



PII S0016-7037(01)00776-1

Sources of fine-sized organic matter in North Atlantic Heinrich Layers: $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ tracers

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(Received February 22, 2001; accepted in revised form July 12, 2001)

Abstract—Organic carbon (OC) and total nitrogen (TN) concentrations and stable isotope ratios ($\delta^{13}\text{C}$, $\delta^{15}\text{N}$) of fine (<50 μm) size fractions of deep-sea sediments from the central North Atlantic were employed to identify changes in sources of organic matter over the past 50 ka BP. Ambient glacial sediments are characterised by values that reflect mixtures of marine and terrestrial inputs (averages $\pm 1\sigma$: OC/TN = 7.6 ± 0.8 ; $\delta^{13}\text{C} = -22.8 \pm 1.0\text{‰}$; $\delta^{15}\text{N} = 5.5 \pm 0.6\text{‰}$). $\delta^{13}\text{C}$, OC, and TN concentrations shift to higher values during the Holocene, indicating a gradual decrease of fine terrigenous supply to the North Atlantic. The unchanged $\delta^{15}\text{N}$ record between last glacial and Holocene stages indicates that the central North Atlantic region remained oligotrophic at least during the past 50 ka BP, but additional studies are required to support this result in terms of nitrogen oceanic budget. During the phases of enhanced ice-rafted detrital supply corresponding to prominent Heinrich events (HL₁, HL₂, HL₄, and HL₅), fine-sized sedimentary organic matter has lower OC and TN concentrations, contrasting sharply with those of ambient glacial sediments. Lower $\delta^{13}\text{C}$ (down to -28‰) and $\delta^{15}\text{N}$ (down to 1.6‰) values and high OC:TN ratios (up to 14.7 ± 1.1) are found for HL₁, HL₂, and with lesser extent for HL₄. These values reflect enhanced detrital supply originating from poorly differentiated soil horizons that characterise periglacial climate conditions and from organic matter-bearing rock sources of the underlying geological basement. During HL₅, only the $\delta^{13}\text{C}$ offset records the input of fine size ice-rafted organic matter. Gradually changing soil development conditions during the time interval covering HL₅ to HL₁ (marine isotope stages 5 to 2), as well as varying erosion levels, have been hypothesized on the basis of constant $\delta^{13}\text{C}$, increasing OC/TN and decreasing $\delta^{15}\text{N}$ values. Copyright © 2002 Elsevier Science Ltd

1. INTRODUCTION

During the past 70,000 yr BP, marine sedimentation in the NE Atlantic is interrupted by six phases of enhanced ice-rafting detritus (IRD) supply called Heinrich events (HL = Heinrich layer; Heinrich, 1988; Broecker et al., 1992; Bond et al., 1992; Andrews and Tedesco, 1992; Andrews, 1998). There is now convincing evidence that these episodes are also observed in various climate records (Bond et al., 1993; Grimm et al., 1993; Porter and An, 1995; Lowell et al., 1995; Benson et al., 1996; Sanchez-Goni et al., 2000). Direct links between Heinrich events, oceanic circulation, and ice sheet dynamics have also been shown (Alley and McAyeal, 1994; Paillard and Labeyrie, 1994; Broecker, 1994; Maslin et al., 1995; Dowdeswell et al., 1995; Manabe and Stouffer, 1997; Cortijo et al., 1997; Vidal et al., 1997; Zahn et al., 1997; Elliot et al., 1998; McManus et al., 1998; Bard et al., 2000; Grousset et al., 2000; Van Kreveld et al., 2000). Each event appears to be an episode of very rapid sediment accumulation, associated with a drop in foraminifer concentration due either to a decrease of marine productivity or to a dilution of marine input by IRD supply (Bond et al., 1992; Grousset et al., 1993). Dilution or reduction of marine supply is a question of great interest because changes in the thermohaline circulation mode due to freshwater influx during Heinrich events have been hypothesized to account for some of the rapid

climate oscillations observed in Greenland ice-core records (Broecker et al., 1990; Keigwin et al., 1991; Paillard and Labeyrie, 1994; Maslin et al., 1995; Zahn et al., 1997). Mineralogical and isotopic studies of the detrital supply in Heinrich Layers point to continental source areas located at high latitudes, with contrasting differences during Heinrich events 3 and 6 that are attributed to reduced Laurentide ice-sheet contributions (Jantschik and Huon, 1992; Bond et al., 1992; Grousset et al., 1993; Robinson et al., 1995; Revel et al., 1996; Gwiazda et al., 1996a, 1996b, 1998; Hemming et al., 1998). The enhanced supply of detrital organic matter of continental origin and its preservation under reduced bottom water oxygen content have also been shown by means of specific biomarkers (Rosell-Melé et al., 1997; Madureira et al., 1997) and sediment mass accumulation studies (Manighetti and McCave, 1995) in various North Atlantic settings.

In this study, we provide a high-resolution elemental (organic carbon and total nitrogen) and isotopic ($\delta^{13}\text{C}$ and $\delta^{15}\text{N}$) record of fine-sized (<50 μm) particulate organic matter in North Atlantic deep-sea sediments covering the HL₁ to HL₅ time interval (back to ~ 50 ka BP; Bond et al., 1993). This study was performed in order: (1) to estimate the contribution of terrestrial organic matter in glacial marine sediments due to enhanced IRD supply, and (2) to discuss some of the factors controlling the isotopic signature of preserved sedimentary organic matter in the North Atlantic during the last glaciation. Indeed, identification of terrigenous and marine supplies is necessary when estimating ocean paleo-productivity (or paleo-

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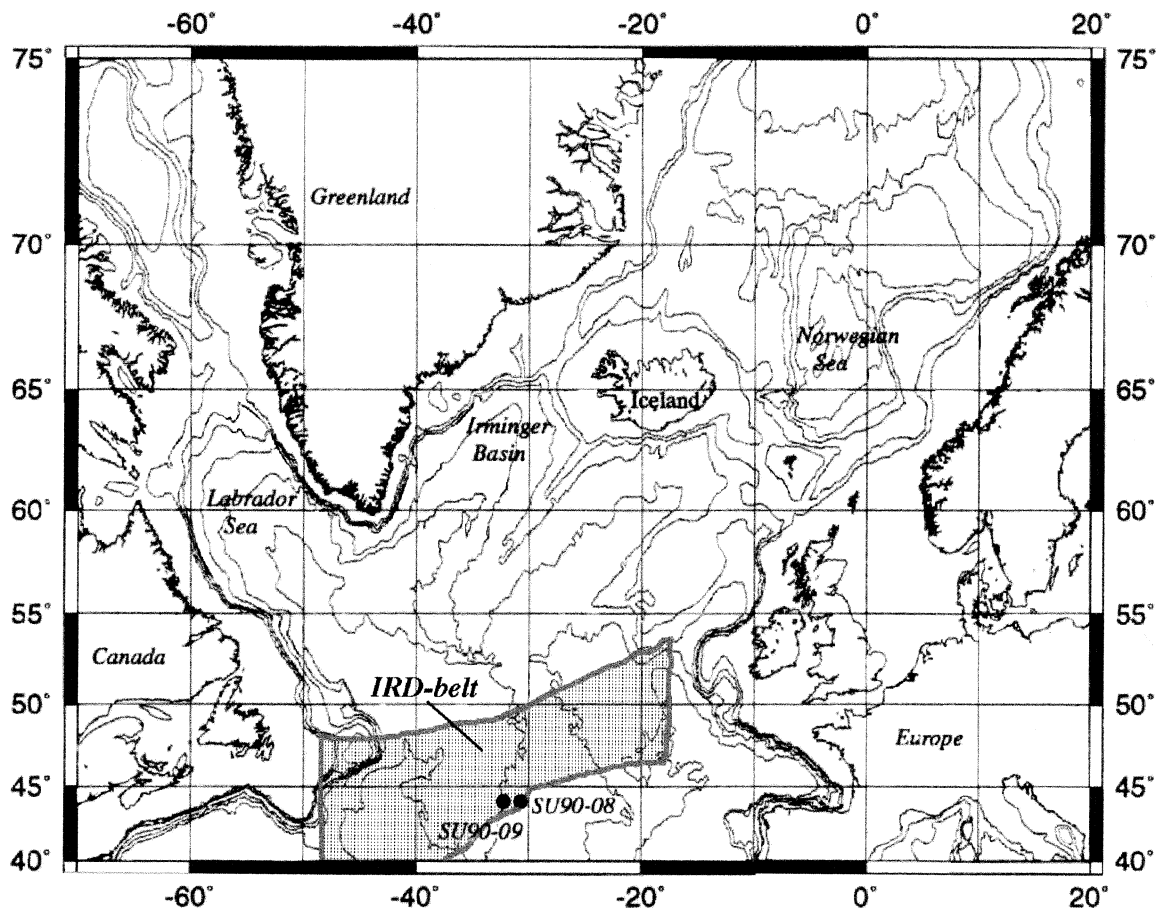


Fig. 1. Location of core SU90-09 in the central North Atlantic. This map was obtained using Online Map Creation (www.aquarius.geomar.de/omc/). The location of the "Ruddiman ice-rafted detritus belt" (Ruddiman, 1977) is also displayed.

pCO₂ level) using the organic matter content of deep-sea sediments (Pedersen et al., 1991; Sancetta, 1992; Sarthein et al., 1992; Bentaleb et al., 1996). Moreover, better links between open sea environments (in the oligotrophic zone) and productive continental margins (François et al., 1997; Ganeshram et al., 2000; Kienast, 2000) are also expected, using the well-dated Heinrich events for stratigraphic correlations.

2. SEDIMENTARY AND STRATIGRAPHIC FRAMEWORK

Sediment samples were recovered from piston core SU90-09 (43°05'N-31°05'W; water depth: 3375 m), located in the North Atlantic on the western side of the Mid Atlantic Ridge (Fig. 1). Core SU90-09 is ~1000 m shallower than the abyssal plain, and sedimentary input is mainly due to vertical fluxes (Grousset and Chesselet, 1986). Cross-correlations with reference core SU90-08 (43°31'N-30°24'W) and down-core position of HL₁-HL₅ were performed using coarse lithic grain (>150 μm) counts, low-field magnetic susceptibility, reflectance ("grey scale") records, and Accelerator Mass Spectrometry (AMS) ¹⁴C ages on monospecific *N.pachyderma s.* shells, following the methods described in Grousset et al. (1993), Cortijo et al. (1995), and Grousset et al. (2001). All ¹⁴C age values are uncalibrated radiometric ages, corrected for a 400 yr reservoir

age effect (Bard, 1988). HL₁, HL₂, HL₃, HL₄, and HL₅ were identified at core depths 50.0 to 61.5 cm, 81.0 to 91.5 cm, 107.0 to 114.0 cm, 144.0 to 153.5 cm, and 187.0 to 193.5 cm, respectively (Fig. 2). HL₃ is weakly represented for core SU90-09, which was located at that time near the southern limit of polar waters extent and IRD supply (Ruddiman, 1977; Grousset et al., 1993). All radiometric ages obtained for HL₁-HL₃ are consistent with published data from several North Atlantic settings where limited bioturbation and sediment reworking have already been shown (Bond et al., 1992, 1993; Bond and Lotti, 1995; Cortijo et al., 1995; Vidal et al., 1997; Cortijo et al., 1997; Elliot et al., 1998; Grousset et al., 2000).

