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Deglacial export of pre-aged terrigenous carbon to the Bay of Biscay

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Abstract. The last deglaciation is the most recent relatively well-documented period of pronounced and fast climate warming and, as such, it holds important information for our understanding of the climate system. Notably, while research into terrestrial organic carbon reservoirs has been instrumental in exploring the possible sources of atmospheric carbon dioxide during periods of rapid change, the underlying mechanisms are not fully understood. Here we investigate the mobilization of organic matter to the Bay of Biscay at the mouth of the Channel River, where an enhanced terrigenous input has been reported for the last glacial-interglacial transition. A suite of biomarker and isotopic analyses on a high-resolution sedimentary archive provided the first direct evidence for the fluvial supply of immature and ancient terrestrial organic matter to the core location. In the light of what has been reported for other regions with present or past permafrost conditions on land, this result points to the possibility of permafrost carbon export to the ocean, caused by processes that likely furthered the observed changes in atmospheric carbon dioxide.

1 Introduction

High-latitude permafrost soils hold immense amounts of carbon (C) in the form of frozen organic matter (OM), the thawing of which induces positive feedback mechanisms that have implications for the C cycle on a global scale (Zimov et al., 2006; Schuur et al., 2008, 2009; Hugelius et al., 2014; Schuur et al., 2015). While current climate change raises concerns about the stability of these massive pools of organic C (Vonk et al., 2012; Schneider Von Deimling et al., 2015), the dynamic character of Earth's climate means that past trends and variability can be examined to improve future projections of this effect. The hypothesis of ancient terrestrial C potentially derived from thawing permafrost contributing to elevated atmospheric levels of carbon dioxide (CO_2) and methane (CH_4) during the last deglaciation is discussed in several studies (Ciais et al., 2012; Köhler et al., 2014; Crichton et al., 2016; Simmons et al., 2016). Over the course of the Last Glacial Maximum (LGM), large expanses of continuous permafrost were found in much of the Eurasian continent, including Northwest and Central Europe, covering the region from Poland through Germany, the Netherlands and Belgium into France and Great Britain, in areas where permafrost cover no longer extends (Vandenberghe and Pissart, 1993). These regions comprise the southern edge of the LGM permafrost

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area and, according to Köhler et al. (2014), are likely to have undergone thawing during the last deglaciation. However, while direct evidence for the deglacial remobilization of ancient C from permafrost has been reported for the Arctic (Tesi et al., 2016; Keskitalo et al., 2017; Martens et al., 2019, 2020; Wu et al., 2022) and subarctic (Winterfeld et al., 2018; Meyer et al., 2019), similar data are still lacking for the European realm where the phenomenon has been suggested on the basis of enhanced terrigenous biomarker concentrations in sediment cores (Ménot et al., 2006; Rostek and Bard, 2013; Soulet et al., 2013).

Petrogenic material carried by glacial meltwater may have been an additional source of aged or fossil OM to the oceans during the last deglaciation. Following glacial retreat, the mechanical erosion of bedrock such as oil shales mobilizes petrogenic C, which is transported as finely ground glacial meal to the oceans (Koppes and Hallet, 2002, 2006). Data from the Bering Sea, for example, provide evidence of a rapid supply of petrogenic fossil OM, relevant on a local scale and only during short and specific time periods (Meyer et al., 2019). The remineralization of allochtonous rock-derived C may further contribute to fossil greenhouse-gas emissions, at least on geological time scales (Schillawski and Petsch, 2008; Bouchez et al., 2010; Hilton et al., 2014; Hemingway et al., 2018; Wu et al., 2022). Therefore, if we are to accurately quantify the impact of the permafrost C feedback on Earth's climate, it is imperative to distinguish between the possible origins of the OM deposited on the continental margins over the course of the last deglaciation.

During the LGM, continental glaciers were part of the European landscape. The Fennoscandian (FIS) and the British-Irish (BIIS) ice sheets covered most of Britain, Ireland, Northern Europe and the North Sea (Bowen et al., 2002; Svendsen et al., 2004; Mangerud et al., 2004), contributing to the lower eustatic sea level and altering coastlines (e.g., Fairbanks, 1989; Lambeck, 1997; Lambeck et al., 2014). This sea-level lowstand, paired with the configuration of the BIIS and the FIS, led to a reorganization of major European drainage basins, with continental runoff being funnelled through the English Channel (Gibbard, 1988). The so-called Fleuve Manche or Channel River received the runoff of major European rivers, carrying meltwaters from glaciers and ice sheets (e.g., Antoine et al., 2003; Bourillet et al., 2003) (Figure 1). As a consequence, changes in the hydrological cycle in Europe during the last glacial-interglacial transition have induced a strong response from this system (e.g., Ménot et al., 2006; Toucanne et al., 2009, 2010). Permafrost developed in the glacier-free areas of the continent and towards the end of the last glaciation it is likely to have reached its maximum extent, with discontinuous permafrost present in regions almost as far south as the Mediterranean Sea (Vandenberghe et al., 2014). Notably, the European deglaciation was marked not only by the decay of ice sheets but also by the permanent and complete loss of this permafrost cover (e.g., Vandenberghe and Pissart, 1993; Levavasseur et al., 2011; Vandenberghe et al., 2012; Žák et al., 2012; Schaefer et al., 2014; Vandenberghe et al., 2014), which raises the possibility of permafrost-derived OM being deposited on the continental shelf at the mouth of the Channel River. Here, organic biomarkers and compound-specific radiocarbon (^{14}C) measurements of *n*-alkanoic acids isolated from a high-resolution well-dated marine sediment core retrieved from the outflow of the Channel River were used as the primary tool to evaluate this hypothesis. Together, our results led to the identification of ancient and immature OM, likely sourced from European permafrost.

