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Biomarker evidence for "Heinrich" events

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Abstract—The so-called Heinrich layers, found in North Atlantic sediments, have been attributed to quasi-periodic discharges of armadas of icebergs originating from the Laurentide ice sheet. Using the distribution of biomarkers in a sediment core (BOFS 5K) we have attempted to provide more information about their origin and the effect of the Heinrich events on oceanic circulation and the climatic system. Estimates of sea surface temperature changes, via $U^{K'}_{37}$ measurements, show that the surface ocean underwent significant cooling during the events, probably as a result of incoming iceberg meltwater. The low sea temperatures and the rapid variation in the accumulation of chlorophyll-derived pigments suggest that the events provoked a major change in oceanographic conditions, which may have affected the thermohaline circulation in the Atlantic Ocean. Within the most recent layers we have also found vanadyl alkyl porphyrins and aryl isoprenoid hydrocarbons, diagenetic products of photosynthetic pigments (chlorophylls and carotenoids, respectively). These components are not expected to occur in late Quaternary sediments, so their presence demonstrates a contribution to the layers of ancient, organic rich sedimentary material of continental origin. The presence of vanadyl porphyrins and absence of their nickel counterparts, and the distributional features of the aryl isoprenoids (e.g., presence of the C_{40} reduced carotenoid isorenieratane of green sulphur bacterial origin) indicate the existence of anoxic conditions in the photic zone of a marine water column in the original depositional setting of the contributed ancient sediment. These results suggest that it should be possible, using a biomarker correlation approach, to determine the source area of the ancient sediment eroded by the icebergs. *Copyright © 1997 Elsevier Science Ltd*

1. INTRODUCTION

Intense, quasi-periodic ice-rafting pulses have been identified in North Atlantic marine sediments (Heinrich, 1988; Bond et al., 1992) and correlated with shifts in various climate records (Bond et al., 1993; Grimm et al., 1993; Porter and An, 1995; Benson et al., 1996). These Heinrich events (HE) are believed to be the consequence of massive iceberg releases from the Laurentide ice-sheet (Heinrich, 1988; Andrews and Tedesco, 1992; Bond et al., 1992) and have been linked to rapid climatic variations in the North Atlantic region (Bond et al., 1993; Broecker, 1994; Paillard and Labeyrie, 1994). Although their cause and effect on the thermohaline circulation of the North Atlantic is still under debate, a favoured hypothesis is that fresh water released from the melting icebergs caused sea surface temperatures to drop considerably (Bond et al., 1992) and disrupted deep-water formation (Paillard and Labeyrie, 1994; Maslin et al., 1995). In the present study, to provide further information about the origin of the Heinrich layers (HL) and the effect of the HE on oceanographic conditions, we have examined the distributions of selected types of biomarkers (C_{37} alkenones, tetrapyrrole pigments and aromatic hydrocarbons) in the core BOFS 5K (East Thulean Rise; 50°41.3N, 21°51.9′W, 3547m water depth; Fig. 1; McCave, 1989), in which the HL (I-IV) were located from the relative abundance of coarse fraction lithic debris (ice rafted debris, IRD) and whole core magnetic susceptibility (Fig. 2a,b Maslin, 1993; Maslin et al., 1995).

2. METHODS

2.1. Sample Extraction and Spectrophotometry

After retrieval, core samples were kept cool in the dark before being subsampled at 1 to 5 cm intervals. Subsamples were freeze dried, and then weighed and solvent-extracted (dichloromethane/methanol, 3:1 x 3) using a robotic workstation (Rosell-Melé, 1994; Rosell-Melé et al., 1995a). Identification of the tetrapyrrole pigment types (porphyrins vs. chlorins) was carried out using electronic spectrophotometry (Phillips PU8730 spectrophotometer) (Rosell-Melé and Maxwell, 1996). With a few exceptions, chlorins and porphyrins have electronic spectra with maxima in the near-UV and visible range (350–850nm), the Soret band (S) being the one with the highest extinction in the near-UV range (360–420nm) (Dolphin, 1978). The relative abundances of the total photosynthetic pigments (tetrapyrroles) in the samples were estimated by measuring the absorbance of the extracts in the S band (410 nm) and satellite band (I, 665 nm) regions. The ratio between these bands can be used to classify pigments (Baker and Louda, 1986). Chlorin-like pigments yield S/I of ca. 1 to 5, whereas porphyrins yield considerably higher values (e.g., <10), because of the shift in the satellite bands.

