



# Hydrological changes in eastern Europe during the last 40,000 yr inferred from biomarkers in Black Sea sediments



Frauke Rostek\*, Edouard Bard

CEREGE, Aix-Marseille Université, CNRS, IRD, Collège de France, 13545 Aix-en-Provence, France

## ARTICLE INFO

### Article history:

Received 10 December 2012

Available online 31 August 2013

### Keywords:

Terrigenous biomarkers

*n*-Alkanes

Methyl ketones

Drainage basin

Russian Plain

Fennoscandian Ice Sheet

Paleorivers

Permafrost

Atmospheric CH<sub>4</sub>

## ABSTRACT

The Black Sea is connected to a large drainage area including the European Russian Plain, part of the Alps and southeastern Europe. To study the hydrological changes in this basin over the last 40,000 years, we measured specific terrigenous biomarkers for wetland vegetation in well-dated sediments from the northwestern Black Sea, spanning the last glacial period (lacustrine phase) and the Holocene (marine phase). Low abundances of these biomarkers are observed during the North Atlantic ice melting and cooling events known as Heinrich Events 4 to 2, the Last Glacial Maximum and the Younger Dryas Event. Increased biomarker inputs characterize the mild climate phases known as Dansgaard–Oeschger Interstadials, the Bølling/Allerød and Preboreal Warmings indicating increased erosion due to permafrost degradation, higher primary productivity and/or wetland extension in the drainage basin. The final retreat of the Fennoscandian Ice Sheet from the Russian Plain occurs during the early part of Heinrich Event 1 and is characterized by increased biomarker concentrations in a typical series of four deglacial clay layers. For the last glacial period, the correspondence in timing between the biomarker records and the atmospheric CH<sub>4</sub> record from ice cores, suggests an important CH<sub>4</sub> contribution due to boreal permafrost thawing and wetland emission.

© 2013 University of Washington. Published by Elsevier Inc. All rights reserved.

## Introduction

Well-dated and high-resolution studies of eastern Europe environmental conditions during the last deglaciation are still very scarce, in particular those relating to the development of wetlands and peatlands following the decay of the Fennoscandian Ice Sheet and its drainage through the river system. After the thawing of carbon-rich permafrost soils during the last deglaciation, major peat zones accumulated between 50 and 67°N in northeastern Europe (Gorham, 1991; Gajewski et al., 2001; Yu et al., 2010). Variations of atmospheric CH<sub>4</sub> concentrations recorded in Greenland ice cores (Chappellaz et al., 1990, 1993; Blunier et al., 2007; Loulergue et al., 2008) suggest an important contribution from wetlands and permafrost thawing over the full glacial–interglacial cycle (Fischer et al., 2008; Baumgartner et al., 2012).

In order to study these processes and their timing, we investigate well-dated sediments from the Black Sea by analyzing a suite of terrigenous biomarkers. Our objective is then to compare these new records with other regional and global climate records to follow the deglacial dynamics in northeastern Europe. Specific *n*-alkan-2-ones and *n*-alkanes are used as indicators for peat-forming *Sphagnum* mosses which develop especially in boreal areas with cool temperatures, positive water balance and more than 500 mm of annual precipitation (Halsey and Vitt, 2000). The abundances of these biomarkers are shown to covary with climate,

hydrology/erosion, the dynamics of the Fennoscandian Ice Sheet and local environmental changes throughout the Black Sea drainage basin. The comparison between biomarker records and the CH<sub>4</sub> concentrations in Greenland ice cores illustrates the CH<sub>4</sub> contribution from wetland and permafrost from northeastern Europe.

### Modern and past environments in the Black Sea drainage basin

Together with the northern European Plain, the Russian Plain is the largest lowland landscape in Europe. Numerous peat bogs and one of Europe's biggest swamp areas (Polesia) are situated in the center of the Russian Plain and are drained by the tributaries of the Dnieper River (Göttlich, 1990; Struk, 1993). The vegetation in the Black Sea drainage basin is composed by a cool temperate forest zone north of 50°N and by a dry steppe zone between 50°N and the northeastern Black Sea coast. In the Black Sea lowland, branches of the Dnieper flow through muddy flatlands with islands of deciduous forests, wet meadows, lakes and swamps. The mountain regions (Alps and Carpathians) are covered by closed boreal forests (Struk, 1993) and are drained by the Danube and Dniester Rivers, respectively.

During the last glacial period, the northwestern part of the Russian Plain was covered by the Fennoscandian Ice Sheet (Svendsen et al., 2004; Rinterknecht et al., 2006). Its maximum southern extent occurred during the Last Glacial Maximum (LGM) and corresponded to a permafrost extension as far south as 47°N (Velichko et al., 2002; Renssen and Valderberghe, 2003; Wohlfahrth et al., 2007). Pollen analyses show that most of the ice-free areas (south of 50°N) in the Russian Plain were

\* Corresponding author. Fax: +33 4 42 50 74 21.

E-mail address: [rostek@cerege.fr](mailto:rostek@cerege.fr) (F. Rostek).

occupied by large periglacial tundra- and forest steppes in the northern part, and periglacial steppes to semi-deserts in the central and southern parts (Rousseau et al., 2001; Sidorchuk et al., 2001; Simakova, 2006; Wohlfahrth et al., 2007; Markova et al., 2009). Palynological reconstructions for the LGM show that *Sphagnum* moss was abundant in the northern vegetation zone closest to the Fennoscandian Ice Sheet and decreased towards the southern drier steppe zones (Markova et al., 2009).

In the Alps, glaciers extended to their maximum limit before 21,000 to 19,000 yr ago (Florineth and Schlüchter, 2000; Ivy-Ochs et al., 2006) and the continuous permafrost limit lowered about 600 m during the LGM and the Younger Dryas (YD), (Sailer and Kerschner, 2000; Gruber and Reitner, 2007).

Rapid climate instabilities like Dansgaard–Oeschger Events (DO; Dansgaard et al., 1993) and Heinrich Events (HE; Bond et al., 1992; Heinrich, 1988) left a near-global imprint in the ocean (Broecker et al., 1992; Clark et al., 2001; Hemming, 2004), on the continents in European pollen and lake sediment records (Tzedakis et al., 2002; Ménot and Bard, 2012), and in loess and soil deposits (Vanderberghe and Nugteren, 2001; Antoine et al., 2009). For the Russian Plain, paleoclimate studies are based on ice sheet relicts (Rinterknecht et al., 2006), paleoriver terraces (Sidorchuk et al., 2001), loess/soil sequences (Rousseau et al., 2001) and palynological data bases (Wohlfahrth et al., 2007; Markova et al., 2009). These records are of limited resolution because periglacial processes hamper a continuous recording of millennial-scale climate variations.

Relicts from large meandering paleochannels and their hydro-morphological reconstructions for the last deglaciation show that permafrost soils on the Russian and the Romanian Plains were drained and eroded by river channels and water flows several times larger and stronger than those of today (Sidorchuk et al., 2001; Howard et al., 2004). After the main melting processes, parts of these periglacial channels developed into floodplain lakes and peat bogs.

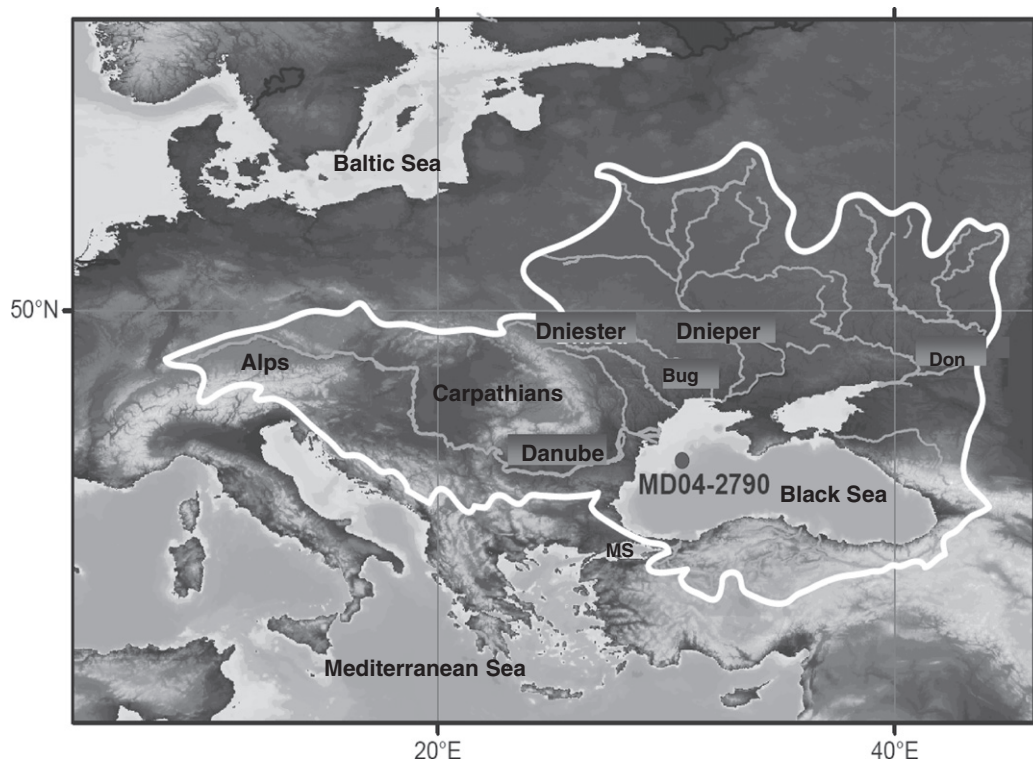
The NW Black Sea collected these large volumes of water and sediment which were transported by the Dniester and Dnieper Rivers from the European Russian Plain and by the Danube River from the Alps and southeastern Europe. Consequently, sediments from the northwestern Black Sea are an ideal archive for the reconstruction of climate-related variations in hydrology and erosion in this large drainage basin (Fig. 1).