Using *N.pachyderma s.* ¹⁴C ages, an average sedimentation rate of $3.4 \pm 0.4 \text{ cm} \cdot \text{ka}^{-1}$ can be estimated for ambient glacial sediments (outside Heinrich Layers) between HL₁ and HL₂ and below HL₂ until 110 cm (Fig. 2). This average value shifts to $4.7 \text{ cm} \cdot \text{ka}^{-1}$ if Heinrich Layers are included in the calculation. With the ¹⁴C age of foraminifers sampled immediately below and above HL₁ ($14.74 \pm 0.04 \text{ ka BP}$ at 63 to 64 cm; $13.37 \pm 0.05 \text{ ka BP}$ at 49 to 50 cm), the sediment accumulation rate increases to $10.3 \pm 1.4 \text{ cm} \cdot \text{ka}^{-1}$. This estimate is consistent with the average value reported for HL₁ for core SU90-08 recovered in the same physiographic setting ($11.7 \text{ cm} \cdot \text{ka}^{-1}$,

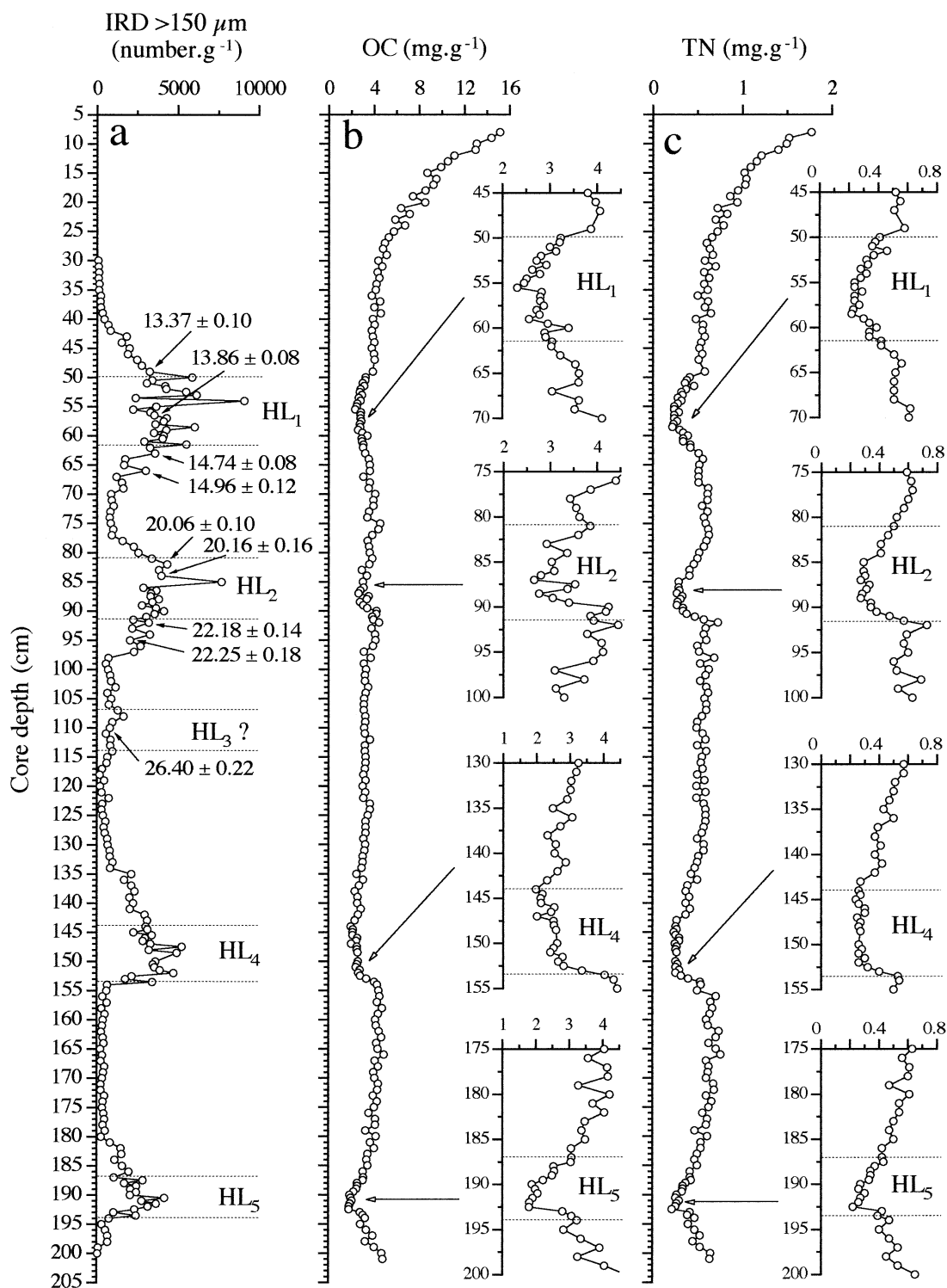


Fig. 2. Plots of down-core variations of: (a) IRD (>150 μm) content, (b) OC concentration with corresponding enlargements for prominent Heinrich Layers, and (c) TN content with corresponding enlargements for prominent Heinrich Layers, for fine (<50 μm) size fractions of carbonate-free samples (core SU90-09). ¹⁴C ages on monospecific *N.pachyderma s.* shells are from Grousset et al. (2001).

Table 3 in Elliot et al., 1998). However, taking into account an additional ¹⁴C value of 13.86 ± 0.04 ka BP measured within HL₁ (56 to 56.5 cm), it shows large variations, ranging from

$8.4 \pm 1.7 \text{ cm} \cdot \text{ka}^{-1}$ to $14.6 \pm 4.2 \text{ cm} \cdot \text{ka}^{-1}$ for 63 to 56 cm and 56 to 49 cm sediment depths, respectively. Our calculated sedimentation rate is lower in HL₂ ($4.4 \pm 0.4 \text{ cm} \cdot \text{ka}^{-1}$), but

Table 1. Organic carbon and total nitrogen elemental and stable isotope data for size fractions of selected samples (core SU90-09).

Nominal depth (cm)	Sediment type	Grain size fraction (μm)	[OC] ($\text{mg} \cdot \text{g}^{-1}$)	[TN] ($\text{mg} \cdot \text{g}^{-1}$)	OC/TN ($\text{mol} \cdot \text{mol}^{-1}$)	$\delta^{15}\text{N}$ vs. AIR (‰)	$\delta^{13}\text{C}$ vs. PDB (‰)
41.0		<50	4.03	0.56	8.4	5.3	-22.5
		50–200	2.06	0.29	8.3	nd	-26.0
47.0		<50	4.05	0.51	9.3	5.3	-23.6
		50–200	2.0	0.21	11.1	5.3	-26.5
62.0		<50	3.03	0.42	8.4	4.5	-24.8
		50–200	2.8	0.28	11.7	5.1	-26.9
148.0	HL ₄	<50	2.52	0.26	11.3	4.5	-27.8
		50–200	0.64	0.05 ^a	14.9	nd ^b	-29.7
150.5	HL ⁴	<50	2.51	0.28	10.5	4.5	-27.6
		50–200	0.86	0.05 ^a	20.1	nd ^b	-30.6
151.0	HL ⁴	<50	2.41	0.26	10.8	4.8	-27.9
		50–200	0.51	0.05 ^a	11.9	nd ^b	-29.9
152.0	HL ⁴	<50	2.64	0.26	11.8	3.5	-27.3
		50–200	0.69	0.05 ^a	16.1	nd ^b	-29.1

nd = not determined.

^a High uncertainty on TN measurement and OC:TN ratio.

^b Low yield.

is not supported by the $9.1 \text{ cm} \cdot \text{ka}^{-1}$ determined for core SU90-08 (Table 3 in Elliot et al., 1998). Therefore, it was not used in this study. Our sedimentation rate estimates are consistent with other published values (Grousset et al., 1993; Revel et al., 1996; Vidal et al., 1997; Cortijo et al., 1997). The high uncertainty attached to these values is mainly due to the low resolution of our ^{14}C dates, with respect to the submillimetric successions of laminated and coarse IRD deposits that compose Heinrich Layers (Grousset et al., 2001). The Younger Dryas event (11 to 10 ka BP, Mangerud et al., 1974) could not be precisely positioned in core SU90-09 sedimentary record. According to foraminifer assemblages (Duprat, personal communication) and assuming a high sedimentation rate during the Younger Dryas event (in the range of the mean estimate for HL₁, $\sim 10 \text{ cm} \cdot \text{ka}^{-1}$), the upper boundary would be placed at $31.1 \pm 1.4 \text{ cm}$, providing a thickness of $\sim 10 \text{ cm}$. The use of a high sedimentation rate is based on the assumption that this event is interpreted in the North Atlantic as an ultimate melt-water and ice-rafting event (HL₀; Andrews et al., 1995; Björck et al., 1996).

3. MATERIALS AND METHODS

3.1. Sample Collection

Sampling was carried out between 8 and 201 cm, at a spacing of every centimeter for ambient glacial sediments and for HL₃ and every half-centimeter for prominent Heinrich Layers (HL₁, HL₂, HL₄, and HL₅; Jantschik and Huon, 1992). We performed an almost continuous collection of samples except at 48 to 49 cm and 149 to 150 cm sediment depths. Assuming an average accumulation rate of $3.4 \pm 0.4 \text{ cm} \cdot \text{ka}^{-1}$ for ambient glacial sediments, sample spacing is 260 to 310 yr. For HL₁ sampling every half-centimeter with variable sediment accumulations ($8.4 \pm 1.7 \text{ cm} \cdot \text{ka}^{-1}$ to $14.6 \pm 4.2 \text{ cm} \cdot \text{ka}^{-1}$) provides data every 27 to 75 yr and, more likely in the same order of magnitude for the other Heinrich Layers due to their high sedimentation rates. In all tables and figures, sediment depths are reported using the upper boundary of each sampling interval (nominal depth 70 cm for sample depth 70 to 71 cm). Bulk sediment densities were calculated for samples between 46 and 67 cm (bracketing HL₁) using their water content (weight %) and assuming particle and water "densities" of $2.65 \text{ g} \cdot \text{cm}^{-3}$ and $1.00 \text{ g} \cdot \text{cm}^{-3}$, respectively (Table 1).