2.2. Fractionation of Extracts and Mass Spectrometry

After solid phase extraction of the total extracts on silica, gas chromatography-mass spectrometry (GC-MS) with ammonia chemical ionization (CI) was used to obtain the $U^{K'}_{37}$ index from the C_{37} alkenones (Rosell-Melé et al., 1995a). Further biomarker analyses were carried out on combined samples from HL II and IV. The

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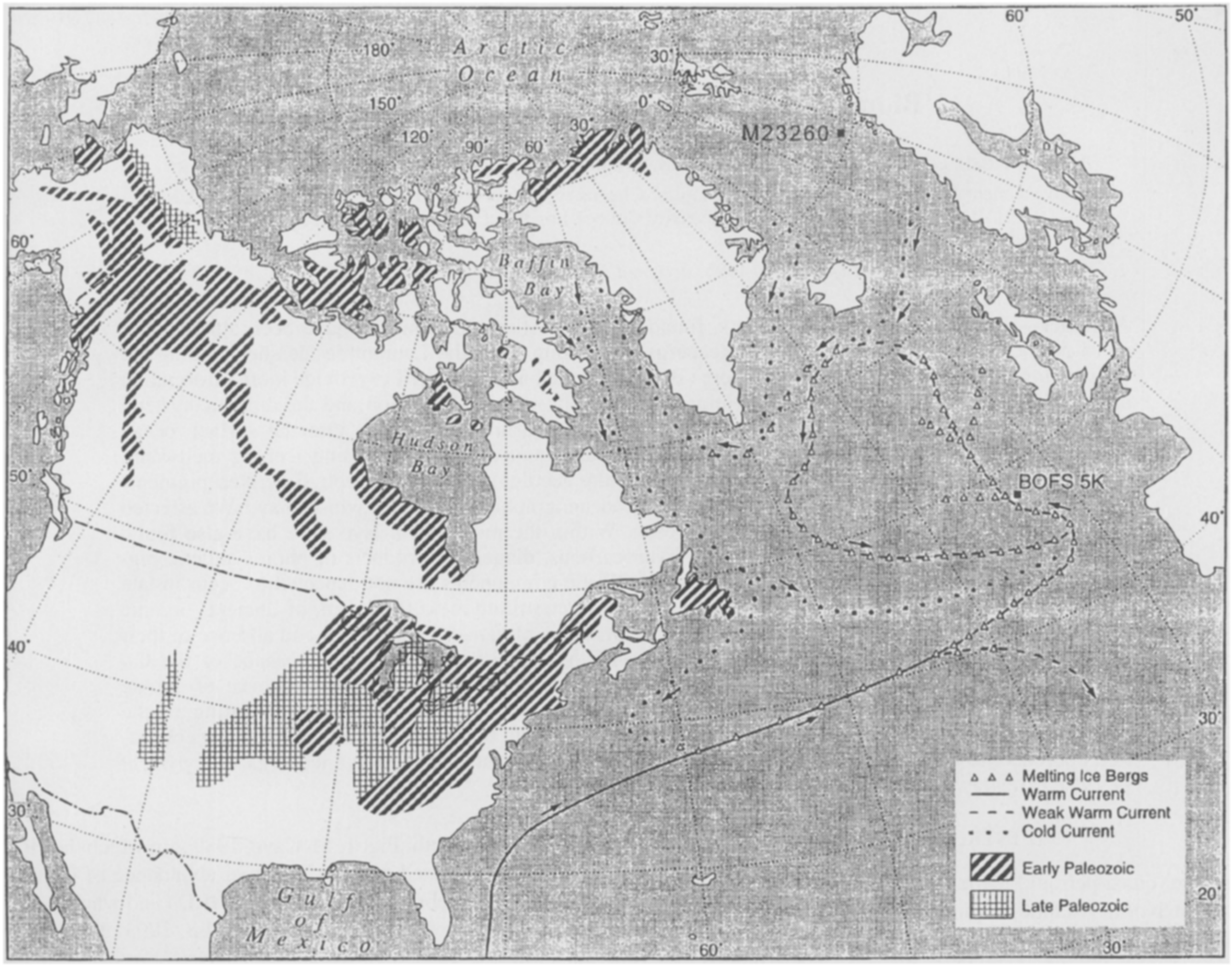


