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Climate-driven changes in lake conditions during late MIS 3 and MIS 2: a high-resolution geochemical record from Les Echets, France

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ABSTRACT

Ice-core (Dansgaard *et al.* 1993; Johnsen *et al.* 2001; NGRIP members 2004) and marine sediment records (Bond *et al.* 1992; Moreno *et al.* 2004; Rasmussen & Thomsen 2004) spanning the last glacial cycle provide compelling evidence of multiple reorganizations of the climatic system triggered by changes thought to originate in the North Atlantic region (Broecker *et al.* 1992; Clark *et al.* 2002). Sudden shifts in air temperature from a cool climate to interstadial values, known as Dansgaard-Oeschger events (DO), have been active most notably during Marine Isotope Stage (MIS) 3. Abrupt and large in amplitude, DO cycles operated on a millennial to centennial time scale and are best expressed in the North Atlantic region (Dansgaard *et al.* 1993; Allen *et al.* 1999; NGRIP members 2004; Moreno *et al.* 2005; Grimm *et al.* 2006; Wohlfarth *et al.* 2008), though recent research suggests that these events were probably important on a global scale (e.g. Voelker *et al.* 2002). Iceberg surges, known as Heinrich events (H events), appear in marine records as sudden cold spells associated with a drastic reduction in sea surface temperature, a southern shift of the Polar Front, disruption of North Atlantic thermohaline circulation and substantial delivery of ice-borne detritus to the open ocean, reaching as far south as Portugal (Bond *et al.* 1992; Broecker *et al.* 1992; Bard *et al.* 2000; Hemming 2004).

On the European mainland, lake sediments are the most promising archives for recording long-term and short-term climatic changes (Voelker *et al.* 2002). The few long lacustrine records from continental Europe show that, on a broad scale, long-term palaeoclimate variations are expressed clearly through changes in vegetation composition and dynamics (Woillard & Mook 1982; de Beaulieu & Reille 1984; Guiot *et al.* 1989; Allen & Huntley 2000; de Beaulieu *et al.* 2001; Guiter *et al.* 2003). However, in the context of abrupt climate change (e.g. for most of MIS 3), only limited palaeoecological information is available: most of the data come from sites located on the southern peninsulas of Mediterranean Europe (Voelker *et al.* 2002). It has been suggested that changes in plant cover varied in this region in concert with climatic fluctuations recorded in Greenland ice cores, with a diverse range of thermophilous taxa present at any time (Allen *et al.* 1999; Sánchez Goñi *et al.* 2002; Tzedakis *et al.* 2004). Much less floristic variability is seen, however, during MIS 3-2

in pollen records from sites located north of the main mountain ranges of central and northern Europe. Here, data from peat deposits (Behre 1989; Preusser 2004), lacustrine sediments (Woillard & Mook 1982; de Beaulieu & Reille 1984; Helmens *et al.* 2000; Müller *et al.* 2003; Sirocko *et al.* 2005; Engels *et al.* 2008) and terrestrial proxies in marine cores (Sánchez Goñi *et al.* 2008) reveal long cold intervals interrupted sporadically by weakly expressed interstadials marked by rises in boreal tree pollen (Allen & Huntley 2000; Guiter *et al.* 2003). Such significant differences in ecological responses point to strong regional and local climatic gradients associated with these events, issues that are not sufficiently considered when inferring synchronicity of events between various records.

In order to improve the understanding of how the European mainland was affected by rapid climate changes, we show that important palaeoecological information can be extracted from geochemical lake records (e.g. Lallier-Vergès *et al.* 1993; Bernasconi *et al.* 1997; Meyers 1997; Dean 1999; Meyers & Lallier-Vergès 1999; Meyers & Teranes 2001; Talbot 2001; Leng *et al.* 2005). Les Echets (Fig. 1A, B) is situated in a region sensitive to current climate changes at the boundary between humid Atlantic air masses and Mediterranean influences. The physical and chemical properties of the former lake and catchment area underwent significant changes on millennial to centennial time scales, changes that we attempt to quantify in palaeoenvironmental terms through multi-proxy geochemical analyses of the organic fraction within sediments. We demonstrate that the region was greatly influenced by the rapid climate variability specific to MIS 3, as seen in marine sediments (Bond *et al.* 1992; Moreno *et al.* 2004; Rasmussen & Thomsen 2004; Sánchez Goñi *et al.* 2008) or ice cores (Johnsen *et al.* 2001; NGRIP members 2004) hundreds of kilometres away.

Depositional setting, lithostratigraphic units and chronology

Les Echets (45°54'N, 4°56'E) is a large (~13 km²), overgrown, palaeo-lake located c. 15 km northeast of Lyon, France (Fig. 1A, B). Its watershed extended over 40 km² in a glacier terminus landscape formed during the Rissian (MIS 6) and pre-Rissian glaciations (de Beaulieu & Reille 1984 and references therein). The catchment consists mainly of unconsolidated late Quaternary glaciofluvial sediments locally covered by thick loess deposits. The surface of the mire is currently at 267 m a.s.l. and the basin itself contains 60–65 m of post-Rissian lacustrine sediments and peat.

The site was not overridden by the Alpine Würmian glaciers, but the basin was ultimately filled during the Late Würmian and an extensive peat bog formed during the Holocene. Artificial drainage of the peat bog started during the Medieval Period (de Beaulieu & Reille 1984) and agricultural activities greatly affected the surrounding vegetation and uppermost sediment.

Two new long cores (EC1 and EC3; Fig. 1B) were mechanically recovered in 2001 and a comprehensive lithological description and correlation between the two sequences is presented in Veres *et al.* (2007). Core EC1 was retrieved from the central and deepest part of the basin (Fig. 1B), 700 m from core EC3 (Veres *et al.* 2008). Core EC1 is 44 m in length and consists of thick alternations of silts and organic-rich sediments in the lower and middle sections and faintly laminated clayey gyttja silts in the upper 15 m. The sequence was subdivided into lithostratigraphic units based on sediment visual appearance, sedimentary structures, grain size and

organic matter content (Veres *et al.* 2007). The down-core lithological variations, clearly reflected in the organic content, are also closely replicated by changes in all geochemical proxies (Fig. 2). Therefore, in interpreting the geochemical data we follow the same unit subdivision. All analyses presented in this article were performed on core EC1 between 30.06 and 3.31 m depth (Figs 2, 3).

The age model follows Wohlfarth *et al.* (2008) and is based on 48 radiocarbon ages on terrestrial and limnic/riparian plant macrofossils, pollen concentrates and bulk sediment. Additionally, 22 luminescence (IRSL) age estimates were obtained on the polymineral fine-grain fraction (4–11 μm) using the modified single-aliquot regenerative-dose protocol of Preusser (2003). The age model (for more details see Wohlfarth *et al.* 2008) was constructed using the Bayesian software Bpeat of Blaauw & Christen (2005). All ages discussed in the text are in calendar years.

According to the age model, the sequence presented in this study covers the time interval from *c.* 46.1 kyr BP at 30.06 m depth to *c.* 15.0 kyr BP at 5.49 m depth (Figs 2, 3). Unit H (30.06–27.48 m) covers the time interval from 46.1 to 36.1 kyr BP, with several large hiatuses (Fig. 2). Unit G (27.48–22.49 m) is dated to 36.1–31.6 kyr BP, unit F (22.49–18.55 m) to 31.6–27.8 kyr BP, unit E (18.55–16.20 m) to 27.8–26.4 kyr BP, unit D (16.20–11.55 m) to 26.4–18.6 kyr BP and unit C (11.55–5.91 m) to 18.6–15.5 kyr BP. In unit B (5.91–3.31 m), the age model extends only to 5.49 m, where we obtained a modelled age of 15.0 kyr BP. No age estimates are available between 5.49 and 3.31 m depth, but most likely the core is not older than 14–15 kyr BP, since palynological investigations of core G recovered from the same area as EC1 (Fig. 1B), suggested that the Les Echets basin was already filled-in during the early part of the last Termination (de Beaulieu & Reille 1984).

