PALEOCEANOGRAPHY, VOL. 20, PA2001, doi:10.1029/2004PA001025, 2005

Variability of unusual distributions of alkenones in the surface waters of the Nordic seas

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Received 5 March 2004; revised 9 November 2004; accepted 23 November 2004; published 6 April 2005.

[1] Samples of filtered particulate organic matter (POM) were obtained during the summers of 1999 and 2000 from the surface waters of the Nordic seas to monitor the spatial distribution of long-chain alkenones. The aim of the study was to appraise existing alkenone-based climatic proxies in northern high latitudes. Unusually high percentages of the tetraunsaturated alkenone were measured in the polar waters of the East Greenland Current, with $C_{37:4}$ of up to 77% in 80% of sea-ice cover. Values of percent $C_{37:4}$ across the Nordic seas showed a strong association with water mass type. Analysis of coccoliths in filters indicated that calcified *Emiliania huxleyi* could not be discounted as the biological precursor of alkenones in all the water masses. A combined data set of 69 samples of POM revealed a stronger correlation of percent $C_{37:4}$ to sea surface salinity (SSS; $R^2 = 0.72$) than to sea surface temperature (SST; $R^2 = 0.50$). Values of percent $C_{37:4}$ in sea surface POM were much higher than those in surficial sediments of the northern North Atlantic. To explain the discrepancy in sedimentary and surface water column percent $C_{37:4}$, we propose that the alkenone contents in surface sediments underlying arctic and polar waters are a combination of autochthonous and allochthonous inputs of alkenones. Our results show that percent $C_{37:4}$ can be used to reconstruct the relative extension of arctic/polar water masses in the North Atlantic. However, the results prevent confirmation of percent $C_{37:4}$ as a paleo-SSS proxy in the Nordic seas, given its multivariate nature in our data set and the decoupling between its range of values in surface waters and sediments.

Citation: Bendle, J., A. Rosell-Melé, and P. Ziveri (2005), Variability of unusual distributions of alkenones in the surface waters of the Nordic seas, *Paleoceanography*, *20*, PA2001, doi:10.1029/2004PA001025.

1. Introduction

[2] At present there are no well-established sea surface salinity (SSS) proxies available to paleoceanographers. The prospect of a proxy that can estimate paleosalinity changes is highly desirable. Such data would contain information on past evaporation, precipitation and runoff inputs to the surface mixed layer and (combined with estimates of past sea surface temperature (SST)) would allow the investigation of paleodensities and past boundary conditions for deepwater formation. In this manuscript we evaluate further the use of an alkenone based index as a potential SSS proxy.

[3] Over the last decade, the alkenone unsaturation index $U_{37}^{K'}$ has been widely adopted as a proxy to estimate past SSTs. This index measures the relative abundance of the diunsaturated and triunsaturated C_{37} alkenones ($C_{37:2}$, $C_{37:3}$) in sediments. Recent studies have shown that in the Nordic seas alkenone SST indices are subject to increasing error in regions where present SST falls below ~6°C (annual mean 0–30 m) [*Levitus and Boyer*, 1994; *Rosell-Melé*, 1998; *Rosell-Melé et al.*, 1994]. Coincidentally, in these subpolar and polar regions the abundance of $C_{37:4}$, relative to the other C_{37} alkenones (%$C_{37:4}$),

$$\%C_{37:4} = \frac{C_{37:4}}{C_{37:2} + C_{37:3} + C_{37:4}} \times 100,$$

increases significantly [*Rosell-Melé*, 1998; *Rosell-Melé et al.*, 1994]. In the northern latitudes, some studies have highlighted an empirical relationship between percent $C_{37:4}$

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0883-8305/05/2004PA001025

and sea surface salinity (SSS) [*Harada et al.*, 2003; *Rosell-Melé*, 1998; *Rosell-Melé et al.*, 2002; *Sicre et al.*, 2002]. Moreover, some have applied the percent $C_{37:4}$ measurement down core as a tentative proxy to infer paleosalinity variations [*Bard et al.*, 2000; *Rosell-Melé*, 1998; *Rosell-Melé et al.*, 2002]. On a global scale it has been demonstrated that there is no discernable relationship of percent $C_{37:4}$ to SSS [*Sikes and Sicre*, 2002]. However, in the Nordic seas and North Atlantic, $\%C_{37:4}$ in surface sediments does show a correlation to ocean atlas SSS [*Rosell-Melé*, 1998; *Rosell-Melé et al.*, 2002].

[4] In this paper we further investigate the potential of the information contained in percent $C_{37:4}$ by reporting the distribution of percent $C_{37:4}$ measured in situ in the surface waters of the Nordic seas. Detailed reports of other alkenone data obtained (e.g., U^{K}_{37} and $U^{K'}_{37}$) have been published elsewhere [*Bendle and Rosell-Melé*, 2004]. Further investigation of alkenone distributions in the Nordic seas surface waters is necessary, as previous North Atlantic water column studies have reported none or very few results from the arctic and polar water masses [*Conte and Eglinton*, 1993; *Sicre et al.*, 2002; *Thomsen et al.*, 1998] and a new sea surface data set is needed to complement more geographically expansive studies of alkenone distributions in surface sediments[*Rosell-Melé*, 1998; *Rosell-Melé et al.*, 1994]. In this study we report alkenone contents in sea surface (~6 m depth) particulate organic matter (POM) obtained from across the spectrum of the characteristic water masses of the Nordic seas, during two cruises of the RRS *James Clark Ross* (JCR) in 1999 and 2000. This is an area with strong east to west hydrographic gradients; characterized by seasonal and spatial variations in SST, SSS, sea ice distribution and winter densification. The latter process results in the formation of deep water masses and hence plays a key role in driving the global thermohaline circulation. The present surface current system is characterized by the interaction of relatively warm (6–15°C) and saline (>35 psu) Atlantic source waters, and cold (<5°C) and less saline (<34.4 psu) polar source waters, the main features of which are illustrated in Figure 1.

[5] Alkenone distributions in POM collected from filtering seawater can be directly compared to ocean parameters measured during sampling, moreover, it is also relatively easy to collect a large number of samples over a large area. However, the approach is limited in that it provides only a temporal and spatial "snap shot" measurement of environmental conditions, not an integrated seasonal and depth signal as can be derived from the analysis of sediments or materials in sediment traps. Senescent bloom material may also be a significant component of the water filtrates, which may lead to temporal offsets between the time of alkenone synthesis and the collection of samples and the measurement of water properties. In this study sampling was conducted from late July to early September, therefore in the period after the peak in phytoplankton standing stocks in the Nordic seas (which develops northward through May and June) [*Longhurst*, 1998]. In the midsummer, grazing by zooplankton reaches a peak and, although primary productivity is high, the standing stock of the phytoplankton is greatly reduced. Therefore, owing to the rapid grazing by zooplankton, the chances of obtaining samples consisting of a significant proportion of old/senescent material should be minimized during this period.

2. Materials and Methods

2.1. Sample Retrieval

[6] Seawater POM was obtained onboard the RRS *James Clark Ross* during the NERC Arctic Ice and Environmental Variability (ARCICE) summer cruises "JR44" in 1999 (25 July to 28 August) and "JR51" in 2000 (28 July to 29 August). Sample details are given in Tables 1 and 2, sample locations are indicated in Figure 1. The POM was filtered from the uncontaminated seawater supply which was continuously pumped to the ship laboratories from a tube protruding half a meter beneath the hull. The depth of the tube inlet beneath the sea surface was approximately at 6 m. Between 60 and 153 L of seawater were collected into carboys and filtrated through Whatman 70 mm GF/F glass fiber filters (precleaned by firing them at 450°C) (during cruise JR44 the particulate suspension was concentrated prior to filtering using a Millipore Pellicon tangential flow system). The POM laden filters for a station were placed into clean 50 mL Teflon capped (aluminum foil lined) glass bottles using clean forceps. A 100 mL of a mixture of dicloromethane (DCM)/methanol (MeOH) (3:1) was added and the sample was then sealed and stored in a freezer until analysis.

[7] During cruise JR51 (excluding stations 15 to 17) part of the water sample was filtered to analyze coccolithophoral contents (GF/F, 0.7 micron pore size). The filter used, while typical for POM analysis, is not ideal to investigate coccolith contents; however, we wanted to directly investigate the source organisms of polar water alkenones in the same samples taken for organic geochemical work. In order to obtain the transparency of GF/F necessary for using the polarized light microscope (LM), a portion of the top layer of the GF/F was piled and mounted on a glass slide. The transparency was obtained by using immersion oil. The use of GF/F filters did not allow a highly detailed taxonomic study but we were able to quantify coccospheres and coccoliths of the principal species by using LM at 1600X. The numbers of coccoliths were transformed to coccospheres using an average number of coccoliths per coccosphere (12 coccoliths for *E.huxleyi*, 10 coccoliths for *Coccolithus pelagicus*). The cell density (number of coccosphere L-1) is an indicator of coccolithophorid production. The recalculation was necessary since the high vacuum pump probably caused breakage and collapse of most coccospheres. Scanning electron microscope (SEM) was used for determining the preservation, and to verify species composition and species ratios (mainly between *E.huxleyi* and *C.pelagicus*). Delicate species, such as those belonging to genera *Pappomonas* and *Syracosphaera*, were also found. They were usually not abundant, with the exception of sample 18 where high cell densities of *Syracosphaera sp.* were recorded.