Today the Black Sea is connected to the Marmara Sea and to the Mediterranean Sea via the Bosphorus (sill depth: –35 m). During the last glacial periods this connection was interrupted several times due to global sea-level lowering and changes in the precipitation/evaporation budget (Degens and Ross, 1974). During periods of low sea level, the hydrology of the northwest Black Sea “lake” was mainly controlled by fluvial input from the Dniester and especially from the Dnieper which was more sizeable than it is today (Bahr et al., 2005, 2006). Today the largest sediment and freshwater water input to the Black Sea derives from the Danube River (Jaoshvili, 2002; Panin and Jipa, 2002).

Complementary to continental morphological, soil and pollen climate proxies, lacustrine/marine sediments record paleoenvironmental changes continuously and at high resolution. Land plant-derived biomarkers transported by rivers document useful information about regional climate, hydrology and erosion through the strength of river runoff, and about the main vegetation changes in the drainage basin.

#### Biomarker proxies for peatlands and wetlands

Long-chain *n*-alkan-2-ones with strong odd over even dominance have been found in various environments such as soils and paleosoils (Xie et al., 2003, 2004), peat deposits (Lehtonen and Ketola, 1990, 1993; Xie et al., 2004; Zheng et al., 2010, 2011), lacustrine and marine sediments (Volkman et al., 1983; Cranwell, 1984) as well as in modern plant leaves and roots and in blue-green algae and macrophytes including seagrass



**Figure 1.** Drainage basin of the Black Sea (white contour), major tributary rivers and the position of Core MD04-2790 (ASSEMBLAGE cruise, 44°13'N/30°59'E, 28 m core length, 358 m water depth, MS = Marmara Sea).

(Wenchuan et al., 1999; Baas et al., 2000; Hernandez et al., 2001; Nichols and Huang, 2007; Jansen and Nierop, 2009; Ortiz et al., 2011). Together with indices based on mid- to long-chain *n*-alkanes (C23 to C27), *n*-alkan-2-ones are interpreted to reflect peat-forming plant inputs, especially from *Sphagnum* mosses (Lehtonen and Ketola, 1990, 1993; Pancost et al., 2002; Nichols and Huang, 2007; Bingham et al., 2010; Ortiz et al., 2010). *Sphagnum* grows in very wet and nutrient-poor areas and is abundant in the top layer of peat bogs and in moist tundra areas. Commonly, the C27 numbered homologue is the dominant *n*-alkan-2-one reported in peat plants and in peat or organic matter-rich soils (Rieley et al., 1991; Hernandez et al., 2001; Xie et al., 2003; Nichols and Huang, 2007; Ortiz et al., 2010; Huang et al., 2012).

In several studies long-chain *n*-alkan-2-ones have been interpreted as degradation products of *n*-alkanes and fatty acids due to increased microbial oxidation or decarboxylation, respectively (Albaigés et al., 1984; Cranwell et al., 1987; Rieley et al., 1991; Xie et al., 2004; Jansen and Nierop, 2009; Andersson and Meyers, 2012). In these studies, similar chain length distributions are reported for *n*-alkanes and *n*-alkan-2-ones. In peat sequences in China, the presence of *n*-alkan-2-ones is interpreted both as an authentic terrestrial biomarker from *Sphagnum* and during warmer and drier periods as a mixed signal of enhanced microbial oxidation of *n*-alkanes and direct plant input (Zheng et al., 2010, 2011).

The origin of mid- to long-chain *n*-alkanes as ubiquitous lipids in sediments is generally allocated to the input of higher plant epicuticular waxes (Eglinton and Hamilton, 1963). These leaf wax compounds are known to be resistant to degradation (Prah et al., 1997) and represent valuable biomarkers for climate reconstructions (Nichols et al., 2006; Bingham et al., 2010; Ortiz et al., 2010). While terrestrial plants such as trees, grasses and shrubs are characterized by long-chain *n*-alkanes (C27 to C31), odd mid-chain length *n*-alkanes are attributed to submerged or floating macrophytes (C21 to C25), and to *Sphagnum* mosses (C23, C25) (Baas et al., 2000; Nott et al., 2000; Pancost et al., 2002; Xie et al., 2003, 2004; Nichols et al., 2006; Vonk and Gustafson, 2009; Huang et al., 2012). Some *Sphagnum* species show a bimodal distribution with a second maximum at the C31 *n*-alkane (Nott et al., 2000; Pancost et al., 2002; Nichols et al., 2006).

In paleoenvironmental studies of peat sequences, different *n*-alkane indices have been proposed to reflect humidity around tropical lakes ( $P_{aq}$  index; Ficken et al., 2000), dominant vegetation in peat bogs (Average Chain Length (ACL) index; Pancost et al., 2002), and the presence of sub-arctic *Sphagnum* species based on the C25/(C25 + C29) ratio (Vonk and Gustafson, 2009). Interestingly, the C23 *n*-alkane has been found to be predominant in peat bogs and in numerous *Sphagnum* species (Baas et al., 2000; Nichols et al., 2006; Bingham et al., 2010; Ortiz et al., 2010). Consequently, the C23/C29 or C23/C31 ratios have been used to discriminate between the dominance of *Sphagnum* versus other higher terrestrial plants (Nott et al., 2000; Nichols et al., 2006; Bingham et al., 2010).

## Material and analytical methods

Core MD04-2790 is 2800 cm long and was taken on the NW shelf of the Black Sea at 352 m water depth (Fig. 1; 44° 12.79' N; 30° 59.61' E, *Assemblage I* cruise, 2004). Core MD04-2790 provides a continuous record of the three main sediment units of the last glacial to the Holocene Period in the northwestern Black Sea (Ross and Degens, 1974; Soulet et al., 2011a). The lacustrine sediments consist of homogenous, partly laminated muddy clay with low carbonate (CaCO<sub>3</sub>: 8–13%) and total organic carbon (TOC: 0.3–0.5%), a series of characteristic red clay layers and two authigenic carbonate layers (CaCO<sub>3</sub>: ≤65%; TOC: ≤2%). Marine sediments consist of a 75 cm thick sapropelic layer with a TOC content of 15% due to enhanced preservation of organic matter in a stratified and oxygen-poor water column. The sapropelic layer is

overlain by late Holocene laminated coccolith ooze (Soulet et al., 2011a).

Using the facilities at CEREGE, biomarker analysis was carried out every 10 cm from 2800 to 900 cm core depth and every 5 cm from 900 cm to the core top. One to five grams of freeze-dried and mortar-ground sediment was extracted with an accelerated solvent extraction system ASE200 (Dionex) using an extraction temperature of 120°C, a pressure of 100 bars and a mixture of dichloromethane/methanol (v/v: 9/1) as extraction solvent (Pailler and Bard, 2002). Gas chromatographic (GC) analyses were performed using a FID-equipped *Fisons Instrument GC8065* and a *Thermo Electron Trace GC*, a 60 m × 0.25 mm × 0.1 μm non-polar fused-silica column DB-5-MS (J&W) fitted with a 2.5 m × 0.53 μm deactivated retention gap and using hydrogen as the carrier gas. GC oven parameters were 45–200°C at 17°C/min and 200–300°C at 3°C/min. Biomarker concentrations were determined in comparison to an internal standard (ethyl triacontanoate). Several samples were measured by GC–MS using a *Trace GC* coupled to a *DSQ* quadrupole mass spectrometer (*Thermo Electron*) with similar GC conditions but using helium as the carrier gas. The identification of C23 to C33 *n*-alkanes and C23 to C31 *n*-alkan-2-ones is based on full scan analysis (40–650 amu) and the selection of single ion traces with the characteristic masses of *m/z* 59 for *n*-alkan-2-ones and *m/z* 57 for *n*-alkanes, respectively (Fig. 2; Lehtonen and Ketola, 1990). Typical single-ion trace chromatograms demonstrate a strong odd over even distribution of the carbon chain lengths in both biomarkers (Fig. 2).