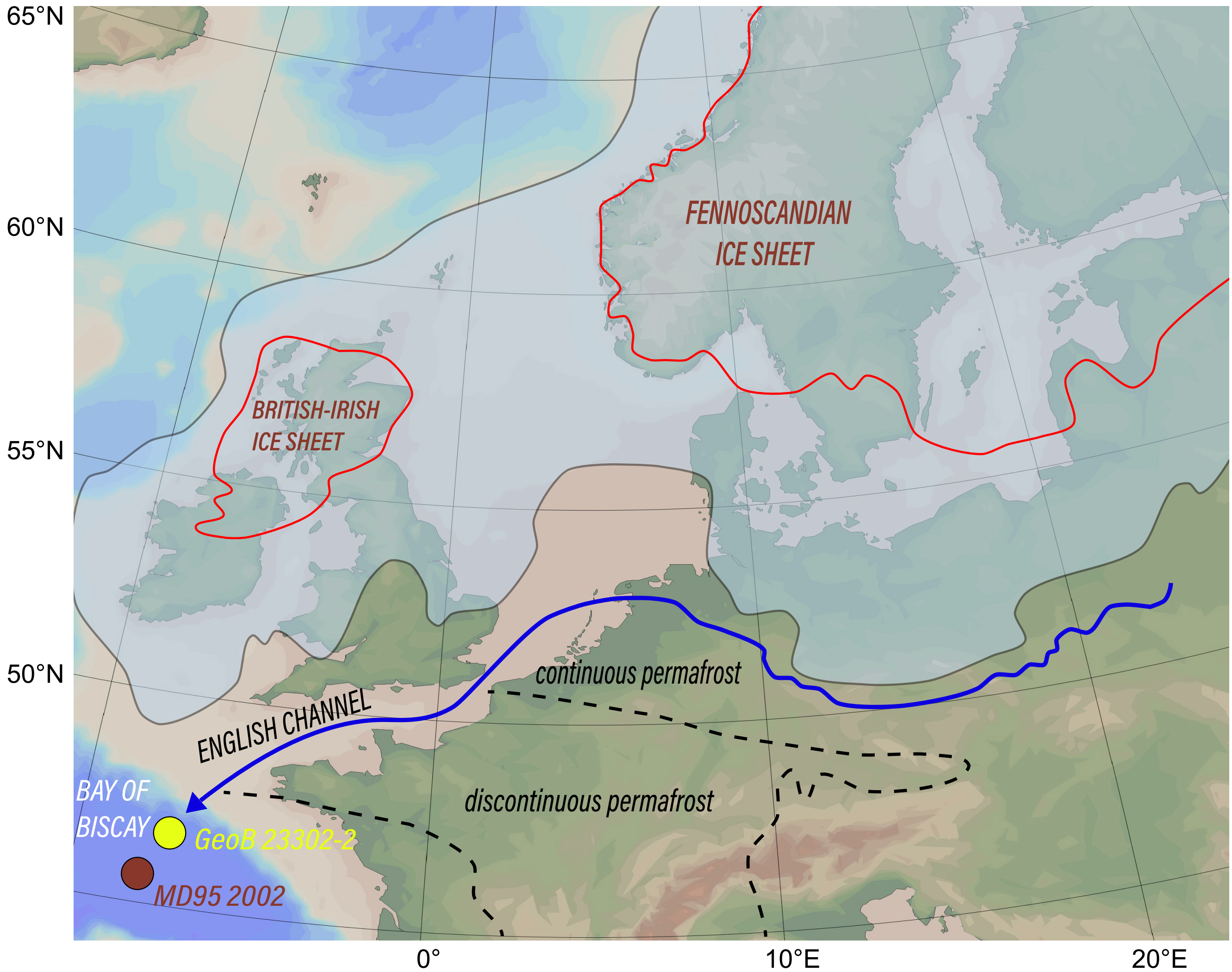

Figure 1. Northwest Europe during the LGM. The blue arrow indicates the downstream course of the Channel River from the eastern flank of the FIS. The dashed lines show the distribution of permafrost (Renssen and Vandenberghe, 2003, and references therein) and the red contours indicate the approximate limits of the ice sheets at ca. 17 ka BP (Patton et al., 2017). The yellow dot illustrates the location where core GeoB23302-2 was retrieved. Map based on that in Ménot et al. (2006), who studied core MD95 2002 from a nearby location (red dot).

