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Origin and Fate of Organic Biomarker Compounds in the Water Column and Sediments of the Eastern North Atlantic [and Discussion]

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Origin and fate of organic biomarker compounds in the water column and sediments of the eastern North Atlantic

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SUMMARY

This paper focuses upon lipid biomarkers as tracers of the biological carbon cycle and our efforts to derive and validate 'molecular tools' for oceanography and palaeoceanography as part of the 1989–1991 UK–JGOFS Biogeochemical Ocean Flux Study (BOFS). Biomarker concentrations and composition in water column particulates and bottom sediments in the North Atlantic show a strong correspondence to seasonal and interannual patterns of productivity. Biomarkers document the rapidity with which vertical flux processes operate in the high latitude North Atlantic: for example, the massive sedimentation of phytodetritus following a coccolithophorid bloom in the Iceland Basin and its subsequent resuspension, and the benthic biological response to this pulse of biologically available carbon. Sedimentary biomarker distributions indicate that organic material decomposition in sediments is dominated by processes at or near the sediment water interface and that downmixing of labile material into the sediments is largely controlled by advective rather than diffusive-like processes.

1. INTRODUCTION: SOURCE AND FATE OF ORGANIC CARBON

The eastern North Atlantic encompasses the extremes of biogeographical provinces, from oligotrophic, nutrient-poor, warm waters of subtropical latitudes to highly productive, nutrient-rich, cold subarctic waters near Iceland. The mid to high latitude North Atlantic is characterized by an extensive spring phytoplankton bloom which is followed by a large vertical flux of incompletely degraded bloom materials ('phytodetritus') (e.g. Lampitt 1985; Rice *et al.* 1986). The factors initiating and limiting bloom development in this region of high surface nutrient concentrations are unclear, as are the aggregation and flux processes responsible for the huge seasonal export of carbon to the seafloor.

The organic geochemist seeks to study the organic carbon cycle by utilizing key organic compounds (biomarkers) as tracers of organic matter sources and remineralization processes. Specific lipid compounds are excellent source indicators as the biochemistry of plants, animal and bacteria exhibits characteristic differences. Furthermore, alteration products often retain structural information enabling one to link them to their original sources. This molecular imprint of sources and transformation processes is preserved, to varying extents, in sediments. Thus, the molecular stratigraphic record contains valuable information for palaeoceanographic reconstruction. In this paper we present selected results from recent organic geochemical studies in the North Atlantic which were conducted largely as part of the U.K. component (Biogeochemical Ocean Flux Study, BOFS) of JGOFS. The examples presented illustrate how biomarker studies help to unravel the processes which control the marine organic carbon cycle.

2. BIOMARKER SIGNALS OF SURFACE WATER PRODUCTIVITY AND WATER COLUMN FLUX

Marine particles contain compounds derived from primary synthesis by marine organisms, allochthonous inputs and the degradative products of primary synthetic compounds. In surface waters, the biomarker signal reflects ecosystem structure and phytoplankton composition. For example, sterol distributions in surface water particulates collected during BOFS North Atlantic cruises vary with phytoplankton species composition (see figure 1). The sample shown in figure 1*a* was collected at the initiation of the spring bloom when nitrate and silicate concentrations were > 6 and > 3 μmoles l^{-1}, respectively. Diatoms, haptophytes and microflagellates predominated while dinoflagellate abundances were very low (D.S. Harbour, unpublished data; Barlow *et al.* 1993). The sterol distribution is

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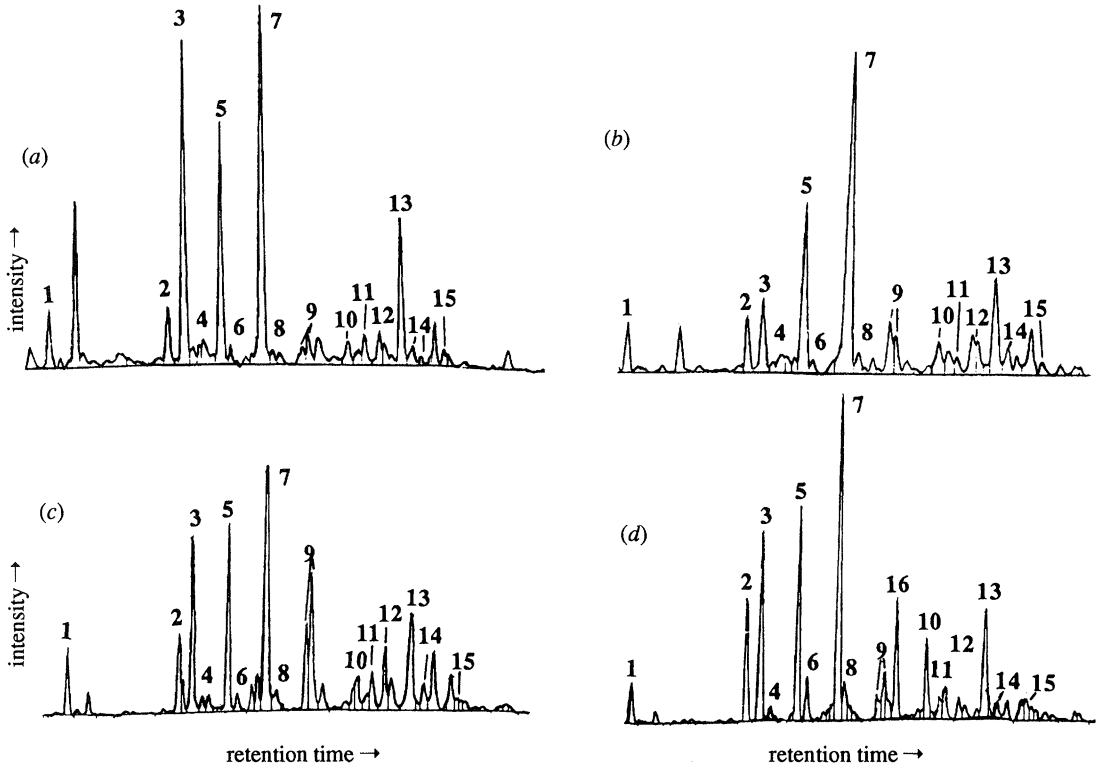

Figure 1. Partial gas chromatograms of sterol fractions extracted from > 1 μm sized euphotic zone particulates. (*a*) 50° N, 18° W, May 1990, 15 m depth. Sample collected near initiation of spring bloom; diatoms and haptophytes predominated. (*b*) 61° N, 20° W, June 1991, 4 m depth. Sample collected at end of massive *Emiliania huxleyi* bloom. (*c*) 59° N, 20° W, June 1989, 15 m depth. Sample collected near end of spring bloom; diatoms and haptophytes predominated. (*d*) 47° N, 20° W, July 1989, 10 m depth. Sample collected during summer in nutrient-depleted waters.