Analysis of total organic carbon (TOC) was carried out at the CEREGE for the same depths as the biomarkers (Soulet et al., 2011a). The analytical method is described elsewhere (Pailler and Bard, 2002).

In order to take into account the dilution effect due to enhanced accumulation and/or enhanced preservation of TOC, the C27 *n*-alkan-2-one (Ket27) and C23 *n*-alkane (C23) concentrations (in ng/g) are normalized to %TOC (Ket27/TOC and C23/TOC, respectively in Figs. 3c,d). The C23/C31 ratio (Fig. 3e) illustrates the relative concentration differences between the odd mid-chain length *n*-alkanes (C23 and C25) and the odd long-chain *n*-alkanes (C27, C29 and C31) and represents the abundance of *Sphagnum* versus vascular land plant vegetation.

## Core chronology

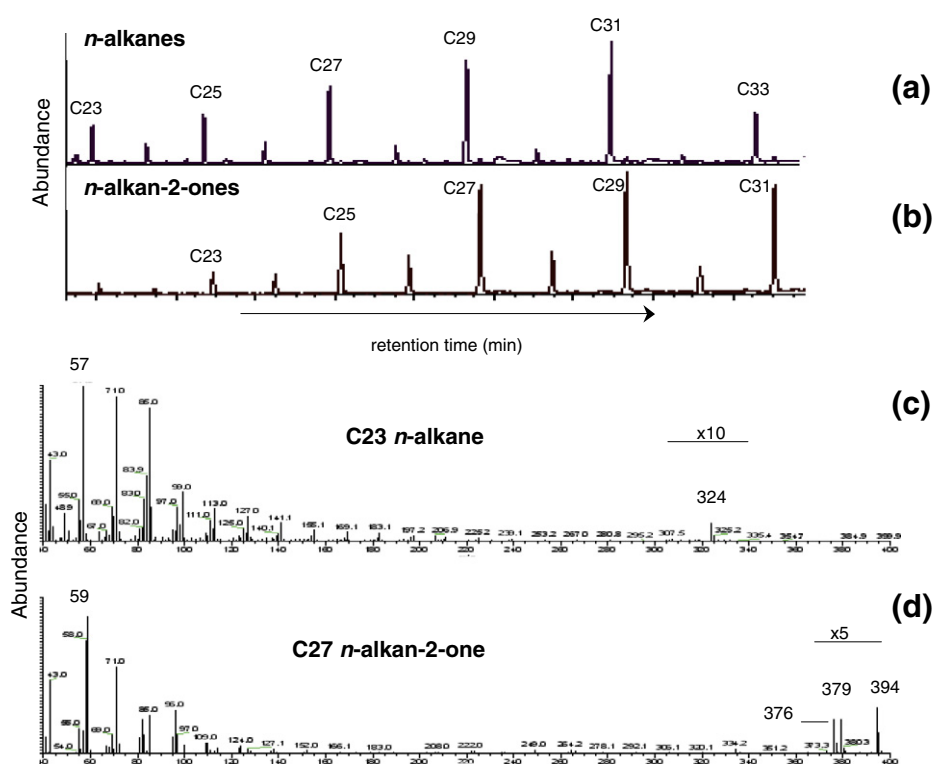
The detailed chronology for core MD04-2790 is based on 30 radiocarbon ages and was refined by varve counting and tuning to climatic records dated independently (Soulet et al., 2011a,b). For the last 17,700 yr a high-resolution XRF–Ca and the TOC record were tuned to the Hulu Cave  $\delta^{18}O$  record (Wang et al., 2001). In the red clay layers the chronology was refined by varve counting. From 17,700 to 32,000 yr ago, a lake temperature record for core MD04-2790 based on the TEX86 paleothermometer (Ménot and Bard, 2012) was tuned to the  $\delta^{18}O$  record of the Hulu Cave (Wang et al., 2001). The comparison between radiocarbon ages and tuned ages allowed the reconstruction of a high-resolution reservoir age record for the last glacial Black Sea “Lake” (Soulet et al., 2011a). For this study, the core stratigraphy was extrapolated from 32,000 yr at 22 m to the core base at 28 m, giving an age of 39,850 yr, by assuming a constant sedimentation rate.

Throughout the paper and figures, we will refer to ages obtained in core MD04-2790 with this combination of geochronological techniques. These ages are thus equivalent to calendar ages before present (1950) obtained by the U–Th method or by calibrating <sup>14</sup>C ages. In order to avoid using the term “cal yr BP” that is restricted to calibrated <sup>14</sup>C ages, we will simply refer to these ages as years (or yr ago).

## Results

Figure 2 reveals differences in chain length distribution of *n*-alkanes and *n*-alkan-2-ones in the lacustrine sediments. The *n*-alkanes are maximizing at the C31 (Fig. 2a; average chain length ACL<sub>C23–31</sub>: 28.8, st.dev.





**Figure 2.** Single-ion traces of the typical masses of (a) *n*-alkanes ( $m/z$  57) and (b) *n*-alkan-2-ones ( $m/z$  59) and mass spectra of (c) with molecular ion masses of C23 *n*-alkane ( $M^+$  324) and (d) of C27 *n*-alkan-2-one ( $M^+$  394) and M-18 (376) and M-15 (379). The sample is from a core depth of 260 cm and corresponds to an age of 13,577 yr. The difference in the chain length distribution of *n*-alkanes and *n*-alkan-2-ones and high carbon preference index (CPI) values ( $CPI_{C_{25-33}} > 6$  for *n*-alkanes and  $CPI_{Ket_{25-31}}$  of 4 for *n*-alkan-2-ones) makes it unlikely that the latter are exclusively a degradation product due to  $\alpha$ -oxidation of *n*-alkanes (Meyers and Ishiwatari, 1993; Andersson and Meyers, 2012).

0.24,  $n = 342$ ) whereas the *n*-alkan-2-ones maximize at the C29 homologue (Fig. 2b;  $ACL_{Ket_{23-31}}$ : 28.1, st.dev. 0.44,  $n = 344$ ).

The carbon preference index (CPI) indicates the degree of diagenesis (Meyers and Ishiwatari, 1993). The mean  $CPI_{C_{25-33}}$  value for *n*-alkanes in the lacustrine sediments of Core MD04-2790 is 6.6 (st.dev. 1.2;  $n = 342$ ) and the mean  $CPI_{Ket_{C_{25-31}}}$  is 4 (st.dev. 1.1;  $n = 344$ ) for the *n*-alkan-2-ones. Typical *n*-alkane CPI values for non-mature lake sediments from mid-latitude are higher than 5 (Huang et al., 2004) and higher than 3.7 in surface sediment from a periglacial paleoriver transect from northeastern Siberia (Vonk et al., 2010). In the latter, degraded sediments show CPI values lower than 2.5. Therefore the relatively high CPI values for *n*-alkanes and *n*-alkan-2-ones in the Black Sea sediments suggest that these biomarkers are not strongly affected by diagenesis.

The C23/TOC and Ket27/TOC records show a relatively tight concordance suggesting a common origin (Figs. 3c,d). The ratio C23/C31 is flatter in the lower part of the core but bears a resemblance to the C23/TOC and Ket27/TOC records in the upper core part.

