et al., 2008; Holdgate et al., 2009). The first two factors can be affected by orbital-forced climate changes, while orbital control on third is unlikely. The overall poor correlation of δ\(^{13}\)C with lithology (tephra, fluvial and coal) (Fig. 5.4) suggests that the bulk δ\(^{13}\)C records are only reflecting peat mire environmental changes to a minor extent, since these different environments are characterized by different vegetation. The bulk δ\(^{13}\)C variation deviating to the compound-specific δ\(^{13}\)C record (Fig. 5.6) suggests that bulk δ\(^{13}\)C was significantly affected by other factors, since \(n\)-alkanes less vulnerable to diagenesis (e.g. Kuypers et al., 1999). The increasing bulk δ\(^{13}\)C trends deviating from compound-specific δ\(^{13}\)C can be explained by early-stage diagenetic processes of kinetic fractionation during plant/peat litter decomposition causing an increase in δ\(^{13}\)C of the residual bulk organic matter (Esmeijer-Liu et al., 2012). Other differentiations between bulk and compound-specific δ\(^{13}\)C are most likely affected by a combination of vegetation-compositional (e.g. Jones et al., 1997) and overburden compaction during peat to mainly lignite, and occasionally, sub-bituminous C coal transformation (Collier and Knechtel, 1939). In contrast, the plant-wax compound-specific δ\(^{13}\)C is not easily affected by post-depositional diagenetic processes and possibly represents the in situ δ\(^{13}\)C signal mainly determined by atmospheric \(pCO_2\) (Pancost and Boot, 2004). Since we observe similar bulk δ\(^{13}\)C variations in the SCR-ZY and HCR-Z coals as Arens and Jahren (2000) we cannot agree with their interpretation stating that the bulk carbon isotopic signature of these lignites reflect atmospheric \(pCO_2\).
Bulk $\delta^{15}N$

Clusters of low $\delta^{15}N$ fluvial clastic sediment and high $\delta^{15}N$ coal (Fig. 5.4) imply a depositional-environmental control on bulk $\delta^{15}N$. The gradually increasing trend in $\delta^{15}N$ accompanying sediment to coal lithological changes may reflect drying-upward (terrestrialization) intervals (e.g. Korasidis et al., 2016) since enhanced $\delta^{15}N$ may result from $^{14}N$-enriched gas emissions in an aridifying environment leaving the soil relatively enriched in $^{15}N$ (Storme et al., 2012). Relatively low $P_{aq}$ values in the coal intervals of the SCR section support that peat layers represent relatively drier depositional environments than the fluvial sediments. These drying upward fluvial sediment-coal alternations, as possibly reflected by both bulk $\delta^{15}N$ and $P_{aq}$, can result from allogenic climate (i.e. orbital forcing) control on river flooding, as well as autogenic channel avulsion or lateral migration. Other variations in $\delta^{15}N$ might be ascribed to diagenesis such as early-stage decomposition (Esmeijer-Liu et al., 2012).

Short-eccentricity recorded by compound-specific $\delta^{13}C$ variations

The comparable 60-cm-scale cyclic patterns for the weighed mean of the mid-chain ($C_{21}$, $C_{23}$, $C_{25}$) n-alkanes ($\delta^{13}C_{mac}$) and the long-chain ($C_{29}$) n-alkane ($\delta^{13}C_{hip}$) in SCR (Fig. 5.5) suggest that macrophytes and higher plants used the same atmospheric $pCO_2$ source for leaf wax synthesis (Pancost and Boot, 2004). Since the $n$-$C_{29}$-alkanes are solely produced by higher terrestrial plants (e.g. Eglinton and Hamilton, 1967; Diefendorf et al., 2015), the $\delta^{13}C_{hip}$ changes likely reflect changes in atmospheric $pCO_2$. Nevertheless, the three 60-cm-scale 1-2‰ negative excursions in the $\delta^{13}C_{mac}$ record are accompanied by up to 3‰ lighter negative excursions in $\delta^{13}C_{hip}$. The latter record probably reflects a drowned peat mire where submerged macrophytes ($n$-$C_{21-25}$) use relatively $^{13}C$-enriched dissolved CO$_2$ in the water with respect to relatively $^{13}C$-depleted atmospheric CO$_2$ used by higher plants ($n$-$C_{29}$). Since the 60-cm-scale divergent $\delta^{13}C_{mac/hip}$ negative excursions occur within coal or clastic intervals and are accompanied by $P_{aq}>0.7$, it can be inferred that sustained peat or clastic environments generally were subaqueous. The lower convergence of $\delta^{13}C_{mac}$ and $\delta^{13}C_{hip}$ at 20 cm height, accompanied with a $P_{aq}$ value of 1, suggests a sedimentary input of emerged macrophytes and higher plants (i.e. same atmospheric CO$_2$ source) into a submerged macrophyte lake environment (Ficken et al., 2000). The middle convergence of $\delta^{13}C_{mac}$ and $\delta^{13}C_{hip}$ at 65 cm height, with a $P_{aq}$ value of 0.4, suggest the in situ presence of emerged macrophytes and higher plants colonizing a drying peat mire (Ficken et al., 2000). The upper convergence of $\delta^{13}C_{mac}$ and $\delta^{13}C_{hip}$ at 160 cm height with a $P_{aq}$ value of 0.7 suggest the in situ presence of submerged/float macrophytes in a shallow lake that derived input of higher plant material (Ficken et al., 2000). The middle convergence ($P_{aq}=0.4$) likely involves a small exposure hiatus. The occurrence of a hiatus is supported by the shape of the $\delta^{13}C_{mac}$ and $\delta^{13}C_{hip}$ peaks, which are sharper than the gentle negative $\delta^{13}C$ excursions (Figs. 5.5 and 5.6). The lower and upper convergences $\delta^{13}C_{mac}$ and $\delta^{13}C_{hip}$ suggesting input of external organic material can be both controlled by external climate or internal autogenic forcing. The middle convergence of $\delta^{13}C_{mac}$ and $\delta^{13}C_{hip}$ and the under/overlying divergent negative excursions of $\delta^{13}C_{mac}$ and $\delta^{13}C_{hip}$ do not show indications of external input of organic material and, therefore, are likely reflecting atmospheric $pCO_2$ changes. The divergent-convergent-divergent $\delta^{13}C_{mac}$ - $\delta^{13}C_{hip}$ interval may represent 1.5 to 2 atmospheric $pCO_2$ cycles covering a time span of ca 100-kyr (Figs. 5.2 and 5.7). Such 100-kyr scale $CO_2$ changes in the early Paleocene would be unambiguously paced by the short-eccentricity orbital cycle (D’Hondt et al., 1996; Kroon et al., 2007). If the coals/carbonaceous shales are connected to short-eccentricity minima (Noorbergen et al., 2018), these phases cohere with relatively $^{13}C$ enriched atmospheric $pCO_2$. The hiatal boundary at 65 cm connected to a short-eccentricity maximum chore with relatively $^{13}C$ depleted atmospheric
The lack of higher-frequency amplitude variations of CO₂ within the negative δ¹³C excursions might be due to low-amplitude precession cycles supporting the phase relation with short-eccentricity minima. The expression of precession cycles most pronounced in the short-eccentricity maxima would than coincide with the lithological boundary hiatal surface (65 cm). Precession, therefore, cannot be clearly identified in SCR neither in the four other bulk isotope records where orbitally induced climate signals were not recognized in the first place.