Sterol fractions were isolated from transesterified (methanolic HCl) extracts of total lipids by TLC (silica). Recovered sterols were analysed as trimethylsilyl derivatives on a 50 m × 0.32 mm CPSil5CB (Chrompack) column, temperature programmed from 50–150 °C at 10 °C min^{-1}, and 150–320 °C at 4 °C min^{-1} using H_2 as carrier gas.

Key: 1: 24-*nor*cholesta-5,22E-dien-3β-ol;
2: 27-*nor*24-methylcholesta-5,22E-dien-3β-ol;
3: cholesta-5,22E-dien-3β-ol;
4: 5α-cholest-22E-en-3β-ol;
5: cholest-5-en-3β-ol [cholesterol];
6: 5α-cholestan-3β-ol;
7: 24-methylcholesta-5,22-dien-3β-ol;
8: 24-methyl-5α-cholest-22-en-3β-ol;
9: unidentified C_{28}steradienols;
10: 24-ethylcholesta-5,22-dien-3β-ol;
11 + 12: unidentified C_{29}steradienols;
13: 24-ethylcholest-5-en-3β-ol;
14: 24-ethyl-5α-cholestan-3β-ol;
15: 4α-23,24-trimethyl-5α-cholest-22E-en-3β-ol [dinosterol] + 24-propylcholesta-5,24(28)E-dien-3β-ol?;
16: 4α-methyl-5α-cholestan-3β-ol.

relatively simple, with 24-methylcholesta-5,22E-dien-3β-ol (7), and cholesta-5,22E-dien-3β-ol (3), predominating. The C_{29} sterol, 24-ethylcholesta-5-en-3β-ol (13), is also abundant, confirming its phytoplankton sources (Volkman 1986).

The sample in figure 1 *b* was collected during the later stages of a massive bloom of the coccolithophorid *E. huxleyi* in the Iceland Basin in June 1991 (Holligan *et al.* 1993). The major sterol of *E. huxleyi*, 24-methylcholesta-5,22E-dien-3β-ol (7), predominates. Diatoms were also abundant (D.S. Harbour, unpublished data), and there was probably an earlier diatom-dominated bloom. Diatom-derived carbon is indicated by two C_{27} sterols, cholesta-5,22E-dien-3β-ol (3) and 27-*nor* 24-methylcholesta-5,22-dien-3β-ol (2), and the C_{29} sterol 24-ethylcholesta-5,22-dien-3β-ol (7) (cf. figure 1 *a*). The sample in figure 1 *c* was collected at the end of the spring bloom in the Iceland Basin in 1989, a year in which diatoms and coccolithophorids were equally abundant (Weeks *et al.* 1993). The greater complexity of the sterol distribution is consistent with the more diverse phytoplankton community. The change in relative abundances of the minor C_{28} and C_{29} sterols (e.g. the C_{28} steradienols, (9)) is consistent with the different species composition in this bloom. The last sample, shown in figure 1 *d*, was collected during the post-bloom stratified summer situation when nitrate and silicate concentrations were

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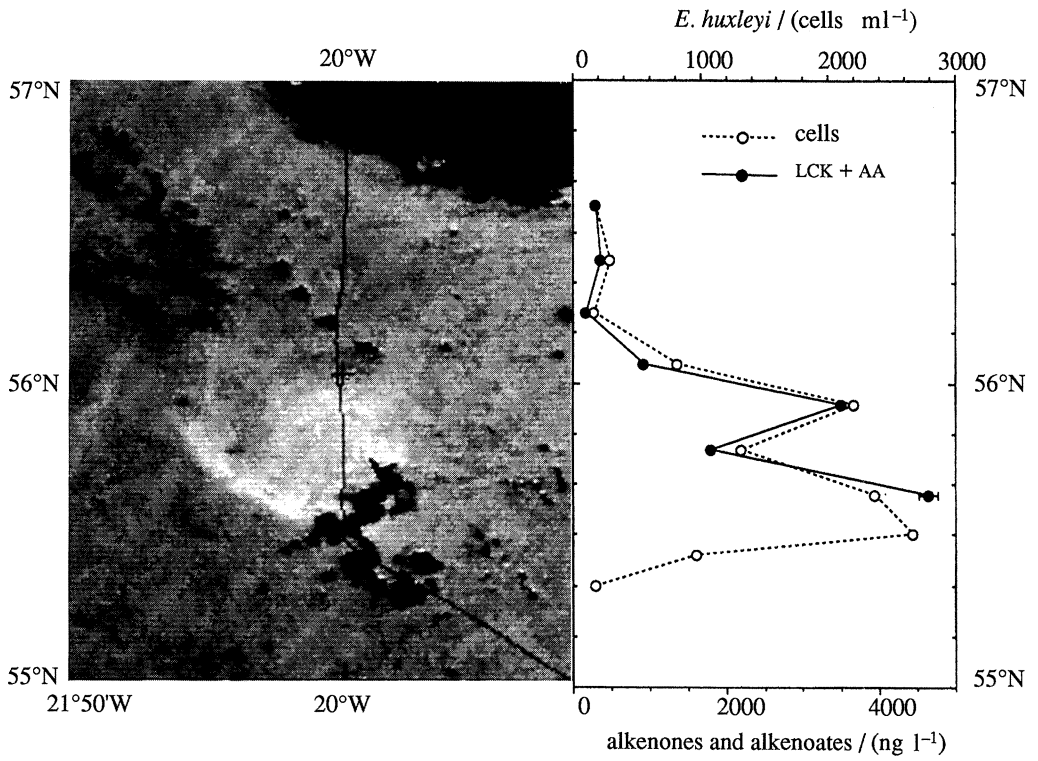

Figure 2. *Emiliania huxleyi* bloom at 56° N, 20° W, July 1991. The AVHRR satellite image of 23 July shows the bloom as a high reflectance feature in a cold core eddy (image courtesy of S. Groom, U. Plymouth, U.K.). The reflectance feature enlarged by approximately 50 % between 23–27 July. The ship's transect on 25 July is indicated by solid line. The second panel shows *E. huxleyi* cell counts (no. ml^{-1}) and summed long-chain alkenone and alkyl alkenoate (LCK + AA) concentrations (ng l^{-1}) at 4 m depth along the transect.