## Discussion

### Hydrological and vegetation changes in the Black Sea drainage basin

#### The glacial period

Figure 3 shows the terrigenous biomarker records in comparison to the  $\delta^{18}O$  NGRIP ice core record reflecting Greenland air temperatures. The glacial interval of Core MD04-2790 between 39,850 and 17,400 yr is characterized by homogenous mud and shows major variations of terrestrial organic matter input as demonstrated by the Ket27/TOC and C23/TOC records. Intervals with lower biomarker ratios between 39,850 and 38,200 yr, 31,200 and 29,900 yr, and between 26,200 and 23,700 yr correspond stratigraphically to the North Atlantic cooling phases Heinrich Events HE4, HE3 and HE2, respectively and those between 23,700 and

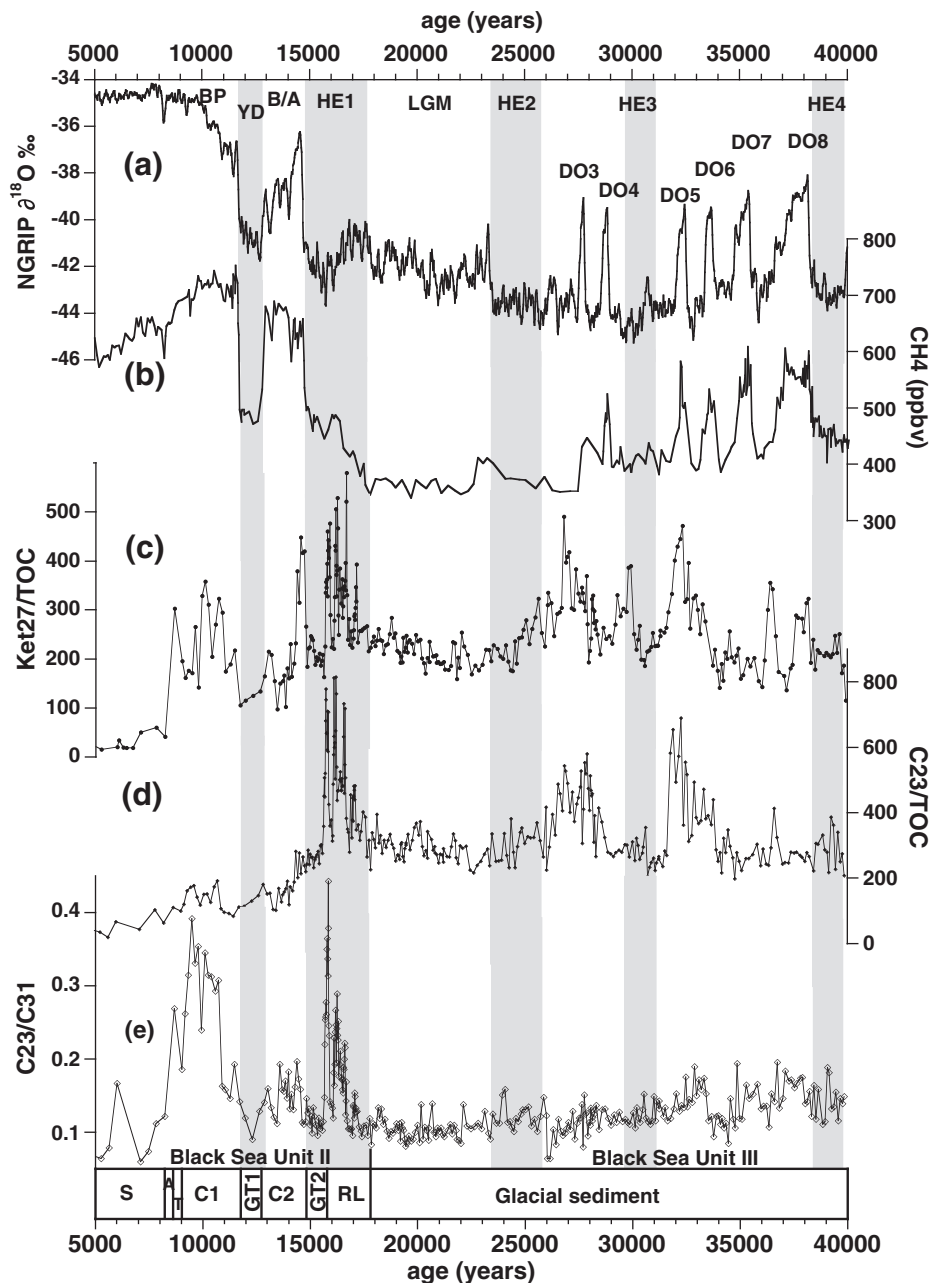
17,400 yr corresponds to the LGM. The low biomarker ratios during these cold periods suggest that permafrost extended over the Russian Plain stabilizing the soil and that erosion was decreased.

Between HE4 and HE3 (38,200–31,200 yr ago) and between HE3 and HE2 (29,900–26,200 yr ago) increased biomarker variability corresponds to the Dansgaard–Oeschger Interstadials DO 8-5 and DO 4-3 (Figs. 3c,d). During these warm phases, permafrost thawing phases occurred in the Black Sea drainage basin, decreasing the soil stability and increasing erosion in the wetlands.

During the glacial period the Black Sea drainage basin was strongly reduced because its northern part was covered by the Fennoscandian ice sheet. Riverine transport through the different environments and vegetation zones integrates a biomarker signal from the border of the ice sheet to the Black Sea. The northern periglacial tundra- and forest steppe zone were humid and rich in organic matter with abundant *Sphagnum* moss (Markova et al., 2009). In this area, the increased mobilization and runoff of soil organic matter during the DO events was most likely limited by the frozen sub-surface layer (Vonk et al., 2010). By contrast, the soils of the southern dry steppic zone contained less organic matter which diluted the river-eroded material as it flowed to the Black Sea.

The Ket27/TOC and C23/TOC biomarker records suggest that during the last glacial period, permafrost on the Russian Plain was affected by millennial-scale climate variability of the North Atlantic region probably via atmospheric circulation patterns (Broccoli and Manabe, 1987; Florineth and Schlüchter, 2000).

In contrast, the relatively constant C23/C31 ratios (between 0.06 and 0.2; mean: 0.12, st.dev. 0.04,  $n = 220$ ) show no clear relationship to millennial-scale climate variability (Fig. 3e) during this time period. This suggests that only limited changes in vegetation composition occurred in the Black Sea drainage basin. Interestingly stable and persisting ecosystems on the Russian Plain during the last glacial period have been attested from palynological studies (Markova et al.,



**Figure 3.** High-resolution paleoclimate records of Core MD04-2790 compared to (a) the  $\delta^{18}O$  record of NGRIP ice core (Andersen et al., 2004) and to (b) the composite atmospheric  $CH_4$  record from Greenland (Blunier et al., 2007). (c) C23/TOC, (d) Ket27/TOC and (e) C23/C31 as an indicator for vegetation changes in the Black Sea drainage basin. The geochemical subunits of the Black Sea sediments are given below panel (e) with Black Sea Unit II: S = Sapropel; A = Aragonite layer; T = Transitional layer; C1 = Carbonate peak 1 with up to 65% authigenic  $CaCO_3$ ; GT1 = Glacial sediment Type 1: homogenous lacustrine mud with low TOC and detrital carbonates; C2 = Carbonate peak 2 with up to 45% authigenic  $CaCO_3$ ; GT2 = Glacial sediment Type 2 as described for GT1; RL = Red Layers; Black Sea Unit III: G = Glacial sediment as described for GT1 (Bahr et al., 2005; Soulet et al., 2011a).

2009) and from recent vegetation modeling (Huntley et al., 2013). Consequently, for the glacial period, the biomarker ratios suggest mainly soil destabilization during DO events due to permafrost degradation and increased erosion, but no major vegetation changes.

#### The early part of the deglaciation

During the deglaciation between 17,400 and 15,600 yr, the Ket27/TOC and C23/TOC records show very distinct increases concomitant with the deposition of four red clay layers (RL; Fig. 3). These “Red Layers” are described as typical features in several cores from the western Black Sea (Bahr et al., 2005, 2006; Major et al., 2006). The deposition of each Red Layer took place over about 200 yr and was interrupted by typical glacial sediments for about 100 to 300 yr (Soulet et al., 2011a,

2013) with lower values of the three biomarker ratios. The deposition of the Red Layers is concomitant with the early part of HE1.

The origin of the Red Layers in the Black Sea sediments is probably related to a sporadic overflowing of a proglacial lake which formed at the southern edges of the Fennoscandian Ice Sheet (Soulet et al., 2013). Accordingly, the important and conspicuous increases of Ket27/TOC and C23/TOC in the Red Layers are related to the emerging meltwater masses which were drained through large meandering paleochannels, eroding and transporting fine argillaceous particles and terrestrial organic matter into the Black Sea. The C23/C31 ratio increases systematically in the Red Layers, suggesting an important increase of *Sphagnum* vegetation in the floodplains of the paleochannels during the deglaciation.

The particularly strong imprint of HE1 in the Black Sea is entirely related to the collapse of the Fennoscandian Ice Sheet with extremely strong fluvial erosion processes. The strong correlation of C23/TOC, Ket27/TOC and C23/C31 with changes in abrupt meltwater input manifested by inorganic geochemical proxies (Soulet et al., 2013) suggests that the biomarker ratios reflect hydrological processes and vegetation changes. In contrast, for the older Heinrich Events, low biomarker ratios suggest that the Fennoscandian Ice Sheet was stable and that riverine activity was reduced.