Methods

Loss-on-ignition parameters

For loss-on-ignition analyses, the sediment was sampled volumetrically in contiguous 2 cm increments (occasionally 1.5 cm) without crossing lithological boundaries. The sediment was combusted for 4 h at 550 °C, to estimate organic matter content (OM), and then 925 °C, to estimate inorganic carbon content (IC). The minerogenic content (MM) represents the detrital residue (including siliceous microfossils) remaining after combusting the samples at 925 °C. All parameters are given as percentage (%) loss of the dry weight (Heiri *et al.* 2001). Dry density (DD) was calculated as the dry mass of the sample divided by its wet volume and is expressed as g cm^{-3} .

Organic matter carbon and nitrogen elemental and isotopic analyses

The organic carbon and total nitrogen concentrations were determined on a Carlo Erba NC2500 elemental analyser using freeze-dried and homogeneously ground sediment samples of 2 cm increments. The core was generally subsampled every 5 cm, but with finer sampling in sections displaying marked lithological changes. Prior to the total organic carbon (C_{org}) analysis, the sediment was treated with 2N HCl to remove carbonates. The residual nitrogen (N_{tot}) was determined before carbonate removal. The relative error was <1% for both measurements. The $C_{\text{org}}/N_{\text{tot}}$ ratios were calculated from the mean C_{org} (%) and N_{tot} (%) and multiplied by 1.167 to yield $C_{\text{org}}/N_{\text{tot}}$ atomic ratios (Meyers & Teranes 2001).

Organic matter carbon and nitrogen stable isotopes were determined with a Finnigan MAT Delta^{plus} mass spectrometer coupled with the elemental analyzer. The isotopic analysis was done in two steps: $\delta^{15}\text{N}_{\text{tot}}$ values were determined on the chemically untreated sediment, while the $\delta^{13}\text{C}_{\text{org}}$ was measured after carbonate removal. Reproducibility is estimated to better than 0.15‰ for both measurements. The $\delta^{13}\text{C}_{\text{org}}$ is given relative to the Vienna PeeDee Belemnite (VPDB) standard and $\delta^{15}\text{N}_{\text{tot}}$ is expressed relative to atmospheric dinitrogen.

Rock-Eval pyrolysis

Samples of about 80 mg of dried (at 40 °C) and ground sediment were used for determining organic matter oxygen (OI) and hydrogen (HI) indices using a Rock-Eval Turbo 6 device. The analysis followed two steps: a pyrolysis phase during which the sediment sample was heated under a nitrogen atmosphere (between 200 and 650 °C) and an oxidation phase under an air stream (between 400 and 850 °C). Both phases were performed under a stepwise controlled rise in temperature, which permitted the identification of a suite of organic components (e.g. HC, CO, CO₂) produced during the process (Lafargue *et al.* 1998). HI represents the hydrocarbonaceous products liberated per gram of C_{org} (mg HC g⁻¹ C_{org}) during the pyrolytic phase, while OI represents milligrams of CO₂ produced per gram of C_{org} (mg CO₂ g⁻¹ C_{org}) below 390 °C, during the pyrolytic phase. Details of this method and applications to palaeolimnology are described thoroughly in Lafargue *et al.* (1998), Meyers & Lallier-Vergès (1999) and Jacob *et al.* (2004).

Results and discussion

Productivity variations in Les Echets as indicators of climatic events

Percentages of organic matter, C_{org} and N_{tot} are normally used in palaeolimnology for describing lake productivity in general terms, and recognize climatic events. The quantity of organic matter preserved in lake sediments depends largely on the organic sedimentation rate and the degree of biological/chemical degradation during transport, burial and postdepositional remineralization (Bertrand & Lallier-Vergès 1993; Patience *et al.* 1996; Meyers 2003). At Les Echets, C_{org} content is extremely low in unit H (1%–2%), but increases to 3%–12% in the silty gyttjas of unit G (Fig. 2). C_{org} contents in units F and E are c. 5% in the clayey silt gyttjas, but only 2%–3% in the clayey gyttja silt layers. At the onset of unit D, C_{org} decreases to around 1%, a trend more or less maintained to the top of the sequence. N_{tot} closely mirrors the trend in C_{org}, with values oscillating between 0.2% in the clayey gyttja silts and 0.8% in the silty gyttjas. From 15 m upwards, N_{tot} are stable around medium to low values, while IC oscillates between 3% and 15%, reflecting the lithological composition of units C and B, i.e. partly oxidized and faintly laminated, calcareous clayey gyttja silts (Fig. 2).

The lithological variations, which are closely followed by changes in organic matter, C_{org} and N_{tot} contents, have been shown by Wohlfarth *et al.* (2008) to reflect the lacustrine sedimentary expression of rapid climate variability during late MIS 3 and most of MIS 2. The trends in C_{org}, N_{tot} and organic matter stable isotopes (Figs 2, 3), as well as significant correlations between these proxies (Fig. 4), suggest that they reflect productivity variations. Therefore, we interpret the silty gyttja layers as reflecting interstadial conditions, i.e. relatively moist and warm climates during which the lake was productive (Wohlfarth *et al.* 2008). Nonetheless, it should be taken into

account that the concentration of organic matter in lake sediments is also related to the rate of delivery of mineral detritus fraction which can dilute the organic fraction or inhibit primary productivity. Detrital minerogenic particles comprise over 90% of the sediment in Les Echets core EC1, with the exception of the silty gyttja layers in units G and F and the carbonate sediments of unit B, where it accounts for 70%–80% of the bulk sediment (Fig. 2). Such high values show that the sequence of EC1 is overall highly minerogenic, a fact also reflected in the record of dry density (DD) (Fig. 2). DD shows high and oscillatory values in unit H, repeated changes between low and high values in units G–E in accordance with lithological changes, and medium to high values in units D–B. The minerogenic horizons (clayey gyttja silts) have been interpreted as representing periods of limited primary production due to less favourable climatic conditions during DO stadials and H events (Wohlfarth *et al.* 2008) (Figs 2, 3).

Sources of sediment organic matter based on C_{org}/N_{tot} and stable isotopes

Bulk sediment C_{org}/N_{tot} ratios are widely used in palaeolimnology for assessing the abundance of terrestrial and aquatic components of organic matter, useful criteria for inferring past lake productivity and climate-related changes in vegetation communities in and around a lake (Meyers & Lallier-Vergès 1999; Talbot & Lærdal 2000). Overall, low C_{org}/N_{tot} ratios (<10) for most of our record indicate that algal productivity dominated input of organic matter to the sediments (Fig. 2). A few intervals in units G to E (silty gyttjas) show C_{org}/N_{tot} between 10 and 22, values likely reflecting mixed lacustrine and terrestrial contribution to the organic matter pool. Although various biochemical constituents of both terrestrial and algal organic matter could be severely affected by diagenesis, the general elemental signature of sources is usually preserved after sedimentation (Meyers & Lallier-Vergès 1999). Therefore, the major concern in the use of C_{org}/N_{tot} in the present study is the contribution (if any) of inorganically bound nitrogen to this ratio. Although we had no analytical means in determining the inorganic nitrogen content, a strong correlation between C_{org} and N_{tot} (Fig. 4B) suggests that most of the N_{tot} in EC1 is organically bound. Biasing of the N_{tot} values by inorganic nitrogen is of major concern for sediments with <0.3% C_{org} (Meyers & Lallier-Vergès 1999). Nevertheless, we can use the regression line (cf. Talbot 2001) in Fig. 4B and estimate that a small portion of N_{tot} might be derived from inorganic forms. However, we have chosen not to subtract these values without analytical control, as doing so might result in incorrect C_{org}/N_{tot} ratios, i.e. most N_{tot} contents in unit H will be negative. Moreover, the C_{org}/N_{tot} interpretation is fully supported by estimates of algal palaeoproductivity based on biogenic silica analysis and diatom flora distribution in the same core (Ampel *et al.* 2008). Ongoing organic petrography and biomarker analyses are expected to provide results for validating/invalidating the use of C_{org}/N_{tot} for inferring sources of organic matter at Les Echets.