< 0.5 and 2 μmoles l^{-1}, respectively (Weeks *et al.* 1993). A diatom bloom was followed by increasing nanoplankton abundance as nutrients were depleted (Sieracki *et al.* 1993). At the time of sampling, dinoflagellates and microflagellates predominated (D.S. Harbour, unpublished data). 4-Methylsterols of presumed dinoflagellate origin [4α-23,24-trimethyl-5α-cholest-22E-en-3β-ol (dinosterol, 15) and 4α-methyl-5α-cholestan-3β-ol (16)], sterols found only in trace amounts in the samples shown in figure 1*a–c*, were present in significant quantities, as were stanols, the degradation products of stenols as well as primary biosynthetic products.

These samples illustrate that although most sterols have multiple sources, the phytosterol signature of euphotic zone particles varies with species composition and increases in complexity over time in parallel with the increasing complexity of the plankton community. Lipid biomarkers provide important information on the phytoplankton composition complementary to that of algal pigments (e.g. Barlow *et al.* 1993). Biomarker-based algorithms should be further developed as quantitative indices of plankton community structure.

(*a*) *Tracing the production and fate of* Emiliania huxleyi *blooms using long-chain alkenones and alkyl alkenoates*

Lipid biomarkers also provide important information on transport and remineralization processes. In this regard it is important to note that the biogeochemical behaviour of a specific compound is controlled to a large extent by its bioreactivity. For example, the biogeochemical behaviour of a strongly bioaccumulated compound (e.g. polyunsaturated ω3 fatty acids, Harvey *et al.* 1987), is largely controlled by biological activities, including vertical migrations (Conte 1989). In contrast, the behaviour of a weakly bioaccumulated, 'bioinert' compounds (e.g. dinosterol, Harvey *et al.* 1989) is controlled largely by aggregation and disaggregation processes which affect settling rates. Most compounds fall somewhere between these two extremes. In this section we illustrate the application of lipid biomarkers in water column studies by following the production and fate of the haptophyte algae-derived long-chain alkenones and alkyl alkenoates (LCK + AA). These compounds are known to be synthesized in the open ocean solely by *E. huxleyi* and the closely related *Gephyrocapsa* spp. (Conte *et al.* 1995; Volkman *et al.* in press). They are presumed to be relatively 'bioinert' and hence their transport through the water column depends upon the strength of aggregation and flux processes.

LCK + AA concentrations in surface water particulates in the eastern North Atlantic are correlated with cell concentrations of *E. huxleyi* (plus *Geophyrocapsa* spp.) (Conte & Eglinton 1993). Figure 2 illustrates the remarkable correspondence between physical location of an *E. huxleyi* bloom as seen from the AVHRR reflectance and both *E. huxleyi* cell and LCK + AA concentrations in the same surface water (4 m) samples (Conte *et al.*, unpublished results). The correspondence is encouraging for the future use of satellites for areal estimation of the extent of such coccolithophorid

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Table 1. *Surface and water column inventories for Emiliania huxleyi cells (no. ml^{-1}) and for summed long-chain alkenones and alkyl alkenoates (LCK+AA) in > 1 μm particles (ng l^{-1}) from two sites in the* 1991 *bloom region of the Iceland Basin* (cf. figures 1*b* and 3)

(Cell counts and C_{org} data from Derek Harbour, Plymouth Marine Laboratory.)

(*a*) *Bloom and post-bloom concentrations in surface waters*

	concentration	
period	cells (no. ml^{-1})	LCK+AA (ng l^{-1})
June 18–20 (bloom)		
61° N	2000–4000	1800–2200
62° N	4000–10,000	6000–15,000*
July 20–25 (post-bloom)		
60° N	100–200	100–200
62° N	< 100	n.d.

(*b*) *Bloom mixed layer and post-bloom water column inventories (mg m^{-2})*

		inventory		water column
		June mixed layer (0–20 m)	July water column (> 200 m)	percentage of mixed layer
61° N	LCK+AA	44	27	61 %
	C_{org}	800	540[a]	67 %
62° N	C_{org}	1600	1000[a]	63 %

[a] Indicates estimated value using biomarker/cell conversions of 1.5 pg LCK+AA cell^{-1} and LCK+AA comprises 5 % cellular organic carbon (Conte *et al.* 1994*b*).
n.d. denotes not determined.

blooms and the ensuing flux of biomarkers to the seafloor. However, quantification of the relation between biomarker production, as determined from satellite imagery, and the benthic flux will require a quantitative understanding of the extent of biomarker remineralization with depth and in different oceanic regimes.

A close correspondence between biomarker and cell concentrations and satellite estimates of bloom intensity was also observed in the 1991 *E. huxleyi* bloom in the Iceland Basin which was intensively studied by BOFS (Holligan *et al.* 1993). Cell concentrations in the most intense region of satellite reflectance were up to two orders of magnitude higher than in post-bloom waters; lower cell concentrations were measured nearer the periphery (see table 1). The intensity of this very specific biomarker signal of Gephyrocapsid production (e.g. *E. huxleyi*) is registered in particles throughout the water column, even at depths of 2 to 4.5 km (see figure 3). In the Iceland Basin, where surface water concentrations during the bloom were up to two orders of magnitude above those of non-bloom periods, samples collected from the water column approximately one month after the Iceland Basin bloom (cf. figure 1*b*) show biomarker concentrations 1–2 orders of magnitude higher than during periods when large *E. huxleyi* blooms were absent (cf. figure 1*c*). Water column concentrations at 62° N, where the bloom was maximal, are higher than at 61° N, near the bloom periphery. The inference to be drawn is that biomarkers in water column particulates quantitatively reflect recent past surface water productivity and that examination of the lower water column may provide a better overall integrated signal of seasonal productivity than snapshot measurements in highly variable surface waters.

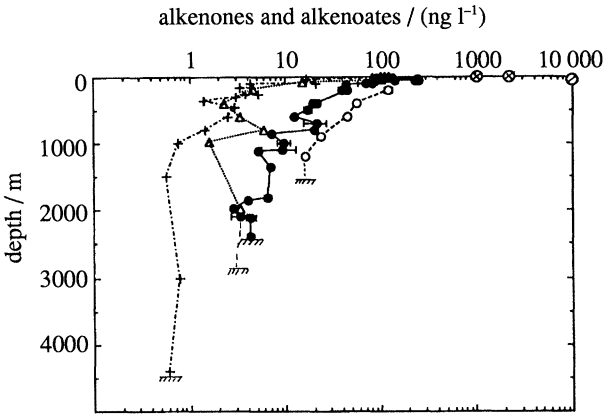

Figure 3. Concentration profiles (ng l^{-1}, log scale) of summed long-chain alkenone and alkyl alkenoates in the water column for stations along the 20° W JGOFS transect, following periods of high and low *E. huxleyi* production in surface waters. The large circles show approximate concentrations in surface waters at 62° N (slashed circle) and 61° N (crossed circle) in the Iceland Basin, June 1991 during the latter stages of a massive *E. huxleyi* bloom (cf. figure 1*b*). The smaller circles show water column concentrations at 62° N (○) and 61° N (●) approximately one month later. The profile at 59° N (△) was measured in June 1989 at the end of a spring bloom which had no *E. huxleyi* predominance (cf. figure 1*c*); the profile at 47° N (+) was measured in July 1989 during the post-bloom period. Shaded bars indicate seafloor depths. Samples were collected using *in situ* filtration (Conte *et al.* 1992). The total transesterified lipid extract was analysed as described in figure 1.