The youngest part of HE1 between 15,400 and 14,800 yr is characterized by typical glacial sediment (GT2; Fig. 3) and biomarker ratios as low as those observed in the older Heinrich Events, reflecting cold climate conditions with strengthened permafrost and reduced erosion.

The biomarker records show that the onset of the melting of the Fennoscandian Ice Sheet on northeastern Europe occurred at 17,400 yr. This is within the error limits of  $^{10}\text{Be}$  moraine dating ( $19,000 \pm 1600$  yr) (Rinterknecht et al., 2006), but about 3600 yr later than on the western European continent where the deglaciation started early at about 21,000 yr ago (Ménot et al., 2006). The abrupt decrease of biomarker ratios in the younger part of HE1 is compatible and concomitant with the rerouting of ice-sheet meltwater towards the Baltic Sea (Kvasov, 1979; Ehlers and Gibbard, 2004; Mangerud et al., 2004; Soulet et al., 2013) and concomitant with an extreme cooling in this second phase of HE1 (Bard et al., 2000; Denton et al., 2006).

The Bølling Warm Period between 14,800 and 14,300 yr is expressed by a sharp increase of Ket27/TOC whereas C23/TOC stays low. As mentioned above, the southern edge of the Fennoscandian Ice Sheet drained into the Baltic and the Arctic Seas at that time. Therefore a considerable input to the Black Sea came through the melting of the alpine ice domes (Darnault et al., 2011) which contributed to tributaries of the Danube River. Increasing lake temperatures and greater productivity led to authigenic calcite precipitation (C2; Fig. 3; Bahr et al., 2005). In addition, a higher lake level could have built a favorable environment for aquatic macrophytes and algae in the extended Danube and Dnieper floodplains and on the flooded shelf of the northwestern Black Sea. Macrophytes and algae could represent an additional local source of *n*-alkane-2-ones (Wenchuan et al., 1999; Hernandez et al., 2001) explaining the decoupling between Ket27/TOC and C23/TOC.

During the Allerød Period between 13,900 and 12,900 yr, low biomarker ratios suggest lower alpine meltwater input and/or reduced soil erosion due to reforestation (Bahr et al., 2005). Slightly increased C23/C31 ratios during the Bølling/Allerød (B/A) suggest a relative increase of wetland vegetation in the Black Sea drainage basin.

#### *The late part of the deglaciation*

During the YD Cold Event between 12,900 and 11,500 yr, Ket27/TOC, C23/TOC and C23/C31 show minimum values (Fig. 3). Typical glacial sediment (GT1; Fig. 3) and low biomarker ratios point to re-extending dry and cold permafrost conditions (Renssen and Valderbergh, 2003; Gruber and Reitner, 2007) and decreasing soil erosion in the Black Sea drainage basin.

At the abrupt beginning of the Preboreal warming (PB) at 11,600 yr increasing lake temperature, productivity and lake level led again to authigenic calcite precipitation (C1; Fig. 3). Ket27/TOC, C23/TOC and C23/C31 ratios increase (Fig. 3) indicating a relative increase of wetland vegetation. However, river input and terrigenous sediment supply remained low during this time interval (Bahr et al., 2005; Soulet et al., 2011a). This paradox can be explained by a major extension of boreal peat areas in the now ice-free regions (Gajewski et al., 2001; Yu et al., 2010) and/or by increased aquatic macrophyte growth in the extended Danube Delta and Dnieper Estuary regions due to lake-level rise. Indeed, pollen analyses from the Black Sea region confirm an increasing presence of freshwater marshes and swamps related to warm and humid climate conditions (Mudie et al., 2007).

Due to global sea-level rise during the mid-Holocene, the Black Sea started reconnecting to the Mediterranean Sea via the Marmara Sea

9000 yr ago (Soulet et al., 2011b). The marine phase is characterized by low Ket27/TOC and C23/TOC due to increased TOC values related to marine productivity and to the preservation of organic matter in a euxinic water column. The inflow of marine water led to intense water-column stratification and euxinic conditions at water depth >400 m and resulted in the deposition of a sapropelic layer (Bahr et al., 2006; Major et al., 2006; Soulet et al., 2011a,b).

#### *Permafrost degradation on the Russian Plain and the atmospheric CH<sub>4</sub> record*

Ice-core analyses show that atmospheric methane (CH<sub>4</sub>) concentration has varied by a factor of about two (350–800 ppbv) on orbital and millennial time scales during the last 800,000 yr, following the Dansgaard–Oeschger cycles closely during the last glacial period (Chappellaz et al., 1990, 1993; Blunier et al., 2007; Louergue et al., 2008). These past CH<sub>4</sub> variations are mostly attributed to emissions from wetlands, a third of which are located in the boreal zone (Chappellaz et al., 1990, 1993; Fischer et al., 2008; Louergue et al., 2008). A recent study shows that the inter-hemispheric difference in CH<sub>4</sub> has been relatively stable over the last 40,000 yr and that boreal wetland sources were never completely shut off during the glacial periods (Baumgartner et al., 2012). In addition to continental wetlands, a further contribution could have come from the flooding of the continental shelves in the tropics and subtropics during periods of rapid sea-level rise (Ridgwell et al., 2012).

In order to fingerprint the wetland and permafrost contributions from northeastern Europe to global atmospheric CH<sub>4</sub> concentrations, we compare the biomarker record from the Black Sea with the CH<sub>4</sub> record from ice cores (Figs. 3b,c). For the last glacial period between 40,000 and 25,000 yr, Ket27/TOC and C23/TOC maxima correspond to warmer/more humid DO interglacial events, concomitant with atmospheric CH<sub>4</sub> increases. The correspondence suggests that permafrost thawing, subsequent soil availability and wetland areas on the Russian Plain potentially may have represented a boreal CH<sub>4</sub> source during DO events. During the cold LGM, Ket27/TOC, C23/TOC and CH<sub>4</sub> are low and stable suggesting permafrost stability due to low air temperatures. Our results for the DO events and the LGM are compatible with the calculated CH<sub>4</sub> source distribution – tropical or northern hemisphere wetlands – reconstructed from polar ice-core records (Baumgartner et al., 2012).

The time period of HE1 is of particular interest because North Atlantic sea-surface temperature records suggest extremely cold temperatures (Bond et al., 1992; Bard et al., 2000). However, due to increasing insolation continental ice sheets and mountain glaciers diminished in volume and snowlines retreated (Denton et al., 2006; Williams et al., 2012). In addition, global sea level rose during the same period (Bard et al., 1990; Peltier and Fairbanks, 2006; Carlsen and Clark, 2012). Atmospheric CH<sub>4</sub> starts to increase at the onset of HE1 at about 17,400 yr and is accompanied by prominent biomarker increases (Fig. 3). This abrupt start also corresponds to the deposition of the Red Layers, which mark the beginning of the melting of the eastern Fennoscandian Ice Sheet.

By contrast, during the younger part of HE1 (corresponding to H1a; Bard et al., 2000) between 15,600 and 14,700 yr, Ket27/TOC and C23/TOC decrease to glacial values suggesting similar dry and cold conditions on the Russian Plain to those of the older HE. Interestingly atmospheric CH<sub>4</sub> did not drop but rather paused at a value of 450 ppbv above the glacial level of 350 ppbv (Fig. 3). This may be linked to a CH<sub>4</sub> contribution from the shelves, flooded due to rapid sea-level rise (Ridgwell et al., 2012) and to the now larger ice-free areas on the continents.

Greenland temperatures, atmospheric CH<sub>4</sub> and Black Sea biomarker ratios increase abruptly at the beginning of the warm Bølling Period at 14,800 yr. This suggests a causal relationship between northern hemisphere temperature increase, permafrost degradation and/or wetland extension and CH<sub>4</sub> emission. Due to the increasing contribution of



both boreal and tropical sources, the atmospheric CH<sub>4</sub> concentrations increase to typical full interglacial values (Chappellaz et al., 1997) and exhibit a larger interhemispheric difference (Baumgartner et al., 2012). The correspondence of the records suggests that the final retreat of the Fennoscandian Ice Sheet from the eastern European Plain contributes to increasing global CH<sub>4</sub> concentrations by increasing wetland areas or thaw lakes.

The shutdown of CH<sub>4</sub> emissions to low values during the Younger Dryas is related to the re-extension of stable permafrost (Fischer et al., 2008) and is mirrored by low values of biomarkers (Fig. 3). By contrast, the abrupt Early Holocene temperature increase led to deep thawing of large boreal permafrost areas, and CH<sub>4</sub> emissions increased rapidly to full interglacial values. The lowering of atmospheric CH<sub>4</sub> concentrations in the Mid-Holocene results from a drying period of the tropics (Flückiger et al., 2002) whereas the concomitant decrease in biomarkers in the Black Sea record is mainly related to sea-level rise and the reconnection of the Black Sea with the Mediterranean Sea.