Decreasing δ¹³C-CO₂ following the KPB

The ca 2 ‰ depletion in δ¹³C_mac superimposed on the 60-cm-scale negative δ¹³C excursions may reflect a longer-term trend of ¹³C depletion in atmospheric pCO₂. In the open marine realm, the bulk δ¹³C record of ODP site 1262 (Walvis Ridge, S-Atlantic, Kroon et al., 2007) also shows a marked negative trend of ca 1 ‰ from ca 66 to 65.8 Ma (Fig. 5.7). This coeval δ¹³C decrease on the continent and in the ocean following the ca first 200 kyr after the KPB (66 Ma) can be explained by both enhanced terrestrial and oceanic primary productivity as the result of post-KPB global warming (e.g. Alegret et al., 2012).
CONCLUSIONS

To identify the imprint of Milankovitch cyclicity in five early Paleocene coal sections of the Fort Union Formation in north-eastern Montana (USA), multi-proxy high-resolution stratigraphic records of bulk δ13C and δ15N variables and compound-specific δ13C records have been established. The bulk δ13C records generally show a poor correlation with lithological changes thought to interrelate. Comparison with compound-specific δ13C records using n-alkanes, that do reflect autogenic-lithologic and Milankovitch cyclicity, implies that bulk δ13C was likely affected by post-depositional diagenetic processes related to early-stage decomposition. Nevertheless, the bulk δ15N record persistently shows 15N depletion among fluvial sediment and 15N enrichment among coal, reflecting lithological changes, hence, changes in the peat-forming environment. Based on bulk δ15N, however, it cannot be stated if these lithological variations reflect Milankovitch cycles or if they might also have resulted from autogenic processes. Comparable trends in δ13C in mid-chain (C21–25) n-alkanes derived from macrophytes (δ13Cmac) and long-chain (C29) n-alkanes representing higher plants (δ13Chip) suggest that the carbon isotope variations originate from atmospheric pCO2. The δ13Cmac relative to δ13Chip diverging in the gentle negative isotope excursions and converging in a sharp intercalated δ13C peak indicate macrophyte submergence-emergence-submergence, respectively. The gentle diverging δ13Cmac - δ13Chip negative excursions (submergence) occurring within coal and carbonaceous shale lithological intervals, with Paq values around 0.7, suggest peat-shale accumulation in a drowned mire. The sharp converging δ13Cmac - δ13Chip peak (emergence) aligning at a carbonaceous shale-coal boundary, with a Paq values of 0.4, suggest non-deposition in a drying peat mire. The 100-kyr duration of this drowning-drying-drowning interval is in line with 100-kyr short-eccentricity orbital forcing. Because the gentle δ13Cmac excursions do not show significant higher-frequency variations, these phases might be linked to low amplitudes of the precession cycle prevailing during short-eccentricity minima. Such a phase relation is in agreement with Noorbergen et al. (2018) proposing peat-carbonaceous shale formation linked to short-eccentricity minima. The superimposed negative trend in δ13Cmac parallel to a same negative carbon isotope excursion in the oceanic realm can be ascribed to enhanced global productivity during a ca 200-kyr time interval of post-K-Pg global warming.