The rapid lithological changes are also clearly expressed in $\delta^{13}C_{org}$, which shows large isotopic shifts (8‰–10‰) between lithological horizons (Figs 2, 3). The most depleted values (–25‰ to –28‰) are found in unit H, as a whole, and in units F (22.54–21.82 m; 31.7–30.9 kyr BP) and D (14.88–16.18 m; 23.5–26.4 kyr BP), i.e. sediments with very low C_{org} . The other carbon-poor intervals (clayey gyttja silts) show values between –22‰ and –25‰, while $\delta^{13}C_{org}$ is progressively enriched in the silty gyttjas to values as high as –18‰ to –16‰ (Figs 2, 5A). While the C_{org}/N_{tot} ratios indicate a mixture of algal and C3 land plant material, the $\delta^{13}C_{org}$ in the silty gyttjas is

outside the ranges defined for such organic matter sources (Fig. 5A). These observations imply that the more carbon-rich the sediment is, the more enriched is its organic matter isotopic composition, reaching values characteristic of C4 terrestrial plants (i.e. -9‰ to -17‰ ; Leng *et al.* 2005). As C4 plants are mostly adapted to arid and warm climates, a contribution of this type of material to the organic pool at Les Echets is very unlikely during the studied interval. Therefore, we presume that biogeochemical changes related to increased primary productivity are responsible for the enriched $\delta^{13}\text{C}_{\text{org}}$ values in the silty gyttjas (Meyers 1997; Fuhrmann *et al.* 2003 and references therein). According to Talbot & Lærdal (2000), two factors are of great importance in controlling the isotopic composition of aquatic organic matter, namely the isotopic range of the dissolved inorganic carbon pool and isotopic effects related to the availability of dissolved CO_2 in the lake water. Moreover, variables such as rapid changes in species composition and growth rate (Ficken *et al.* 1998), varying $p\text{CO}_2$ (Street-Perrott *et al.* 2004) and diagenesis (Lehmann *et al.* 2002) have also been shown to complicate the interpretation of bulk $\delta^{13}\text{C}_{\text{org}}$ values (Meyers 1997; Leng *et al.* 2005). During periods of enhanced aquatic productivity, which we assume was the case during deposition of the silty gyttjas, the transfer of organic matter to the hypolimnion or its rapid burial in the sediment may have triggered temporary or permanent depletion of ^{12}C in the productive surface waters, and in turn led to a progressive isotopic enrichment of the subsequently produced organic matter (Meyers 1997; Talbot & Lærdal 2000; Meyers & Teranes 2001; Filippi & Talbot 2005). Similar shifts to less negative values for algal organic matter have already been reported from a number of sites, e.g. in Meyers (1997 and references therein). Significant changes of the carbon isotopic signal can also occur when the availability of dissolved CO_2 decreases and aquatic producers use dissolved HCO_3^- ($\delta^{13}\text{C}=1\text{‰}$) as their source of carbon (Meyers & Lallier-Vergès 1999; Fuhrmann *et al.* 2003; Street-Perrott *et al.* 2004). Both enrichment of the dissolved inorganic carbon and the uptake of HCO_3^- during intense epilimnetic photosynthesis (when the availability of CO_2 decreases) may result in the production of isotopically enriched aquatic organic matter reaching values as high as -9‰ (Meyers & Lallier-Vergès 1999), i.e. in the range of C4 plants. Uptake of dissolved HCO_3^- is the most likely explanation for the enriched $\delta^{13}\text{C}_{\text{org}}$ values observed in the calcareous sediments of unit B and for the intervals rich in carbonates in units E and D (Figs 2, 5A). Calcified *Chara* sp. identified within those intervals point to a biogenic origin for the carbonates, while low $\text{C}_{\text{org}}/\text{N}_{\text{tot}}$ ratios confirm that the organic matter originates mostly from in-lake sources (Figs 2, 5A).

Diagnostic evidence for the sources of organic matter may also be provided by the stable nitrogen isotopes, a proxy useful for determining past availability of nitrogen to aquatic producers (Talbot 2001; Meyers & Teranes 2001). The isotopic composition of organically fixed nitrogen depends largely on the composition of the dissolved inorganic nitrogen pool and on the metabolic pathway which the organic matter producers follow during nitrogen assimilation (Talbot & Lærdal 2000). Lacustrine algae that form organic matter using dissolved nitrate (NO_3^-) have $\delta^{15}\text{N}$ values between 7‰ and 10‰ (the $\delta^{15}\text{N}$ of NO_3^-), whereas aquatic producers and land plants that directly assimilate atmospheric nitrogen ($\delta^{15}\text{N}=0\text{‰}$) produce organic matter with values close to $0\pm 2\text{‰}$ (Meyers 1997; Talbot & Lærdal 2000).

The high $\delta^{15}\text{N}_{\text{tot}}$ in the clayey gyttja silts (7‰ – 10.4‰) in units G–E might be interpreted as resulting primarily from algal fixation of dissolved nitrate. This would

add evidence of an algal origin of the organic matter in the clayey gyttja silts, in accordance with the C_{org}/N_{tot} ratios, which, with values mainly of <10 , suggest that algal biomass is the dominant source of organic matter. Interestingly, the enrichment in $\delta^{13}C_{org}$ coincides with depletion in $\delta^{15}N_{tot}$ from around 8‰ to 10.4‰ in the clayey gyttja silts to less than 5‰ in the silty gyttjas (Figs 2, 4E). Such depletion in $\delta^{15}N_{tot}$ over a productive interval might actually result from restricted availability of dissolved nitrogen following intense algal production, rapid sedimentation and limited remineralization of organic matter during/after burial (Meyers 1997; Talbot & Lærdal 2000; Meyers & Teranes 2001). However, the lack of correlation between $\delta^{15}N_{tot}$ and N_{tot} (Fig. 2) confirms that the processes behind nitrogen biochemical dynamics in lakes are complicated by a multitude of factors which can affect the nitrogen cycle (see review in Talbot 2001; Lehmann *et al.* 2002), and therefore interpretation of the data is not straightforward (Meyers & Teranes 2001; Leng *et al.* 2005). Overall, $\delta^{15}N_{tot}$ is generally more depleted in units G to E (clayey gyttja silts) and enriched in units D to B, while unit H and the silty gyttjas in units G to E exhibit medium values (Fig. 2). Such differences may occur because of changes in nitrogen availability in the surface waters, shifts in fixation patterns, changes in phytoplankton assemblages and/or organic matter sources (lacustrine or terrigenous), or due to the release of nitrogenous compounds after organic matter incorporation into the sediment (Talbot & Lærdal 2000). An alternative explanation for the low $\delta^{15}N_{tot}$ values in the silty gyttjas (Fig. 2) might be that they indicate periods of soil leaching and delivery of terrestrial organic material to the lake, processes that could have depressed the $\delta^{15}N_{tot}$ to values showing a mixture of algal and terrestrial organic matter. Soil organic matter has typical $\delta^{15}N_{tot}$ values of around 5‰, while C_{org}/N_{tot} higher than 10 in the silty gyttjas indicate contributions of higher-plant detritus rich in cellulose to the sediment.

Above 16.90 m (<27.1 kyr BP) $\delta^{15}N_{tot}$ drops and oscillates in a narrow range between 0.6‰ and 3.9‰ (units D–B). It is possible that these values reflect a major change in biota composition, with direct fixers of atmospheric nitrogen becoming the dominant organic matter producers, in contrast to the nitrogen dynamics in the underlying units (Fig. 2). Shifts to low $\delta^{15}N_{tot}$ (≈ 3 ‰) for aquatic-derived organic matter in a Late Pleistocene sequence from Lake Victoria have been interpreted by Talbot & Lærdal (2000) as an indication of enhanced atmospheric nitrogen fixation by aquatic communities. Nevertheless, low $\delta^{15}N_{tot}$ values in units D and C may on the other hand derive (at least partially) from the incorporation of degraded terrestrial organic matter washed-in from the watershed; however, this interpretation is in conflict with the low C_{org}/N_{tot} ratios and relatively high hydrogen index (HI) contents in sediments above 16.90 m. Figure 4B shows that relatively low C_{org} values are associated with medium N_{tot} values; it is possible that some inorganic nitrogen depresses the C_{org}/N_{tot} ratios to the extremely low values observed during this period. In other words, the terrestrial component in the C_{org}/N_{tot} ratios may be underestimated in these sediments.