## Conclusions

Long-chain *n*-alkan-2-ones (Ket27/TOC) and *n*-alkanes (C23/TOC) in Black Sea sediments are useful indicators for the variation of permafrost thawing and/or of wetland extension as well as for fluvial periglacial soil erosion in its drainage basin during the last 40,000 yr.

During the last glacial period, the biomarker records correlate clearly with paleohydrological changes in eastern Europe due to millennial climate variations known as Dansgaard–Oeschger and Heinrich events. DO interstadials are characterized by biomarker increases whereas biomarkers decrease during the LGM and cold Heinrich events 4 and 2.

During the last deglaciation, the biomarker ratios increase precisely with the start of the Fennoscandian Ice Sheet retreat during the oldest part of HE1 which is accompanied by the deposition of the typical series of Red Layers. During the youngest part of HE1 between 15,500 and 14,800 yr, the biomarker ratios are compatible with rerouting of ice sheet meltwaters toward the Baltic Sea. Further biomarker variations are coherent with subsequent climatic phases such as the Bølling/Allerød, the Younger Dryas and the Preboreal periods.

The comparison between the Black Sea terrigenous biomarkers and the global atmospheric CH<sub>4</sub> record for the last 40,000 yr suggests that boreal wetland and permafrost changes contributed to global atmospheric CH<sub>4</sub> variations over the glacial and deglaciation periods.

## Acknowledgments

Core MD04-2790 was collected during a RV *Marion Dufresne* cruise in 2004 as part of the ASSEMBLAGE project conducted by G. Lericolais, funded by the European Commission (EVK3-CT-2002-00090) and supported by the Institut Polaire Français (IPEV). We thank T. Blunier for providing numerical CH<sub>4</sub> data. Paleoclimate work at CEREGE is supported by the European Community (Project Past4Futur) and the Collège de France.

## References

Albaigés, J., Algaba, J., Grimalt, J., 1984. Extractable and bound neutral lipids in some lacustrine sediments. *Organic Geochemistry* 6, 223–236.

Andersen, K.K., Azuma, N., Barnola, J.M., et al., 2004. High-resolution record of Northern Hemisphere climate extending into the last interglacial period. *Nature* 431, 147–151.

Andersson, R., Meyers, P.A., 2012. Effect of climate change on delivery and degradation of lipid biomarkers in a Holocene peat sequence in the Eastern European Russian Arctic. *Organic Geochemistry* 53, 63–v72.

Antoine, P., Rousseau, D.-D., Moine, O., Kunesch, S., Hatté, C., Lang, A., Tissoux, H., Zöller, L., 2009. Rapid and cyclic aeolian deposition during the Last Glacial in European loess: a high-resolution record from Nussloch, Germany. *Quaternary Science Reviews* 28 (25–26), 2955–2975.

Baas, M., Pancost, R., van Geel, B., Sinninghe, Damsté, J., 2000. A comparative study of lipids of *Sphagnum* species. *Organic Geochemistry* 31, 535–541.

Bahr, A., Lamy, F., Arz, H., Kuhlmann, H., Wefer, G., 2005. Late glacial to Holocene climate and sedimentation history in the NW Black Sea. *Marine Geology* 214, 309–322.

Bahr, A., Arz, H., Lamy, F., Wefer, G., 2006. Late glacial to Holocene paleoenvironmental evolution of the Black Sea, reconstructed with stable oxygen isotope records obtained on ostracod shells. *Earth and Planetary Science Letters* 241, 863–875.

Bard, E., Hamelin, B., Fairbanks, R.G., Zindler, A., 1990. Calibration of the 14C timescale over the past 30,000 years using mass spectrometric U–Th ages from Barbados corals. *Nature* 345, 405–410.

Bard, E., Rostek, F., Turon, J.-L., Gendreau, S., 2000. Hydrological impact of Heinrich events in the subtropical Northeast Atlantic. *Science* 289, 1321–1324.

Baumgartner, M., Schilt, A., Eicher, O., Schmitt, J., Schwander, J., Spahni, R., Fischer, H., Stocker, T.F., 2012. High-resolution interpollar difference of atmospheric methane around the Last Glacial Maximum. *Biogeosciences Discussions* 9, 5471–5508.

Bingham, E.M., McClymont, E.L., Välranta, M., Mauquoy, D., Roberts, Z., Chambers, F.M., Pancost, F.M., Evershed, R.P., 2010. Conservative composition of *n*-alkane biomarkers in *Sphagnum* species: implications for palaeoclimate reconstruction in ombrotrophic peat bogs. *Organic Geochemistry* 41, 214–220.

Blunier, T., Spahni, R., Barnola, J.-M., Chappellaz, J., Loulergue, L., Schwander, J., 2007. Synchronization of ice core records via atmospheric gases. *Climate of the Past* 3, 325–330.

Bond, G., Heinrich, H., Broecker, W., Labeyrie, L., McManus, J., Andrews, J., Huon, S., Jantschik, R., Clasen, S., Simet, C., 1992. Evidence for massive discharges of icebergs into the North Atlantic ocean during the last glacial period. *Nature* 360, 245–249.

Broccoli, A.J., Manabe, S., 1987. The influence of continental ice, atmospheric CO<sub>2</sub>, and land albedo on the climate of the last glacial maximum. *Climate Dynamics* 1, 87–99.

Broecker, W., Bond, G., Klas, M., Clark, E., McManus, J., 1992. Origin of the northern Atlantic's Heinrich events. *Climate Dynamics* 6, 265–273.

Carlsen, A.E., Clark, P.U., 2012. Ice sheet sources of sea level rise and freshwater discharge during the last deglaciation. *Reviews of Geophysics* 50, RG4007.

Chappellaz, J., Barnola, J.M., Raynaud, D., Korotkevich, Y.S., Lorius, C., 1990. Ice-core record of atmospheric methane over the past 160,000 years. *Nature* 345. <http://dx.doi.org/10.1038/345127a0>.

Chappellaz, J., Blunier, T., Raynaud, D., Barnola, J.-M., Schwander, J., Stauffer, B., 1993. Synchronous changes in atmospheric CH<sub>4</sub> and Greenland climate between 40 and 8 kyr BP. *Nature* 366. <http://dx.doi.org/10.1038/366443a0>.

Chappellaz, J., Blunier, T., Kints, S., Dällenbach, A., Barnola, J.-M., Schwander, J., Raynaud, D., Stauffer, B., 1997. Changes in the atmospheric CH<sub>4</sub> gradient between Greenland and Antarctica during the Holocene. *Journal of Geophysical Research* 102, 15987–15997.

Clark, P.U., Marshall, S.J., Clarke, G.K.C., Hostetler, S.W., Licciardi, J.M., Teller, J.T., 2001. Freshwater forcing of abrupt climate change during the last glaciation. *Science* 293, 283–287.

Cranwell, P.A., 1984. Alkyl esters, mid chain ketones and fatty acids in late glacial and postglacial lacustrine sediments. *Organic Geochemistry* 6, 115–124.

Cranwell, P.A., Eglinton, G., Robinson, N., 1987. Lipids of aquatic organisms as potential contributors to lacustrine sediments – II. *Organic Geochemistry* 11 (6), 513–527.

Dansgaard, W., Johnsen, S.J., Clausen, H.B., Dahl-Jensen, D., Gundestrup, N.S., Hammer, C.U., Hvidberg, C.S., Steffensen, J.P., Sveinbjörnsdóttir, A.E., Jouzel, J., Bond, G., 1993. Evidence for general instability of past climate from a 250-kyr ice-core record. *Nature* 364, 218–220.

Darnault, R., Rolland, Y., Braucher, R., Bourlès, D., Revel, M., Sanchez, G., 2011. Timing of the last deglaciation revealed by receding glaciers at the Alpine-scale: impact on mountain geomorphology. *Quaternary Science Reviews* 31, 127–142.

Degens, E.T., Ross, D.A., 1974. The Black Sea – Geology, Chemistry, and Biology. American Association of Petroleum Geologists, Tulsa, Oklahoma (633 pp.).

Denton, G.H., Broecker, W.S., Alley, R.B., 2006. The mystery interval 17.5 to 14.5 kyrs ago. *PAGES News* 14 (2), 14–16.

Eglinton, G., Hamilton, R.J., 1963. The distribution of alkanes. In: Swain, T. (Ed.), *Chemical Plant Taxonomy*. Academic Press, New York, pp. 187–218.

Ehlers, J., Gibbard, P.L., 2004. Quaternary Glaciations – Extent and Chronology, Part I: Europe. Elsevier 461.