[8] Surface sediments analyzed in this study were part of a series of box cores obtained by successive cruises of the

Table 1. JR44 Filter Sample Information: Collection and Analytical Data[a]

	Coordinates							GC-CI-MS C_{37} Isomer Response, mV × min			
Sample	Latitude, deg N	Longitude, deg E	Date in 1999	Volume Filtered, L	SST, deg C	SSS, PSU	ΣLCK, ng/L	$C_{27:4}$	$C_{37:3}$	$C_{37:2}$	$C_{37:4}$, %
1	62°21.36	3°20.60	24 July	140	13.2	34.73	54.5	0	206,929	153,591	0
2	64°17.57	5°40.33	25 July	140	12.7	34.72	43.8	-	2,053,900	11,272,000	0
3	65°98.46	8°88.64	26 July	140	11.9	34.21	16.4	5,975,508	91,459,560	35,478,504	4
4	67°90.32	6°74.48	27 July	140	11.0	35.12	7.7	0	79,296,864	45,364,996	0
5	68°20.02	6°37.71	27 July	140	10.9	35.12	2.6	0	40,803,472	20,873,120	0
6	69°57.68	4°55.16	28 July	140	9.6	35.10	59.9	2,878,132	66,447,996	19,934,856	3
7	70°79.43	2°71.61	29 July	140	9.3	35.06	36.5	748,907	65,685,644	22,069,924	0
8	71°13.66	2°15.05	29 July	140	9.3	35.17	0	1,269,309	40,100,300	9,470,588	2
9	72°55.85	−0°39.61	30 July	130	6.6	34.92	13.4	236,993	25,049,286	5,860,770	1
10	73°07.34	−1°47.05	30 July	140	5.4	34.72	0	-	-	-	-
11	74°13.35	−3°82.23	31 July	140	5.1	34.71	0	-	-	-	-
12	75°56.82	−7°75.95	1 Aug.	140	5.0	34.61	0	-	-	-	-
13	76°03.46	−9°24.27	2 Aug.	140	0.3	30.71[b]	0	4,248,410	1,400,932	186,463	73
14	76°37.29	−10°45.94	2 Aug.	140	2.1	30.69[b]	6.9	21,389,678	5,363,385	1,058,775	77
15	80°41.69	5°54.62	10 Aug.	140	4.9	34.41[b]	7.9	2,644,676	18,029,870	4,616,426	10
16	79°86.56	1°02.52	13 Aug.	140	2.1	34.28[b]	3.0	7,610,967	9,445,704	1,929,831	40
17	78°88.35	1°77.0.3	14 Aug.	140	1.8	33.03[b]	5.4	18,877,274	8,972,016	1,634,382	64
18	78°83.32	8°72.3.5	15 Aug.	140	7.1	34.81[b]	2.5	1,393,344	7,569,482	2,178,028	13
19	78°71.48	9°05.20	15 Aug.	140	7.0	34.81[b]	1.9	391,375	3,699,818	1,313,646	7
20	77°51.98	7°28.52	16 Aug.	140	6.7	35.04[b]	0	-	-	-	-
21	77°39.36	6°68.68	16 Aug.	140	6.7	35.03[b]	0	-	-	-	-
22	76°34.34	2°66.92	17 Aug.	140	6.0	34.90[b]	0	-	-	-	-
23	76°00.41	1°51.32	17 Aug.	140	5.7	34.88[b]	0	-	-	-	-
24	74°76.20	−2°16.21	18 Aug.	110	5.3	34.74[b]	0	-	-	-	-
25	71°25.01	−9°59.78	20 Aug.	140	6.4	34.71[b]	13.2	72,028,552	159,000,000	24,361,404	28
26	69°22.85	−12°66.74	21 Aug.	140	6.8	34.66[b]	3.2	896,431	5,648,757	1,328,236	12
27	66°86.66	−17°39.28	22 Aug.	140	8.5	34.41[b]	12.4	94,041	1,723,457	568,590	4
28	67°48.49	−21°51.18	23 Aug.	140	6.1	34.06[b]	33.3	765,802	9,333,642	2,038,687	6
29	68°71.13	−23°01.14	24 Aug.	140	4.2	29.65[b]	0	-	-	-	-
30	69°22.79	−23°70.43	24 Aug.	140	2.5	30.93[b]	0	-	-	-	-
31	68°13.55	−22°28.25	25 Aug.	140	4.4	33.07[b]	0	-	-	-	-
32	66°69.35	−18°36.52	26 Aug.	140	7.2	33.58[b]	30.4	559,376	8,531,252	2,315,096	4

[a] Volume filtered is the volume (in liters) of sea surface seawater filtered for lipid extraction. SST, SSS, and fluorescence were measured using the ships data logging systems, except where indicated, and correspond to the seawater pumped to the ship laboratory from ~6 m below sea surface. ΣLCK is the total abundance of all the C_{37} and C_{38} alkenones.

[b] Derived from CTD rather than the ship thermosalinograph.

Table 2. JR51 Filter Sample Information: Collection and Analytical Data[a]

	Coordinates							GC-CI-MS C_{37} Isomer Response, mV × min			
Sample	Latitude, deg N	Longitude, deg E	Date in 2000	Volume Filtered, L	SST, deg C	SSS, PSU	ΣLCK, ng/L	$C_{27:4}$	$C_{37:3}$	$C_{37:2}$	$C_{37:4}$, %
1	67°78.83	7°75.10	28 July	60	10.6	34.75	19.1	138,944	28,403,218	11,128,898	0.3
2	69°39.56	5°50.00	28 July	100	10.1	35.32	5.9	0	5,571,485	3,113,115	0
3	69°94.05	7°09.67	5 Aug.	96	10.0	35.42	82.8	0	42,972,372	18,199,352	0
4	73°16.66	9°66.82	6 Aug.	153	8.0	35.45	-	-	-	-	-
5	74°66.67	10°49.99	6 Aug.	85	7.5	35.40	3.2	1,075,359	20,662,586	9,024,364	3
6	74°49.86	5°36.53	8 Aug.	78	7.3	35.39	-	0	1,866,330	1,053,238	0
7	74°81.77	−0°06.03	9 Aug.	153	5.9	35.15	-	-	-	-	-
8	76°02.65	−7°64.46	10 Aug.	120.5	−0.6	30.72	2.9	17,006,148	9,001,958	2,214,277	60
9	75°29.56	−5°18.79	11 Aug.	148.5	5.6	34.70	-	-	-	-	-
10	73°44.07	−9°43.56	14 Aug.	119	3.4	31.96	-	-	-	-	-
11	73°02.72	−13°43.83	17 Aug.	151	3.5	31.20	-	-	-	-	-
12	72°42.87	−15°52.58	24 Aug.	127.5	1.8	30.87	5.4	276,985	218,103	46,982	51
13	69°81.30	−19°39.40	25 Aug.	149.5	0.8	30.12	-	5,043,562	3,519,187	1,136,476	52
14	67°87.74	−21°32.05	26 Aug.	100.5	7.0	34.24	109.5	7,565,562	44,364,412	7,282,673	13
15	67°55.15	−17°12.47	26 Aug.	110	7.6	34.71	39.4	6,097,162	37,779,684	9,193,764	11
16	67°52.07	−12°08.94	27 Aug.	104.5	9.1	34.87	13.2	4,041,261	22,381,554	5,469,366	13
17	65°09.01	−9°40.69	28 Aug.	142	8.8	34.98	-	2,974,084	40,025,916	6,498,169	6
18	60°66.16	−3°59.03	29 Aug.	79	12.9	35.60	6.9	0	19,853,816	12,809,840	0

[a] Volume filtered is the volume (in liters) of sea surface seawater filtered for lipid extraction. SST, SSS, and fluorescence were measured using the ships data logging systems and correspond to the seawater pumped to the ship laboratory from ~6 m below sea surface. ΣLCK is the total abundance of all the C_{37} and C_{38} alkenones.