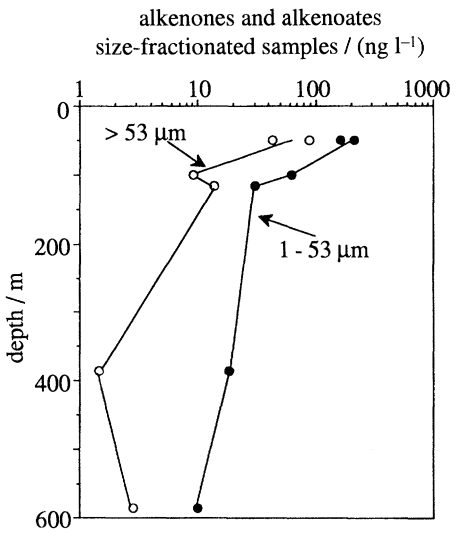

Figure 4. Concentration profile in the upper water column of summed long-chain alkenone and alkyl alkenoates (ng l^{-1}, log scale) in 1–53 μm suspended (●) and > 53 μm sinking (○) particles in samples at 61° N station, July 1991 (cf. figure 3). From 8–34 % of the total concentration of alkenones and alkenoates was present in > 53 μm particles.

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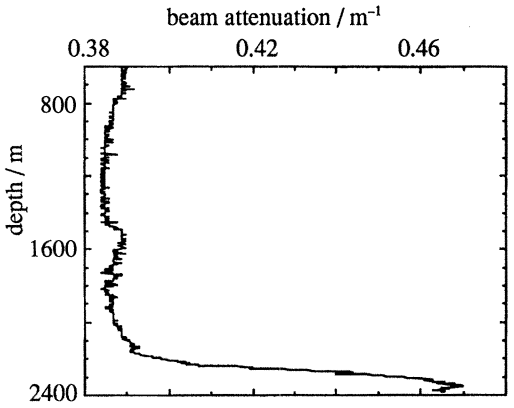

Figure 5. Representative CTD trace of beam attenuation (532 nm, m^{-1}) of the lower water column showing the nepheloid layer in the cold core eddy at the 61° N station (cf. figure 3). The nepheloid layer extended from 2200 m to the bottom (2400 m).

The *E. huxleyi* cells that biosynthesize LCK+AA average < 5 μm diameter and therefore cannot settle through the water column without first being incorporated into larger particles through aggregation or herbivory. Preliminary information on the size distribution of these biomarkers (figure 4) indicates that 8–34% of the total LCK+AA were present in > 53 μm particles, attesting to the strength of aggregation processes in this environment.

Minimum bloom production can be roughly estimated from 18 June concentrations (see table 1) by assuming uniform cell distribution within the mixed layer (Holligan *et al.* 1993) and negligible export fluxes prior to this date. The inventory of bloom material in the underlying water column one month later can be roughly estimated by assuming negligible biomarker concentrations in the water column prior to the bloom period. Comparison of these very rough estimates indicates that, at a maximum, only about 60% of the total production of either biomarkers or organic carbon can be accounted for in the underlying water column. This discrepancy suggests that LCK+AA have been extensively remineralized within the water column (Conte *et al.* 1992) and/or that much of the bloom production has been removed, either by advection or loss to the sediments. This latter possibility is discussed in §3.

(*b*) *Nepheloid layers*

The nepheloid layer observed at the 61° N site one month following the Iceland Basin bloom (see figure 5) is typical of those observed throughout the high latitude eastern North Atlantic. Relative to the underlying surficial sediment, this nepheloid layer was greatly enriched in labile compounds (e.g. PUFAS) but depleted in other compounds that are usually more abundant in sediments (e.g. hopanoids and $> C_{22}$ saturated acids) (see figure 6). This indicated that this nepheloid layer at this site was not comprised primarily of resuspended sediment but contained a large fraction of relatively undegraded material. Disaggregated 'phytodetritus' can easily be resuspended by bottom currents as low as 7–9 cm s^{-1}, commonly observed during the passage of mesoscale eddies (Lampitt 1985; Auffret *et al.* 1994). Thus, biomarker data support other indications (e.g. Walsh 1988) that 'rebound flux' of phytodetritus is a major contributor to nepheloid layers.

Rapid deposition of relatively undegraded phytodetritus, and subsequent degradation and disaggregation followed by resuspension seems to be a general feature of the high latitude North Atlantic. Resuspension exposes organic materials to degradative