2 Materials and methods

In this research we used several analytical tools to examine core GeoB23302-2 (47°26'N, 8°28'W; 2184 m water depth) (Figure 1). We report elemental ratios for zirconium (Zr), rubidium (Rb), iron (Fe) and calcium (Ca), i.e., Zr/Rb and Fe/Ca. The former is an elemental measure of grain size that has been used as a proxy for, e.g., river runoff (Dypvik and Harris, 2001; Kylander et al., 2011; Wang et al., 2011; Wu et al., 2020) while the latter is a provenance indicator, reflecting variations

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in terrigenous sediment delivery (Arz et al., 1999; Itambi et al., 2009; Dickson et al., 2010). We also calculated *n*-alkane-derived indices, namely the carbon-number preference index (CPI_{alk}) (e.g., Bray and Evans, 1961; Marzi et al., 1993) and the proxy ratio P_{aq} (Ficken et al., 2000), which are commonly used in environmental investigations (e.g., Nichols et al., 2006; Rommerskirchen et al., 2006; Zhou et al., 2012; Bush and McInerney, 2013; He et al., 2020; Feurdean et al., 2021) to assess the degree of OM degradation and reconstruct the temporal evolution of continental vegetation systems. The CPI_{alk} is based on the predominance of odd over even *n*-alkanes while the P_{aq} reflects the predominance of long-chain *n*-alkanes in terrestrial vascular plants as opposed to algae and macrophytes, which primarily synthesize short- to mid-chain *n*-alkanes (Bianchi and Canuel, 2011). While both indices indicate the relative input of aquatic macrophytes and terrestrial plants to the sediment (Ficken et al., 2000; Bush and McInerney, 2013), the CPI_{alk} is also an indicator of OM degradation (Bray and Evans, 1961; Marzi et al., 1993). Here, the branched and isoprenoid tetraether (BIT) index (Hopmans et al., 2004) is used as a proxy for the input of terrestrially-sourced OM and the f$\beta\beta$ (Meyer et al., 2019) as an indicator of petrogenic OM. Radiocarbon and $\delta^{13}C$ analyses were carried out for the construction of a dual-carbon isotope mixing model to estimate the relative contributions of different C sources to the bulk organic carbon (OC) in our samples. Finally, given that the results of bulk ^{14}C dating reflect the ^{14}C content of a heterogeneous mixture of compounds possibly derived from distinct sources, here we further address the provenance of the OM by using compound-specific ^{14}C analyses of high molecular weight *n*-alkanoic acids ($C_{26:0}$, $C_{28:0}$ and $C_{30:0}$) - which are typically derived from vascular plants (Bianchi and Canuel, 2011) - from specific depths in the core. This approach has been successfuly employed for the identification of ancient terrigenous material export at other sites (e.g., Winterfeld et al., 2018; Meyer et al., 2019; Wu et al., 2022). For methodology details, the reader is referred to the supplementary material.

3 Results

The age-depth model for core GeoB23302-2 shows a period of enhanced deposition between approximately 20 and 15 kcal BP (Supplementary Figure 1). An outlier analysis shows that the model represents well the foraminifera ^{14}C ages, with an OxCal overall agreement index of 99%. Apart from our results, Figure 2 shows the NGRIP $\delta^{18}O$ record (Andersen et al., 2004) and a time series for atmospheric CO_2 concentration (Köhler et al., 2017) (Figure 2a) as well as records for sea surface temperature (SST) in the North Atlantic Ocean (Bard et al., 2000) and $\delta^{13}C$ from European speleothems (Wainer et al., 2011) (Figure 2b). From approximately 20.6 until 15 kcal BP, the Zr/Rb ratio shows a long-term increase, whereas a period of relatively high Fe/Ca values is observed at ca. 21 - 16.4 kcal BP (Figure 2c). Values for the proxy P_{aq} are relatively low during the LGM and show a pronounced increase at approximately 21 kcal BP with higher values towards the late glacial and a sudden decrease at the onset of Heinrich event 1 (H1; ca. 17.2 kcal BP) (Figure 2d). This is followed by a sharp increase at approximately 16.5 kcal BP and a drop to Holocene values around 16.3 kcal BP. The $\mathrm{CPI_{alk}}$ and the f$\beta\beta$ proxy show relatively low values in the late glacial/early deglaciation when compared to the Holocene (Figure 2e). During the LGM, the $\mathrm{CPI_{alk}}$ values are broadly constant while an increase is observed at the beginning of H1 followed by a sharp drop around 16.5 kcal BP and a return to higher values at approximately 16.2 kcal BP. The f$\beta\beta$ record shows fluctuations during the LGM, followed by a gradual decrease starting at approximately 18 kcal BP and a sharp drop around 16.5 kcal BP before returning to higher values