Sources and preservation of sediment organic matter based on hydrogen and oxygen indices

Autochthonous lacustrine organic material deposited and preserved in an oxygen-poor environment will normally exhibit high (>600 mg HC g^{-1} C_{org}) HI values (Talbot & Lærdal 2000). Following lake-level lowering or increased oxygen availability in the

water column due to changing mixing regimes or at the water–sediment interface, algal organic matter is progressively oxidized during sinking and sedimentation (Ariztegui *et al.* 2001; Jacob *et al.* 2004). In such cases, C_{org} and HI decrease to very low values, while the oxygen content progressively increases as a function of oxidation strength (Meyers 1997). In many circumstances, algal organic matter can become highly degraded under oxygenated conditions to produce low HI and high OI values characteristic of terrestrial organic matter, leading to complications of source assignments (Patience *et al.* 1996; Sifeddine *et al.* 1996).

High HI values (400–700 mg HC g⁻¹ C_{org}) in the silty gyttjas (Figs 2, 3) suggest that sediment organic matter in these layers is rich in hydrogenous compounds which could derive mostly from algal biomass and/or from microbial biomass, and to a lesser extent also from the waxy material of higher plants (Meyers & Lallier-Vergès 1999; Talbot & Lærdal 2000; Lüniger & Schwark 2002). Support for a dominant algal origin in the silty gyttjas is provided by the $\delta^{13}\text{C}_{\text{org}}$, which show the most enriched values when HI is high (Fig. 4F), although intermediate $C_{\text{org}}/N_{\text{tot}}$ ratios in the same horizons point also to a terrestrial component in the sediment.

High OI values (>200 mg CO₂ g⁻¹ C_{org}), on the other hand, are regarded as representing the contribution of oxygen-rich organic matter originating mainly from land-derived plant debris (Wilkes *et al.* 1999; Dean 2006). Most of the minerogenic-rich intervals in units H and F–D have medium to very high OI (Figs 2, 3, 5B). These intervals also produced HI values of <400 mg HC g⁻¹ C_{org} (and in some instances of <250 mg HC g⁻¹ C_{org}) and $\delta^{13}\text{C}_{\text{org}}$ between –24‰ and –28‰, which could indicate the presence of terrestrial organic matter in the sediment. However, this interpretation contrasts with the low $C_{\text{org}}/N_{\text{tot}}$ ratios (<10) in these intervals. There are a few intervals in the sequence that exhibit very high OI (>500 mg CO₂ g⁻¹ C_{org}) and low C_{org} and HI (100–200 mg HC g⁻¹ C_{org}) contents, notably in unit H at 29.40–29.05 m (c. 45.7–45.0 kyr BP), in unit E at 22.54–21.82 m (31.7–30.9 kyr BP) and in unit D at 14.88–16.18 m (26.4–23.5 kyr) (Figs 2, 3, 5B). OI as presented in this study represents the CO₂ released during the pyrolytic phase at temperatures below 390 °C. Despite this, due to the occurrence of carbonates in the sediment, the highest OI values (>500 mg CO₂ g⁻¹ C_{org}) have to be interpreted with caution, although no correlation of OI with IC (Fig. 2), mineral carbon (Rock Eval) and CaO contents (ICP-AES) has been observed in the ongoing analyses. It is difficult to explain why such OI values occur and whether they are related to organic matter degradation or carbonate oxidation, although these high OI intervals correlate precisely with the highest dry density values. The latter proxy is commonly employed for quantifying catchment erosion and minerogenic deposition in a lake basin (Zolitschka & Negendank 1996; Brauer *et al.* 2000). As such, we could argue that these intervals represent times of limited in-lake productivity, erosion and supply of terrestrial material (including also terrestrial organic matter) into the lake. It is possible that the intervals with OI values could be associated with the presence of highly oxidized/refractory terrestrial organic matter (Talbot & Lærdal 2000; Fuhrmann *et al.* 2003). These intervals show the lowest $C_{\text{org}}/N_{\text{tot}}$ ratios in the sequence, but also the lowest HI values (Figs 2, 3, 5B). There is a possibility that $C_{\text{org}}/N_{\text{tot}}$ ratios (during intervals poor in C_{org}) are indeed biased by inorganic nitrogen, or by the adherence to the mineral matrix of nitrogen compounds released during organic matter degradation, processes that could depress the $C_{\text{org}}/N_{\text{tot}}$ ratios to low values (Freudenthal *et al.* 2001; Lehmann *et al.* 2002). Therefore, we consider that

additional optical microscopy and mineralogical investigations seem necessary for securely explaining the trends in the C_{org}/N_{tot} ratio and hydrogen and oxygen indices over intervals with low organic content.

The occurrence of *Phragmites* macrofossils mainly in the clayey gyttja silts with medium to high OI values suggests that the coring location was in shallower waters during their deposition (e.g. Talbot & Livingstone 1989). Therefore, the alternating layers of silty gyttja and clayey gyttja silts probably reflect also lake level oscillations (Ampel *et al.* 2008), partly explaining the trends in the HI-OI plot (Fig. 5B). The lack of geomorphological evidence of major inflow or outflow suggests that the Les Echets palaeo-lake was primarily fed by precipitation or precipitation-controlled groundwater. Large variations in precipitation reconstructed for Europe in general (Sánchez Goñi *et al.* 2002), and Les Echets in particular (Guiot *et al.* 1989), during MIS 3-2 were likely associated with variations in lake size. Changing hydrodynamic properties and circulation regimes in the water column, together with rapid migration of shorelines, could have shifted the sediment limit and caused erosive events and/or changes in the contributing plant group to the organic matter pool (Talbot & Livingstone 1989). As the lake had no significant inflow, most of the organic matter should be autochthonous as suggested by the C_{org}/N_{tot} , HI and biogenic silica data (Ampel *et al.* 2008), although intensification of aeolian activity during stadials may have added terrestrial organic matter (with variable degrees of degradation) to the lake. The coring location of EC1 is about 1 km from the closest shoreline, indicating that the palaeo-lake was large in the past (>13 km²). It may be that the terrigenous organic matter is actually a minor constituent of the sediment in core EC1 (as indicated by C_{org}/N_{tot} ratios), since the core site is in a distal location at an appreciable distance from the shore (Fig. 1B). In large lakes, land-derived material typically becomes negligible beyond a few hundred metres from the shore (e.g. Lake Pyramid, Nevada; Meyers & Teranes 2001). We consider that at the time of deposition of the silty gyttja layers the water column was most likely high and stratified (Ampel *et al.* 2008) and algal productivity resulted in a significant transfer of organic matter to the lake bottom. Good preservation of organic matter is inferred from the high C_{org} and HI values in those intervals (Fig. 2), both proxies pointing to enhanced organic preservation due to both high productivity and reducing environments (Bertrand & Lallier-Vergès 1993; Ariztegui *et al.* 2001; Eusterhues *et al.* 2005). The more organic the lake bottom the greater the chances that the hypolimnion/sediment pore waters turn anoxic/corrosive (Dean 1999). Such a development might have influenced the cycling of carbonate and productivity limiting elements in Les Echets (Bernasconi *et al.* 1997), partly explaining the trends in the organic matter stable isotopes which became enriched at times of high lake productivity (Fig. 2). On the other hand, a lowering of the lake level or ventilation changes leading to enhanced oxygen availability in the water column (and therefore enhanced organic matter degradation) at the time of deposition of clayey gyttja silts could be an explanation for the moderate to high OI observed in the minerogenic-rich sediments (Fig. 5B).

Palaeoenvironmental reconstruction and comparison with other records

Climate and environment at Les Echets between c. 46.1 and 36.1 kyr BP

Early to middle MIS 3 is characterized in Greenland ice cores (Dansgaard *et al.* 1993; Johnsen *et al.* 2001; NGRIP members 2004) and marine sediment records (Sánchez Goñi *et al.* 2002; Moreno *et al.* 2005; Roucoux *et al.* 2005) by several interstadial events (17–9), of which, DO 12 and 14 are of considerable length. DO 12 and 14 have also been the warmest intervals of MIS 3 and are clearly recognizable in pollen records from terrestrial sites (Allen *et al.* 1999; Tzedakis *et al.* 2004) and land-sea climate proxies in marine cores from Mediterranean Europe (Sánchez Goñi *et al.* 2002, 2008; Moreno *et al.* 2005; Roucoux *et al.* 2005).