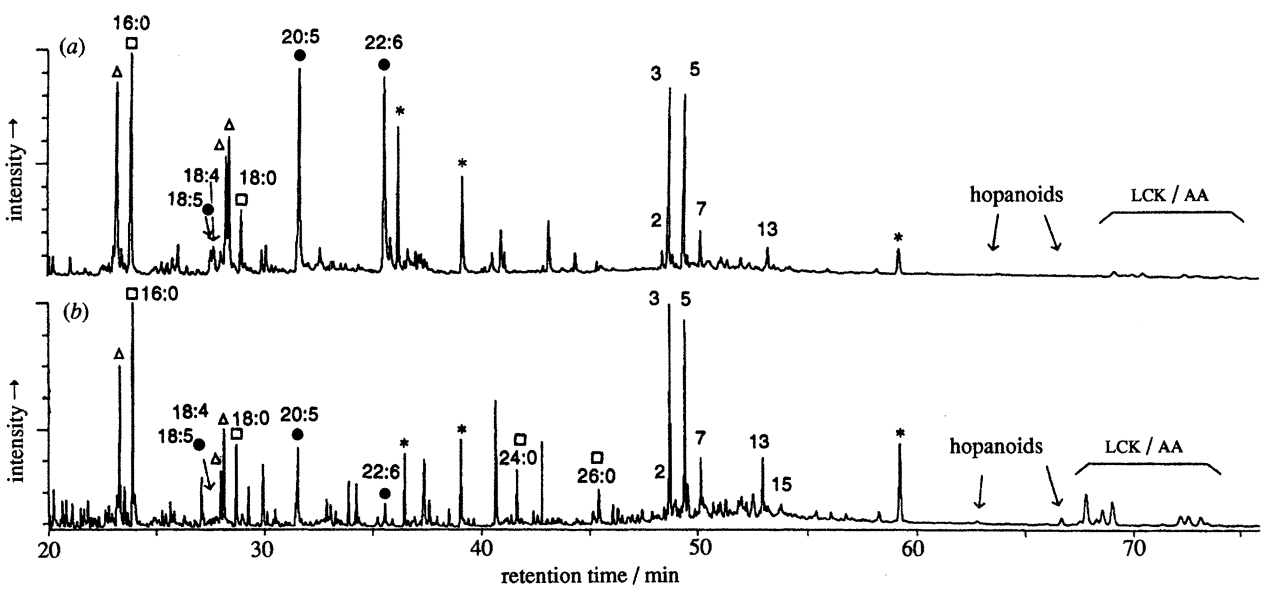

Figure 6. Partial gas chromatograms of trimethylsilylated derivatives of transesterified products of total lipid extracts of > 1 μm size particulates from the nepheloid layer (cf. figure 5) and in underlying surficial sediments (0–1 mm depth). (*a*) Nepheloid layer, 30 m above bottom. (*b*) 0–1 mm sediment. KEY: □: saturated fatty acids; △: 18:1 monounsaturated fatty acids; ●: polyunsaturated fatty acids; 1–15: sterols using figure 1 key; hopanoids: C_{31} hopanol and C_{32} hopanoic acid; LCK/AA: long-chain alkenones and alkyl alkenoates; *: internal standards. Gas chromatographic conditions as in figure 1.

influences which differ somewhat from those at the seafloor and serves to transport and redistribute the flux. This will average out mesoscale variability in overlying production, but it may also result in localized sediment focusing. These processes may contribute to the small-scale patchiness observed in this region (e.g. Brand & Shimmield 1992; Santos *et al.* 1994). The effects of low-energy horizontal transport processes on sedimentary signals in the North Atlantic is an important area for additional research.

3. BIOMARKER DIAGENESIS AT THE SEDIMENT/WATER INTERFACE

Most organic material arriving at the seafloor is rapidly remineralized by the benthic community living at or near the sediment/water interface. Any remaining material is downmixed by the feeding and locomotory activities of benthic animals (bioturbation) and further remineralization takes place within the sediments. Thus, the reconstruction of palaeoenvironment from the molecular stratigraphic record requires that we understand how benthic boundary layer processes affect the preservation of key lipid biomarker classes.

(*a*) *The role of bioturbation and microbial processes in organic matter remineralization*

Concentration profiles of specific biomarkers in the topmost sediments reflect rates of degradation and down-mixing as well as overlying water column fluxes. Mixing rates over short time scales ($< \approx 100$ years) are insufficient to obliterate the fine scale structure of relatively short-lived components within the bioturbated zone, as illustrated by downcore concentration profiles of excess ^{210}Pb and the major lipid classes in the abyssal Biscay Abyssal Plain (see figure 7). Thus, biomarker concentrations vary by nearly a factor of two over a several mm depth range and some decrease by up to 90% over the upper 10 mm. Similar concentration gradients are seen in cores underlying both productive and oligotrophic regimes (Madureira 1994). These results indicate that diagenetic processes occurring at, or near the sediment/water interface dominate the early diagenetic losses of these and other labile compounds in abyssal sediments.

Subsurface concentration maxima (cf. figure 7) are often observed for excess ^{210}Pb and biomarkers (Smith *et al.* 1986, 1987; Brand & Shimmield 1992; Madureira 1994). Reactive biomarker compounds such as sterols and fatty acids are extremely sensitive to the type of the mixing. High resolution biomarker profiles provide strong evidence that downmixing of labile material in oxic sediments is largely controlled by advective rather than diffusive-like processes (Conte *et al.* 1994*a*). For example, downmixing due to bulk physical displacement, such as localized focusing in depressions, burrows and other feeding structures, results in subsurface concentration maxima in which biomarker composition is minimally altered. In contrast, downmixing due to macrofaunal feeding and subsurface egestion results in subsurface maxima in which biomarker composition is altered to that characteristic of faecal material. Thus, biomarkers provide complementary information to that of radiotracers, which can provide valuable information on rates of downmixing but relatively little insight on the downmixing process itself.

In §2, we presented evidence that the water column inventory of *E. huxleyi* derived long-chain alkenones and alkenoates (LCK + AA) sampled one month after a major bloom was depleted relative to estimated bloom production. One explanation is that some bloom material may have been incorporated into the sediments (e.g. Graf 1989; Pfannkuche 1993). In figure 8 we compare two cores from the Iceland Basin. The first (59° N) was collected in May 1989, before any spring

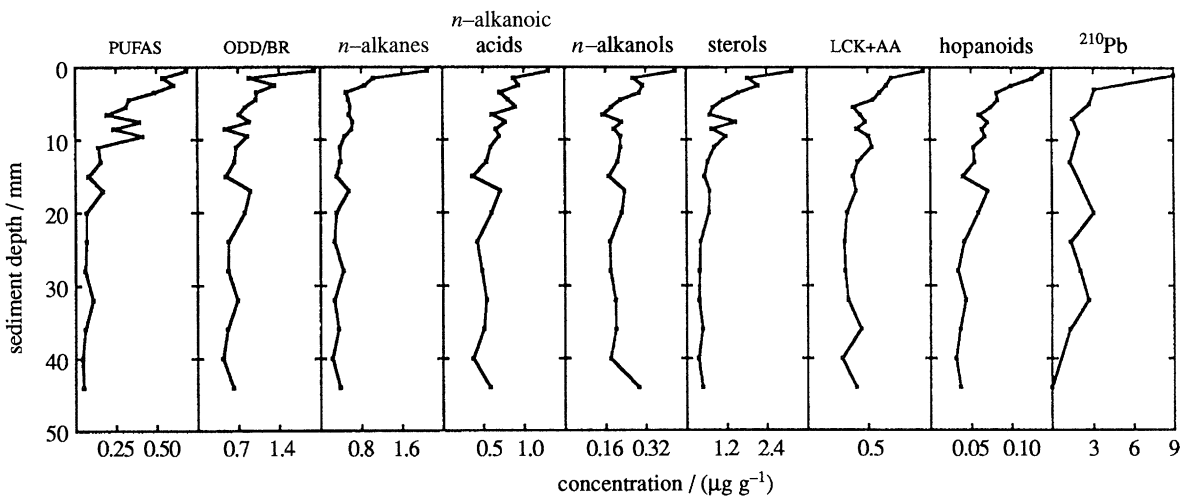

Figure 7. Downcore concentration profiles of excess ^{210}Pb (dpm gram^{-1}) and summed abundances of selected lipid classes (μg gdw^{-1}) in near surface sediments (0–45 mm depth) in the Biscaye Abyssal Plain (redrawn from Madureira *et al.* 1995). The core was obtained using the Multicorer (Barnett *et al.* 1984) and sectioned at 1–4 mm depth intervals using the Precision Core Extruder (Conte *et al.* 1994*a*). Analytical conditions as in figure 6. Key: PUFAs [20:2, 20:5, 22:6 polyunsaturated fatty acids]; ODD/BR [$C_{15}$and C_{17} *iso*, *anteiso* and linear fatty acids]; *n*-Alkanes [$C_{25}-C_{33}$]; *n*-Alkanoic acids [$C_{22}-C_{30}$]; *n*-Alkanols [$C_{22}-C_{28}$]; Sterols [4-methyl and 4-desmethyl sterols]; LCK + AA [alkenones and alkyl alkenoates]; hopanoids [C_{32} bishomohopanoic acid and hopanol].