3.2. Elemental and Stable Isotope Measurements

Organic carbon (OC), total nitrogen (TN), $\delta^{13}\text{C}$, and $\delta^{15}\text{N}$ isotope ratios were measured, after carbonate removal, on the same sample aliquot by EA-IRMS (Carlo-Erba NA-1500 NC Elemental Analyser on line with a Fisons Optima Isotope Ratio Mass Spectrometer) at the Laboratoire de Biogéochimie Isotopique in Paris. Results for isotope abundance are reported in per mil (‰) relative to Pee Dee Belemnite (PDB) standard and relative to air N_2 , for $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$, respectively (Coplen et al., 1983). OC and TN are reported in $\text{mg} \cdot \text{g}^{-1}$ of dry sample (equivalent to weight %). During the course of this study, analytical precision was better than the means ($\pm 1\sigma$): $\pm 0.1\text{‰}$ for $\delta^{13}\text{C}$, $\pm 0.3\text{‰}$ for $\delta^{15}\text{N}$, $0.1 \text{ mg} \cdot \text{g}^{-1}$ for OC, and $0.05 \text{ mg} \cdot \text{g}^{-1}$ for TN. The uncertainty on OC:TN ratios averages 1.1, due to low nitrogen content and high OC and TN analytical uncertainties. Data reproducibility was checked by replicate analysis of samples (50%) and of a tyrosine standard which yielded $-23.2 \pm 0.1\text{‰}$ and $10.05 \pm 0.30\text{‰}$, for $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$, respectively (mean values for 610 measurements: $\delta^{13}\text{C} = -23.2\text{‰}$, $\delta^{15}\text{N} = 10.0\text{‰}$). All elemental and isotope values are displayed in Figures 2–7.

3.3. Grain Size Fractionation

Bulk sediment samples were sieved at $50 \mu\text{m}$. The choice of a fine size fraction for this study is justified by three main reasons: (1) terrigenous organic matter, transported "far off" its continental source, is rather concentrated in the fine size fraction, either dispersed in the sediment or linked to clay minerals (Keil et al., 1994, Christensen, 1996); (2) resistant soil organic matter is more concentrated in fine size fractions (Balesdent and Mariotti, 1996) and therefore, a better characterisation of continental sources of organic matter is expected; (3) the ratio of OC versus lithic content of bulk sediment is very low, in particular for Heinrich Layers which are enriched in coarse IRD, leading to high mineral matrix effects and reducing as much the resolution of the elemental analysis. To control the relevance of this procedure, coarser size fractions (50 to $200 \mu\text{m}$) were also separated for selected ambient glacial sediment and Heinrich Layers samples (Table 1). After carbonate removal, the coarse fractions of ambient glacial sediments yield OC and TN concentrations of 2.0 to $2.8 \text{ mg} \cdot \text{g}^{-1}$ and 0.21 to $0.29 \text{ mg} \cdot \text{g}^{-1}$, respectively. Although lower than for the corresponding $<50 \mu\text{m}$ size fractions, these values are in the range of those determined for fine size fractions. In contrast, the coarse size fractions of HL₄ samples provide much lower OC concentrations (0.5 to $0.9 \text{ mg} \cdot \text{g}^{-1}$), and their TN content ranges at the detection limit of the elemental analyser ($\sim 0.05 \text{ mg} \cdot \text{g}^{-1}$). Working with bulk samples in which more than 50 weight % is represented by the $>50 \mu\text{m}$ size

Table 2. Values used for sediment and organic carbon mass accumulation rate calculations in HL₁.

Nominal depth (cm)	Water content (wt · %)	Bulk sediment density (g · cm ⁻³)	[IRD > 150 μm] (number · g ⁻¹)	Total foraminifer content (number · g ⁻¹)	[<50 μm] (wt · %)	[OC] (mg · g ⁻¹)	δ ¹³ C vs. PDB (‰)
46	40.4	1.983	1,888	nd	42.08	3.97	-22.2
47	37.8	2.027	2,472	9,831	45.75	4.05	-23.6
48	37.2	2.036	2,767	7,513	nd	nd	nd
49	35.9	2.058	3,236	7,254	35.48	3.87	-23.4
50	31.9	2.123	5,857	11,607	39.82	3.23	-24.9
50.5	28.4	2.181	3,392	13,981	41.05	3.21	-25.3
51	27.6	2.194	3,066	9,257	45.67	3.00	-25.9
51.5	27.9	2.190	4,191	13,753	50.11	3.13	-25.0
52	26.9	2.207	4,273	8,545	41.80	2.81	-25.7
52.5	25.8	2.224	5,481	5,684	43.55	2.72	-26.3
53	22.1	2.285	6,137	5,431	44.18	2.93	-27.0
53.5	22.4	2.28	2,381	4,793	36.22	2.63	-27.3
54	22.1	2.285	9,095	7,311	32.71	2.79	-26.7
54.5	19.6	2.327	nd	nd	32.93	2.51	-26.8
55	17.7	2.357	3,641	1,458	27.70	2.46	-27.4
55.5	18.8	2.340	2,231	485	40.15	2.31	-27.4
56	17.5	2.362	3,299	2,465	26.76	2.83	-27.6
56.5	18.8	2.339	3,538	3,264	35.83	2.8	-27.8
57	18.4	2.347	4,284	1,423	36.37	2.8	-27.7
57.5	17.9	2.355	4,119	1,336	31.55	2.87	-27.5
58	17.2	2.366	3,604	179	43.70	2.72	-27.2
58.5	16.7	2.374	6,012	418	41.89	2.78	-28.0
59	18.4	2.347	4,273	648	35.77	2.56	-27.2
59.5	18.9	2.339	3,504	3,532	39.82	2.96	-27.3
60	19.7	2.324	4,122	3,440	40.06	3.4	-26.6
60.5	20.7	2.309	4,037	9,341	46.94	2.89	-26.6
61	27.7	2.192	2,922	7,807	43.08	2.91	-26.7
61.5	33.2	2.103	5,518	16,900	44.36	3.05	-25.8
62	30.8	2.142	3,262	6,568	43.56	3.03	-24.8
63	34.7	2.077	3,581	8,898	40.01	3.22	-24.4
64	40.5	1.982	1,746	25,474	36.86	3.54	-24.6
65	43.0	1.941	1,675	24,525	35.45	3.62	-24.3
66	45.3	1.903	3,008	22,230	34.23	3.61	-24.5
67	44.2	1.921	1,212	25,550	36.92	3.05	-23.4

nd = not determined.

fraction (Table 2) would forbid direct δ¹⁵N comparison between Heinrich Layers and ambient glacial sediments.

3.4. Carbonate Removal Procedure

To reduce possible leaching effects on sedimentary organic matter during carbonate removal, the size fractions were carefully treated with 1N HCl at 70°C in a way that pH was always maintained at 3.0. Preliminary experiments, together with X-ray diffraction controls,

showed that complete dissolution of carbonates following this procedure requires heating. When applied at room temperature, dissolution of calcite grains is complete but that of dolomite, more concentrated in prominent Heinrich Layers (HL₁, HL₂, HL₄, and HL₅) is always incomplete, leading to variable ¹³C enrichment with respect to the low δ¹³C usually obtained for organic matter (Table 3). All samples were rinsed in deionised water to remove dissolved salts. The solid residue was recovered by high-velocity centrifugation (6000 rounds · min⁻¹ for 3 h), dried at 35°C, and hand-grounded with a mortar, following a

Table 3. Comparison of elemental and stable isotope data for two different carbonate dissolution procedures applied to fine size (<50 μm) fractions of selected samples.

Nominal depth (cm)	Sediment type	δ ¹³ C vs. PDB (‰)	δ ¹³ C vs. PDB (‰)	[OC] (mg · g ⁻¹)	[OC] (mg · g ⁻¹)	[TN] (mg · g ⁻¹)	[TN] (mg · g ⁻¹)
<i>Sample treatment</i>		(1)	(2)	(1)	(2)	(1)	(2)
49		-19.1	-23.4	6.8	3.9	0.7	0.6
55.5	HL ₁	-16.1	-27.4	8.0	2.3	0.5	0.2
58	HL ₁	-19.6	-27.2	6.2	2.7	0.4	0.2
61	HL ₁	-24.4	-26.6	4.6	2.9	0.5	0.3
64		-25.4	-24.6	6.0	3.5	0.8	0.6
86.5	HL ₂	-15.0	-27.4	6.7	2.8	0.4	0.3
88	HL ₂	-20.1	-27.7	6.3	3.4	0.4	0.3
90	HL ₂	-18.4	-26.9	7.9	3.4	0.4	0.3
93		-23.4	-23.4	6.8	3.8	1.1	0.6

1 = dissolution at room temperature; 2 = dissolution at 70°C.

Table 4. Organic carbon concentrations [OC] of carbonate-free <50 μm size fractions of selected samples and dissolved organic carbon (DOC) concentrations of their filtered leachate solutions.

Nominal depth (cm)	Sediment type	Dry sample weight (g)	[OC] ($\text{mg} \cdot \text{g}^{-1}$)	OC (mg)	Leachate volume (mL)	DOC content ($\text{mg} \cdot \text{L}^{-1}$)	DOC content (mg)	OC loss ^a (%)
139		0.9626	2.57	2.47	13.6792	17	0.23	8.59
140		1.0621	2.54	2.70	13.9421	32	0.45	14.19
142		1.0787	2.62	2.83	13.1840	20	0.26	8.53
143		0.8423	2.31	1.95	13.8276	11	0.15	7.25
144	HL ₄	1.0592	1.98	2.10	12.6825	21	0.27	11.27
145	HL ₄	0.9176	2.12	1.95	11.9715	14	0.17	7.93
146	HL ₄	0.9621	2.53	2.43	12.1269	19	0.23	8.65
148	HL ₄	1.1055	2.52	2.79	13.1472	15	0.20	6.61
150	HL ₄	1.0851	2.61	2.83	10.0527	16	0.16	5.37
151	HL ₄	1.1487	2.41	2.77	13.6641	30	0.41	12.90
152	HL ₄	1.1800	2.64	3.11	13.0205	21	0.27	8.07
153	HL ₄	1.0712	3.35	3.59	13.5413	15	0.20	5.36
154		0.7850	4.30	3.38	13.2135	20	0.26	7.26
155		0.6898	4.41	3.04	13.7498	19	0.26	7.91
156		0.5975	4.53	2.71	14.5352	30	0.44	13.88
157		0.4354	4.29	1.87	13.3885	9	0.12	6.07

^a OC loss = DOC/(OC + DOC).

procedure commonly used for stable isotope studies of sedimentary organic matter (Schubert and Nielsen, 2000). The washing step is required as chlorine has a high water retention capacity. If not removed from the samples, high Cl^- content introduces large uncertainties during sample weighting for elemental analysis and thus, incorrect OC and TN weight percentage determinations. Moreover, dissolved salts interfere with the silica reduction columns of the Elemental Analyser, leading to incomplete OC-CO₂ and TN-N₂ conversions and variable ¹³C/¹²C and ¹⁵N/¹⁴N fractionations.