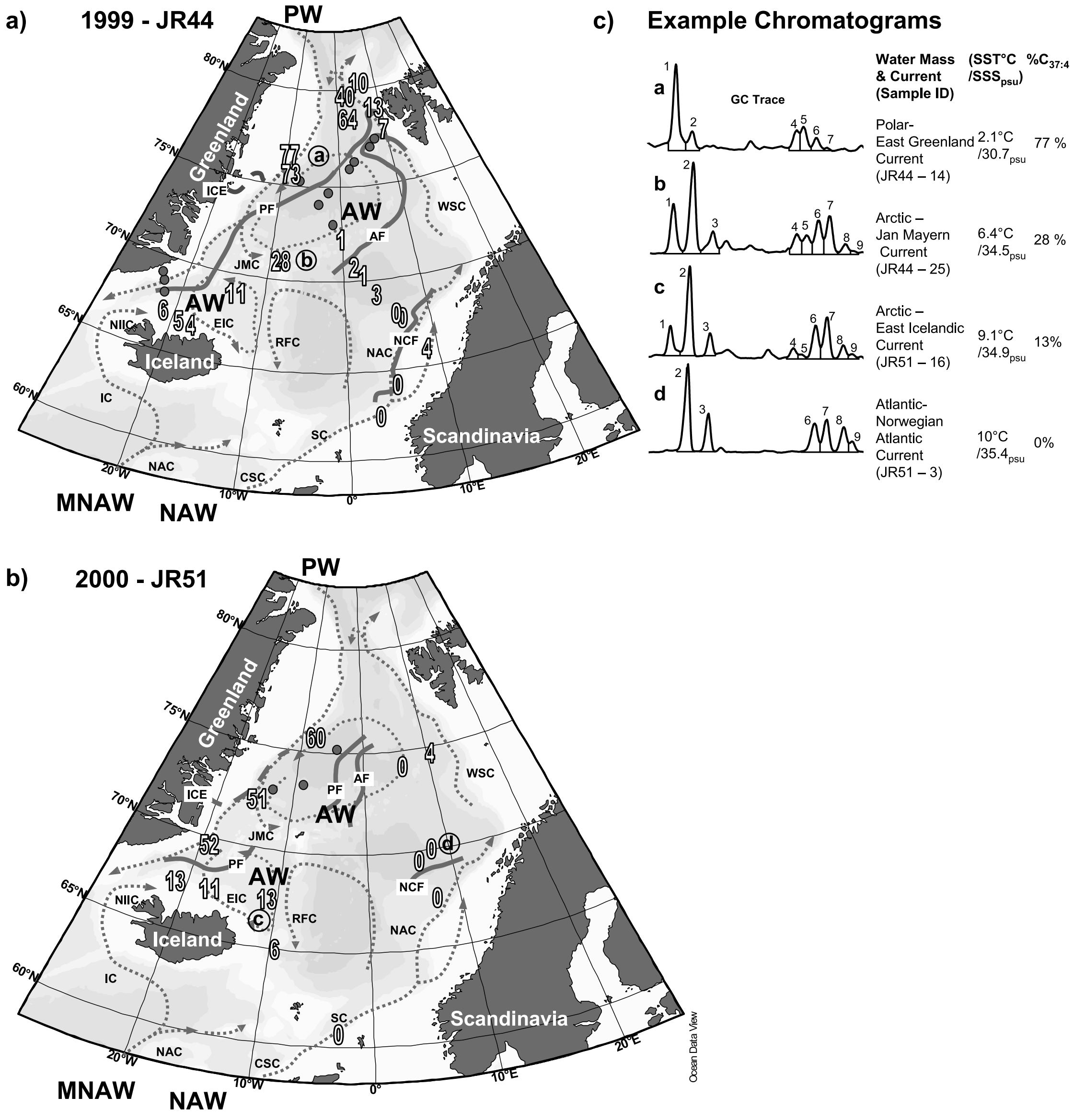

Figure 1. Maps showing the sampling locations during two ARCICE cruises on the RRS *James Clark Ross* from mid-July to September in (a) 1999 (JR44) and (b) 2000 (JR51). Numbers represent measured values of percent $C_{37:4}$ (dots represent samples where no alkenones were detected). Main features of the surface to near-surface circulation in the Nordic seas are illustrated by thin dashed arrows. From *Hansen and Østerhus* [2000], *Johanessen* [1986], and *Swift* [1986]. Position of oceanographic fronts are indicated by solid gray lines. Frontal positions are estimated from continuous in situ measurements made during the cruises. Currents are as follows: EGC, East Greenland Current; EIC, East Icelandic Current; IC, Irminger Current; NAC, North Atlantic Current; NIIC, North Icelandic Irminger Current; RFC, Recirculated Faroe Current; SC, Shetland Curren; WSC, West Spitsbergen Current; JMC, Jan Mayen Current. Water masses are as follows: AW, arctic water; MNAW, Modified North Atlantic Water; NAW, North Atlantic Water; PW, polar water. Ocean fronts are as follows: PF, polar front; AF, arctic front; NCF, Norwegian Coastal Front. Southern extent of dense (>80%) sea ice was estimated from SeaWiFs satellite data and is indicated by gray bold dashed lines. (c) Representative chromatograms: GC-FID traces of alkenone patterns from different water masses are illustrated. Alkenone peak assignation: (1) $C_{37:4}$ Me, (2) $C_{37:3}$ Me, (3) $C_{37:2}$ Me, (4) $C_{38:4}$ Et, (5) $C_{38:4}$ Me, (6) $C_{38:3}$ Et, (7) $C_{38:3}$ Me, (8) $C_{38:2}$ Et, and (9) $C_{38:2}$ Me. The sample location is indicated by encircled letters a–d.

German vessel *Meteor* between 1987 and 1989. The cores were subsampled at 1 cm intervals (for the top 5 cm) and at 5 cm intervals below 5 cm. The samples used in this study had been freeze-dried and stored, sealed, at room temperature since ~1993, prior to analysis in 2001. Additional core-top samples for the Icelandic shelf region of the Nordic seas were taken from gravity cores collected during ARCICE cruises JR44 and JR51, and subsampled in similar fashion as the other sediments.

2.2. Analytical Methods

[9] The glass fiber filters containing the particulate material were extracted by ultrasonication (x3) with 20 mL of DCM/MeOH (3:1), after addition of an internal standard. The combined extracts were hydrolyzed in sealed test tubes with a 3 mL solution of KOH in MeOH (8%) for 36 hrs. The neutral fraction was recovered with 3 mL of hexane (x3) and the combined extract was washed with water (previously distilled and solvent extracted), in a test tube to remove residual KOH traces. The extract was re-dissolved, dried with Na_2SO_4 and stored sealed, at −20°C, until chromatographic analysis.

[10] Sediment samples were freeze dried and ground, an internal standard added and extracted with DCM/MeOH at 70°C for 5 minutes using a MARS 5 microwave extractor (see *Kornilova and Rosell-Melé* [2003] for details). The solvent extract was concentrated to dryness with a centrifugal evaporator or with nitrogen blow-down, re-dissolved in DCM and dried with Na_2SO_4. The extracts were fractionated by high performance liquid chromatography (HPLC). This was performed using a system consisting of a Thermo Hypersil column (50 × 4.6 mm) packed with Lichospher Si100 5 m silica, and a Thermo Hypersil guard column. Fractions were collected using a Foxy Jr automatic collector. The solvent program was adapted from *Schulz et al.* [2000]. Four fractions were collected in test tubes by eluting at 1 mL min^{-1} with hexane (1.4 mL, aliphatic and cyclic alkanes), hexane/DCM (17:3; 3.5 mL, aliphatic ketones), DCM (2.25 mL, cyclic ketones), acetone (2.25 mL, sterols, alcohols and polars). Fractions 1 and 2 were combined, dried under nitrogen and derivatized using bis-trimethylsilyl-trifluoroacetamide (BSTFA) prior to gas chromatographic analysis.

[11] Quantification of the absolute abundance of alkenones was performed using a Fisons 8000 Series gas chromatograph fitted with a flame ionization detector (GC-FID) and a split/splitless injector. Baseline separation of the alkenones was obtained using a SGE BP-1 fused silica column (60 m length, 0.25 mm i.d., 0.25 μm film thickness), and an oven temperature program as follows: 60°C for 1 min, 60°C to 200°C at 20°C min^{-1}, 200°C to 305°C at 6°C min^{-1}, held at 305°C for 35 min, 305°C to 320°C at 15°C min^{-1} and held at 320°C for 2 min. Hydrogen was used as a carrier gas.