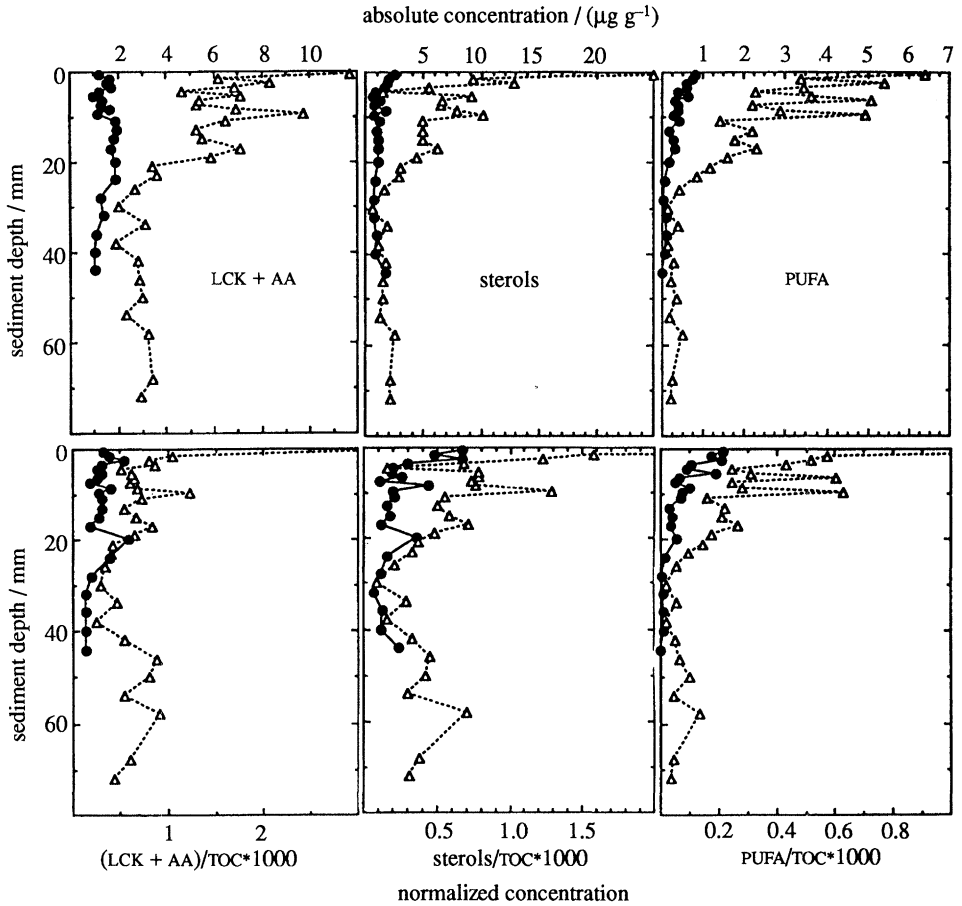

Figure 8. Downcore concentration profiles of total long-chain alkenones and alkyl alkenoates (LCK + AA), PUFA and sterols in near surface sediments in cores at 61° N, 20° W (△) and 59° N, 20° W (●) in the Iceland Basin. The 61° N core was collected July 1991, one month after the *E. huxleyi* bloom (cf. figure 3). The 59° N core was collected May 1989, prior to any spring bloom. The top panels show absolute concentrations (μg gdw^{-1}), the bottom panels concentrations normalized to organic carbon ([x]/TOC) × 1000). Sampling as per figure 7.

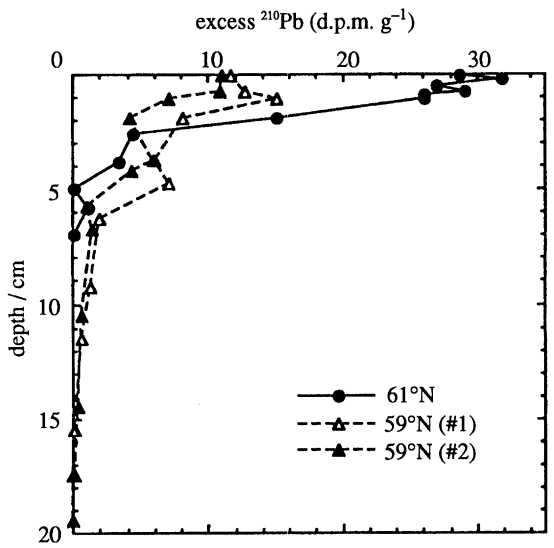

Figure 9. Downcore concentration profiles of excess ^{210}Pb (dpm g^{-1}) in near surface sediments in the Iceland Basin. (*a*) 61° N, 20° W, 2450 m water depth (from Madureira 1994). (*b*) 59° N, 20° W, 2790 m water depth (from Brand & Shimmield 1992). Cores collected using the Multicorer.

bloom in the overlying waters; the second (61° N) was collected in July, approximately one month after the 1991 *E. huxleyi* bloom (cf. figure 3). Concentrations of LCK + AA in the 61° N (post-bloom) core are over three times greater than in the 59° N (pre-bloom) core. Is this enrichment the result of localized focusing or a seasonal pulse of phytodetritus? In support of the first possibility, the excess ^{210}Pb in the 61° N core is nearly three times that of the 59° N core (figure 9). This indicates a higher rate of recent organic carbon deposition at 61° N, and suggests that the difference in biomarker concentrations between the sites reflects sediment focusing (e.g. Cochran *et al.* 1990). However, the organic carbon normalized concentrations of LCK + AA and also of labile non-specific eucaryote-derived sterols and polyunsaturated fatty acids are substantially higher in the 61° N core (see figure 8, bottom panel). This indicates that organic material at 61° N was significantly more labile than that at 59° N, and strongly suggests a recent pulse of phytodetritus which by the time of sampling had already been downmixed by the benthic macrofauna to depths exceeding 20 mm.