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at approximately 16.2 kcal BP (Figure 2e). At the peak of our BIT record, around 18 kcal BP, compounds pre-aged by up to ca. 25,000 ^{14}C yr were delivered to the continental shelf. Pre-depositional ages broadly follow the BIT record, with younger compounds observed from the end of the BIT peak (ca. 16 kcal BP) towards the Holocene. The results of our Bayesian mixing model (Supplementary Figure 2) corroborate the BIT index record, with samples from the period of enhanced terrigenous OM deposition showing relatively high contributions of terrestrial and petrogenic C while Holocene samples are mostly marine. During the terrigenous OM peak, OC_{petro} varies from 29 ± 13.1 to 61.6 ± 13.7 %, $OC_{mar-bio}$ varies from 9.4 ± 3.9 to 39.6 ± 7 % and $OC_{ter-bio}$ from 16.4 ± 9.3 to 49.3 ± 17.2 % (Figure 3).

4 Discussion

4.1 Source of the OM in the sedimentary record

Our results corroborate the previous findings of Ménot et al. (2006), and the expanded set of elemental, geochemical and isotopic proxies analyzed here sheds light on the possible sources of the terrestrial OM reaching the Bay of Biscay during the LGM-Holocene transition. Between ca. 20.6 and 15 kcal BP, the values of the Zr/Rb ratio reflect the deposition of coarser-grain sediments at the core location. A period of relatively high Fe/Ca values (ca. 21 - 16.4 kcal BP) is indicative of a greater influx of sediment from land (Figure 2c). This is consistent with periods of enhanced terrestrial contribution to the bulk OM present in the sediment, namely from approximately 20.5 to 19 and from 19 to 16.5 kcal BP, as revealed by the BIT index (see e.g., Hopmans et al., 2004; Herfort et al., 2006; Kim et al., 2006; Schouten et al., 2013; Grotheer et al., 2020) (Figure 2f). These Fe/Ca and BIT patterns are also recorded in core MD95 2002 (see Supplementary Figures 3 and 4; Toucanne et al., 2015; Ménot et al., 2006, respectively) and a similar pattern of marked Fe/Ca peaks, sometimes associated with peaks in OM content, during Heinrich events and much lower values throughout the Holocene has been observed at other sites (Jennerjahn et al., 2004; Lebreiro et al., 2009; Zhang et al., 2015; Crivellari et al., 2018). Values for the P_{aq} proxy point to a major contribution of OM from aquatic plants between approximately 20.2 and 17.2 kcal BP, suggesting the presence of OM sourced from peat and wetland vegetation (Figure 2d). Values displayed by the CPI_{alk} (Figure 2e) are in agreement with this interpretation and together the applied proxies point to a dominance of the relative contribution of aquatic vegetation to the deposited OM towards the end of the LGM and a growing contribution of vascular plants starting at ca. 17.2 kcal BP. This result is consistent with pollen-based vegetation reconstructions that point to prevailing steppe and tundra landscapes in western and central Europe from 21 to 17 kcal BP, when woody biomes started to develop (Binney et al., 2017). Our CPI_{alk} record also provides clues to the degree of preservation of the sedimentary OM and, therefore, degradation processes happening during transportation (Bröder et al., 2018) as well as the presence of petrogenic material (Farrington and Tripp, 1977; Jeng, 2006) are additional factors to be considered for the interpretation of this record. The signal of more mature OM fluvially transported to the continental shelf is detected in our $\mathrm{CPI_{alk}}$ and f$\beta\beta$ records, which reach relatively low values during the peak of deposition when compared to the Holocene (Figure 2e). However, these two proxies are not always correlated throughout the core. For instance, at ca. 18.5 kcal BP f$\beta\beta$ values start to decrease due to the influx of more mature terrigenous OM in the sediment while $\mathrm{CPI_{alk}}$ values show an increase. This indicates that the $\mathrm{CPI_{alk}}$ record is a proxy for vegetation change rather than OM degradation during