Ficken, K.J., Li, B., Swain, D.L., Eglinton, G., 2000. An *n*-alkane proxy for the sedimentary input of submerged/floating freshwater aquatic macrophytes. *Organic Geochemistry* 31, 745–749.

Fischer, H., Behrens, M., Bock, M., Richter, U., Schmitt, J., Loulergue, L., Chappellaz, J., Spahni, R., Blunier, T., Leuenberger, M., Stocker, T.F., 2008. Changing boreal methane sources and constant biomass burning during the last termination. *Nature* 452, 864–867.

Florineth, D., Schlüchter, C., 2000. Alpine evidence for atmospheric circulation patterns in Europe during the Last Glacial Maximum. *Quaternary Research* 54, 295–308.

Flückiger, J., Monnin, E., Stauffer, B., Schwander, J., Stocker, T.F., Chappellaz, J., Raynaud, D., Barnola, J.-M., 2002. High-resolution Holocene N<sub>2</sub>O ice core record and its relationship with CH<sub>4</sub> and CO<sub>2</sub>. *Global Biogeochemical Cycles* 16 (1), 1010. <http://dx.doi.org/10.1029/2001GB001417>.

Gajewski, K., Viau, A., Sawada, M., Atkinson, D., Wilson, S., 2001. *Sphagnum* peatland distribution in North America and Eurasia during the past 21,000 years. *Global Biogeochemical Cycles* 15 (2), 298–310.

Gorham, E., 1991. Northern peatlands – role in the carbon-cycle and probable responses to climatic warming. *Ecological Applications* 1, 182–195.

Göttlich, K. (Ed.), 1990. Moor- und Torfkunde. E. Schweizerbart'sche Verlagsbuchhandlung, Stuttgart, p. 529.

Gruber, A., Reitner, J.M., 2007. Dating of mass movements by rock glaciers: examples from the eastern Alps. *Geophysical Research Abstracts*, 9. European Geosciences Union, p. 03945 (SRef-ID: 1607-7962/gra/EGU2007-A-03945).

Halsey, L.A., Vitt, D.H., 2000. *Sphagnum*-dominated peatlands on North America since the Last Glacial Maximum: their occurrence and extent. *The Bryologist* 103 (2), 334–352.

Heinrich, H., 1988. Origin and consequences of cyclic ice rafting in the Northeast Atlantic Ocean during the past 130,000 years. *Quaternary Research* 29 (2), 142–152.

Hemming, S., 2004. Heinrich Events: massive late Pleistocene detritus layers of the North Atlantic and their global climate imprint. *Reviews of Geophysics* 42, RG1005. <http://dx.doi.org/10.1029/2003RG000128>.