Biomarkers furthermore suggest a rapid microbial response to this pulse of phytodetritus (e.g. Gooday & Turley 1990). Concentrations of bacteria-derived compounds (odd and branched chain fatty acids and hopanoids) were higher in the 61° N core and they strongly covaried with those of labile eucaryote-derived biomarkers (PUFAS, sterols) (see figure 10). Similar

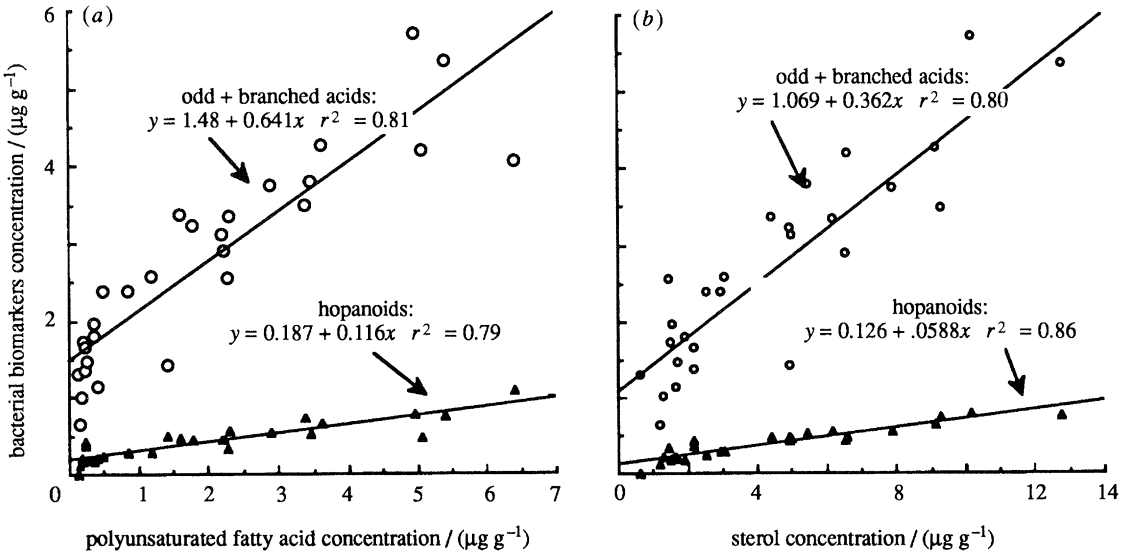

Figure 10. Concentration plots (μg gdw^{-1}) of bacteria-derived biomarkers (Y axis) versus labile eucaryote-derived polyunsaturated fatty acids (*a*) and sterols (*b*) in samples of sediment layers from the 61° N core (cf. figure 9). Least square regressions for bacterial biomarkers also shown.

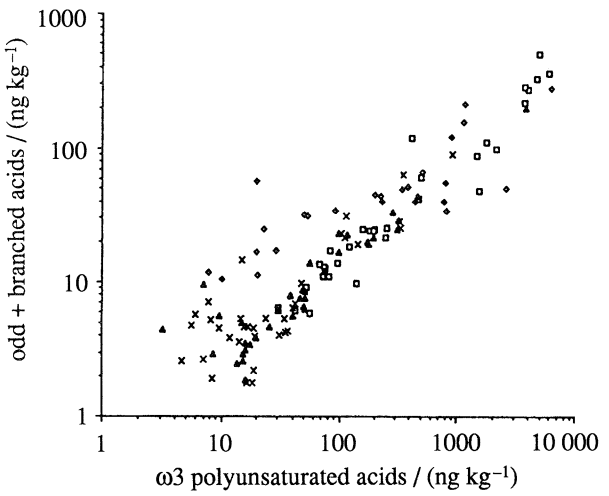

Figure 11. Concentration plot (ng kg^{-1}, log scales) of bacteria-derived odd and branched chain fatty acids (*y*-axis) *vs.* labile eucaryote-derived ω3 polyunsaturated fatty acids (*x*-axis) in 1–53 μm size particulates in the upper 1000 m of the western North Atlantic (Conte 1989). Samples are from the Slope Water and warm-core Gulf Stream rings in April (◇), June (□), August (△) and September (×) 1982.

covariance between concentrations of bacteria-derived biomarkers and labile eucaryote-derived biomarkers is also observed in the western North Atlantic water column (see figure 11). These linear correlations provide strong evidence that the distribution of bacterial biomass and, by extension, activity is closely coupled to the distribution of the labile organic carbon substrate.

4. CONCLUSIONS AND QUESTIONS TO BE ADDRESSED IN FUTURE STUDIES

This paper has considered potential applications of biomarkers in assessment of a number of processes relating to the organic carbon cycle in the North Atlantic. Biomarker distributions in the water column provide qualitative and semi-quantitative information on recent past surface water productivity. More research is needed to assess biomarker loss rates with depth and under different oceanic conditions so that water column data can be used to estimate productivity in a more quantitative way. Biomarker data presented here further document the rapid vertical sedimentation of bloom-derived material to abyssal depths within a matter of weeks to months, its subsequent resuspension, and a rapid biological response to this pulse of biologically available carbon. A number of studies have reported on the multiplicity of components imbedded in the large mucous aggregates which dominate this flux (e.g. Thiel *et al.* 1988, 1989). Recent BOFS studies (Lampitt *et al.* 1993; our own observations from pump studies) suggest animal activities in subeuphotic zone waters contribute significantly to aggregate production. However, we still have a poor understanding of particle aggregation and disaggregation. Detailed biomarker analyses of water column particulates should provide valuable insights into processes controlling vertical flux.

Timelapse photography, microbiological/foraminifera studies and organic geochemical studies have shown that biological activity on the deep seafloor varies in response to inputs from the overlying water column. Is the seasonal variance observed in deep sea properties proportional to the seasonal variance of surface water properties, as attenuated by some function of water depth? More time series at key locations, such as the repeated observations at the BIOTRANS station, are needed to fully understand seasonal and interannual variability in the North Atlantic and its effects on sedimentary biomarker signals.

Lastly, we have discussed low-energy sediment transport processes which resuspend and redistribute the benthic flux. Excess ^{210}Pb and biomarker data suggests that in the short term, the deposition of organic carbon in the high latitude North Atlantic is spatially patchy. How much of the variability which we see in the North Atlantic sediments and, by

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extension, in the sedimentary record, is due to bottom current redistribution processes rather than changes in overlying production? More work is required to identify optimal methods for distinguishing temporal variations in sediment focusing from the palaeo productivity changes in the sedimentary records from this area.