To monitor the effect of acid dissolution on the organic matter content of samples, dissolved OC measurements were carried out on the HCl leachates of 16 selected samples, previously filtered with GF/F silicon filters (pore size $\sim 0.8 \mu\text{m}$). These measurements were performed on a Shimadzu 5000 Carbon Analyser with an average 2% analytical uncertainty. Dissolved OC content ranges from 9 to 32 $\text{mg} \cdot \text{L}^{-1}$ (Table 4). With respect to the leaching volumes used, these concentrations correspond to OC losses of 0.12 mg to 0.45 mg, which represent 5.5% to 14.2% of the total OC content of the samples. However, almost all losses are lower than 9%. As very fine grain particulate OC (<0.8 μm) has also been released during desegregation of sediment samples in the liquid phase, these losses must be considered as overestimates of the OC resulting from selective HCl dissolution of sedimentary organic matter. A complete recovery of organic matter, particulate and hydrolysable (dissolved) OC, was also attempted. For this purpose, the leaching solutions of selected samples were passed through a Cl^-/OH^- strong anion exchanger (Dowex Marathon A2 polystyrene exchanger) to remove Cl^- with respect to dissolved OC. Complete exchange was assumed when the pH of the solution coming out of the columns rises to ~ 5.6 (CO₂-H₂O equilibrium pH for deionised water in the laboratory). Although the exchange resins have been previously thoroughly rinsed several times with deionised water, contamination due to the release of OC by the polystyrene exchanger has been noticed for several experiments. This contribution is small (~ 12 to $24 \text{ mg} \cdot \text{L}^{-1}$) but is in the same range as the dissolved OC concentration released in the leaching solutions. Moreover, the polystyrene balls of the anion exchanger display isotopic compositions ($\delta^{13}\text{C} = -33.3\%$ and $\delta^{15}\text{N} = -1.7\%$) that may artificially bias results toward depleted values, with respect to isotope fractionation between solid and liquid phases. Accordingly, the washing procedure was preferred to a complete recovery. Although more than 90% recovery was attained and only a very low amount of more "labile" organic matter has been lost during carbonate removal, we considered that our carbonate-free size fractions are mainly composed of resistant organic matter (-refractory; Zegouagh et al., 1999).

4. RESULTS

The down-core variation of OC and TN concentrations is displayed for fine sedimentary organic matter, together with IRD counts, in Figure 2. OC concentrations of $1.8 \text{ mg} \cdot \text{g}^{-1}$ to $15.2 \text{ mg} \cdot \text{g}^{-1}$ and TN concentrations of $0.22 \text{ mg} \cdot \text{g}^{-1}$ to $1.77 \text{ mg} \cdot \text{g}^{-1}$ are obtained. These contents decrease from $15.2 \text{ mg} \cdot \text{g}^{-1}$ and $1.77 \text{ mg} \cdot \text{g}^{-1}$ at 8 cm to $\sim 4.4 \text{ mg} \cdot \text{g}^{-1}$ and $0.6 \text{ mg} \cdot \text{g}^{-1}$ at 30 cm, respectively. This later depth corresponds to our first-order estimation of the Younger Dryas event termination. For convenience, the samples collected above 30 cm will be referred to as Holocene in the following text. Ambient glacial sediments below 30 cm display roughly constant concentrations with depth (averages $\pm 1\sigma$: OC = $3.7 \pm 0.6 \text{ mg} \cdot \text{g}^{-1}$, TN = $0.56 \pm 0.08 \text{ mg} \cdot \text{g}^{-1}$), although a slight increasing trend is displayed by the samples between HL₄ and HL₅. Noticeable decreases with sediment depth are also observed a few centimeters above the prominent Heinrich Layers (HL₁, HL₂, HL₄, HL₅), whereas rather steep increases characterise their bottom terminations (Fig. 2). Prominent Heinrich Layers display the lowest concentrations with maximum deviations of $1.9 \text{ mg} \cdot \text{g}^{-1}$ for OC and of $0.34 \text{ mg} \cdot \text{g}^{-1}$ for TN from ambient glacial sediment averages. HL₃ cannot be distinguished from ambient glacial sediments on the basis of its OC and TN concentrations that average ($\pm 1\sigma$) $3.3 \pm 0.2 \text{ mg} \cdot \text{g}^{-1}$ and $0.55 \pm 0.05 \text{ mg} \cdot \text{g}^{-1}$, respectively.

OC and TN concentrations are correlated (Fig. 3a). Such a correlation is required to check if the nitrogen content of samples is organic in nature with respect to OC (Stein and Rack, 1995). Because the zero-intercept value reveals the magnitude of possible inorganic nitrogen excess, the reliability of the correlation method depends on the accuracy of the linear regression fit. We used a least square fitting method with a reduced major axis procedure, recommended for such applications (Payne, 1991). Each set of samples (Holocene, ambient glacial and HL₃, prominent Heinrich Layers) displays linear relationships with very close slopes. Intercepts at $0 \text{ mg} \cdot \text{g}^{-1}$ OC yield values that are either slightly positive (0.102 ± 0.022

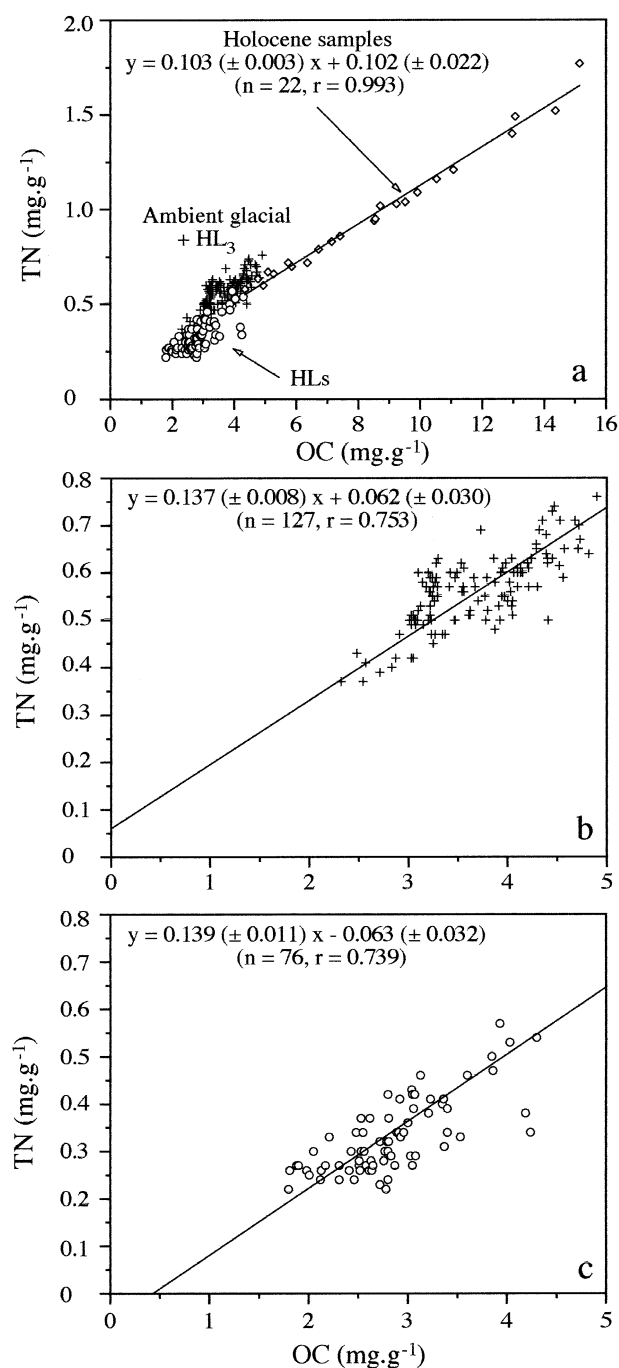


Fig. 3. Plots of OC vs. TN concentrations for fine (<50 μm) size fractions of carbonate-free samples (core SU90-09). (a) All samples. (b) Ambient glacial sediments + HL₃. (c) Prominent Heinrich Layers (HL₁, HL₂, HL₄, HL₅). Regression lines are calculated using a least square fit with a reduced major axis procedure (Payne, 1991). All Pearson's r coefficients are significant from zero at 99.9%.

$\text{mg} \cdot \text{g}^{-1}$ for Holocene samples, Fig. 3a) or fall to zero according to their statistical uncertainty ($0.062 \pm 0.030 \text{ mg} \cdot \text{g}^{-1}$ for ambient glacial and HL₃ samples, Fig. 3b; $-0.063 \pm 0.032 \text{ mg} \cdot \text{g}^{-1}$ for Heinrich Layers, Fig. 3c). Possible nitrogen excess can only be hypothesized for Holocene sediments. Such excess, when existing, is statistically interpreted as reflecting the pres-

ence of bound inorganic nitrogen ($-\text{NH}_4^+$); in particular for sediments having high clay and low OC contents (Stein and Rack, 1995). However, the intercept value calculated for Holocene samples only exceeds the maximum analytical uncertainty ($\pm 0.05 \text{ mg} \cdot \text{g}^{-1}$, 1σ) by a factor of 2. Typical inorganic nitrogen excesses are usually reported on the basis of higher intercepts around 0.3 to $0.5 \text{ mg} \cdot \text{g}^{-1}$ (Emmer and Thunell, 2000; Schubert and Calvert, 2001). Therefore, we estimate that our TN concentrations are organic in nature and that the influence of inorganic nitrogen on $\delta^{15}\text{N}$ values, if any, can be neglected.

The down-core variation of OC:TN ratio (also quoted as C/N) is displayed in Figure 4. The values are expressed as molar ratios ($\text{mol} \cdot \text{mol}^{-1}$ as in the Redfield ratio, Redfield et al., 1963). Most of the values for ambient glacial and HL₃ sediments (average $\pm 1\sigma$: 7.6 ± 0.8) are in the range of the mean ratio for marine phytoplankton (6.6; Redfield et al., 1963), recently reconsidered at 7.4 ± 1.3 ($117 \pm 14/16 \pm 1$; Anderson and Sarmiento, 1994). High OC/TN are obtained for the late Heinrich events, contrasting sharply with the values displayed by ambient glacial and HL₃ sediments. Increases up to 14.7 ± 1.1 are observed in HL₁ and HL₂. However, the maximum shift is lower for HL₄ (up to 11.8 ± 1.1), and no significant increase is noticed for HL₅. The OC/TN record follows that of IRD abundance, in particular for HL₅ where low OC/TN correspond to low IRD deliveries (Figs. 2 and 4).