- Hernandez, M.E., Mead, R., Peralba, M.C., Jaffé, R., 2001. Origin and transport of *n*-alkan-2-ones in a subtropical estuary: potential biomarkers for seagrass-derived organic matter. *Organic Geochemistry* 32, 21–32.
- Howard, A.J., Macklin, M.G., Bailey, D.W., Mills, S., Andreescu, R., 2004. Late-glacial and Holocene river development in the Teleorman Valley on the southern Romanian Plain. *Journal of Quaternary Science* 19 (3), 271–280.
- Huang, Y., Shuman, B., Wang, Y., Webb, T., 2004. Hydrogen isotope ratios of individual lipids in lake sediments as novel tracers of climatic and environmental change: a surface sediment test. *Journal of Paleolimnology* 31, 363–375.
- Huang, X., Xue, J., Zhang, J., Qin, Y., Meyers, P., Wang, H., 2012. Effect of different wetness conditions on *Sphagnum* lipid composition in the Erxianyan peatland, central China. *Organic Geochemistry* 44, 1–7.
- Huntley, B., Allen, J.R.M., Collingham, Y.C., Hickler, T., Lister, A.M., Singarayer, J., Stuart, A.J., Sykes, M.T., Valdes, P.J., 2013. Millennial climatic fluctuations are key to the structure of last glacial ecosystems. *PLoS One* 8 (4), e61963.
- Ivy-Ochs, S., Kerschner, H., Kubik, P.W., Schlüchter, C., 2006. Glacier response in the European Alps to Heinrich Events 1 cooling: the Gschnitz stadial. *Journal of Quaternary Sciences* 21 (2), 115–130.
- Jansen, B., Nierop, K.G.J., 2009. Methyl ketones in high altitude Ecuadorian Andosols confirm excellent conservation of plant-specific *n*-alkane patterns. *Organic Geochemistry* 40, 61–69.
- Jaoshvili, S., 2002. The rivers of the Black Sea. In: Khomerki, I., Gigineishvili, G., Kordzadze, A. (Eds.), Technical Report No 71, European Environment Agency. European Environment Agency, Copenhagen, Denmark.
- Kvasov, D.D., 1979. The Late-Quaternary history of large lakes and inland seas of eastern Europe. *Annales Academiae Scientiarum Fennicae AIII* 127, 1–71.
- Lehtonen, K., Ketola, M., 1990. Occurrence of long-chain acyclic methyl ketones in *Sphagnum* and *Carex* peats of various degrees of humification. *Organic Geochemistry* 15 (3), 275–280.
- Lehtonen, K., Ketola, M., 1993. Solvent-extractable lipids of *Sphagnum*, *Carex*, *Bryales* and *Carex-Bryales* peats: content and compositional features vs peat humification. *Organic Geochemistry* 20 (3), 363–380.
- Loulergue, L., Schilt, A., Spahni, R., Masson-Delmotte, V., Blunier, T., Lemieux, B., Barnola, J.-M., Raynaud, D., Stocker, T., Chappellaz, J., 2008. Orbital and millennial-scale features of atmospheric CH<sub>4</sub> over the past 800,000 years. *Nature* 453, 383–386.
- Major, C., Goldstein, S.L., Ryan, W., Lericolais, G., Piotrowski, A.M., Hajdas, I., 2006. The co-evolution of Black Sea level and composition through the last deglaciation and its paleoclimatic significance. *Quaternary Science Reviews* 25, 2031–2047.
- Mangerud, J., et al., 2004. Ice-dammed lakes and rerouting of the drainage of northern Eurasia during the Last Glaciation. *Quaternary Science Reviews* 23, 1313–1332.
- Markova, A.K., Simakova, A.N., Puzachenko, A.Y., 2009. Ecosystems of Eastern Europe at the time of maximum cooling of the Valdai glaciation (24–18 kyr BP) inferred from data on plant communities and mammal assemblages. *Quaternary International* 201, 53–59.
- Ménot, G., Bard, E., 2012. A precise search for drastic temperature shifts of the past 40,000 years in southeastern Europe. *Paleoceanography* 27, PA2210. <http://dx.doi.org/10.1029/2012PA002291>.
- Ménot, G., Bard, E., Rostek, F., Weijers, J.W.H., Hopmans, E.C., Schouten, S., Sinninghe Damsté, J.S., 2006. Early reactivation of European rivers during the last deglaciation. *Science* 313, 1623–1625.
- Meyers, P.A., Ishiwatari, R., 1993. Lacustrine organic geochemistry – an overview of indicators of organic matter sources and diagenesis in lake sediments. *Organic Geochemistry* 20 (7), 867–900.
- Mudie, P.J., Marret, F., Aksu, A.E., Hiscott, R.N., Gillespie, H., 2007. Palynological evidence for climatic change, anthropogenic activity and outflow of Black Sea water during the late Pleistocene and Holocene: centennial- to decadal-scale records from the Black and Marmara Seas. *Quaternary International* 167–168, 73–90.
- Nichols, J.E., Huang, Y., 2007. C23–C31 *n*-alkan-2-ones are biomarkers for the fresh *Sphagnum* in genus water peatlands. *Organic Geochemistry* 37, 1972–1976.
- Nichols, J.E., Booth, R.K., Jackson, S.T., Pendall, E.G., Huang, Y., 2006. Paleohydrologic reconstruction based on *n*-alkane distributions in ombrotrophic peat. *Organic Geochemistry* 37, 1505–1513.
- Nott, C.J., Xie, S., Avsejs, L.A., Maddy, D., Chambers, F.M., Evershed, R.P., 2000. *n*-Alkane distributions in ombrotrophic mires as indicators of vegetation change related to climatic variation. *Organic Geochemistry* 31, 231–235.
- Ortiz, J.E., Gallego, J.L.R., Torres, T., Diaz-Bautista, A., Sierra, C., 2010. Paleoenvironmental reconstruction of Northern Spain during the last 8000 cal yr BP based on the biomarker content of the Ronanzas ombrotrophic bog (Asturias, northern Spain). *Organic Geochemistry* 41, 454–466.
- Ortiz, J.E., Diaz-Bautista, A., Aldasoro, J.J., Torres, T., Gallego, J.L.R., Moreno, L., Estébanez, B., 2011. *n*-Alkane-2-ones in peat-forming plants from the Ronanzas ombrotrophic bog (Asturias, northern Spain). *Organic Geochemistry* 42, 586–592.
- Pailler, D., Bard, E., 2002. Geochemistry and sea-surface temperature reconstruction for sediment cores of the Iberian Margin. *Palaeogeography Palaeoclimatology Palaeoecology* 181 (4), 431–452.
- Pancost, R.D., Baas, M., Van Geel, B., Sinninghe Damsté, J.S., 2002. Biomarkers as proxies for plant inputs to peats: an example from a sub-boreal ombrotrophic bog. *Organic Geochemistry* 33, 675–690.
- Panin, N., Jipa, D., 2002. Danube river sediment input and its interaction with the north-western Black Sea. *Estuarine, Coastal and Shelf Science* 54, 551562.
- Peltier, W.R., Fairbanks, R.G., 2006. Global glacial ice volume and Last Glacial Maximum duration from an extended Barbados sea level record. *Quaternary Science Reviews* 25, 3322–3337.
- Prahl, F.G., de Lange, G.J., Scholten, S., Cowie, G.L., 1997. A case of post-depositional aerobic degradation of terrestrial organic matter in turbidite deposits from the Madeira Abyssal Plain. *Organic Geochemistry* 27, 141–152.
- Renssen, H., Valderbergh, J., 2003. Investigation of the relationship between permafrost distribution in NW Europe and extensive winter sea-ice cover in the North Atlantic Ocean during the cold phases of the last glaciation. *Quaternary Science Reviews* 22, 209–223.
- Ridgwell, A., Maslin, M., Kaplan, J.O., 2012. Flooding the continental shelves as a contributor to deglacial CH<sub>4</sub> rise. *Journal of Quaternary Science*. <http://dx.doi.org/10.1002/jqs.2568>.
- Rieley, G., Collier, R.J., Jones, D.M., Eglinton, G., 1991. The biogeochemistry of Ellesmere Lake, U.K.—I: source correlation of leaf wax inputs to the sedimentary lipid record. *Organic Geochemistry* 17 (6), 901–912.
- Rinterknecht, V.R., Clark, P.U., Raisbeck, G.M., Yiou, F., Bitinas, A., Brook, E.J., Marks, L., Zelts, V., Lunkka, J.-P., Palvlovskaya, I.E., Piotrowski, J.A., Raukas, A., 2006. The last deglaciation of the southeastern sector of the Scandinavian Ice Sheet. *Science* 311, 1449–1452.
- Ross, D.A., Degens, E.T., 1974. Recent sediments of the Black Sea. In: Degens, E.T., Ross, D.A. (Eds.), *The Black Sea—Geology, Chemistry, and Biology*. AAPG, Tulsa, OK, pp. 183–199.
- Rousseau, D.-D., Gerasimenko, N., Matviichina, Z., Kukla, G., 2001. Late Pleistocene environments of the Central Ukraine. *Quaternary Research* 56, 349–356.
- Sailer, R., Kerschner, H., 2000. Equilibrium line altitudes and rock glaciers in the Ferwall Group (Western Tyrol, Austria) during the Younger Dryas cooling event. *Annals of Glaciology* 28, 141–145.
- Sidorchuk, A., Borisova, O., Panin, A., 2001. Fluvial response to the Late Valdai/Holocene environmental change on the East European Plain. *Global and Planetary Change* 28, 303–318.
- Simakova, A.N., 2006. The vegetation of the Russian Plain during the second part of the Late Pleistocene (33–18 ka). *Quaternary International* 149, 110–114.
- Soulet, G., Ménot, G., Garreta, V., Rostek, F., Zaragosi, S., Lericolais, G., Bard, E., 2011a. Black Sea “Lake” reservoir age evolution since the Last Glacial – hydrologic and climatic implications. *Earth and Planetary Science Letters* 308, 245–258.
- Soulet, G., Ménot, G., Lericolais, G., Bard, E., 2011b. A revised calendar age for the last reconnection of the Black Sea to the global ocean. *Quaternary Science Reviews* 30, 1019–1026.
- Soulet, G., Ménot, G., Bayon, G., Rostek, F., Ponzevera, E., Toucanne, S., Lericolais, G., Bard, E., 2013. Abrupt drainage cycles of the Fennoscandian Ice Sheet. *Proceedings of the National Academy of Science* 110 (17), 6682–6687.
- Struk, D.H., 1993. *Encyclopedia of Ukraine*. University of Toronto Press, Toronto (864 pp.).
- Svensden, J.L., et al., 2004. Late Quaternary ice sheet history of northern Eurasia. *Quaternary Science Reviews* 23, 1229–1271.
- Tzedakis, P.C., Lawson, I.T., Frogley, M.R., Hewitt, G.M., Preece, R.C., 2002. Buffered tree population changes in a Quaternary Refugium: evolutionary implications. *Science* 297, 2044.
- Vanderbergh, J., Nugteren, G., 2001. Rapid climate changes recorded in loess successions. *Global and Planetary Change* 28, 1–9.
- Velichko, A.A., Catto, N., Drenova, A.N., Klimanov, V.A., Kremenetski, K.V., Nechaev, V.P., 2002. Climate changes in East Europe and Siberia at the Late glacial–holocene transition. *Quaternary International* 91 (1), 75–99.
- Volkman, J.K., Farrington, J.W., Gagosian, R.B., Wakeham, S.G., 1983. Lipid composition of coastal marine sediments from the Peru upwelling region. In: Björøy, M., et al. (Ed.), *Advances in Organic Geochemistry*. Wiley, Chichester, pp. 228–240.
- Vonk, J.E., Gustafson, Ö., 2009. Calibrating *n*-alkane *Sphagnum* proxies in sub-Arctic Scandinavia. *Organic Geochemistry* 40, 1085–1090.
- Vonk, J.E., Sanchez-García, L., Semiletov, I., Dudarev, O., Eglinton, T., Andersson, A., Gustafsson, Ö., 2010. Molecular and radiocarbon constraints on sources and degradation of terrestrial organic carbon along the Kolyma paleoriver transect, East Siberian Sea. *Biogeosciences* 7, 3153–3166.
- Wang, Y.J., Cheng, H., Edwards, R.L., An, Z.S., Wu, J.Y., Shen, C.-C., Dorale, J.A., 2001. A high-resolution absolute-dated Late Pleistocene Monsoon record from Hulu Cave, China. *Science* 294, 2345–2348.
- Wenchuan, Q., Dickman, M., Sumin, W., Ruijin, W., Pingzhong, Z., Jianfa, C., 1999. Evidence for an aquatic plant origin of ketones found in Taihu Lake sediments. *Hydrobiologia* 397, 149–154.
- Williams, C., Flower, B.P., Hastings, D.W., 2012. Seasonal Laurentide Ice Sheet melting during the ‘Mystery Interval’ (17.5–14.4 ka). *Geology* 40 (10), 955–958.
- Wohlfahrth, B., Lacourse, T., Bennike, O., Subetto, D., Tarasov, P., Demidov, I., Filimonova, L., Sapelko, T., 2007. Climatic and environmental changes in north-western Russia between 15,000 and 8000 cal yr BP: a review. *Quaternary Science Reviews* 26, 1871–1883.
- Xie, S., Wang, Z.H., Wang, H., Gu, Y., Huang, Y., 2003. Lipid distribution in loess–paleosol sequences from northwest China. *Organic Geochemistry* 34, 1071–1079.
- Xie, S., Nott, C.J., Avsejs, L.A., Maddy, D., Chambers, F.M., Evershed, R.P., 2004. Molecular and isotopic stratigraphy in an ombrotrophic mire for paleoclimatic reconstruction. *Geochimica et Cosmochimica Acta* 68 (13), 2849–2862.
- Yu, Z., Loisel, J., Brosseau, D.P., David, W., Beilman, D.W., Hunt, S.J., 2010. Global peatland dynamics since the Last Glacial Maximum. *Geophysical Research Letters* 37, L13402. <http://dx.doi.org/10.1029/2010GL043584>.
- Zheng, Y., Zhou, W., Meyers, P., 2010. Proxy value of *n*-alkan-2-ones in the Hongyan peat sequence to reconstruct Holocene climate changes on the eastern margin of the Tibetan Plateau. *Chemical Geology* 288, 97–104.
- Zheng, Y., Zhou, W., Liu, X., Zhang, C.L., 2011. *n*-Alkan-2-one distributions in a northeastern China peat core spanning the last 16 kyr. *Organic Geochemistry* 42, 25–30.