Fig. 1. Location of cores BOFS 5K and M23260, and of Palaeozoic sediments above sea-level in North America. The estimated path of the icebergs released from the Laurentide ice-sheet, and surface ocean currents are drawn for illustration purposes.

porphyrin distribution in combined extracts from HL IV was obtained using gel-permeation chromatography-mass spectrometry (Rosell-Melé and Maxwell, 1996). Combined extracts from HL II and IV were fractionated by thin layer chromatography on silica (hexane developer) using dibenzanthracene (Rf 0.1) and lupene (Rf 0.9) as internal reference, to afford the aromatic hydrocarbon fraction, and analyzed by GC-MS using a Carlo Erba GC (Mega series; Chrompack CPSil-5CB, 50 m length, 0.32 mm i.d., 0.25μm film thickness) with on column injection, temperature programmed (from 60 to 300°C at 6°/min and held for 20 min), and coupled to a single quadrupole mass spectrometer with electron ionization (Finningan Mat 4500; 70 eV, m/z 50–700, 2s/scan).

2.3. Age Model

A linear sedimentation rate age model was constructed for the core using corrected AMS ^{14}C dates on monospecific foraminifera samples of *Globigerina bulloides* and *Neogloboquadrina pachyderma* (S), where the species were in abundance (Maslin, 1993; Maslin et al., 1995). In addition, two ash layers, Saksunarvatn (9100 ^{14}C y) and Vedde (10300 ^{14}C y) were identified in the core (Maslin, 1993; Maslin et al., 1995).

3. RESULTS AND DISCUSSION

Solvent extraction of the samples gave extracts whose colour changed abruptly in samples spaced at only 1 cm intervals, varying from colourless to green to orange. This led us to investigate the nature of the pigments and to show that chlorins and porphyrins were present in the HL (Figs. 2 and 3). In green coloured extracts the electronic spectra (Fig. 3a) clearly showed the presence of chlorins, with an absorption maximum at 665 nm, apart from the Soret band at 410 nm. In contrast, the orange coloured extracts showed clearly the presence of vanadyl porphyrins (Fig. 3a), with maxima at 530 and 570 nm; the occurrence of vanadyl cycloalkanoporphyrin (CAP) components maximising at C_{32} (c.f. I) was confirmed by gel permeation chromatography-mass spectrometry (Rosell-Melé and Maxwell, 1996) of extracts from HL IV (Fig. 3b). An estimate of the variation in the concentration of porphyrins relative to chlorins using the S/I ratio from the electronic spectra (Baker and Louda, 1986) showed (Fig. 2d) that the highest porphyrin abundances correlated with maxima in the IRD (Fig. 2a) and magnetic susceptibility (Fig. 2b).

Sedimentary chlorins and porphyrins are diagenetic products of the chlorophylls of phytoplankton (e.g., Callot et al., 1990; Eckardt et al., 1991). Chlorins are, however, early diagenesis products whereas the red metallo porphyrin pigments are formed at a later stage (Baker and Louda, 1983). The youngest sediments where porphyrins (as the free bases) have been found are Late Pliocene lacustrine clays (Keely et al., 1994), and vanadyl porphyrins have never been reported previously in Quaternary sediments. Their unexpected occurrence in extracts from the BOFS 5K core suggests, therefore, that they have an allochthonous origin by way of erosion and advection of much older, organic-rich sedimentary material. Indeed, the correlation between the maxima in S/I and the maxima in magnetic susceptibility and IRD, i.e., when the input of ice rafted material was highest during the HE (Robinson et al., 1995), indicates that the vanadyl porphyrins were transported with the IRD.