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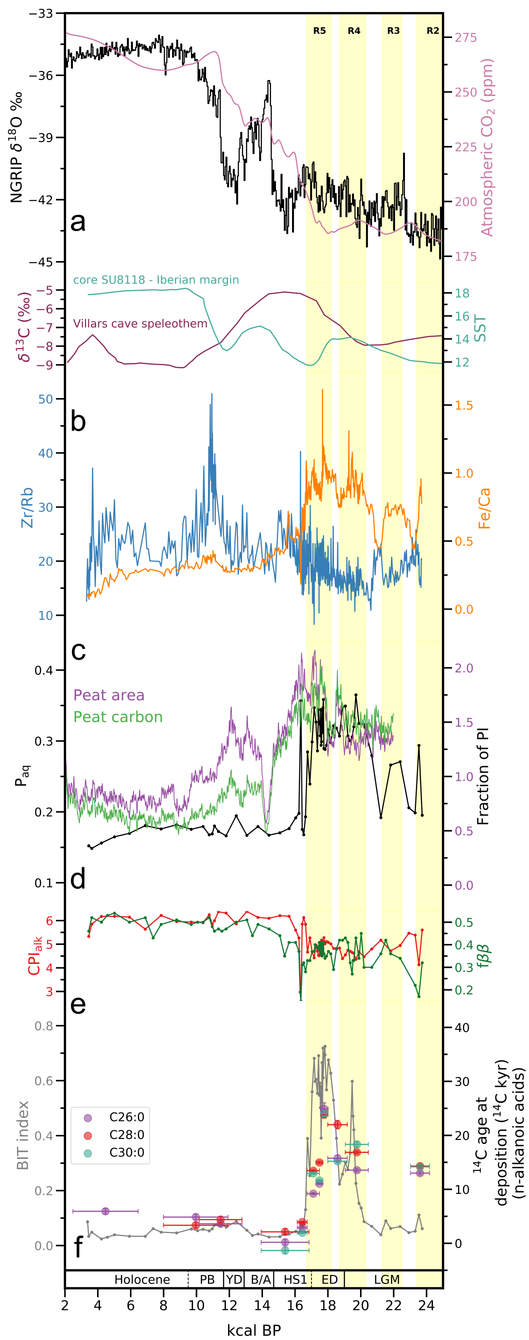

Figure 2. a: NGRIP $\delta^{18}O$ (Andersen et al., 2004) and atmospheric CO_2 (Köhler et al., 2017) records. **b:** Sea surface temperatures in the Northeast Atlantic Ocean (Bard et al., 2000) and $\delta^{13}C$ values from speleothems in Western Europe (Wainer et al., 2011). The data were smoothed to eliminate very high-frequency components. **c:** Zr/Rb and Fe/Ca elemental ratios from XRF data. **d:** Peatland area (purple) and carbon (green) in Europe as a fraction of pre-industrial (PI) values (0.231 Mkm^2 and 19.6 GtC) (Müller and Joos, 2020) and the P_{aq} index record. **e:** $f\beta\beta$ and CPI_{alk} records. **e:** Pre-depositional ^{14}C ages of *n*-alkanoic acids from core GeoB23302-2 and BIT index record. Yellow bands mark major flooding events of the Channel River (Toucanne et al., 2015).

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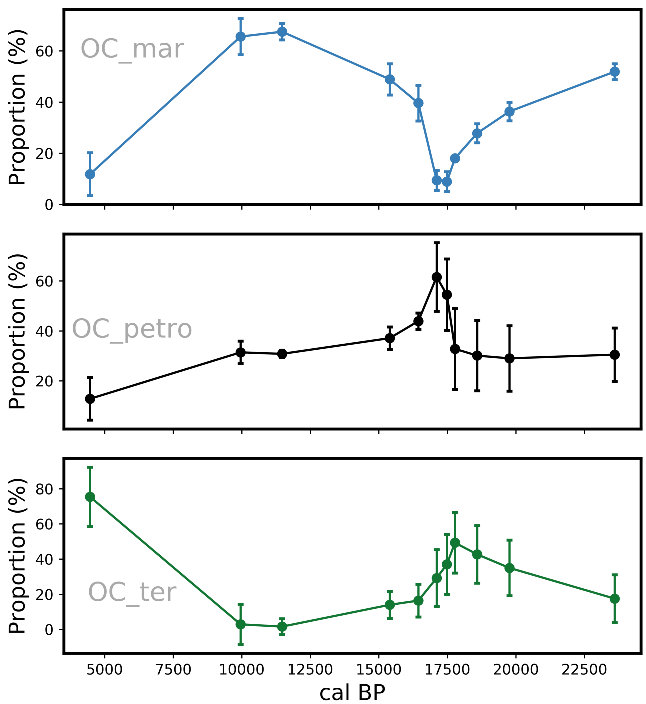

Figure 3. Results of a dual-isotope mixing model to distinguish between the contributions of $OC_{ter-bio}$, OC_{petro} and $OC_{mar-bio}$ to the bulk OM samples.

this interval (Bush and McInerney, 2013). Throughout the archive, the CPI_{alk} values remain above the diagnostic value of petrogenic material (ca. 1) reported by Bray and Evans (1961). Moreover, in contrast with the results of Meyer et al. (2019) for the Bering Sea, in the present study the f$\beta\beta$ proxy is not indicative of petrogenic material in the sediment (see Supplementary Material). This is because the values do not decrease in response to diagenetic transformations but rather due to enhanced inputs of the C31$\alpha\beta$R hopane, which is abundant in peat and lignite (Inglis et al., 2018). The latter is also known as brown coal and is a sedimentary rock that is rich in OM and whose formation process involves the compression of peat. It is, therefore, a carbonaceous material in the intermediate stage between peat and sub-bituminous coal (see e.g., Haque, 2000).