The ages of c. 46.1–36.1 obtained for sediments between 30.06 and 27.48 m place this part of the Les Echets record in early to middle MIS 3 (Fig. 2). There are no indications of interstadial events in these sediments, and it is highly unlikely that there was no response of the Les Echets ecosystem to the interstadial conditions of early to middle MIS 3. Instead, the frequency of erosional contacts points to episodic sedimentation and/or sediment removal in this part of the sequence of Les Echets, distorting the age estimates and making palaeoenvironmental reconstructions and correlations difficult. The presence of sand layers in unit H at such a distance from the basin margin implies either very low water stands and littoral sedimentation or high-energy environments capable of transporting coarse particles to the middle of the lake. On the other hand, it is possible that the sandy layers represent low density sediment flows (turbidite layers) resulting from sediment re-suspension in the basin, although the particular grading specific to such deposits is not apparent for the sandy layers in unit H. Taking also into account the depth of the sediment in the basin (c. 28–30 m) and the distance of the coring site to the basin margin (c. 1 km), a good alternative explanation for the sedimentary gaps would be erosion by bottom/gravity currents or sediment sliding/slumping.

In accordance with lithostratigraphic observations (Fig. 2), the age model indicates the presence of several hiatuses in this part of the record, the largest at 28.1–27.9 m (c. 43.6–36.3 kyr BP) (Wohlfarth *et al.* 2008). The age estimates for this hiatus coincide in part with the time interval suggested for the H 4 (Thouveny *et al.* 2000; Combourieu-Nebout *et al.* 2002; Sánchez Goñi *et al.* 2002; Moreno *et al.* 2004; Rasmussen & Thomsen 2004). We speculate that the severe cold and arid conditions during H 4 over western Europe (Combourieu-Nebout *et al.* 2002; Sánchez Goñi *et al.* 2002; de Abreu *et al.* 2003; Genty *et al.* 2003; Moreno *et al.* 2004; Roucoux *et al.* 2005) led to dramatic changes in the hydrologic regime at Les Echets (changes observed also during other H events), triggering sediment re-suspension and/or erosion. Given the uncertainty of the age model for unit H, it is also possible that the interval with very high OI values between 29.40 and 29.05 m, dated to c. 45.7–45.0 kyr BP, correlates with parts of Heinrich event 5 (H 5), which is dated to that age interval (Cortijo *et al.* 2000; Hemming 2004; Moreno *et al.* 2004; Rasmussen & Thomsen 2004).

Pollen-stratigraphic data (de Beaulieu & Reille 1984) indicate that sedimentation during MIS 5 at Les Echets has been continuous, but sediments of MIS 4 to early MIS 3 age are most likely disturbed/missing in the centre of the basin (Allen & Huntley 2000; de Beaulieu *et al.* 2001; Guiter *et al.* 2003; Veres *et al.* 2007). It is

possible that the coring location of EC1 was either periodically desiccated during MIS 4 to early MIS 3, or, more likely, had fluctuating water levels (Veres *et al.* 2007; Ampel *et al.* 2008). A combination of very dry conditions at Les Echets during MIS 4 (de Beaulieu & Reille 1984) and low water levels during stadials and Heinrich events (Ampel *et al.* 2008) could therefore have triggered rapid and repeated migration of shorelines, resulting in gaps in sedimentation. Higher precipitation at the beginning of interstadial events could in turn have led to a rapid rise of the lake level and changes in the hydrodynamic properties causing erosion of underlying levels (Veres *et al.* 2007, 2008; Wohlfarth *et al.* 2008). Therefore, a combination of climate and internal basin dynamics is probably responsible for the unstable sedimentation conditions in the centre of the basin during this time interval, as evidence for early–middle MIS 3 interstadial events has been documented in the littoral core EC3 (see Veres *et al.* 2007, 2008 for details).

Climate and environment at Les Echets between c. 36.1 and 15.0 kyr BP

The most intriguing attribute of this time period at Les Echets is the alternating deposition of silty gyttja layers rich in organic contents and separated by distinct minerogenic layers (Fig. 2). Apparently, the rise in organic content was very rapid and was followed by a phase during which productivity remained high for hundreds of years. Wohlfarth *et al.* (2008) showed that these lithological variations are the lacustrine sedimentary expression of DO interstadials and stadials from late MIS 3 and MIS 2.

The first of the lake organic productivity events in Les Echets (following the hiatus), occurred between c. 36.2 and 35.7 kyr BP and its double-peak suggests that it most likely correlates with parts of DO interstadial 8 (Fig. 2). At about 35.7 kyr BP, the lake entered a phase dominated by clastic sedimentation which lasted for about 400 years. The temperature rise and increased moisture availability leading into DO interstadial 7 at 35.3 kyr BP corresponds to a shift towards higher productivity in the lake. The lake remained productive for several hundred years before the rapid shift to a new phase of predominantly clastic sedimentation. These conditions persisted for about 300 years (34.7–34.4 kyr BP), after which the productivity gradually increased in a saw-tooth manner, remained high for another 200 years and rapidly declined, reaching stadal levels at about 34.2 kyr BP. The rise in lake productivity at 33.5 kyr BP coincides with maximum temperatures at the start of DO interstadial 6, during which the lake remained highly productive for about 600 years (33.5–32.9 kyr BP). A gradual and oscillatory decline in lake productivity occurred between 33.0 and 32.5 kyr BP, before the lake entered a new phase of low productivity lasting until 32.1 kyr BP. This cold phase most likely coincides with the coldest part of the stadal between DO interstadials 6 and 5. A subsequent rise in productivity at 32.1 kyr BP coincides with the onset of DO interstadial 5 (Figs 2, 3).

Between 30 and 22 kyr BP the record shows only minor increases in organic productivity centred around 29.5 and 28.1 kyr BP (Figs 2, 3), which indicates that general climatic conditions had become colder in the region than during the preceding intervals (Genty *et al.* 2003; Rousseau *et al.* 2007). The age model indicates that these minor productivity events might correlate with DO interstadials 3 and 4, which are considered relatively moist/warm events in other parts of Europe (Chondrogianni *et al.* 2004) and the North Atlantic (Weinelt *et al.* 2003).

The organic matter deposited during the interstadial events at Les Echets consists of a mixture of algal and terrestrial components, suggesting that environmental conditions allowed for both high lake productivity and development of vegetation in the drainage area. The intervals dominated by minerogenic sedimentation represent periods of limited primary production and organic matter degradation, and reflect stadial conditions (Fig. 2). The trends in the geochemical proxies discussed in this article are closely replicated by shifts in the biogenic silica content, diatom communities dynamics (Ampel *et al.* 2008) and vegetation changes (Wohlfarth *et al.* 2008).

Pollen-stratigraphic records from lake sites in southern Europe (Allen *et al.* 1999; Tzedakis *et al.* 2004) and parallel investigations of land–sea climate proxies from marine cores obtained in the Mediterranean (Moreno *et al.* 2004, 2005) and on the Atlantic Margin of Western Europe (Sánchez Goñi *et al.* 2002, 2008; de Abreu *et al.* 2003; Roucoux *et al.* 2005) indicate a quasi synchronous response of vegetation to rapid climate variability for these regions. Variations in pollen composition, which could be directly correlated with isotopic and sea surface temperature estimates from the same samples, showed that vegetation changes were directly related to the succession of relatively wet/warm (interstadial) and cool/dry (stadial) conditions in the nearby Atlantic Ocean. While several periods of high primary productivity are seen at Les Echets between c. 36.2 and 28 kyr BP, only two interstadial events, Hengelo and Denekamp, have been recognized in pollen-stratigraphic records from central and northwest Europe for the same time interval (Behre 1989; Allen & Huntley 2000; Caspers & Freund 2001; Guiter *et al.* 2003; Müller *et al.* 2003; Preusser 2004). The high-resolution geochemical and chronological record for core EC1 indicates that these terrestrial interstadials were not individual events, but may contain several events with alternating interstadial and stadial conditions, partly explaining the discrepancies in the dating (Behre 1989; Caspers & Freund 2001) and environmental reconstructions (Guiter *et al.* 2003) for these events.