OC mass accumulation rates (CAR) have been estimated for fine size fractions of HL₁, using the equation $\text{CAR} = \text{MAR} \times \text{OC}$ ($\text{mgC} \cdot \text{cm}^{-2} \cdot \text{ka}^{-1}$), where $\text{MAR} = d \times F \times S$ is the mass accumulation rate ($\text{g} \cdot \text{cm}^{-2} \cdot \text{ka}^{-1}$), d is the dry bulk sediment density ($\text{g} \cdot \text{cm}^{-3}$, Table 2), S is the sedimentation rate (S , $\text{cm} \cdot \text{ka}^{-1}$), F is the fine (<50 μm) size fraction abundance (wt.%, Table 2), and OC is the fine OC concentration ($\text{mg} \cdot \text{g}^{-1}$, Table 2). The results of CAR estimates are plotted in Figure 5, along with IRD content, total foraminifer content, sediment density, fine OC concentration, and $\delta^{13}\text{C}$ values. Calculated IRD and total foraminifer accumulation rates are also reported. For HL₁ samples, we used the average sedimentation rate previously calculated ($S = 10.3 \pm 1.4 \text{ cm} \cdot \text{ka}^{-1}$). The average value ($S = 3.4 \pm 0.4 \text{ cm} \cdot \text{ka}^{-1}$) was applied to ambient glacial sediments located immediately below (62 to 67 cm) and above (49 to 46 cm) HL₁. The mass accumulation rates calculated for samples located at the upper and lower limits of Heinrich Layers may be underestimated, due to gradually changing IRD delivery. However, this discrepancy is limited because sediment density and OC concentrations are independent parameters. The bulk sediment densities (1.92 to $2.37 \text{ g} \cdot \text{cm}^{-3}$, Table 2) are consistent with the ones reported by Auffret et al. (1996) for prominent Heinrich Layers of the northeast Atlantic. Fine terrigenous fraction fluxes average $2.6 \pm 0.4 \text{ g} \cdot \text{cm}^{-2} \cdot \text{ka}^{-1}$ for MAR and $9.2 \pm 1.6 \text{ mgC} \cdot \text{cm}^{-2} \cdot \text{ka}^{-1}$ for CAR during ambient glacial sedimentation. Due to the rise of sediment density and sedimentation rate in HL₁, MAR and CAR increase to maximum values of $11.3 \pm 2.4 \text{ g} \cdot \text{cm}^{-2} \cdot \text{ka}^{-1}$ and $35.4 \pm 4.8 \text{ mgC} \cdot \text{cm}^{-2} \cdot \text{ka}^{-1}$, respectively.

The down-core variation of $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values for fine-sized organic matter is displayed in Figure 4. The isotope values range from -19.7‰ to -28.0‰ for $\delta^{13}\text{C}$ and 1.6‰ to 7.0‰ for $\delta^{15}\text{N}$. The highest $\delta^{13}\text{C}$ values are obtained for Holocene sediments, which also show a regular increasing

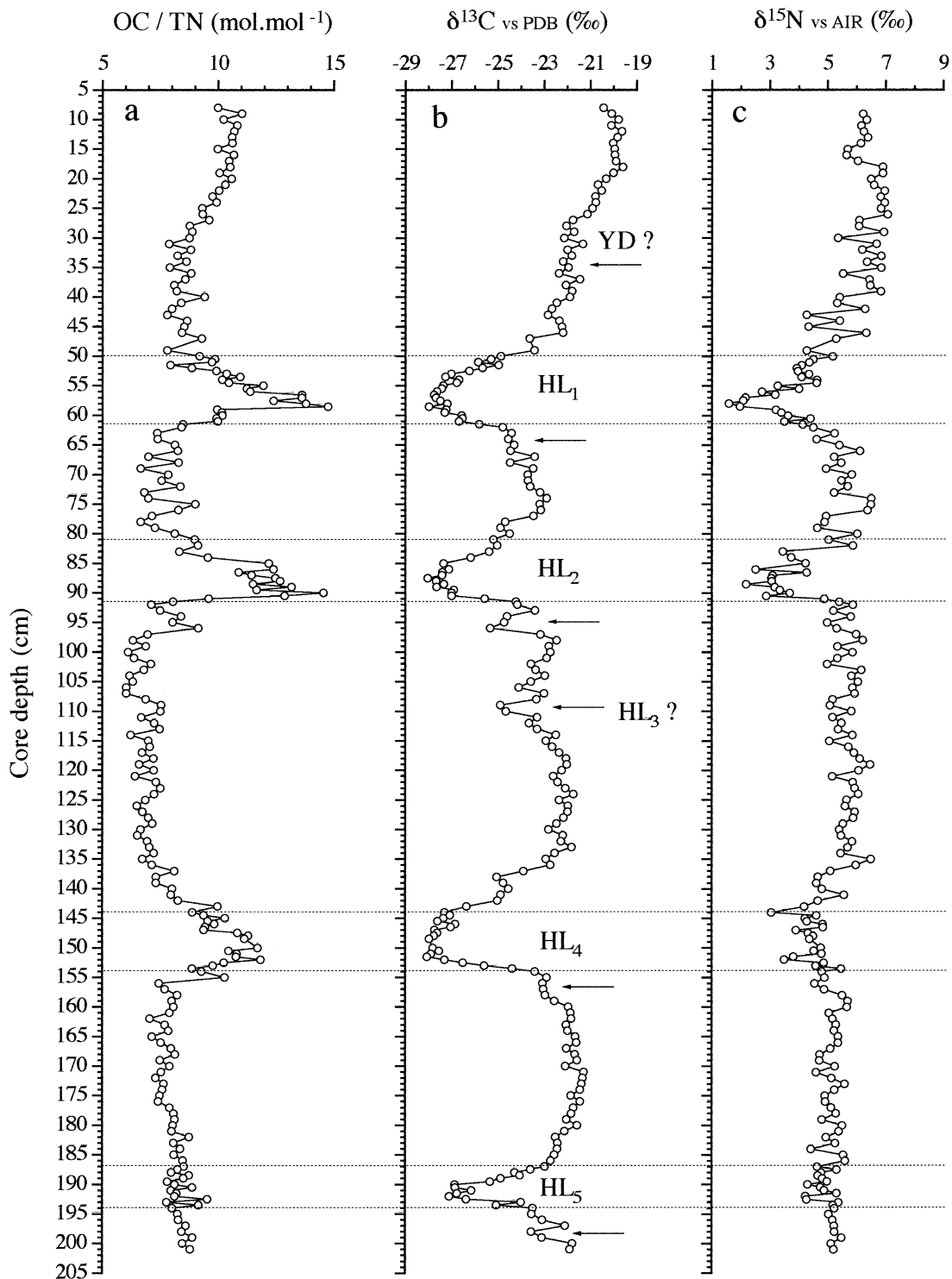


Fig. 4. Plots of down-core variation of: (a) OC:TN molar ratios, (b) $\delta^{13}\text{C}$, and (c) $\delta^{15}\text{N}$, for fine ($<50\ \mu\text{m}$) size fractions of carbonate-free samples (core SU90-09). Black arrows refer to particular sediment depth intervals discussed in the text. YD = Younger Dryas event, HL₁-HL₅ = Heinrich events 1 to 5.

trend toward the core top. The lowest $\delta^{13}\text{C}$ values are recorded during the phases of enhanced ice rafting corresponding to prominent Heinrich Layers (HL₁, HL₂, HL₄, and HL₅). Concomitant decreasing $\delta^{15}\text{N}$ trends are only observed in HL₁,

HL₂, and partly in HL₄. The down-core $\delta^{15}\text{N}$ variation mirrors that of OC:TN ratios. The lowest values are found in Heinrich Layers. They contrast sharply with those measured for ambient glacial sediments that average ($\pm 1\sigma$) $-22.8 \pm 1.0\text{‰}$ (range:

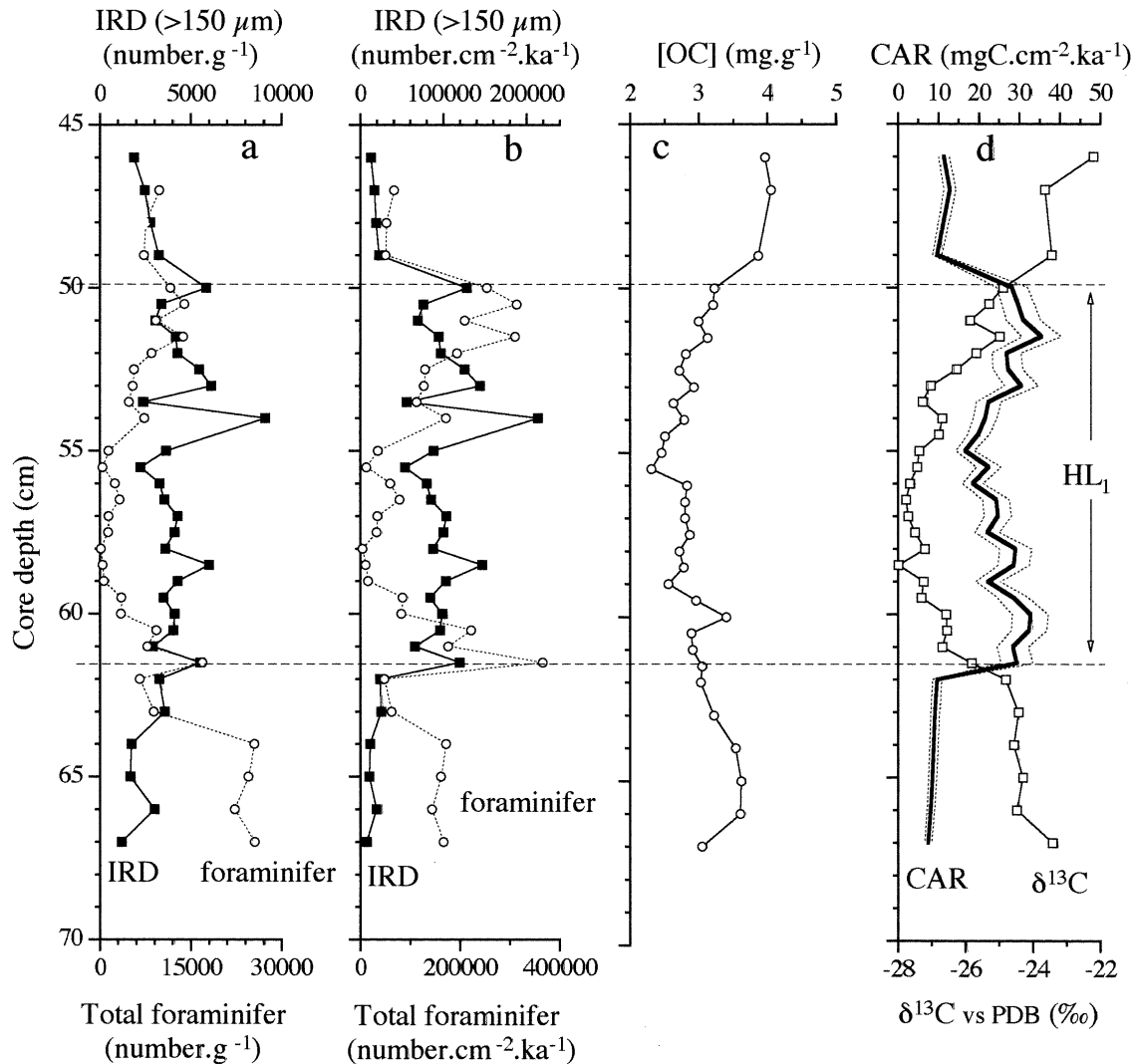


Fig. 5. Plots of (a) IRD (>150 μm) and total foraminifer contents, (b) IRD (>150 μm) and total foraminifer accumulation rates, (c) OC concentration of fine (<50 μm) size fractions of carbonate-free samples (core SU90-09), (d) fine-sized carbon mass accumulation rate (CAR) and δ¹³C values. CAR were calculated with $S = 3.4 \pm 0.4 \text{ cm} \cdot \text{ka}^{-1}$ for ambient glacial sediments and with $S = 10.3 \pm 1.4 \text{ cm} \cdot \text{ka}^{-1}$ for HL₁.