[12] Quantification of the relative abundances of the target components (within-class distributions) was performed using a Varian 3400 gas chromatograph directly coupled to a Finnigan MAT TSQ 700 triple stage quadrupole mass spectrometer (GC-CI-MS), using ammonia chemical ionization [*Rosell-Melé et al.*, 1995]. The GC was fitted with a splitless injector operated in "high performance" nonvaporizing mode, held at 80°C during injection then rapidly heated from 80–300°C at °C min^{-1}. Separation of the analytes was achieved using a 50 m length, 0.32 mm i.d. fused silica column, with 0.12 μm CPSIL5-CB film thickness (Chrompack). The oven temperature program was: 200°C to 300°C at 6°C min^{-1} with no initial hold time and a final isothermal period of 10 minutes. Hydrogen was employed as a carrier gas with a head pressure of 8 psi. Operating conditions for the mass spectrometer were optimized for sensitivity with respect to the C_{37} methyl alkenones. Chemical ionization was achieved using high purity ammonia (BOC micrographic grade). Specific ions, corresponding to the $[M + NH_4]^+$ species of the analytes were monitored.

[13] The sea surface filter samples were analyzed both by GC-CI-MS and GC-FID. Values of $U^{K'}_{37}$ and percent $C_{37:4}$ measured by both techniques were compared. Results for $U^{K'}_{37}$ were compared with those previously reported by *Rosell-Melé et al.* [1995], with both instruments providing similar results but with a slight relative overestimation of $U^{K'}_{37}$ by GC-FID (~0.01 $U^{K'}_{37}$ units). Measurements of percent $C_{37:4}$ by GC-FID and GC-CI-MS displayed a linear relationship ($y = 1.04x + 11.6$, $R^2 = 0.93$); however, estimates of $\%C_{37:4}$ by GC-FID, relative to GC-CI-MS, were often higher by ~10%. This may have been due to coelution of the $C_{37:4}$ with other compounds in the GC-FID system. This has been reported as a problem by other workers [*Sicre et al.*, 2002; E. Bard, personal communication, 2002]. Hence it may be important to use a GC-CI-MS (or GC-SIM) analysis to obtain accurate percent $C_{37:4}$ values and care should be taken when comparing values of percent $C_{37:4}$ measured by GC-CI-MS to values measured by GC-FID in the literature.

[14] Procedural and analytical reproducibility was determined for the analyses with an homogeneous "sediment standard" (analyzed once for every 10 samples to be validated). The overall average reproducibility for the absolute quantification of alkenones by GC-FID had a coefficient of variation (CV) of 5.92% (at 2σ). The overall average reproducibility for percent $C_{37:4}$ by GC-CI-MS had a coefficient of variation (CV) of 0.79 (at 2σ).

3. Results and Discussion

3.1. Surface Hydrography in the Nordic Seas During August 1999 and 2000

[15] The complex systems of warm and cold currents in the Nordic seas (Figure 1) are arbitrarily delimited by a number of ocean fronts, which reflect strong, quasi-permanent, boundaries in the temperature and salinity fields and which are strongly associated with the bottom topography [*Johanessen*, 1986]. During the 1999 and 2000 ARCICE cruises the positions of the polar front (PF), arctic front (AF) and Norwegian Coastal Front (NCF) were estimated by comparison of the monitored sea surface property data and the typical Nordic seas hydrographic provinces described in the literature [*Hansen and Østerhus*, 2000; *Johanessen*, 1986; *Swift*, 1986]. Additionally, depth profile data collected during both cruises were also consulted [*Bendle*, 2003]. Using the conventions of *Johanessen* [1986], the

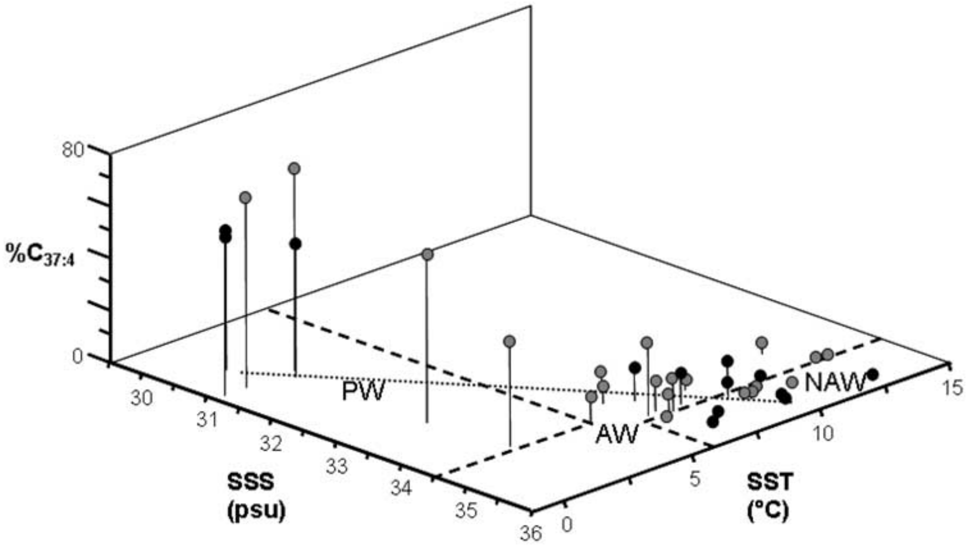

Figure 2. Distributions of percent $C_{37:4}$ in the surface water masses of the Nordic seas. Percent $C_{37:4}$ versus temperature and salinity with major water masses delimited (dashed line). Dark gray circles, samples from JR44; black circles, samples from JR-51. Water masses were delimited using the values from literature [*Hansen and Østerhus*, 2000; *Johanessen*, 1986; *Swift*, 1986]. The dotted line is a linear regression between SSS and SST: y = 1.5x − 44.2, R^2 = 0.54 (n = 50).

SSS isoline at 34.4 psu was used to estimate the position of the PF, likewise the 35 psu isoline was used to estimate the position of the AF (in the northwest) and the NCF (in the southeast). The position and extent of sea ice off the east coast of Greenland was also estimated from SeaWiFs images of Chlorophyll *a*, and true color images [*Bendle and Rosell-Melé*, 2004].

[16] Figure 1 shows that there was considerable variation in the position of fronts between the two cruises in both 1999 and 2000. In 1999, the PF followed the continental shelf (Figure 1a), especially closely south of ~74°N, and dense sea ice did not extend south of 74°N. In 1999 the AF followed, relatively closely, the line of the Mohns ridge, a position often ascribed as typical for the AF in reviews of Nordic seas oceanography [e.g., *Johanessen*, 1986]. This results in a fairly large expanse of AW occupying the Greenland Sea between the polar waters of the EGC in the west and the Atlantic signature waters in the Norwegian Sea to the east. In the northeastern Nordic seas, Atlantic signature waters were measured as far north as ~78°N (presumably carried by the West Spitsbergen Current, WSC), beyond which there was a gradient of change to polar-type waters at ~80°N. In 1999, the NCF followed, fairly closely, the Norwegian continental shelf (see Figure 1). The cruise track in 2000 did not extend as far to the northeast, therefore interannual comparisons for this region are not possible. However, in the central, southern and western Nordic seas, there was a degree of overlap and therefore comparisons can be made. In August 2000 there appeared to be some significant differences in the physical oceanography of the Nordic seas compared to 1999. In the southwest Nordic seas, in August 2000, the PF extended much further away from the continental shelf (Figure 1b). The sea ice also extended further south to 72°N. However, compared to August 1999, a large polynya opened to the northeast of Greenland [*Bendle and Rosell-Melé*, 2004]. In 2000 the PF and AF were, geographically, much closer in the central Nordic seas, due to the PF occupying a position further east and Atlantic signature waters pushing much farther west into the Greenland Sea. In 2000 the NCF pushed father west from the Norwegian continental shelf compared to 1999 (Figure 1b).