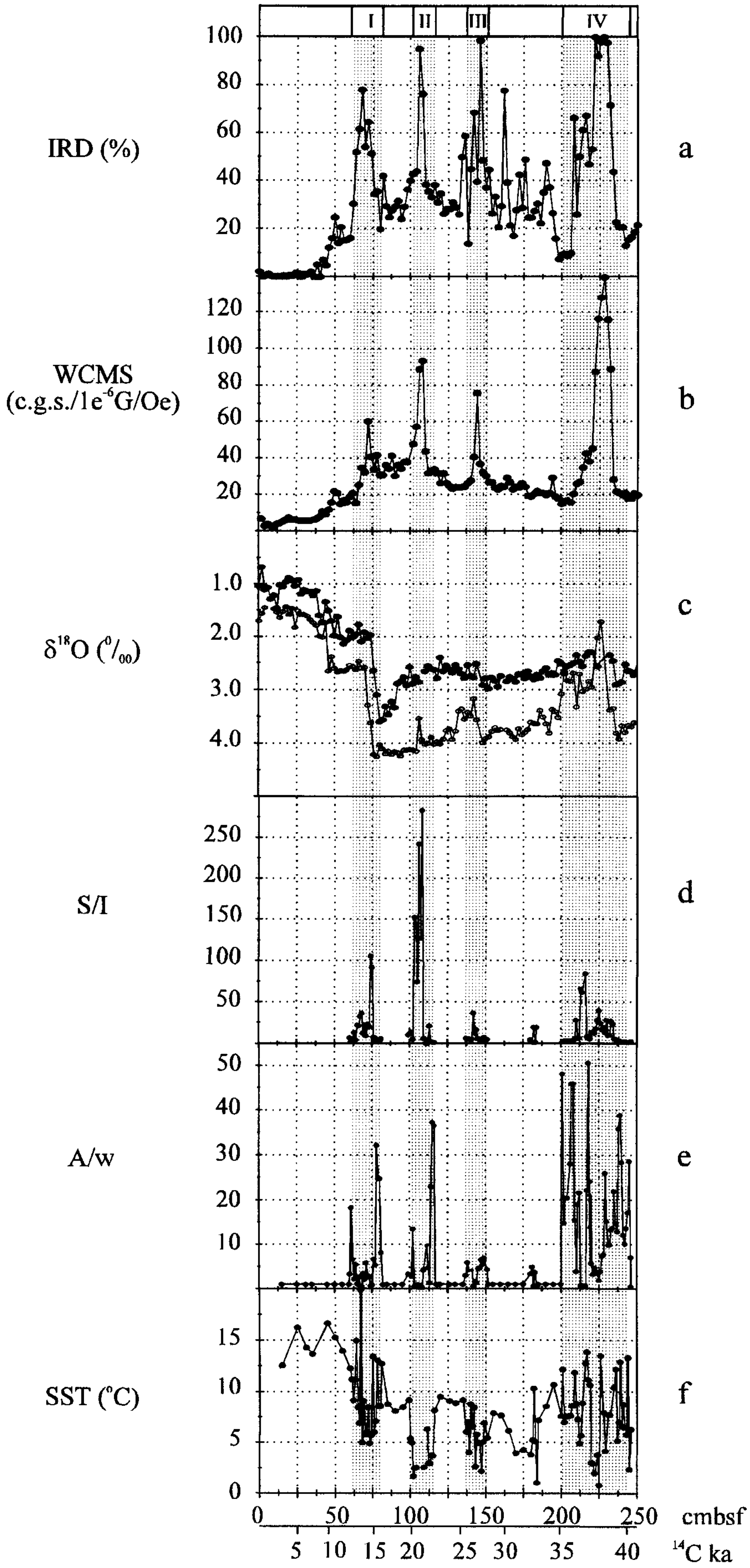
The aromatic hydrocarbon fraction in combined extracts from HL II+IV was characterised by the presence of an homologous series of aryl isoprenoids (the C_{14} component being confirmed by comparison with a standard), 3 isomers of triaromatic isoprenoids (Sinninghe Damsté et al., 1995) and two C_{40} diaromatic components with a carotenoid-derived carbon skeleton (Fig. 4). The later eluting C_{40} component was assigned as isorenieratane from its relative retention time and comparison of its mass spectrum (base peak *m/z* 133) with that of a standard (Schaeflé et al., 1977), and the second C_{40} diaryl isoprenoid corresponding to the component identified previously by Hartgers et al. (1993, 1994a,b). All of these components are diagenetic products of aromatic carotenoid pigments characteristic of green photosynthetic bacteria (e.g., isorenieratene, II), which are obligate anaerobes and are considered to be indicative of the occurrence of photic zone anoxia in the water column of the depositional setting (e.g., Summons and Powell, 1986; Requejo et al., 1992; Hartgers et al., 1994a,b). It is highly unlikely that anoxygenic photosynthesis occurred in the North Atlantic during the Quaternary because of the open ocean setting and the need for a highly stratified water column typically associated with restricted or enclosed water bodies. Hence, as with the vanadyl porphyrins, we associate the presence of the carotenoid-derived hydrocarbons in the HL with the erosion and advection of ancient sedimentary material of continental origin.