−24.1 to −21.3‰) and $5.5 \pm 0.6\text{‰}$ (range: 4.3 to 6.5‰), for δ¹³C and δ¹⁵N, respectively. As for OC and TN concentrations, the isotopic values measured for HL₃ samples (107 to 114 cm) do not show significant deviations from ambient glacial sediments. A slight δ¹³C decrease (~1.5‰) is, however, observed for samples at 109 to 110 cm core depth. The transitions from ambient glacial sedimentation to Heinrich Layers are characterised by sharp δ¹³C decreases, which mirror the behaviour of OC and TN concentrations (Fig. 2). On the contrary, the return to ambient glacial conditions, following prominent Heinrich Layers, is rather progressive and partly initiated before the end of the ice-rafting events, at 53 cm for HL₁ (50 to 61.5 cm), 86 cm for HL₂ (81 to 91.5 cm), or 190 cm for HL₅ (187.0 to 193.5 cm). Temporary δ¹³C decreases (or plateaus) are also observed, shortly preceding Heinrich events (63 to 66 cm for HL₁, 93 to 97 cm for HL₂, 155 to 159 cm for HL₄, and 197 to 200 cm for HL₅).

5. DISCUSSION AND INTERPRETATION

5.1. Fine-Sized Sedimentary Organic Matter Supply

Fine OC concentrations are low (<1.5 wt.%, Fig. 2) but, in the range of the values reported for surface marine sediments in the oligotrophic zone of the North Atlantic (Premuzic et al., 1982). The regular increase of OC and TN above ~30 cm suggests either a gradual increase in fine-sized organic matter supply during the Holocene or a depth-related degradation trend of sedimentary organic matter (Emerson et al., 1985). An argument against degradation is that the change ~30 cm depth corresponds to our first-order estimation of the last glacial/interglacial (-Holocene) boundary. The transition between the Late Glacial and the Holocene is characterised by a major change in sediment composition (Shackleton and Opdyke, 1973; Mayer, 1991). Marl-like sediments (low CaCO₃ content), typical of glacial sedimentation, are gradually replaced by

foraminiferal oozes (high CaCO_3 content). Thus, biologic carbonate supply increases during the Holocene. Evidence of changing source of organic matter is also shown by the $\delta^{13}\text{C}$ and the OC/TN values obtained for samples above ~ 30 cm. Extensive collection of surface organic matter in the open sea has shown that planktonic $\delta^{13}\text{C}$ vary with latitude (Sackett et al., 1965; Fontugne and Duplessy, 1981; Rau et al., 1989; Goericke and Fry, 1994; Bentaleb et al., 1996). Although only scarce data have been reported for SU90-09 core location, our uppermost Holocene $\delta^{13}\text{C}$ mirror present-day marine surface organic matter values (-19‰ to -22‰). The gradually increasing OC/TN trend, from ~ 8.5 at 30 cm to ~ 10.5 at 8 cm, corresponds to an increase of fine OC concentrations in sediments with respect to TN; a first-order estimate of a changing sedimentary organic matter supply during the Holocene.

Bulk sediment mass accumulation rates based on using ^{230}Th data have been reported for HL₁ in a neighbor core ($19 \text{ g} \cdot \text{cm}^{-2} \cdot \text{ka}^{-1}$; François and Bacon, 1994) and in the northeast Atlantic ($12.5 \text{ g} \cdot \text{cm}^{-2} \cdot \text{ka}^{-1}$; Thomson et al., 1995). These values are higher than our fine size fraction estimate ($11.3 \pm 2.4 \text{ g} \cdot \text{cm}^{-2} \cdot \text{ka}^{-1}$ for HL₁). However, if we take into account the amount of fine $<50 \mu\text{m}$ sediment of our samples (30 to 50%), we obtain a value close to that reported by François and Bacon (1994). Because fine size fraction percentages and OC concentrations decrease in HL₁, the observed shift of OC mass accumulation rate is solely linked to the increase of sediment density and accumulation rate, both accompanying enhanced ice-rafting detritus supply. OC fluxes also display minimum values within HL₁ ($16.5 \pm 2.3 \text{ mgC} \cdot \text{cm}^{-2} \cdot \text{ka}^{-1}$ at 55 cm), but they are still above those of ambient glacial sediments sampled immediately below and above HL₁ (average $\pm 1\sigma$: $9.2 \pm 1.6 \text{ mgC} \cdot \text{cm}^{-2} \cdot \text{ka}^{-1}$). As shown in Figure 5, the low OC concentrations also correspond to periods of minimum foraminifer mass accumulation. Fine organic matter $\delta^{13}\text{C}$ values are positively correlated with total foraminifer content, as well as with total foraminifer mass accumulation rates ($r = 0.871$, $n = 23$). Enriched ^{13}C compositions and higher OC concentrations are obtained for periods of high foraminifer fluxes that are observed at the bottom and top parts of HL₁, but the highest $\delta^{13}\text{C}$ values are still lower than those in ambient glacial sediments (average $\pm 1\sigma$: $-22.8 \pm 1.0\text{‰}$). The concomitant decrease of fine OC concentrations, $\delta^{13}\text{C}$, and total foraminifer content suggests a dilution of ambient glacial sedimentary organic matter by IRD organic supply. In that sense, the continental organic matter source is characterised by depleted $\delta^{13}\text{C}$ values and low OC concentrations. This question will be addressed more precisely in the following sections.

5.2. Diagenetic or Source Isotope Signatures for Fine-Sized Sedimentary Organic Matter?

Postdepositional degradation of organic matter in deep-sea sediments is characterised by significant changes due to preferential release of nitrogen and concomitant ^{15}N enrichment (Altabet, 1996; François et al., 1997). The down-core $\delta^{15}\text{N}$ record provides the opposite trend in HL₁, HL₂, and partly HL₄. Moreover, no significant deviation from ambient glacial sediments is shown by HL₅. This does not mean that diagenetic effects are absent (for example, $+4\text{‰}$ $\delta^{15}\text{N}$ offset between settling particles and top core sediment in the southern Ocean;

François et al., 1997), but rather that fine-sized organic matter recovered in sediments is mainly composed of “refractory” OC, less sensitive to postdeposition degradation processes. Indeed, Thomson et al. (1996) reported in northeast Atlantic sediments a diagenetic redistribution with depth of redox elements, consecutive of varying sedimentary mass accumulation rates. Moreover, secondary carbonate precipitation is also suspected in prominent dolomite-rich Heinrich Layers (Jantschik, 1991; Auffret et al., 1996). However, physical protection of settling organic matter particles by the predominant mineral components may account for better preservation of organic matter in the water column as well as in sediments (Hedges et al., 2001). Therefore, as higher sedimentary fluxes characterise Heinrich Layers, enhanced preservation of source organic matter from bacterial oxidation and thus, of source isotope signature, can be expected. Enhanced deposition fluxes due to melting icebergs could have protected the organic-rich surface zone of the sediment. Reduced permeability would induce limited bacterial activity and better preservation of sedimentary organic matter. Moreover, a lowering of bottom ventilation tied to surface meltwater inputs has been reported during Heinrich events in several North Atlantic settings (Sarnthein et al., 1994) and, especially for the neighbor core SU90-08 (Vidal et al., 1997). Reduced oxygen supply to bottom waters may also contribute to better preservation of organic matter from degradation processes. Accordingly, both high mass accumulation rates and reduced bottom water ventilation may account for better preservation of organic matter in Heinrich Layers.

Our results are only partly supported by the depositional fluxes published by Manighetti and McCave (1995) in the northeast Atlantic. In their study, fine ($<63 \mu\text{m}$) OC concentrations of glacial sediments, that are in the same range as those of our fine ($<50 \mu\text{m}$) size fraction values, also decrease during HL₁ in some of the sediment cores studied. However, OC mass accumulation enhancement is only observed for bulk sediment samples; fine-sized OC fluxes remaining apparently unchanged during the major pulse of IRD supply. If degradation under oxic conditions does not account for the observed elemental and stable isotope changes, methanogenic bacteria could also be capable of continuing degradation processes under low oxygen conditions that may prevail in Heinrich Layers. For instance, the concomitant $\delta^{13}\text{C}$ decrease and OC/TN increase in HL₁ and HL₂ could be explained by selective degradation of more labile ^{13}C -rich organic molecules such as carbohydrates and amino acids (Heinrichs, 1992). But this assumption does not hold if OC/TN values are taken into account because the assumed degradation effect tends to fade in HL₄ and is no longer observed for HL₅. Thus, it is unlikely that postdeposition diagenetic effects are responsible for the down-core elemental and stable isotope values, in particular during Heinrich events.