3.2. Percent C37:4 in Sea Surface POM During August 1999 and 2000

[17] Filtered water samples were successfully obtained from Atlantic and polar source water masses in both 1999 and 2000 (Figure 1). The main water domains contained substantially different distributions of alkenones, as can be inferred from the chromatographic traces shown in Figure 1c. The geographical and water mass distributions of values of percent $C_{37:4}$ are shown in Figures 1 and 2, respectively. A feature of the data that stands out is the high values of percent $C_{37:4}$ in samples from the polar waters of the EGC. Values below 5% are typical from open marine settings in mid to low latitudes [*Rosell-Melé*, 1998]. Higher values of percent $C_{37:4}$ above this threshold have been previously observed in a diverse range of lacustrine environments [*Cranwell*, 1985; *Li et al.*, 1996; *Thiel et al.*, 1997; *Volkman et al.*, 1988; *Zink et al.*, 2001], in coastal/brackish sediments [*Ficken and Farrimond*, 1995; *Schöner et al.*, 1998; *Schulz et al.*, 2000] and in the open ocean in high latitudes [*Harada et al.*, 2003; *Rosell-Melé*, 1998; *Sicre et al.*, 2002; *Sikes et al.*, 1997]. The highest previously reported values of percent $C_{37:4}$ in the open ocean water column is 41%, obtained from the subpolar waters of the Bering Sea [*Harada et al.*, 2003], and 35% in the Greenland Sea [*Sicre et al.*, 2002]. We found six polar water samples that yielded percent $C_{37:4}$ > 40%. These were retrieved from locations with up to 80% sea ice cover at the time of collection. The two samples collected on 2 August 1999

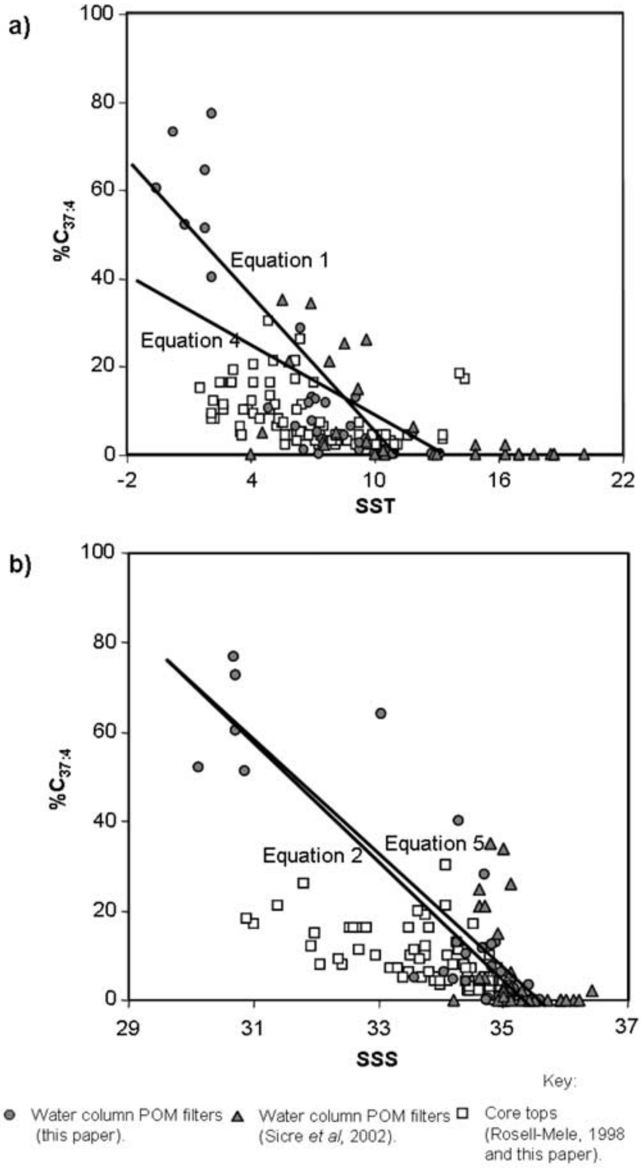

Figure 3. Distributions of percent $C_{37:4}$ in the water column and surface sediments of the Nordic seas and northern north Atlantic. Scatterplots of percent $C_{37:4}$ versus (a) SST and (b) SSS from sample sets illustrated in Figure 4. SST and SSS data was measured in situ for POM samples for sediment samples values are taken from the World Ocean Atlas: mean summer (July, August, and September) at 0 m depth [*Levitus and Boyer*, 1994]. Regression lines correspond to equations cited in text.

from the EGC yielded the highest percent $C_{37:4}$ values (72 and 77%) observed so far in any environment: marine, brackish or lacustrine. This apparently contrasts with a previous investigation by *Sicre et al.* [2002] which did not detect alkenones in the truly polar waters of the Nordic seas (salinity of <34.4 psu). In fact, we found low absolute concentrations of the alkenone class in the polar waters (ΣLCK, see Tables 1 and 2) and did not detect alkenones in a third of all the samples, with samples from the polar and arctic waters being those most likely to have undetectable concentrations.

[18] Figure 2 highlights the clustering of high %$C_{37:4}$ values (40–77%) within the polar waters, and with low values (0–3%) in Atlantic waters. Low to intermediate values (0–28%) were obtained from water masses that are not classified as truly polar or Atlantic. Further inspection of the geographic distribution of the samples from the "intermediate" water masses reveals:

[19] 1. Low %$C_{37:4}$ values of 0–4% in the Shetland current. The Shetland Current is an Atlantic source current which has lowered salinities as a result of mixing with the Norwegian Coastal Current (as opposed to low salinity polar waters).

[20] 2. Low to intermediate %$C_{37:4}$ values of 4–13% in the Icelandic Sea, North Icelandic Irminger and East Icelandic Currents. These are water masses which result from varied mixing of polar and Atlantic sources.

[21] 3. A relatively high %$C_{37:4}$ value of 28% from the Jan Mayen Current, which has a strong source in the East Greenland Current.

[22] 4. Intermediate %$C_{37:4}$ values of 10–12% from the region in the far north in which the West Spitsbergen Current (Atlantic source) mixes with the East Greenland Current.

[23] In Figure 3 Nordic seas sea surface POM and surface sediment percent C_{37} data [*Rosell-Melé*, 1998; *Sicre et al.*, 2002; this paper] are plotted against SST and SSS. Regression of the POM data from this paper against SST and SSS reveals that %$C_{37:4}$ is linearly correlated to SST (equation (1)). While, a correlation of slightly higher significance (higher R^2 and lower relative error of the coefficients) is achieved with SSS (equation (2)) (see Figure 3):

$$\%C_{37:4} = -5.5(\pm 0.5) \times \text{SST} + 56.5(\pm 4.5), \quad R^2 = 0.76 (n = 33), \tag{1}$$

$$\%C_{37:4} = -13.4(\pm 1.2) \times \text{SSS} + 472.6(\pm 42), \quad R^2 = 0.79 (n = 33). \tag{2}$$

A multiple regression of %$C_{37:4}$ versus SST and SSS yields the following equation:

$$\%C_{37:4} = 311(\pm 54.1) - 8(\pm 1.7) \times \text{SSS} - 2.8(\pm 0.7) \times \text{SST}, R^2 = 0.86 (n = 34). \tag{3}$$

[24] The different significance of the coefficients (SSS and SST) can be inferred by looking at their relative error. This is slightly larger for SST (25% of the coefficient) than for SSS (21% of the coefficient). However, a test of significance of the multiple regression coefficients shows that both the SST coefficient ($p < 10^{-4}$) and that of SSS ($p < 10^{-4}$) are highly significant. Hence both SST and SSS

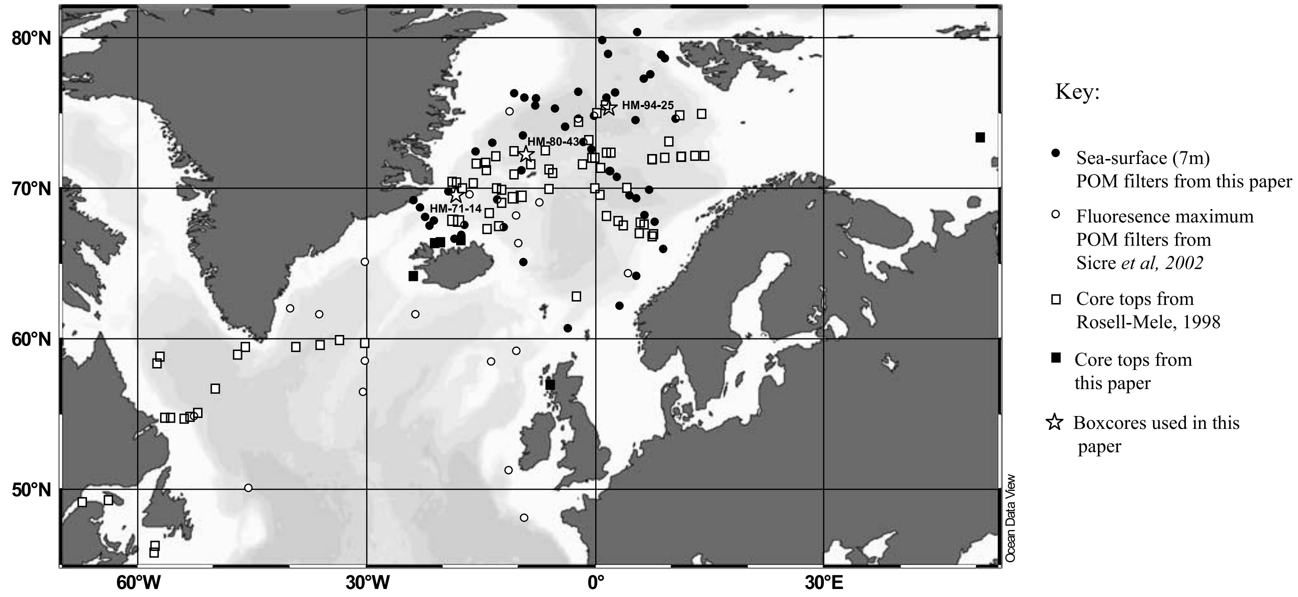

Figure 4. Geographic distribution of percent $C_{37:4}$ samples from the water column and surface sediments of the Nordic seas and northern North Atlantic.

coefficients contribute significantly and almost equally to the predictability of percent $C_{37:4}$.