Compound-specific ^{14}C results disclose an ancient origin for the terrigenous biomarkers analyzed in this study (Figure 2f). Several mechanisms could be invoked to explain pre-aged *n*-alkanoic acids during the most recent part of our record, including deposition-resuspension loops on the continental shelf (Kusch et al., 2021, and references therein). In other words, pre-aged compounds during the Holocene are likely to be the result of lateral transport in the ocean. The pre-depositional ages of some of the compounds present in core GeoB23302-2 are considerably greater than those previously attributed to permafrost-derived OM at other sites and at different timescales (e.g., Gustafsson et al., 2011; Winterfeld et al., 2018). Although petrogenic contributions are commonly thought to be absent from *n*-alkanoic acids, this assumption does not always hold (Kvenvolden, 1966) and the erosion of organic-rich sedimentary rocks can supply OC_{petro} to the ocean, thereby depleting the ^{14}C compound-

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specific signal in the sediment (e.g., Raymond et al., 2004; Copard et al., 2007; Wu et al., 2022, and references therein). However, the OM present in core GeoB23302-2 presents δ^{13}C values heavier than those of organic-rich rocks in the region (e.g., Zhao et al., 2022). These values are rather comparable to those observed in peat (Supplementary Figure 2), corroborating the results of the CPI_{alk} and $f\beta\beta$ proxies and pointing to a pre-aged immature source such as lignite. This is supported by our Bayesian mixing model results, which point to relatively high contributions of fresh peat material ($OC_{ter-bio}$) and lignite (OC_{petro}) to the bulk OM during the peak of OM deposition (Figure 3). The pre-depositional ages during this period are likely to be the result of intermediate storage in a different reservoir and/or transit times before burial in the marine sediment (Kusch et al., 2010; Bröder et al., 2018). In fact, whenever a C reservoir differs in ^{14}C content from the coeval atmosphere a reservoir effect is established (Suiver and Polach, 1977). Indeed, similarly to what happens in the deep ocean, the C pool in deep permafrost deposits is isolated from the atmospheric input of newly formed C species, with its ^{14}C content being only subjected to decay, leading to a reservoir effect. To summarize, our results strongly support previous findings describing a massive remobilization of terrestrial C from the European continent to the North Atlantic Ocean during the last deglaciation (Ménot et al., 2006). In addition, the set of proxies applied in this study allows us to go further and suggest peat-derived material as a major source of OM to the Bay of Biscay during the last deglaciation.

4.2 Landscape development and OM remobilization mechanisms

Wetlands are ecosystems that store C and release CO_2 due to the decomposition of OM (Mitra et al., 2003). Therefore, the establishment of wetlands in the study region towards the end of the LGM (Figure 2d), combined with permafrost distribution data (e.g., Vandenberghe and Pissart, 1993; Levavasseur et al., 2011; Vandenberghe et al., 2012; Schaefer et al., 2014; Vandenberghe et al., 2014) and records of atmospheric CO_2 concentration (Köhler et al., 2017), suggests the need to investigate thawing permafrost as a possible source of OM to the deposition site. Contrary to what happened in the Holocene, large shifts in the atmospheric CO_2 reservoir are not reported for the Eemian (126 – 115 kyr BP), suggesting that vast peatland areas remained relatively stable during the penultimate glacial-interglacial transition (Brovkin et al., 2016, and references therein). Although some of these peatlands were buried by glaciers and mineral sediments, Weichselian ice sheets were not as extensive as the ones from the Saalian and some deposits remained uncovered (e.g., in Northern Germany, on the cliff of the Elbe River; Ehlers et al., 2011). Peat deposits formed during the last interglacial occur widely across the studied region (Turner, 2000), from Belgium (e.g., De Moor, 1983) and the Netherlands (e.g., Schokker et al., 2004) to Poland (e.g., Woronko et al., 2018), through Germany (e.g., Börner et al., 2018; Grube and Usinger, 2017) and Denmark (e.g., Christiansen, 1998). Although the environmental conditions of the last glaciation were unfavorable for the development of peatlands, factors such as the formation of permafrost in Europe resulted in the long-term preservation of OM from older periods (Treat et al., 2014). In Northwest and Central Europe, continuous permafrost prevailed at approximately 27-17 kcal BP (Vandenberghe and Pissart, 1993), with the deposits likely degrading and shrinking due to the warming observed at the end of the LGM. For instance, in the Netherlands, there has been evidence of widespread permafrost degradation between 22 and 21 kcal BP (Van Huissteden et al., 2000), with continuous permafrost in the Dutch coversand region completely disappearing after 20 kcal BP (Bateman and Van Huissteden, 1999). This episode is an example of permafrost thawing that may have contributed to wetland development between ca. 21

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and 16 kcal BP as recorded in our P_{aq} record (Figure 2d). Between 17 and 15 kcal BP, permafrost zones in the study region were restricted to areas near the retreating ice-sheets (Renssen and Vandenberghe, 2003, and references therein). Moreover, apart from a short later period of discontinuous permafrost (ca. 10.9 - 10.5 kcal BP) that has also been reported for Northwest and Central Europe (Vandenberghe and Pissart, 1993), there is evidence of the presence of permafrost in this region during the Younger Dryas (e.g., Isarin, 1997; Petera-Zganiacz and Dzieduszyńska, 2017).