Notably low organic contents between 31.7 and 30.9 kyr (22.54–21.82 m) point to an event when lake primary productivity was drastically reduced (Figs 2, 3). Although the timing of H events is difficult to constrain, and estimates of their strength and environmental impact largely differ from study to study (e.g. Hemming 2004; Roche *et al.* 2004), our age model suggests that this period of low productivity at Les Echets is the terrestrial/lacustrine equivalent of H 3. Furthermore, the impact of H 2 is recognizable in the interval with very low organic content between c. 26.4 and 22.0 kyr BP (14.88–16.18 m), just before the rise in productivity and carbonate content at c. 22–20.0 kyr BP (Unit D; Figs 2, 3). Proxy records from Iberia and the North Atlantic also document a moist and warm interval between 23 and 19 kyr BP (Bard *et al.* 2000; Roucoux *et al.* 2005), and its presence at Les Echets indicates that this moist/warm interval, most likely corresponding to DO 2, was of regional importance (Rousseau *et al.* 2007).

Palynological records from marine cores off the coast of Iberia (Sánchez Goñi *et al.* 2002; Moreno *et al.* 2005; Roucoux *et al.* 2005), as well as loess records from continental Europe (Hatté & Guiot 2005; Rousseau *et al.* 2007), indicate that, in general, H events 3 and 2 led to a drastic reduction in forest cover as a response to aridity and cold air temperatures. Influxes of Polar waters into the Mediterranean further hampered productivity and caused large decreases in sea surface

temperature (Moreno *et al.* 2004; Siervo *et al.* 2005). In our case, H 3 and 2 are associated with a strong reduction in aquatic productivity, minerogenic deposition as well as enhanced organic matter mineralization (Figs 2, 3).

The period between H 3 and H 2 is interpreted in some records as the coldest of MIS 3 and 2 (Roucoux *et al.* 2005) with temperatures and moisture gradually decreasing as full glacial conditions approached. The long period with very low values for organic productivity indicators after *c.* 28 kyr BP (in units D to B) indicates that climate was relatively stable, dry and cold (e.g. Hatté & Guiot 2005) with low aquatic productivity at Les Echets (Ampel *et al.* 2008). During this time, the nearby alpine glaciers expanded to within 10–15 km of the site (de Beaulieu & Reille 1984). Extensive meltwater deposits in front of the glacier lobes would also have been prone to aeolian deflation. Increased influx of aeolian dust from both local and distal sources may also partly explain the relatively high accumulation rates observed at Les Echets at times approaching full glacial conditions (de Beaulieu & Reille 1984; Wohlfarth *et al.* 2008). It is possible, therefore, that the high minerogenic input to the lake either diluted the organic fraction, or, perhaps more likely, that a high percentage of mineral particles in the water column during a cold climate inhibited primary productivity (Ampel *et al.* 2008).

Apart from showing that crucial palaeoenvironmental information can be obtained by studying the organic fraction within lacustrine sediments, the results of this study also demonstrate that the site of Les Echets could represent a link between sites in northern central Europe and the Mediterranean region. In the context of rapid climate variability, Les Echets can provide a basis for the reinvestigation of northern central European records, which, from a vegetation point of view more closely parallel Les Echets than records from Mediterranean Europe (Behre 1989; Allen & Huntley 2000).

Synthesis and conclusions

We have reconstructed past lake organic productivity and catchment erosion based on a sedimentological and geochemical investigation of a 30 m long core from Les Echets spanning the time period *c.* 46 to 15 kyr BP. This reconstruction indicates cyclic alternation of different depositional environments and productivity levels, which seems to reflect the climatic fluctuations that occurred during late MIS 3 and 2, namely DO cycles and H events. Each of the productivity phases in Les Echets relates to regional temperature and humidity changes, which triggered internal basin dynamics such as lake level variations, changes in organic matter inputs and preservation state, erosive events and the ultimate rapid in-filling of the lake. The carbon cycling in Les Echets is primarily the result of increased phytoplankton production during favourable climatic conditions that correlate to DO interstadials 8–2 (Fig. 2). The increases in organic carbon are paralleled by enriched $\delta^{13}\text{C}_{\text{org}}$ and $\delta^{15}\text{N}_{\text{tot}}$, and high hydrogen index values indicating dominance of aquatic primary production during the productive intervals. Variations in organic matter stable isotopes seem to reflect changes/limitations in the productive limiting elements and a mixture of organic matter sources, with periods of abundant contribution of aquatic primary producers, mixed with different types of terrestrial and soil-derived organic components in different oxidation states.

Good preservation of organic matter during the productive events is inferred from trends in the hydrogen and oxygen indices, while minerogenic-rich sediments deposited during DO stadials show moderate organic matter degradation. On the contrary, intense degradation of organic matter, extremely limited primary productivity and high clastic input to the lake occurred at Les Echets during times of large ice-rafted detritus and meltwater discharges in the Atlantic Ocean, i.e. H events 2–5. The dry and harsh environmental conditions reconstructed for western Europe during H events were most likely associated with lake level variations at Les Echets, partly explaining the occurrence of a hiatus in our record corresponding in part to H 4.

In general, the abrupt and high-amplitude oscillations at Les Echets correlate well with the timing and amplitude of climatic events recorded in the Greenland ice-core records (see Wohlfarth *et al.* 2008). Overall, high sedimentation rates allowed for high temporal resolution for constraining the timing of oscillations in lake productivity in Les Echets. Palaeoenvironmental proxies at Les Echets vary in concert during MIS 3 and 2, and these new geochemical data highlight the palaeoclimatic potential of this site in not only linking the Mediterranean records to the northern European records, but also for increasing our understanding of how lake systems respond to rapid climate change in general.