[25] Previous work in the Nordic seas and northern North Atlantic surface sediments [*Rosell-Melé et al.*, 2002] and sea surface POM [*Sicre et al.*, 2002] has found a stronger relationship of percent $C_{37:4}$ to SSS, than to SST. A similar observation was made by *Harada et al.* [2003] for a number of sea surface POM samples from the Bering Sea.

[26] One problem of attempting to assess the relative influence of SST and SSS on alkenone distributions in the Nordic seas is the fact that the two variables are not completely independent (Figure 2). Both SST and SSS decrease in the transition from Atlantic to polar-type waters. However, SST initially decreases more rapidly than SSS, whereas in the colder waters SSS decreases more rapidly compared to SST. A linear regression (between SST and SSS) yields a R^2 value of only 0.54 (Figure 2). Therefore, if only one independent variable (SST or SSS) controlled percent $C_{37:4}$, and the other had no relationship to percent $C_{37:4}$ it should be possible to identify which one was the dominant control. Results from this study, however, find little difference in the significance of the correlations of percent $C_{37:4}$ to SST and SSS. Moreover, with regard to the applicability of percent $C_{37:4}$ as a SSS proxy, the distribution of percent $C_{37:4}$ plotted against SSS (Figure 3) displays considerable scatter, especially in polar waters, and percent $C_{37:4}$ appears unconvincing as a predictor of SSS.

3.3. Regional and Global Correlations of Percent $C_{37:4}$ With SSS and SST From POM

[27] Figure 4 illustrates the geographic distribution of water column and sediment surface samples compiled for this paper, with surface sediments collected by *Rosell-Melé* [1998] and POM samples described in the work of *Sicre et al.* [2002] from the Nordic seas and the North Atlantic. In the Nordic seas region there is considerable overlap of sediment and water column samples; which facilitates a comparison. Figure 3 contains plots of percent $C_{37:4}$ in the water column and surface sediment samples versus SST and SSS (for sediment samples SST and SSS values are taken from the World Ocean Atlas: mean summer (July, August, and September) at 0 m depth [*Levitus and Boyer*, 1994]).

[28] Values of percent $C_{37:4}$ measured in sea surface POM in this study are similar, within a comparable range of SST and SSS values, to those from suspended POM measured in the fluorescence maximum by *Sicre et al.* [2002]. The sampling depth for this study was ~6 m and is probably representative of the surface mixed layer. If the filtered POM data from the present study and that from *Sicre et al.* [2002] are combined and used to derive a regression line of percent $C_{37:4}$ against SSS and SST, the linear correlation for percent $C_{37:4}$ versus SST (equation (4)) becomes weaker, compared to a regression based on just the data from this study (equation (1), $R^2 = 0.78$):

$$\%C_{37:4} = -2.7(\pm 0.3) \times \mathrm{SST} + 37.6(\pm 3.6), \quad R^2 = 0.5(n = 69). \tag{4}$$

[29] The weaker correlation is due to greater scatter in the *Sicre et al.* [2002] data for percent $C_{37:4}$ versus SST. Combining the data sets also results in a slightly weaker linear correlation for percent $C_{37:4}$ versus SSS:

$$\%C_{37:4} = -12.7(\pm 0.9) \times \mathrm{SSS} + 450.1(\pm 33.1), \quad R^2 = 0.72(n = 69). \tag{5}$$

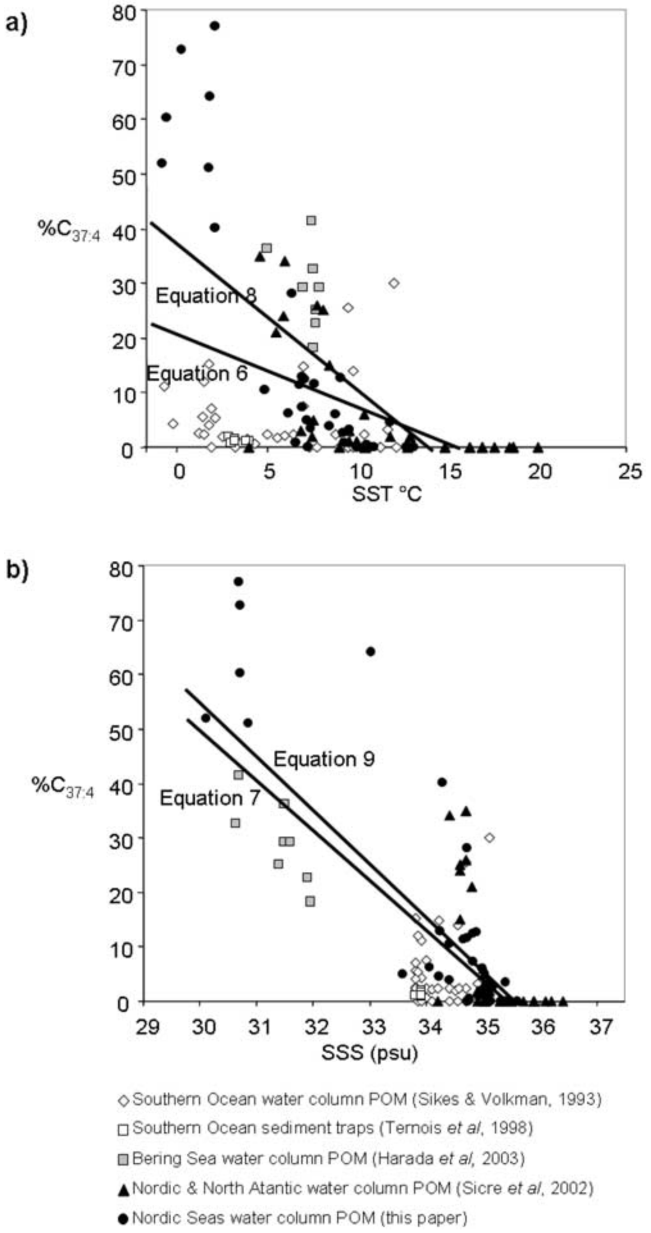

Figure 5. Distributions of percent $C_{37:4}$ in the global water column. Scatterplots of $C_{37:4}$ versus (a) SST and (b) SSS.

[30] However, the combined data set of 69 samples of POM reveals a stronger correlation of percent $C_{37:4}$ to sea surface salinity (SSS, $R^2 = 0.72$) than to SST ($R^2 = 0.50$) Recently, *Sikes and Sicre* [2002] assessed the global relationship of SST and SSS to percent $C_{37:4}$ reporting no discernable relationship of percent $C_{37:4}$ in the water column to SST or SSS on a global scale. Two new data sets are now available to add to the global database since the publication of the *Sikes and Sicre* [2002] work: this study (Nordic seas) and *Harada et al.* [2003] (Bering Sea). Both new studies report high values of percent $C_{37:4}$ in the surface waters from northern high latitudes. Figure 5 illustrates the global distribution of water column percent $C_{37:4}$ versus SSS and SST, with the new data incorporated. Values of percent $C_{37:4}$ showed no significant correlation to SST using the new global data set:

$$\%C_{37:4} = -1.4(\pm 0.3) \times \mathrm{SST} + 21.2(\pm 2.6). \qquad R^2 = 0.17(n = 122) \tag{6}$$

[31] This is partly due to the data from the Southern Ocean, which clearly contrast with that from the Northern Hemisphere in the relationship of percent $C_{37:4}$ to SST. In the surface waters of the southern ocean (temperature range between −1 to 18°C) the $C_{37:4}$ compound was reported to occur in significant relative abundance (up to 30%) in many samples but displayed absolutely no correlation with SST [*Sikes et al.*, 1997]. The global correlation of percent $C_{37:4}$ to SSS was stronger but still not highly significant:

$$\%C_{37:4} = -9.1(\pm 0.8) \times \mathrm{SSS} + 321.3(\pm 27.2). \qquad R^2 = 0.52(n = 122) \tag{7}$$