The remobilization of OM from land to ocean is largely mediated by rivers, with factors such as precipitation and temperature being major regulators of fluvial C fluxes (Bauer et al., 2013, and references therein). Between 21 and 17 kcal BP, a temperature rise (Figure 2a) observed in various Atlantic environmental records (e.g., Arz et al., 1999; Bard et al., 2000; Combourieu Nebout et al., 2002; Pailler and Bard, 2002), marked a transition from cold and dry to warm and wet conditions in continental Europe. For example, a gradual increase in the Northeast Atlantic SST starting at about 25 kcal BP and preceding the peak of terrigenous deposition is recorded in core SU8118 (37°46'N, 10°11'W) (Bard et al., 2000). This same warming trend can be observed on land, reflected in the δ^{13}C signature of a speleothem record from Western Europe (45°30'N, 0°50'E) (Wainer et al., 2011) and starting roughly at the same time (Figure 2b). The speleothem timeseries is not high resolution and long-term trends may be in fact punctuated with short-term oscillations. In any case, it is important to acknowledge that, although speleothem δ^{13}C values can potentially serve as a proxy for temperature (see e.g., Lechleitner et al., 2021, and references therein), the correlation must be interpreted with caution due to several other factors influencing C isotopic ratios in these archives (Fohlmeister et al., 2020). Enhanced precipitation in response to warming led to increases in fluvial runoff and, due to widespread permafrost, increased erosion and transport of sediment from land to the Channel River outlet (Ménot et al., 2006). After approximately 18 kcal BP, as the climate warmed, the area occupied by peatlands in Europe increased (Müller and Joos, 2020). This is in agreement with our P_{aq} index record, which shows the re-establishment of previously frozen peatlands (Figure 2d). Processes such as thermal and physical erosion of these deposits (see e.g., Sidorchuk et al., 2009, 2011) led to pre-aged material reaching the final burial site.

The glacial erosion of underlying OM and its subsequent transport in meltwater constitute an important mechanism of C remobilization at different timescales (Cui et al., 2016; Horan et al., 2017; Meyer et al., 2019; Wadham et al., 2019, and references therein). Therefore, the erosion of European permafrost and peatland deposits by glacial meltwater is also likely to have exported OM to the ocean. The decay of the European ice sheets and glaciers at the onset of the last deglaciation (e.g., Marks, 2002; Rinterknecht et al., 2006; Ó Cofaigh and Evans, 2007; Ballantyne and Ó Cofaigh, 2017; Patton et al., 2017) contributed to strengthening the Channel River discharge at the core location (Antoine et al., 2003; Bourillet et al., 2003) and it has been proposed that this was the main mechanism controlling the river activity during this time period (Toucanne et al., 2009). Deglacial pulses of meltwater emanating from the BIIS (at 22 and 18.6 kcal BP) and the FIS (starting around 19 kcal BP) (Bowen et al., 2002; Rinterknecht et al., 2006) were routed to the North Atlantic via the Channel River. In this way, the activity of the river responded to changes in the European ice masses, being particularly influenced by the dynamics of the FIS (Toucanne et al., 2010).

Although subglacial meltwater can flow through permeable sediments as groundwater, the presence of frozen ground with reduced hydraulic transmissivity, i.e., permafrost, hinders this process (Piotrowski, 1997). This leads to trapped pressurized

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water accumulating underneath ice sheets and eventually draining during catastrophic events. As the climate warmed and the ice sheets retreated and/or permafrost decayed, bursts of subglacial meltwater were released, carving glacial features known as tunnel valleys in the ground and discharging large amounts of eroded material into rivers (Piotrowski, 1994, 1999; Kirkham et al., 2022, and references therein). Subglacial channels from major Pleistocene glaciations are still present today in Europe and serve as evidence of this phenomenon (e.g., Piotrowski, 1999; Piotrowski et al., 1999). Meltwater streams from the FIS discharged through the Elbe River and provoked several flooding events of the Channel River (Mangerud et al., 2004; Toucanne et al., 2015), with remarkable episodes (R2-R5) recorded as peaks in the ratios Ti/Ca and Fe/Ca of both the GeoB23302-2 and the MD95 2002 archives (Supplementary Figure 3). Floods R2-R5 were most likely associated with enhanced processes of erosion and sediment export in the catchment (see e.g., Bogen and Bønsnes, 2003) and the intensified freshwater influx, resulting from riverine discharge due to a mixture of precipitation and glacial meltwaters, is reflected in the terrestrially sourced OM signal shown by our BIT index record, which corroborates that reported for core MD95 2002 (Ménot et al., 2006) (Supplementary Figure 4).