Consideration of the distributional characteristics of the porphyrins and aromatic hydrocarbons allows us to make some inferences about the depositional setting of the ancient sediment contributing to HL II and IV. The presence of vanadyl porphyrins and absence of their nickel counterparts is associated with sediment deposition in epicontinental anoxic seas (e.g., Lewan, 1984; Eckardt et al., 1991). Such conditions occurred during the Palaeozoic and numerous deposits of this age surround the North Atlantic region (Derry, 1980). For instance, we have also found allochthonous vanadyl porphyrins in Quaternary sediments in Meteor core 23260 (Fig. 1) from the Norwegian Sea (Rosell-Melé and Maxwell, 1996). Likewise, the presence of chlorobiaceae-derived aromatic hydrocarbons is related to stratified anoxic environments (see above). Their distributions in the HL of core 5K compares favourably with those reported for a number of Palaeozoic North American sediments (Requejo et al., 1992). In contrast, in the Norwegian Sea core none of these components were detected (A. Rosell-Melé et al., unpubl. data), indicating a different source area for the ice-rafted sedimentary material at this site. Other studies have provided evidence of sources in North America (Heinrich, 1988; Andrews and Tedesco, 1992; Bond et al., 1992; Dowdeswell et al., 1995; Gwiazda et al., 1996), Appalachian Triassic red facies (Lebreiro et al., 1996), and Icelandic and Scandinavian locations (Rahman, 1995; Revel et al., 1996). Our findings would appear to confirm a North American origin for the HL material. in the BOFS 5K core, given the similarity in the aromatic biomarker distributions to those in Palaeozoic sediments from central and western Canada (Requejo et al., 1992). It seems plausible, therefore, that debris from eroded outcrops was transported through the Hudson Strait as IRD from the Laurentide ice-sheet, although determining the location of the organic rich "source rocks" from which the HL material originated will require detailed biomarker correlation studies of possible candidates with the biomarker features we have already determined.

It has been argued that fresh water released from melting icebergs caused sea surface temperatures to fall considerably (Bond et al., 1992; Maslin et al., 1995). Indeed, our U^K_{37} data confirm that sea-surface temperatures dropped during the HE (Fig. 2f), although significant temperature fluctuation occurred during warmer climatic periods in isotopic stage 3 (H4) and near Termination I (H1). There is a discrepancy of several degrees centigrade during glacial times and the HE between the absolute SST values derived from U^K_{37} and those of Maslin et al. (1995) from transfer function estimates. These differences may arise from uncertainties attached to temperature calibrations used for U^K_{37} estimates (cf. Rosell-Melé et al., 1995b), as the estimates may be complicated by variations in the algae which produced alkenones, as well as on seasonality and diagenetic effects, in certain circumstances, independently of the calibration equation used. Such uncertainties may be more significant at the "cold end" of the regression line used for calibration. Thus, caution is required using absolute SST values for future quantitative work.