[32] Figure 5 clearly highlights a difference in the relationship of percent $C_{37:4}$ versus SSS between the Nordic seas and Bering Sea basins. Data from both basins feature high values of percent $C_{37:4}$. However, percent $C_{37:4}$ values are higher for the Nordic seas (50–77%) than for the Bering Sea (18–44%), in polar waters with a similar salinity range (30–32 psu). This may suggest that other parameters not measured in our study, such as nutrients, growth rate or light intensity, may have an additional influence in the relative production of alkenones by algae. Another explanation is that this may reflect regional (e.g., genetic) differences in the physiological response of the of alkenone producers to a given environmental variable [*Broerse et al.*, 2003]. To explore further the relationship of percent $C_{37:4}$ to SSS and SST in the Northern Hemisphere basins, regressions were made using the Northern Hemisphere data only. The equations obtained show stronger relationships for both SST and SSS with percent $C_{37:4}$ for the Northern Hemisphere data set over the global data set:

$$\%C_{37:4} = -2.9(\pm 0.3) \times \mathrm{SST} + 39.9(\pm 3.4), \qquad R^2 = 0.51(n = 77) \tag{8}$$

$$\%C_{37:4} = -9.8(\pm 0.8) \times \mathrm{SSS} + 348.1(\pm 27.6). \qquad R^2 = 0.66(n = 77) \tag{9}$$

[33] However, the relationship to SSS for the Northern Hemisphere is weaker than when the Nordic seas ($R^2 = 0.72$) and the Bering Sea ($R^2 = 0.76$; *Harada et al.* [2003]) are considered separately. This contrasts with the relationship to SST, which is similar in the Nordic seas ($R^2 = 0.0.51$) to the Northern Hemisphere as a whole (0.5), but is insignificant in the Bering Sea data set ($R^2 = 0.17$).

[34] In summary, there is no strong global or even hemispherical relationship of percent $C_{37:4}$ to SSS or SST, although within individual basins a relationship to SSS or SST can appear stronger. In the Nordic seas and N. Atlantic POM, where the distribution of %$C_{37:4}$ is most closely associated with SSS (equation (5)), the relationship displays considerable scatter and takes the form of a cluster of high %$C_{37:4}$ values associated with polar waters and a low value cluster with Atlantic waters, with mixing between these two groups in the intermediate water masses. However, whether an environmental factor or combination of factors promotes the production of relatively high percent $C_{37:4}$ values in polar or polar influenced ocean waters remains to be established. Recent work by *Prahl et al.* [2003] has demonstrated that light and nutrient stress can contribute to the variability in alkenone unsaturation ratios produced by *E. huxleyi*. Although the authors did not address the $C_{37:4}$ alkenone directly (just $C_{37:2}$ and $C_{37:3}$) their work demonstrates that other parameters than SST and SSS, environmental stresses, can influence alkenone unsaturation ratios in the field. In this study we obtained POM samples from across a region of the ocean which displayed sharp gradients in SSS and SST. Other oceanographic properties can also be expected to have varied across the region. In the polar waters in which we observe unusually high percent $C_{37:4}$ values the seasonal nutrient and light regimes differ considerably from the Atlantic source waters to the south and east [*Longhurst*, 1998]. It is a possibility that such factors might have also significantly influenced alkenone distributions by placing environmental stress on alkenone producers, in combination with or independently of the variability in SST or SSS. The influence of other factors might also explain the lack of a consistent relationship to SSS or SST globally, but this remains to be proven.

3.4. Comparison of Percent $C_{37:4}$ Distributions in POM With Surface Sediment Data

[35] In the Nordic seas, higher values of percent $C_{37:4}$ are generally found in POM samples than in proximal underlying sediments (Figure 3). This is especially apparent in the polar water samples (<34.4 psu), where sediment values do not exceed 20% in percent $C_{37:4}$ but water column values are 40–77%. Alkenones (like all lipid compounds) degrade in the water column and in sediments. It is sometimes argued that alkenone ratios may be biased through preferential degradation or incorporation (into macromolecular organic matter) of the components with more double bonds ($C_{37:4}$ > $C_{37:4}$ > $C_{37:2}$) [*Flügge*, 1997; *Freeman and Wakeham*, 1991; *Gong and Hollander*, 1999; *Hoefs et al.*, 1998]. However, studies that report significant biases (e.g., >0.5°C in the $U_{37}^{K'}$ index) are outnumbered by papers reporting no or minor biases as a consequence of C_{37} alkenone degradation in the water column or sediments [*Grimalt et al.*, 2000, and references therein].

[36] To investigate whether $C_{37:4}$ is preferentially degraded to the other C_{37} alkenones in sediments, which may account for the discrepancy between sea surface POM and surface sediments described above, three sediment depth profiles from box cores were analyzed. If the most recently deposited sediments can be retrieved intact, then early diagenesis of the C_{37} alkenones may be investigated. If the preferential degradation of the $C_{37:4}$ alkenone is severe, then a consistent trend of decreasing values of percent $C_{37:4}$ should "overprint" any climatic signal in the top most sediments. Sediments retrieved using box cores were preferred for this investigation as these devices usually preserve the top sediments without disturbance, unlike piston corers that disturb the sediment surface. The location of the box cores collected is illustrated in Figure 4. Figure 6 illustrates for each core the values for percent $C_{37:4}$ and the GC-CI-MS response of the C_{37} alkenones in the sediments (0 to 5 or 10 cm) normalized to the top (0 cm) sample. The results from box cores showed that all of the C_{37} isomers experienced an exponential decrease with depth of ~80% in concentration in the top 5 cm. This was accompanied by some large changes in the values of percent $C_{37:4}$, e.g., up to 8% between minimum and maximum values in core HM71-14. However, $C_{37:4}$ did not consistently degrade faster with depth than the other C_{37} alkenones. In the first 5 or 10 cm values of percent $C_{37:4}$ were observed to increase by 4.7% in core HM94-25, and decrease by 2.2% in core HM71-14, while the overall change in core HM80-43 of 0.05% was insignificant. The results of the three cores give a mean change in percent $C_{37:4}$ of +0.8% ($1\sigma = 2.9$). These results do not support suggestions that the $C_{37:4}$ compound is especially susceptible to early diagenesis relative to the other C_{37} alkenone compounds, at least once sequestered to sediments.

[37] The only previous work to focus significantly on the relative stability of the $C_{37:4}$ alkenone in the water column of the Nordic seas is by *Flügge* [1997]. The mean effect on the percent $C_{37:4}$ value of all the *Flügge* [1997] experiments is a shift of −2.8%, but it should be noted that Flügge used only GC-FID for analysis, which may have added uncertainty to the integration of the $C_{37:4}$ alkenone. Results from this paper and from *Sicre et al.* [2002] have highlighted problems relating to an unidentified compound that coelutes with the $C_{37:4}$ alkenone. This can be circumvented by using GC-CI-MS (this study) or GC-MS Selected Ion Monitoring [*Sicre et al.*, 2002]. Assuming that the *Flugge* [1997] data have not been biased by a coelutant in the chromatographic trace, the $C_{37:4}$ degradation experiments from this and Flugge's unpublished thesis cover timescales of 2 years (laboratory) to centuries (box cores) and give a mean reduction of percent $C_{37:4}$ by 2.1%. We do not think that this is sufficient to account for the huge differences in observed percent $C_{37:4}$ values between the summer water column of the western Nordic seas and the regional surface sediments.

[38] Instead we suggest that given that alkenones with high percent $C_{37:4}$ values are produced in low abundances in polar waters, the autochthonous signal is vulnerable to dilution in the underlying sea surface sediments by resuspension and mixing with advected allochthonous matter containing relatively higher abundances of $C_{37:3}$ and $C_{37:2}$ alkenones. Recent work has highlighted that in certain oceanic environments (Benguela upwelling system, Bermuda rise) alkenone records in sediments may include a significant allochthonous component [*Mollenhauer et al.*, 2003; *Ohkouchi*, 2002]. Moreover, turbulent plume events