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Discussion

C. Rabouille (*CFR, CNRS-CEA, Gif-sur-Yvette, France*). I was under the impression that alkenones were refractory. Dr Conte's data seem to show the contrary especially in surface sediments. Is there any influence on the ratios utilized as sea–surface temperature estimators in deep cores, such as U^{k}_{37}?

M. H. Conte. Long-chain alkenones are certainly more resistant to degradation than other lipids such as fatty acids and sterols, and they were originally presumed to be refractory. However, there is now abundant evidence that alkenones are degraded under oxic conditions, both within the water column and in the sediments. Fortunately, both the di- and tri-unsaturated alkenones are lost at the same rate so that alkenone unsaturation ratios (e.g. U^{k}_{37}, U^{k}_{38Me}) are not altered. Hence, the temperature signal carried by these compounds is not affected by diagenetic losses.

L. Labeyrie (*CFR, CNRS-CEA, Grif-sur-Yvette, France*). How does the ratio of alkenones to *E. huxleyi* cells preserve down the water column?

M. H. Conte. It is likely that most of the alkenones and alkyl alkenoates settling through the water column are contained in detritus rather than in intact cells although this has not yet been rigorously examined. We do know that the (alkenone + alkenoate)/cell ratios measured after *E. huxleyi* blooms are much higher than those measured in cell cultures or within blooms, suggesting that a large percentage of the biomarkers are present in the detrital remains of grazed cells. One problem, however, in exact determination of the alkenone/cell ratio in natural waters is that uncalcified *E. huxleyi* cells cannot as yet be identified as such, so cell decalcification, which is known to occur under cell stress, will obviously affect these estimates.

S. Mudge. From Dr Conte's biomarker distributions in the water column and sediments, can she determine the settling velocity of the particles and therefore their mean effective diameter?

M. H. Conte. One certainly would be able to determine mean settling rates from a better time series sequence of water column and sediment sampling, but I would be reluctant to make any estimates given the limit data presented here for the Iceland Basin bloom. However, we do know that within 40 days of the estimated initiation of the *E. huxleyi* bloom, some of the bloom material had already arrived at 3000 m and had been mixed down into the sediments. This would require a *minimum* settling velocity on the order of 75–100 m d^{-1} for at least some portion of the bloom material, which is consistent with other estimates for phytodetritus settling rates.

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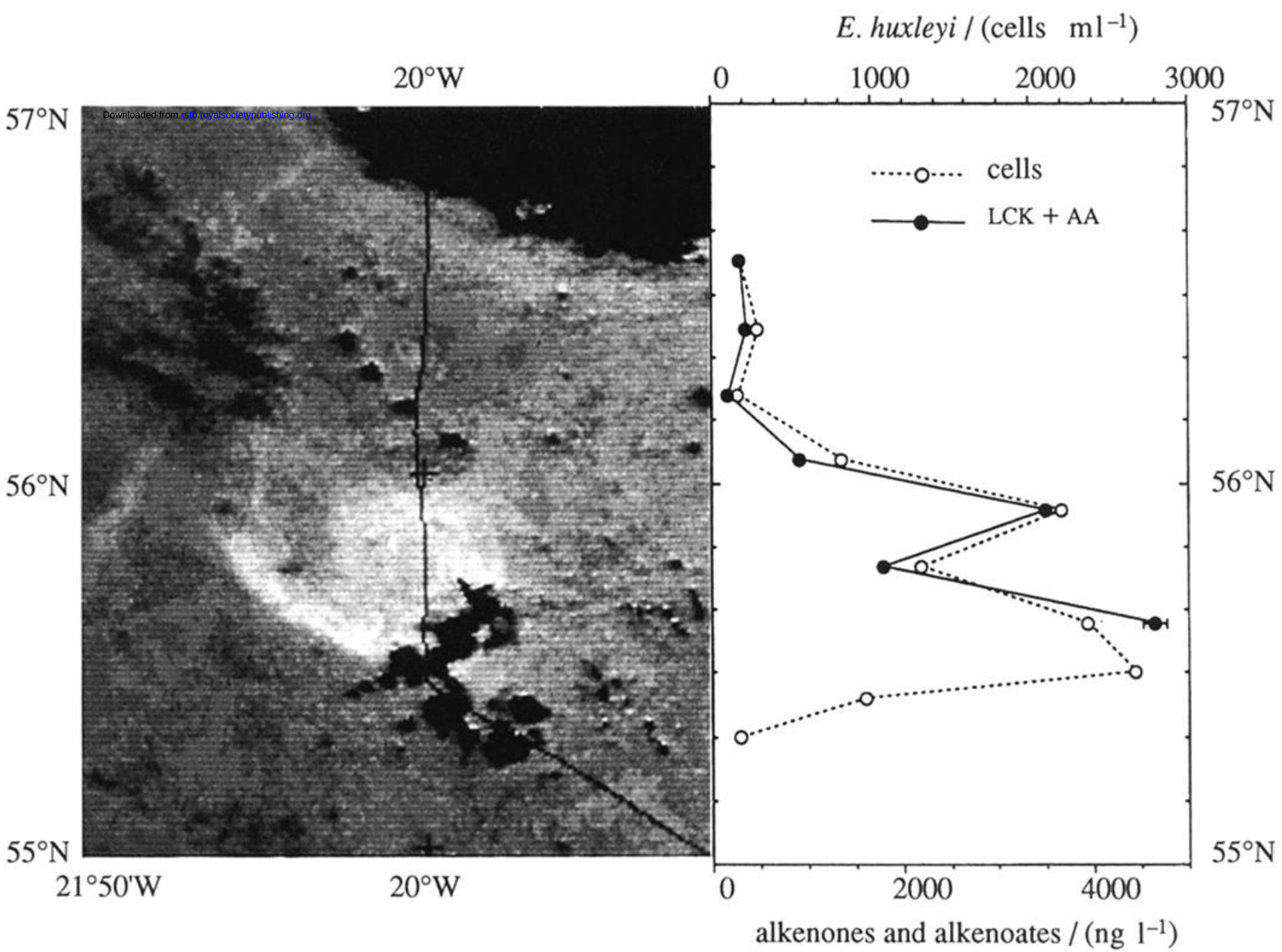

igure 2. *Emiliania huxleyi* bloom at 56° N, 20° W, July 1991. The AVHRR satellite image of 23 July shows the bloom s a high reflectance feature in a cold core eddy (image courtesy of S. Groom, U. Plymouth, U.K.). The reflectance ature enlarged by approximately 50 % between 23–27 July. The ship's transect on 25 July is indicated by solid line. he second panel shows *E. huxleyi* cell counts (no. ml^{-1}) and summed long-chain alkenone and alkyl alkenoate .CK + AA) concentrations (ng l^{-1}) at 4 m depth along the transect.