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Figures

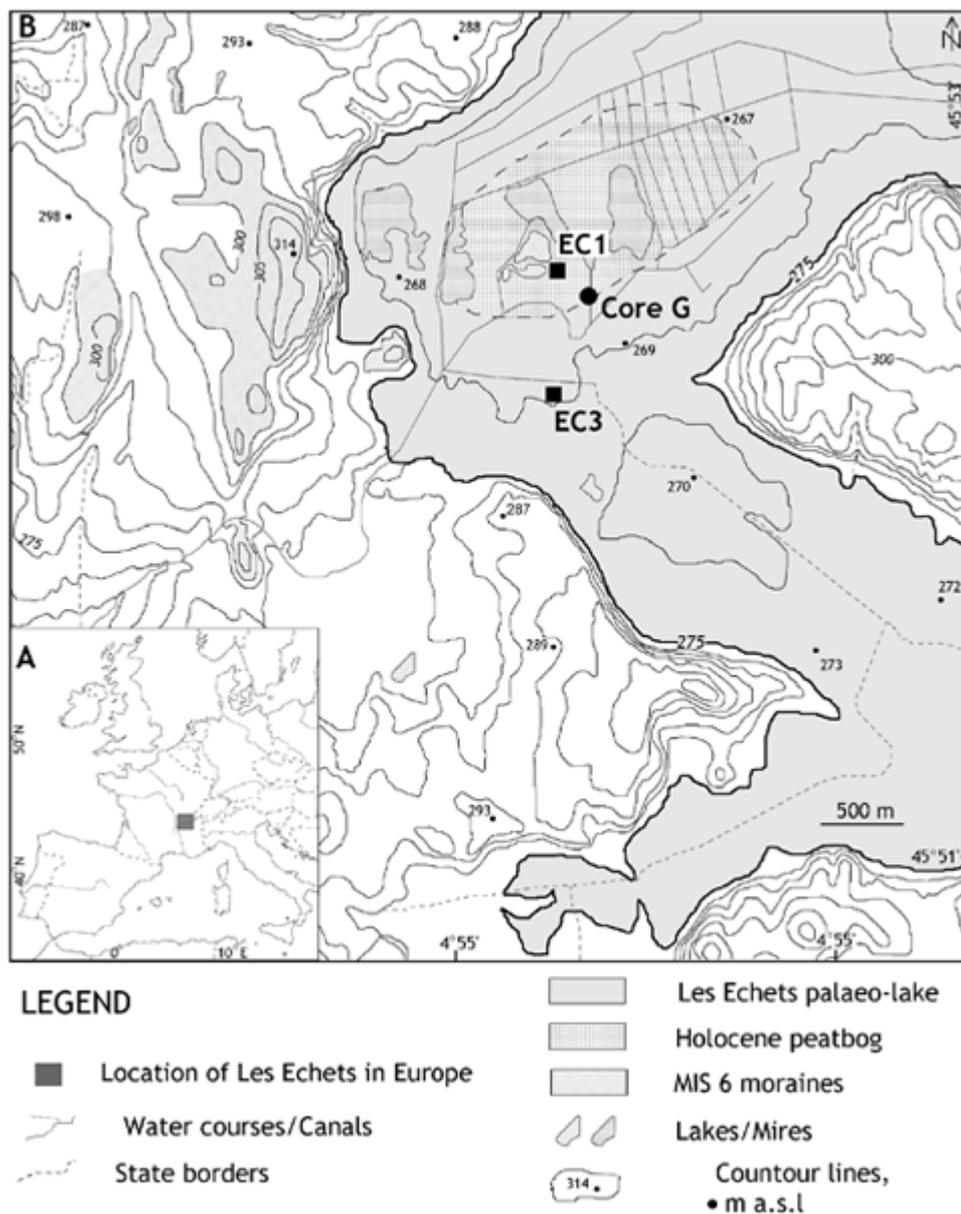


Fig. 1. A. Location of Les Echets palaeo-lake in Europe. B. Les Echets palaeobasin, with the location of the coring sites marked by rectangles (EC1 and EC3) and circle (core G; de Beaulieu & Reille 1984).

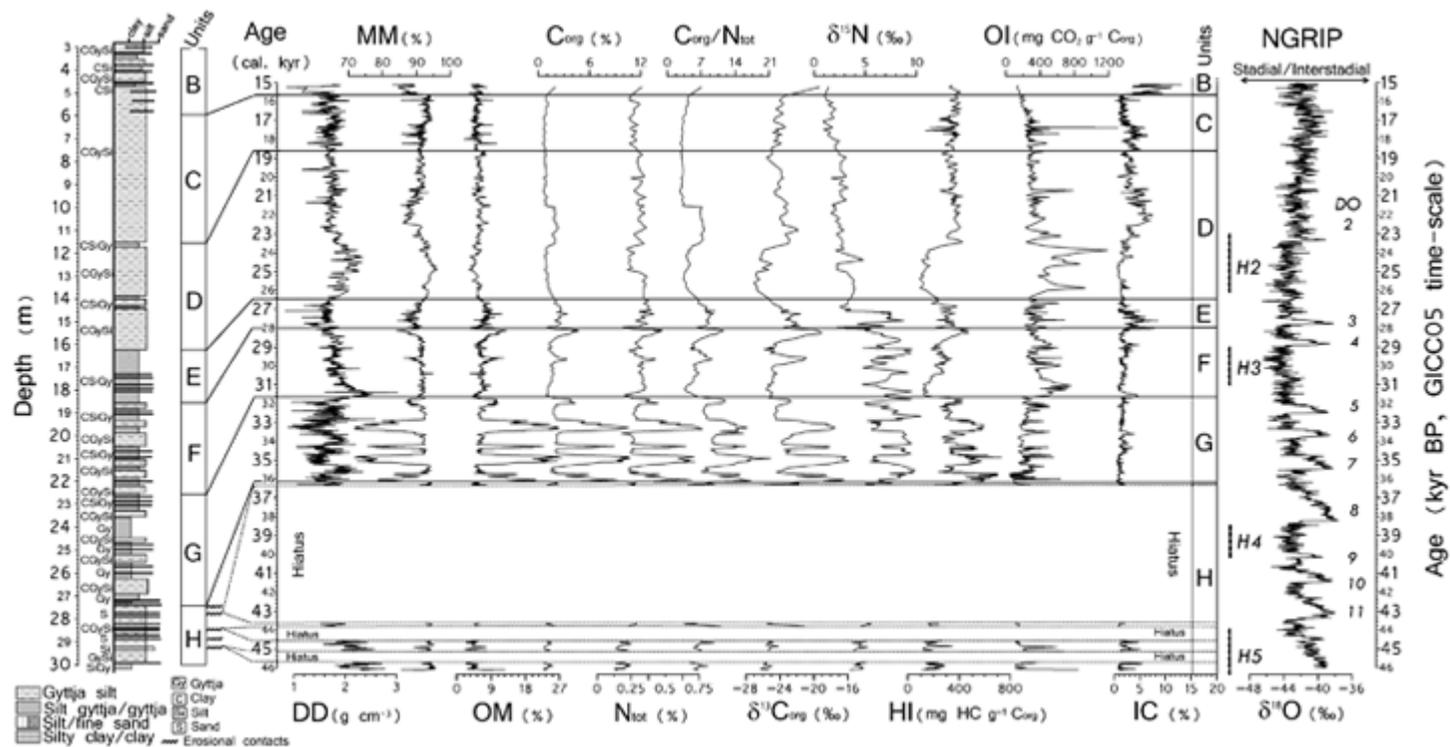


Fig. 2. Lithostratigraphy (on a depth scale) and vertical profiles of minerogenic matter content (MM), dry density (DD), organic matter content (OM), organic carbon content (C_{org}), total nitrogen content (N_{tot}), C_{org}/N_{tot} ratio, organic matter carbon ($\delta^{13}C_{org}$) and nitrogen ($\delta^{15}N_{tot}$) stable isotopes, hydrogen (HI) and oxygen (OI) indices and inorganic carbon content (IC) plotted on an age scale. The horizontal lines delimit stratigraphic units. The stippled vertical lines delimit the calibrated age ranges for Heinrich (H) events 5, 4, 3 and 2 (Bard *et al.* 2000; Thouveny *et al.* 2000; Sánchez Goñi *et al.* 2002; de Abreu *et al.* 2003; Hemming 2004). The $\delta^{18}O$ curve and GICC05 time scale for the NGRIP ice core follow Andersen *et al.* (2006) and Svensson *et al.* (2008). DO refer to Dansgaard–Oeschger interstadials