5.3. Terrestrial versus Marine Sources of Fine-Sized Organic Matter

Sedimentary organic matter in deep-sea sediments from the North Atlantic can be derived from several possible sources: terrestrial biologic, soil and lithic material supplied by wind, surface, and bottom oceanic circulation and ice rafting; and marine organic matter derived from planktonic and benthic sources such as foraminifers. Stable ($\delta^{13}\text{C}$ and $\delta^{15}\text{N}$) isotopes

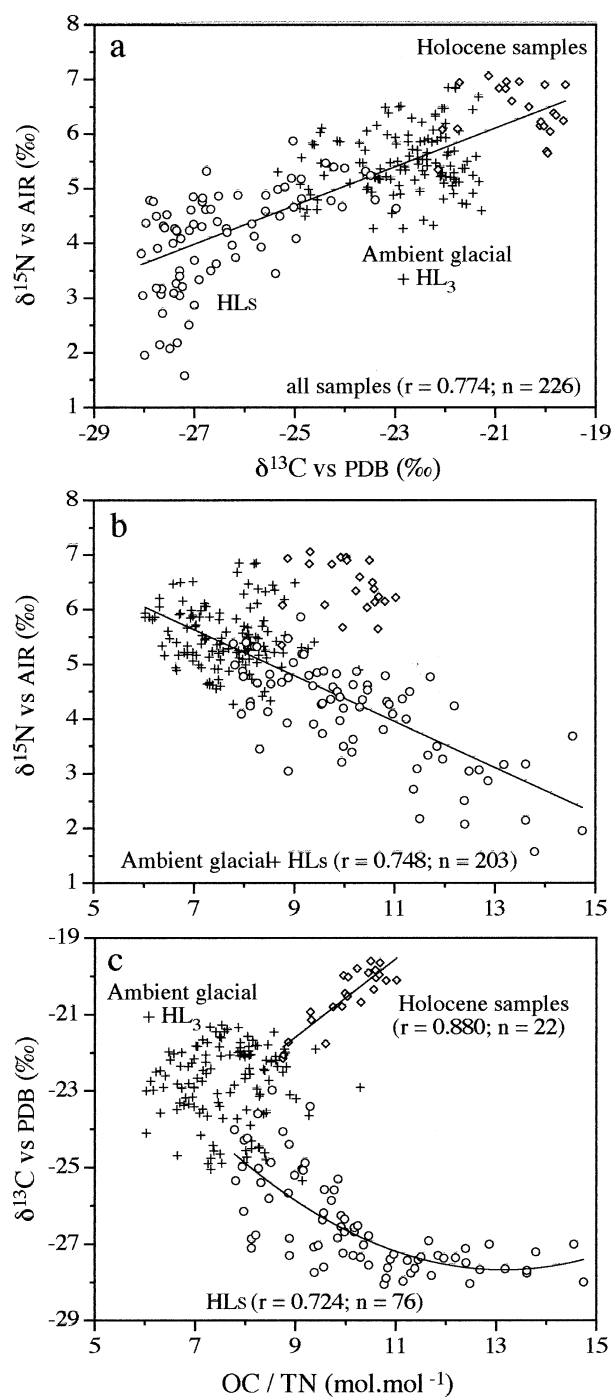


Fig. 6. Plots of (a) $\delta^{15}\text{N}$ vs. $\delta^{13}\text{C}$, (b) $\delta^{15}\text{N}$ vs. OC:TN ratios, (c) $\delta^{13}\text{C}$ vs. OC:TN ratios, for fine ($<50\ \mu\text{m}$) size fractions of carbonate-free samples (core SU90-09). Pearson's r coefficients are significant from zero at 99.9%.

and OC:TN ratios can be used as first-order tools for discriminating between these possible sources (Meyers, 1997). A first-order linear correlation can be drawn between $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values (Fig. 6a). This relationship is usually interpreted as a mixing trend between terrestrial and marine sources of organic matter, providing depleted and enriched isotope ratios, respectively (Peters et al., 1978; Mariotti et al., 1984; Wada et al.,

1987; Thornton and McManus, 1994; Ohkouchi et al., 1997; Muzuka and Hillaire-Marcel, 1999). In core SU90-09, the marine end-member would have an isotopic signature approached by Holocene samples, whereas the terrestrial source end-member corresponds to Heinrich Layers samples.

Plots of $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$ values against OC/TN state more precisely the mixing assumption (Fig. 6b,c). The negative correlations indicate that the terrestrial end-member is best approximated by a fine organic matter component defined with HL₁ and HL₂ samples, which is depleted in nitrogen (high OC/TN), ^{15}N (low $\delta^{15}\text{N}$), and ^{13}C (low $\delta^{13}\text{C}$). The second end-member falls in the range of ambient glacial sediments (averages $\pm 1\sigma$: $\delta^{15}\text{N} = 5.5 \pm 0.6\text{‰}$, $\delta^{13}\text{C} = -22.8 \pm 1.0\text{‰}$; OC/TN = 7.6 ± 0.8) and is more difficult to identify due to a large dispersion of the data. $\delta^{13}\text{C}$ values provide a better discrimination of the potential end-members because the $\delta^{15}\text{N}$ record does not show a marked difference between Late Glacial and Holocene stages.

Two distinct mixing trends can be portrayed. Holocene sediments display a linear relationship corresponding to a binary mixture in which one end-member is best represented by ambient glacial sediments, the second being a source enriched in ^{13}C ($\sim -19\text{‰}$) and in OC (OC/TN > 10), approached by the most recent Holocene deposits. The second mixing trend connects ambient glacial sediments on one side and Heinrich Layer samples on the other. Fine ice-rafted organic matter displays low $\delta^{13}\text{C}$ (-27‰ to -28‰) but varying OC/TN (8.5 to 15.0) and $\delta^{15}\text{N}$ (1.6‰ to 5.5‰). Ambient glacial sediment $\delta^{13}\text{C}$ values can be in the range of possible planktonic production if the source was located at higher latitude than for Holocene sediments. This assumption is consistent with a southward migration of polar waters to midlatitudes during the last glacial maximum (Ruddiman, 1977). The more depleted values found for Heinrich Layers (in the range -28‰) could also reflect marine supply if the source was located at even higher latitudes. However, detailed studies of sedimentary organic matter in polar regions have shown that organic matter can be enriched in ^{13}C , leading to a scattered range of values for sediments and surface waters (-15‰ to -27‰ ; Nakatsuka et al., 1995; Gibson et al., 1999; Muzuka and Hillaire-Marcel, 1999; Schubert and Calvert, 2001). Highly variable isotope fractionation in plankton or algae, low atmospheric CO_2 levels, or local terrestrial inputs were argued to account for this scattering.

For core SU90-09, the high OC/TN values do not support an exclusive marine contribution, at least for HL₁ and HL₂. Indeed, OC/TN greater than 10 are usually interpreted as reflecting soil organic matter of the top horizons that is usually impoverished in nitrogen. Another terrestrial source of organic matter with high OC/TN is supplied by ice rafting of glacially eroded debris of organic matter-bearing sedimentary rocks (Tyson, 1995). They have already been identified for HL₂ and HL₄ in North Atlantic sediments (Rosell-Melé et al., 1997). The origin of particular organic compounds, unexpected in late Quaternary sediments, was attributed to ancient, organic-rich sedimentary material of continental origin, similar to the Paleozoic carbonate rocks overlying the Precambrian basement of North America. Other evidence, among others, of rock-derived sources in North Atlantic sediments is shown by the occurrence of detrital dolomite grains. This component may represent up to 17% of the bulk sediment mineralogical content for prominent

Heinrich Layers (Jantschik, 1991). After complete carbonate removal, the isotopic composition of our samples also accounts for this contribution, although in minor abundance with respect to the other potential sources. Organic matter derived from soil and lithic sources should provide low $\delta^{13}\text{C}$ values. Indeed, soil, peat, and wetland sources of organic matter from taiga- or tundra-like ecosystems release material derived from terrestrial C_3 plants (average $\pm 1\sigma$: $\delta^{13}\text{C} = -27 \pm 6\%$, Deines, 1980; Farquhar et al., 1989; Leawitt and Danzer, 1992; Michelsen et al., 1996). Such terrestrial supply of organic matter to the North Atlantic is still shown by present-day river exports of old (^{14}C -depleted) organic matter with low $\delta^{13}\text{C}$ (-28.2% to -33.7% ; Raymond and Bauer, 2001). Glacial erosion of organic matter-bearing rocks from ancient sedimentary rocks underlying the soil profiles can also provide $\delta^{13}\text{C}$ in the range of C_3 plants as shown by Precambrian-Jurassic geochemical records ($-31\% < \delta^{13}\text{C} < -26\%$; Tyson, 1995; Hayes et al., 1999).

Low $\delta^{15}\text{N}$ marine signatures as for HL_1 and HL_2 are typically found in organic-rich deposits where either nitrate availability is sufficient to allow isotope discrimination in favour of ^{14}N , or N_2 fixation is the dominant fixation process (Altabet, 1996; Haug et al., 1998; Calvert et al., 1992). However, these environments do not correspond to the open sea setting of core SU90-09 and to the low OC content of sediments. The depleted $\delta^{15}\text{N}$ signatures can also reflect terrestrial environments, in particular soils and sediments of periglacial environments (Schubert and Calvert, 2001) and, possibly also organic-rich basement rocks, but few data are available for these lithological sources. For early Heinrich Layers, contrasting results are obtained. $\delta^{15}\text{N}$ and OC/TN values tend to those of ambient glacial sediments for HL_4 or can no longer be distinguished for HL_5 . During soil formation, ^{15}N enrichment with respect to the original vegetation composition (Yoneyama, 1996) leads to higher $\delta^{15}\text{N}$ for soil organic matter, in particular in aging parts of soil profiles and for fine resistant size fractions (Mariotti et al., 1980). Indeed, fine-sized organic matter from differentiated soil horizons (high $\delta^{15}\text{N}$, low OC/TN ratios) could reflect relatively "warmer" climate conditions that prevailed at mid to high latitude regions for the time interval corresponding to marine isotope stage 3 (~ 24 to 59 ka BP, Martinson et al., 1987). Since the two last Heinrich events (~ 21 ka BP and 14 ka BP for HL_2 and HL_1 , respectively; Bond et al., 1993) took place during the Last Glacial maximum, low $\delta^{15}\text{N}$ values and high OC/TN are expected, indicating cooler climate conditions with limited soil development. Rather depleted plant isotope signatures ($-7\% < \delta^{15}\text{N} < 0.9\%$; Schultze et al., 1994) will be transmitted to soil organic matter. It is, however, difficult to compare our data with continental paleo-climate records as $\delta^{15}\text{N}$ measurements are rarely reported. However, the $\delta^{15}\text{N}$ record in prominent Heinrich Layers is consistent with the isotopic record trend of preserved collagen of ancient herbivore bones (Drucker et al., 2000; Iacumin et al., 2001) that point to changing vegetation and soils.

Based on these various end-member assumptions, the following organic matter source estimates can be proposed: (1) a composite terrestrial-marine end-member whose composition is best estimated by ambient glacial sediment averages ($\delta^{13}\text{C} = -22.8 \pm 1.0\%$; $\delta^{15}\text{N} = 5.5 \pm 0.6\%$; OC/TN = 7.6 ± 0.8); (2)

a continental source characterised by low $\delta^{13}\text{C}$ (down to -28%), variable OC:TN ratios ($8.5 < \text{OC/TN} < 15.0$) and variable $\delta^{15}\text{N}$ (1.6 to 5.5%), corresponding to soil and lithic detritus inputs that culminate during Heinrich event maxima; and (3) another composite terrestrial-marine end-member ($\delta^{13}\text{C} \sim -19\%$; $5.5\% < \delta^{15}\text{N} < 7.0\%$; OC/TN > 10), recording a progressive change in the source of fine-sized organic matter during the Holocene. Assuming constant $\delta^{13}\text{C}$ end-member values for marine and terrestrial fine-sized organic matter supply during the last glaciation, we can make a semi-quantitative estimate of the proportion of continental derived organic matter at core SU90-09 location using the following equation: $\delta^{13}\text{C} = f \delta^{13}\text{C}_t + (1-f) \delta^{13}\text{C}_m$. $\delta^{13}\text{C}$ is the measured value ($\%$), f is the proportion of terrestrial supply ($\%$), $\delta^{13}\text{C}_t$ is the terrestrial end-member estimated with Heinrich Layer samples ($-29 \pm 1\%$), and $\delta^{13}\text{C}_m$ is the assumed marine end-member value for ambient glacial sediments ($-20 \pm 1\%$). Results for these estimates are reported in Figure 7. Although the end-member values are only assumptions, our first-order estimate of the continental contribution (f %) is supported by positive and negative correlations with IRD and total foraminifer abundance, respectively (Fig. 7c,d). Enhanced ice-rafted detritus deliveries correspond to the highest continental contributions (in the range 80 to 100% , Fig. 7b). According to our estimates, 30 to 50% of fine-sized organic matter in ambient glacial sediments is derived from terrestrial sources during marine isotope stage 2 (~ 12 to 24 ka BP, Martinson et al., 1987).