Considering that the OM buried in marine sediment is only a relatively small part of the total OM entering rivers, which is predominantly returned to the atmosphere as CO_2 (e.g., Aufdenkampe et al., 2011), the OM export to the Bay of Biscay via the Channel River is likely to have been accompanied by the transfer of CO_2 and CH_4 to the atmosphere (e.g., Schneider Von Deimling et al., 2015; Schuur et al., 2015; Bröder et al., 2018). It follows that our results corroborate the hypothesis of permafrost thawing in the Northern Hemisphere contributing to the observed perturbations in the atmospheric C reservoir (Köhler et al., 2014). This essentially means that Northwest and Central Europe too, similar to other permafrost sites (Winterfeld et al., 2018; Meyer et al., 2019), may have contributed to the deglacial rise in atmospheric CO_2 (Köhler et al., 2014; Marcott et al., 2014). Our high pre-depositional ages at ca. 17.5 kcal BP (up to ca. 15 ^{14}C kyr) may partly explain the steep drop in the ^{14}C signature of atmospheric CO_2 during the period known as the Mystery Interval (17.5 – 14.5 kyr BP) (see e.g., Broecker and Barker, 2007). In other words, this result implies that thawing European permafrost combined with the deep ocean reservoir contributed ^{14}C-depleted CO_2 to the atmosphere during this period. However, our results show that the remobilization of C from this terrestrial pool started as early as ca. 20.2 kcal BP, which considerably precedes estimates of large permafrost contributions to atmospheric CO_2 between 17.5 and 15 kyr BP (Crichton et al., 2016). This suggests the need to investigate leads and lags in the permafrost carbon feedback.

After approximately 18 kcal BP, a re-routing of the Elbe-Weser system meant that FIS meltwater carrying ancient C was being delivered to the Norwegian Channel (Toucanne et al., 2010, and references therein). After 17 kcal BP, sea-level rise caused a shift of the shoreline, with the Bay of Biscay no longer being suitable to record terrestrial runoff during the Holocene (Lambeck, 1997). However, the reported terrigenous input to the Black Sea basin during H1 (Soulet et al., 2013) is likely to carry the same signal of degrading Eemian peatlands. Notably, although our data support what has been previously inferred for the study region (Ménot et al., 2006; Rostek and Bard, 2013; Soulet et al., 2013), the distinct timing for the discharge peak observed in this study compared to other sites may imply different mechanisms of C remobilization and these need to be further investigated. Indeed, factors such as the local hydrology and vegetation have been shown to play a role in the accumulation and degradation pathways of permafrost-influenced peatlands (Hugelius et al., 2020, and references therein).

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Peat-forming wetlands remain an important source of terrestrial OM to the ocean and of CH_4 and CO_2 to the atmosphere, with flux rates likely increasing due to current warming (Freeman et al., 2001; Hodgkins et al., 2014). In high northern latitudes wetlands, it has been shown that permafrost degradation leads to wetland shrinkage (Avis et al., 2011). In the tropics the situation is also critical, with anthropogenic (Moore et al., 2013) and natural (Schefuß et al., 2016; Garcin et al., 2022) factors contributing to the remobilization of pre-aged C from peatlands. Therefore, the release of large amounts of peat-derived OM described here for deglacial Europe has analogues in the present day and may be useful to inform future projections of permafrost peatland loss (e.g., Fewster et al., 2022), with our results advocating for the importance of better constraining the C cycle in wetlands.

5 Conclusions

To reconcile the great pre-depositional ages observed here with geochemical data that do not hint towards highly-degraded petrogenic material, we argue that the OM in core GeoB23302-2 is mostly derived from ancient continental peat deposits. During the last interglacial, peatlands were established in the European landscape. These deposits were widely distributed and remained relatively stable throughout the last glaciation due to the widespread presence of permafrost. Over the course of the last deglaciation, warming and episodes of ice-sheet retreat and associated flooding of the Channel River resulted in the erosion of these permafrost deposits, enhancing the downstream transport of sediment and mobilising ancient C to the core site. Our results suggest that, between 20.2 and 15.8 kcal BP, up to ca. 62% of the OM delivered to the Bay of Biscay was sourced from ancient European peatlands. After approximately 17 kcal BP, our core location was no longer suitable to record terrigenous inputs and, together with the Black Sea, the Norwegian Channel may have become the recipient of fluvially-discharged permafrost-derived C. It is likely that outgassing of part of the ancient C released from the thawing European permafrost contributed to the rapid rise of approximately 30 ppm in the atmospheric CO_2 concentration between 17.5 and 16 kcal BP, but further investigation is needed to accurately quantify the rates and magnitudes of the processes responsible for this contribution. This study provides empirical evidence of a cycle of peat formation during warm periods and long-term storage under colder conditions. Owing to the size of the C pool involved, such a mechanism is likely to bear important consequences for Earth's climate. In this context, our results will be useful to better constrain the role of ancient C mobilization and the permafrost carbon feedback in climate models.

Data availability. Data generated in this study are freely available at https://doi.pangaea.de/10.1594/PANGAEA.954937

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Competing interests. The authors declare that they have no conflict of interest.

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