The concentration of the chlorophyll-derived chlorin pigments also changed markedly and abruptly across the HL, no chlorins being detected when the IRD (Fig. 2a) decreased to background glacial or interglacial levels (Fig. 2e). Within each layer the concentration of chlorins also dropped as S/I (Fig. 2d), magnetic susceptibility (Fig. 2b), and IRD (Fig. 2a) values maximised, although this probably relates to autochthonous material being diluted by IRD.

The marked variation in the chlorin record must result from changes in oceanographic conditions which favoured the accumulation of chlorins during the HE, through increased primary productivity and/or enhanced preservation. One possibility is that productivity increased as a result of nutrients being made available by iceberg melting, either through localised upwelling or released after being trapped in the ice (Neshyba, 1977; Sancetta, 1992). It has been


I
II
III
IV
IRD (%)
a
WCMS (c.g.s./1e-6G/Oe)
b
δ18O (‰)
c
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e
SST (°C)
f
0 50 100 150 200 250 cmbsf
5 10 15 20 25 30 35 40 14C ka
100
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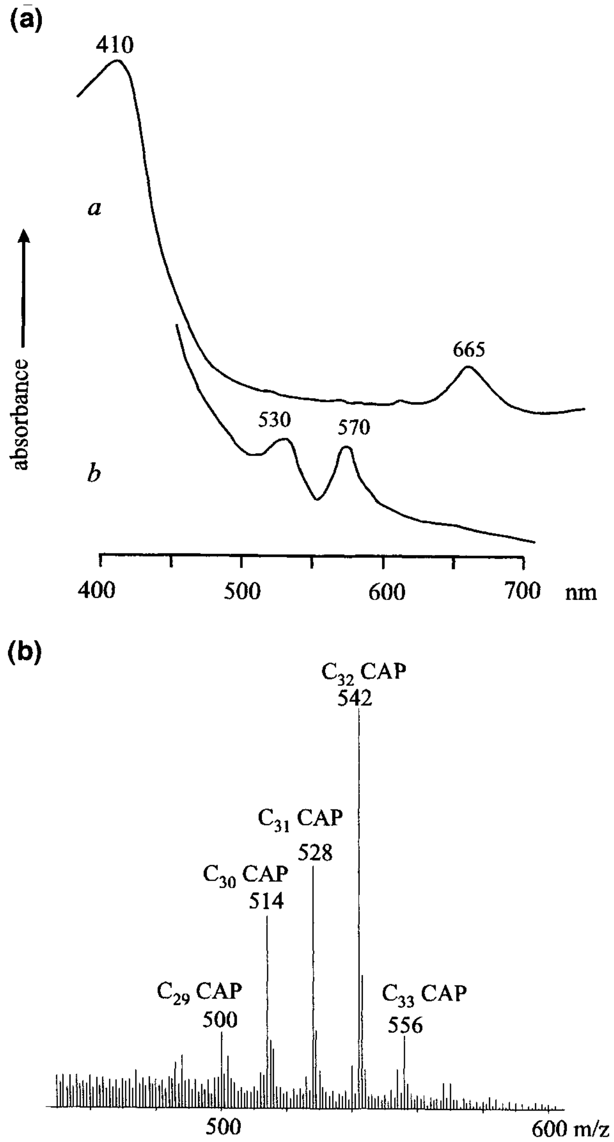


Fig. 3. (a) Absorbance spectra of two representative extracts with low (<10, *a*, containing mainly chlorins) and high (>10, *b*, containing mainly vanadyl porphyrins) S/I values. (b) Mass spectrum of vanadyl porphyrin fraction in combined extracts from Heinrich layer IV.

suggested, however, that primary productivity was low at these times (Bond et al., 1992; Broecker et al., 1992; Maslin, 1993). In addition, we found extremely low abundances of the long-chain alkenones of prymnesiophyte origin (de Leeuw et al., 1980; Volkman et al., 1980) in the sediments. This is based on the observation that no alkenones (generally considered to be more resistant to degradation than other lipid biomarkers) could be detected in the HL using GC with flame ionization detector, although they could be detected by the more sensitive GC-CI-MS technique. Although the latter was not calibrated for determining concentrations, it did appear that the alkenones were in lower abundance in the HL than in sediments above and below.