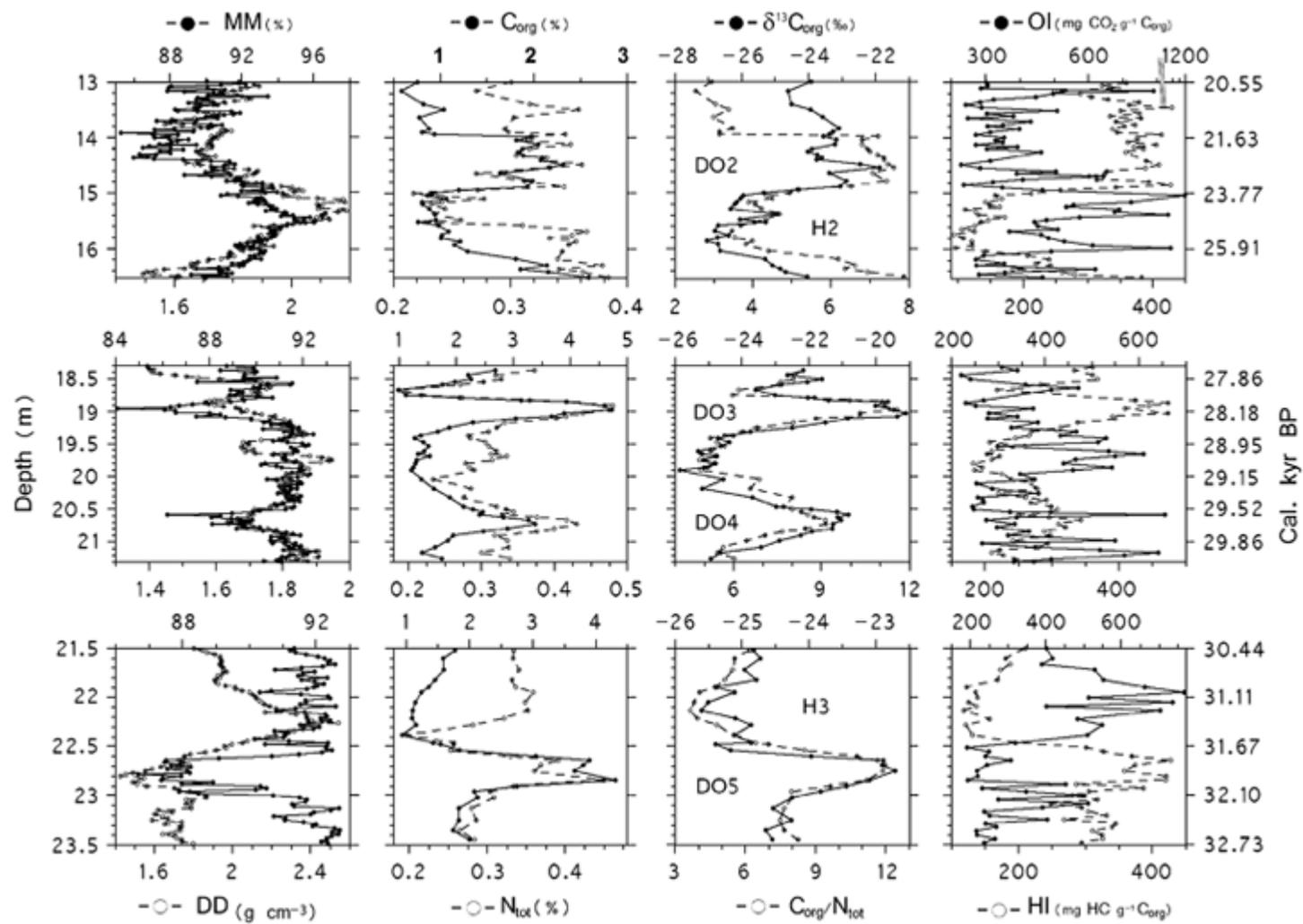


Fig. 3. Detailed plots over selected intervals in core EC1. The age estimates presented in the right-hand scale are exclusively for the major ticks in the depth scale, without linear interpolation between the plotted ages.

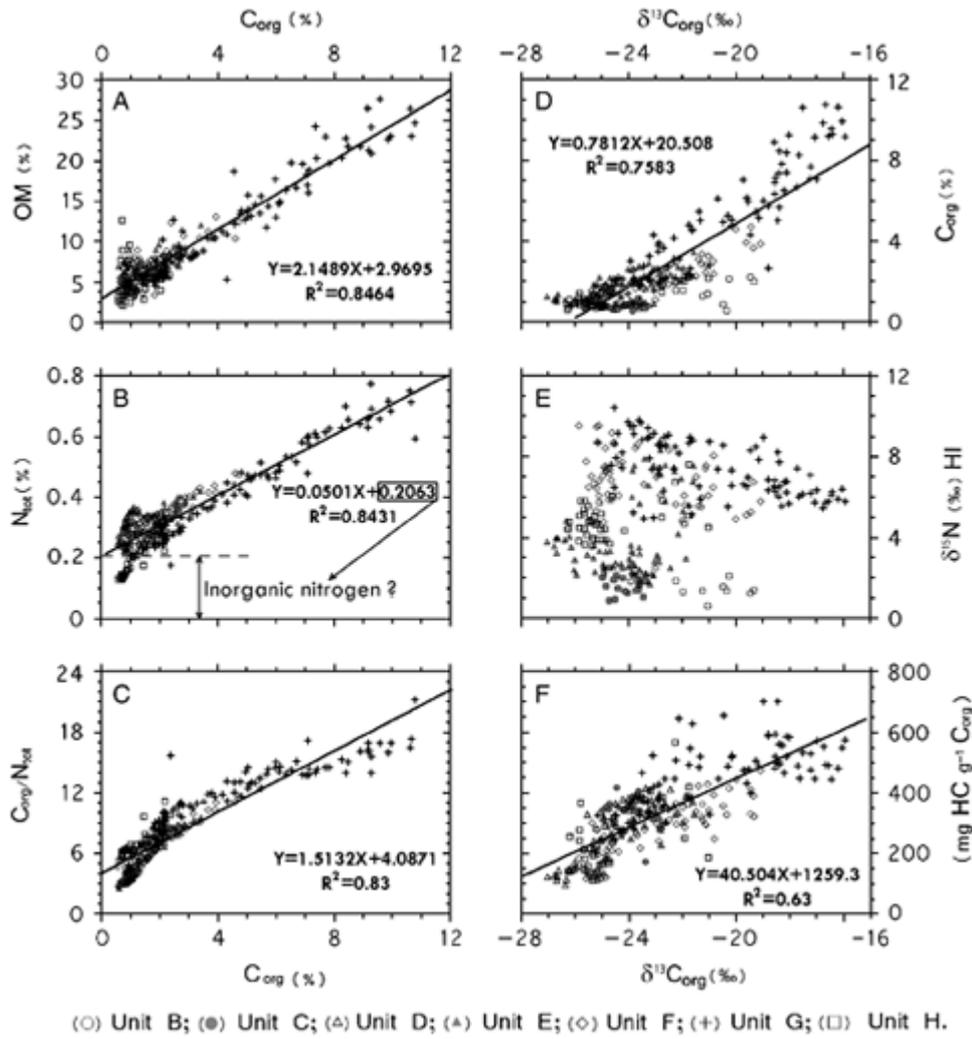


Fig. 4. Cross-plots of (A) organic carbon (C_{org}) and organic matter (OM); (B) organic carbon (C_{org}) and total nitrogen (N_{tot}); (C) organic carbon (C_{org}) and C_{org}/N_{tot} ratio; (D) $\delta^{13}C_{org}$ and organic carbon (C_{org}); (E) $\delta^{13}C_{org}$ and $\delta^{15}N_{tot}$ and (F) $\delta^{13}C_{org}$ and hydrogen index (HI).

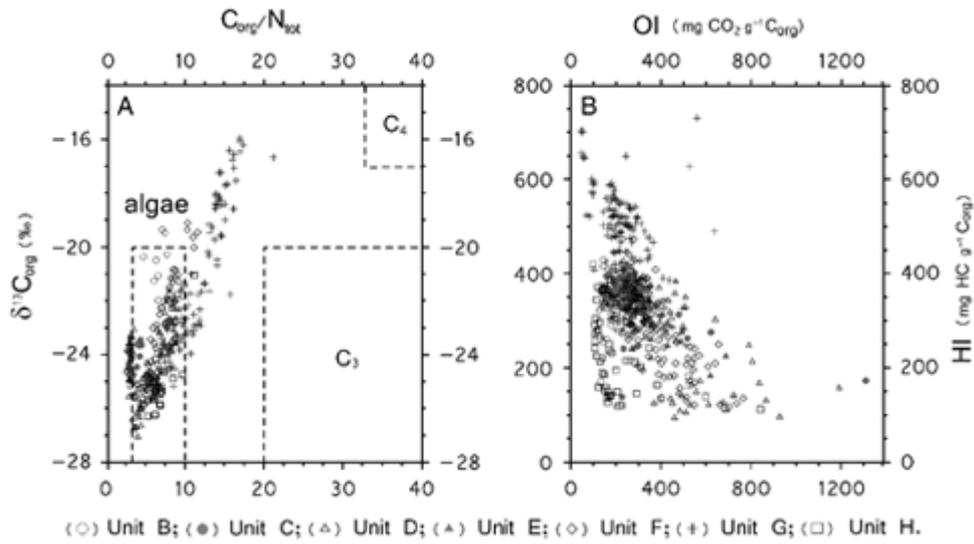


Fig. 5. A. Cross-plots of C_{org}/N_{tot} and $\delta^{13}C_{org}$. B. Pseudo van-Krevelen diagram of hydrogen index (HI) and oxygen index (OI) contents.