The contrasted behaviour of $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ records in early (HL_1 and HL_2) and late (HL_5 and partly HL_4) prominent Heinrich events is best explained by a change in the isotopic composition of the terrestrial source organic matter rather than a change in the source of organic matter. Reduced IRD supply for HL_5 (and with lesser extent for HL_4 , Fig. 2) may correspond to lower erosion level in the continental source region. Organic matter mainly derived from differentiated soil horizons (high $\delta^{15}\text{N}$, low OC/TN) is supplied by ice rafting. In contrast, during HL_1 and HL_2 , high IRD deliveries correspond to enhanced glacial erosion, providing higher amounts of detrital organic matter from lithic sources of the underlying basement rocks. Another significant difference between $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ isotopic records is shown by the glacial-interglacial transition. The $\delta^{15}\text{N}$ record does not provide a marked difference between Late glacial and Holocene sediments, as shown elsewhere (Nakatsuka et al., 1995; François et al., 1997; Emmer and Thunell, 2000; Ganeshram et al., 2000), but not in the South China Sea (Kienast, 2000). These unchanged isotopic values indicate that the deep-sea environment of core SU90-09 mainly remained oligotrophic during the past $50,000$ yr BP. Since only fine-sized organic fractions have been studied, additional sedimentary records are still required to interpret the changes in oceanic nitrogen budget that can be derived from these results (Broecker and Henderson, 1998; Bertrand et al., 2000). Possible links between stable isotope records in Heinrich Layers and bottom water circulation are beyond the scope of this study. However, the asymmetric changes shown by this $\delta^{13}\text{C}$ sedimentary organic matter record resemble the $\delta^{13}\text{C}$ benthic foraminifer record that is interpreted as reflecting oscillatory behaviour of the thermohaline circulation mode (Zahn et al., 1997).

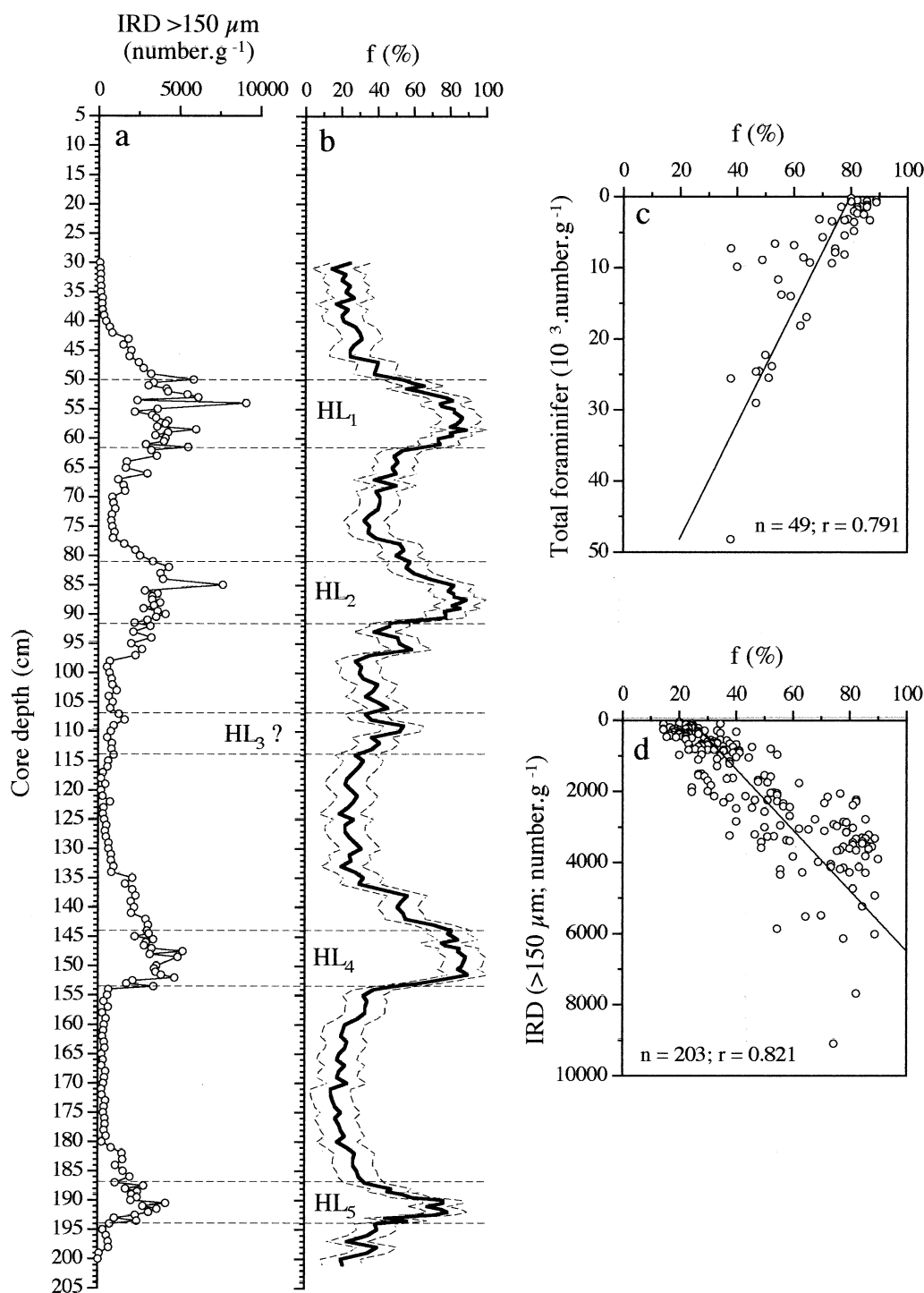


Fig. 7. Plots of (a) down-core variation of IRD ($>150 \mu\text{m}$) abundance, (b) down-core calculated continental fine size OC percentage (f), (c) f vs. total foraminifer abundance, and (d) f vs. IRD ($>150 \mu\text{m}$) abundance. f values were calculated using $\delta^{13}\text{C}_t = -29 \pm 1\text{‰}$ and $\delta^{13}\text{C}_m = -20 \pm 1\text{‰}$. The linear relationships between IRD and total foraminifer abundances and f are based on $\delta^{13}\text{C} = -29\text{‰}$ and $\delta^{13}\text{C} = -20\text{‰}$. Foraminifer data for core SU90-09 are from Grousset et al. (2001).

6. CONCLUDING REMARKS

Discrimination with OC and nitrogen elemental concentrations and stable ($\delta^{15}\text{N}$ and $\delta^{13}\text{C}$) isotope data between sources of fine-sized organic matter in North Atlantic deep-sea sedi-

ments is a difficult challenge due to possibly overlapping values. However, the use of diagrams that combine OC/TN, $\delta^{15}\text{N}$, and $\delta^{13}\text{C}$ values provides constraint on the possible mixtures of terrestrial and marine organic matter. During the

phases of enhanced ice-rafting detritus supply corresponding to prominent Heinrich events (HL₁, HL₂, HL₄, and HL₅) of the past 50 ka BP, the concomitant decrease of fine OC concentrations, $\delta^{13}\text{C}$, and total foraminifer content suggests a dilution of ambient glacial sedimentary organic matter by terrestrial-derived inputs. Preservation and supply of fine organic matter are thoroughly increased due to higher mass accumulation rates as shown for HL₁. During Heinrich events 1 and 2, the source of terrestrial material cannot be located precisely, but is interpreted as originating from poorly differentiated soils that characterise periglacial climate conditions prevailing during the Last Glacial Maximum, and from organic matter-bearing rock sources of the underlying geological basement (e.g., Paleozoic limestones; Bond et al., 1992). The earliest prominent Heinrich events (HL₅ and partly HL₄) display a contrasting sedimentary record. Only low $\delta^{13}\text{C}$ values support the assumption of enhanced terrestrial supply. This discrepancy is best explained by a change in the isotopic signature of the continental organic matter source, linked to “warmer” climate conditions and lower erosion levels. The unchanged $\delta^{15}\text{N}$ record between last glacial and Holocene stages indicates that the central North Atlantic region remained oligotrophic at least during the past 50 ka BP. A constant $\delta^{15}\text{N}$ sedimentary signature suggests a limited change in the rate of denitrification in the North Atlantic, but other deep-sea records are still required to support this preliminary result. On the whole, our study of fine-sized (<50 μm) sedimentary organic matter mainly provides the record of a varying mixture of terrestrial and marine supplies to the central North Atlantic, with little information on marine productivity changes. Although the highest continental supplies are found in prominent Heinrich Layers (up to 80 to 100%), we cannot infer if a complete breakdown of marine supply was attained. Additional data are still required to answer this question, possibly combining high-resolution microsampling in Heinrich Layers, $\Delta^{14}\text{C}$, $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ measurements on organic matter with quantitative organofacies studies.

Acknowledgments—We are grateful to NEB (Naturalia et Biologia, Paris) who supported D. Burdloff through a postdoctoral fellowship at the LBI (Université Pierre and Marie Curie, Paris). This study also benefited from financial support from the French CNRS programs VARIANTE and ECLIPSE. R/V Le Suroit (IFREMER, France) recovered core SU90-09 used in this study. We are indebted to J. Duprat, H. Etcheber, L. Hervé, M. Lafosse, R. Pouvreau (DGO, Université de Bordeaux I); and to M. Grably, C. Girardin (LBI, Université Pierre and Marie Curie, Paris). H. Bocherens, Y. Zegouagh (LBI, Université Pierre and Marie Curie, Paris), P. Bertrand and P. Martinez (DGO, Université Bordeaux I) kindly helped us with their comments and discussions to improve a former draft of this manuscript. Dr. N. E. Ostrom and three anonymous reviewers are gratefully acknowledged for their marked interest and constructive comments. Stable isotope data are available on simple request to S. Huon (E-mail: huon@ccr.jussieu.fr).

Associate editor: N. E. Ostrom

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