Sedimentation rates during the Heinrich events are estimated to be high (10–200cm/ka) (Dowdeswell et al., 1995), so perhaps it could be argued that the chlorins were preserved as a result of a "sealing" effect by the incoming sediment. However, chlorins accumulated (Fig. 2e) before and after IRD levels rose above glacial background (Fig. 2a), when the IRD would have been insufficient to allow such "sealing" and preservation of the chlorins in the sediment, the components being below detection limit outside of the HE horizons. Hence, since the chlorin data indicate that the HE started earlier and finished later than the lithological and magnetic data would indicate, and sediment exhaustion in the icebergs could take place long before melting was complete (Dowdeswell and Dowdeswell, 1989; Dowdeswell et al., 1995), we suggest that the presence of abundant meltwater, and not IRD, gave rise to the accumulation of chlorins during the HE. If the chlorin accumulation in the HL was not a result of increased productivity it is, by default, likely to have been a result of enhanced preservation. Although the factors which bring about the breakdown of chlorophyll in aquatic environments are not clear, oxic conditions appear to be important (Hendry et al., 1987; Brown et al., 1991; Sun et al., 1993). It has been argued that the large meltwater input during HE decreased or stopped deep water formation in the North Atlantic (Bond et al., 1993; Maslin, 1993; Broecker, 1994; Paillard and Labeyrie, 1994; Maslin et al., 1995). This would have reduced the bottom water oxygen content, as oxygen was being consumed and not replenished, so perhaps conditions were created which favoured the preservation and accumulation of chlorins. Hence, the chlorin data appear to endorse the presumed reduction in the thermohaline circulation during the HE, and the rapid switch between two states (on/off) of deep circulation, although we cannot rule out the possibility of productivity changes. Either way, the sudden appearance and disappearance of pigments in the sediment record illustrates the rapid change in oceanographic conditions triggered by these events.

4. CONCLUSIONS

Analysis of the autochthonous C_{37} alkenones in the BOFS 5K core Heinrich layers and measurement of the U^K_{37} index confirm earlier ideas that sea surface temperatures dropped

Fig. 2. Data for core 5K vs. depth (cm below sea floor, cmbsf) and ^{14}C age. (a) Ice rafted debris (%). (b) Magnetic susceptibility (c.g.s./1e^{-6} G/Oe). (c) Oxygen isotopes for *Globigerina bulloides* (solid circles) and *Neogloboquadrina pachyderma* (S) (empty circles). (d) Ratio between solvent extract absorbance at the Soret (410nm) and I (665nm) bands measured by electronic spectrophotometry. (e) Solvent extract absorbance (A) per dry weight of sediment (w) at 665 nm showing chlorin relative concentration. (f) U^K_{37} sea surface temperature estimates (annual average at 0 m depth; Rosell-Melé et al., 1995a). The Heinrich layers are indicated by the shaded bands, and numbered at the top of the plot.

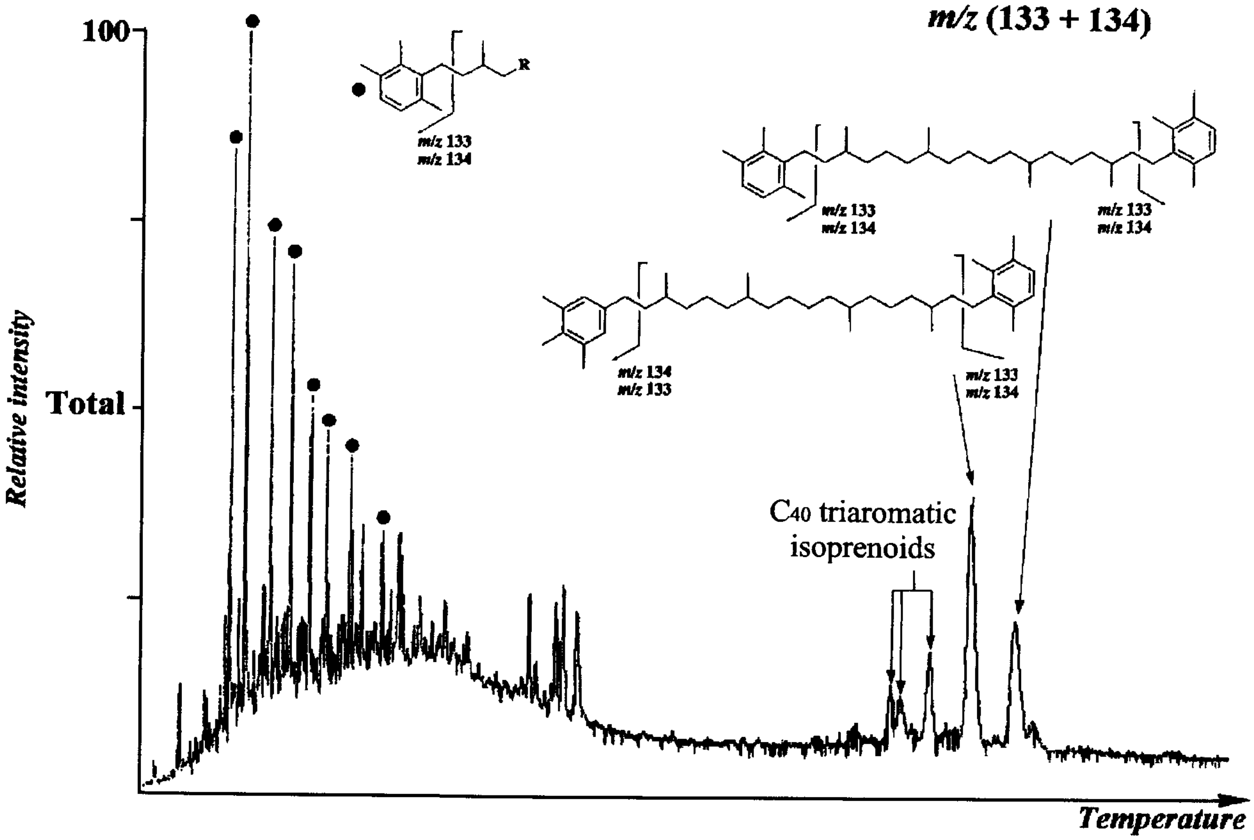


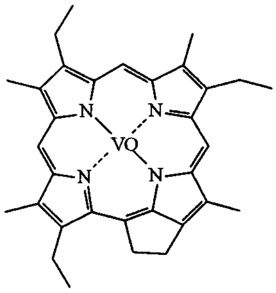
Fig. 4. Mass chromatogram m/z (133+134) of combined extracts of samples from Heinrich layers II and IV. Aryl isoprenoids are indicated by solid circles.

during the Heinrich events, probably as a result of fresh water released from melting icebergs.

Autochthonous chlorin pigments were observed only in the Heinrich layers and their accumulation is tentatively attributed to enhanced pigment preservation. We suggest that the accumulation of chlorins in the Heinrich layers may be the result of reduced bottom water oxygen content, earlier studies having suggested that large meltwater input reduced or stopped deep water formation in the North Atlantic.

Vanadyl porphyrins and carotenoid-derived aromatic hydrocarbons were present in ancient organic-rich sedimentary material of continental origin, contributed as ice rafted debris in Heinrich layers during iceberg melting. The presence of vanadyl porphyrins, together with the absence of their nickel counterparts and presence of specific aromatic hydrocarbons originating from the carotenoids of anaerobic green sulphur bacteria attest to the existence of anoxic conditions in the marine water column of the depositional setting of the ancient organic rich sediment. The distribution of the carotenoid-derived aromatic hydrocarbons is similar to component distributions observed previously in Palaeozoic sediments from North America, although a biomarker survey of potential "source rocks" is required before the location of the allochthonous sedimentary material can be identified.

This preliminary study indicates the potential of a biomarker approach for reconstructing palaeocurrent patterns through mapping of sedimentary molecular distributions.



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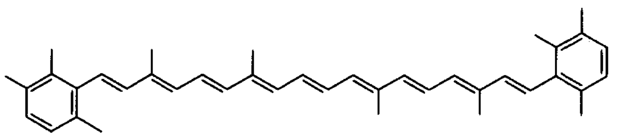

II

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