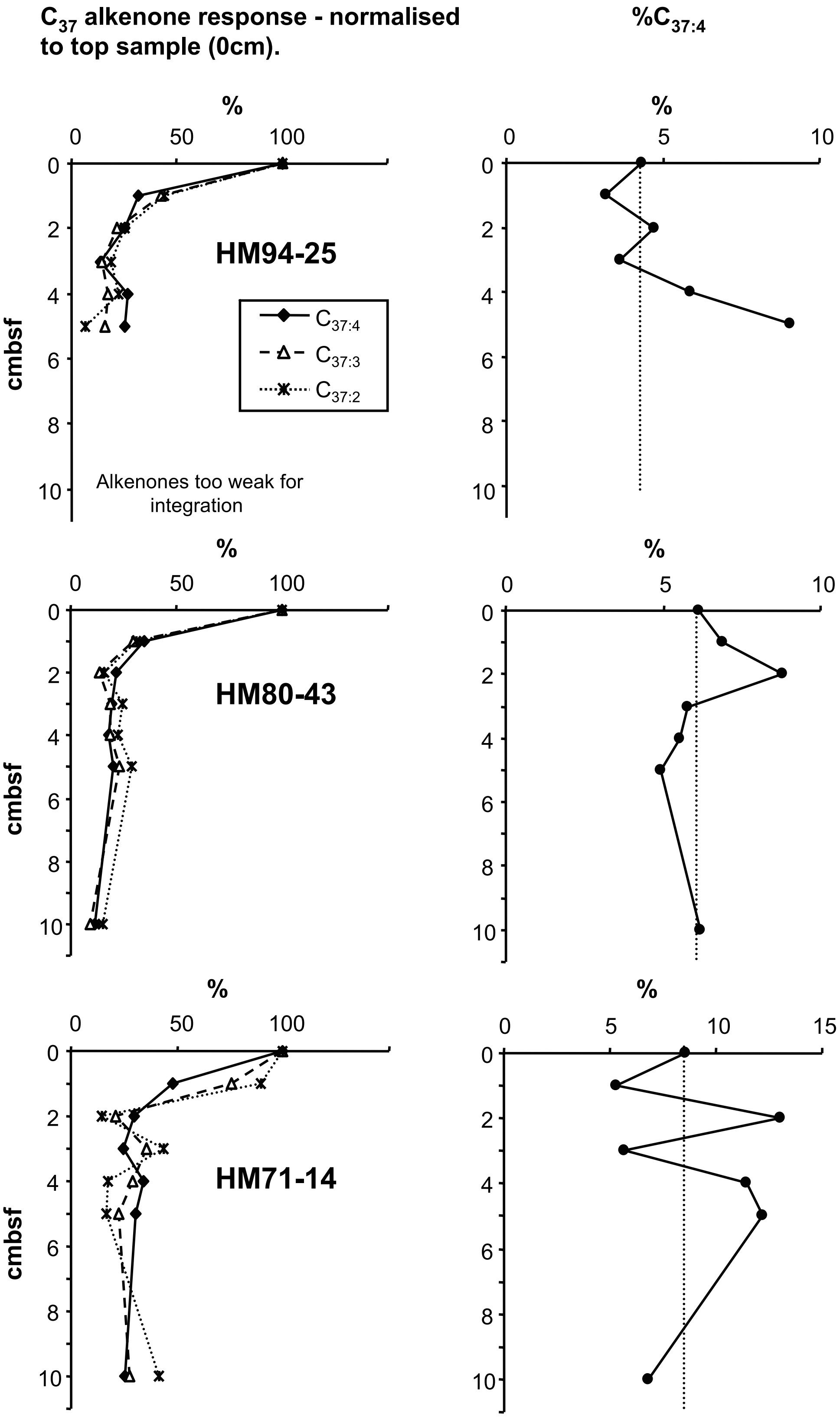

Figure 6. Distributions of alkenones in box cores from the Nordic seas.

Table 3. Coccolithophores Cell Densities (Number of Coccospheres L^{-1}) for JR51 Samples

				Coccospheres L^{-1}						
Sample	SST, deg C	ΣLCK, ng/L	$C_{37:4}$, %	Total L^{-1}	E.huxleyi	C.pelagicus	Unidentified Others	Syracosphaera	E.huxleyi/ C.pelagicusl	Notes From SEM
1	11	19	0	0	0	0	0	0		
2	10	6	0	33,696	30,875	2257	564	0	>1	abundant low calcified *E.huxleyi*
3	10	83	0	0	0	0	0	0		
4[a]	8	-	-	2001	1241	760	0	0	>1	large *E.huxleyi*
5	7	3	3	500	116	384	0	0	<1	
6	7	0	0	5462	122	5340	0	0	<1	
7[a]	6	-	-	1190	520	549	121	0	>1	
8	−1	3	60	859	284	574	0	0	<1	abundant organic matter
9	6	-	-	0	0	0	0	0		
10	3	-	-	161	26	135	0	0	<1	
11	4	-	-	121	91	0	30	0		
12	2	5	51	325	42	134	149	0	<1	
13	1	0	52	8	0	8	0	0	<1	
14	7	109	13	271,382	251,199	19,655	528	0	>1	
18	13	7	0	24,820	11,135	557	1763	11,364	>1	many *S. pulchra*

[a] These samples were part of a batch that was partly spilt during work up for alkenone analysis (up to 90% loss according to internal standard), which may account for the discrepancy between presence of significant numbers of *E. huxleyii* and absence of alkenones.

originating on the Barents sea continental margin could contribute significant quantities of allochthonous alkenones to the Norwegian Sea [*Martrat et al.*, 2003; *Thomsen et al.*, 1998]. Indirect evidence of a potential alkenone bias in the Nordic seas comes from sediment traps which record coccolithophore assemblages. These show that temporal and regional inputs of re-suspended material to depth is highly variable [*Andruleit*, 1997; *Samtleben et al.*, 1995]. Evidence also comes from a sediment trap study which showed that coccolithophore assemblages in sediment traps 300 m above the seafloor in the Greenland and Norwegian Seas were strongly influenced by lateral advection within the nepheloid layer [*Andruleit*, 1997], with *E. huxleyi* increasing from 25 to 51% between 500 and 2300 m in the Greenland Sea, but only from 58 to 66% between 500 and 2300 m in the Norwegian Seas [*Andruleit*, 1997]. Other studies have also shown that surface sediments of the southeast Greenland margin can contain coccolith species from subtropical and midlatitudinal areas (B. Balestra et al., Coccolithophorids in the Southeast Greenland Margin: Production and sedimentation, submitted to *Marine Micropaleontology*, 2004). Overall the evidence suggests that a warm bias "overprints" the local signal by advection and that this is likely to be more severe in the Greenland Sea than in the Norwegian Sea.

3.5. What is the Source Organism Responsible for the Unusual Polar Water Percent $C_{37:4}$ Distributions?

[39] The fact that *E. huxleyi* is rare in polar waters and *Gephyrocapsa* species are absent in those waters suggests that in this region there might be unknown alkenone producers associated with polar waters. To investigate this possibility we have compared coccolithophore biogeography with the alkenone distributions during cruise JR51. The dominant species found were *E. huxleyi* and *C. pelagicus*. The ratio of *E. huxleyi* to *C. pelagicus* is indicative of different water masses in the Nordic Sea. In surface sediments, a ratio of *E. huxleyi*/*C. pelagicus* >1 is indicative of Atlantic source waters, and values <1 are indicative of arctic and polar water masses [*Baumann et al.*, 2000]. In addition, barren or very low coccolithophorid cell density samples are also associated with the northwestern Nordic seas [*Samtleben et al.*, 1995]. This pattern is generally seen in our results from cruise JR51 where ratios between these two species are correlated to SST ($R^2 = 0.75$).

[40] Very high percent $C_{37:4}$ values were found in three of the polar water samples from JR51, in samples 8, 12 and 13. In all three samples the ratio of *E. huxleyi* to *C. pelagicus* was always <1 (Table 3). If the concentrations of alkenones were high for these samples then a novel alkenone source could be invoked, given the low cell densities of *E. huxleyi*. However, the alkenone concentrations were low (<5 ng/L), and some evidence of *E. huxleyi* growth or advection was found in two of the samples. Moreover, *C. pelagicus* does not produce alkenones [*Conte et al.*, 1994b]. Therefore with this evidence in hand there is not a compelling case for the existence of unidentified alkenones producers in polar waters.

[41] Earlier work by Norwegian scientists reported *E. huxleyi* to be generally but not completely absent from truly polar waters (dominated by diatoms) of the Nordic seas [*Gran*, 1929; *Paasche*, 1960; *Winter et al.*, 1994; *Smayda*, 1958]. A study of 410 plankton samples (collected during 1987–1995) found that the large *E. huxleyi* summer blooms are limited to the Norwegian and Barents Seas (>500 × 103 cells/L) [*Baumann et al.*, 2000]. Relatively high numbers (100–500 × 103 cells/L) occurred west of Jan Mayen, but further to the north/northwest in the Greenland Sea and EGC most samples were barren of *E. huxleyi* [*Baumann et al.*, 2000]. However, *E. huxleyi* is known to be an extremely euryhaline and eurythermal species, being able to withstand salinities much lower than the 29 psu of the EGC. For instance, it is found in the Sea of Azov and the Black Sea where salinity is 11 and 17–18 psu respectively [*Bukry*, 1974]. Moreover, it has the largest natural temperature range (1–30°C) exhibited by any coccolithophore [*Okada and McIntyre*, 1977]. Furthermore, *E. huxleyi* is tolerant of different nutrient and light conditions as demonstrated by its natural distribution in both eutrophic (e.g., Norwegian fjords; *Conte et al.* [1994a]) and oligotrophic

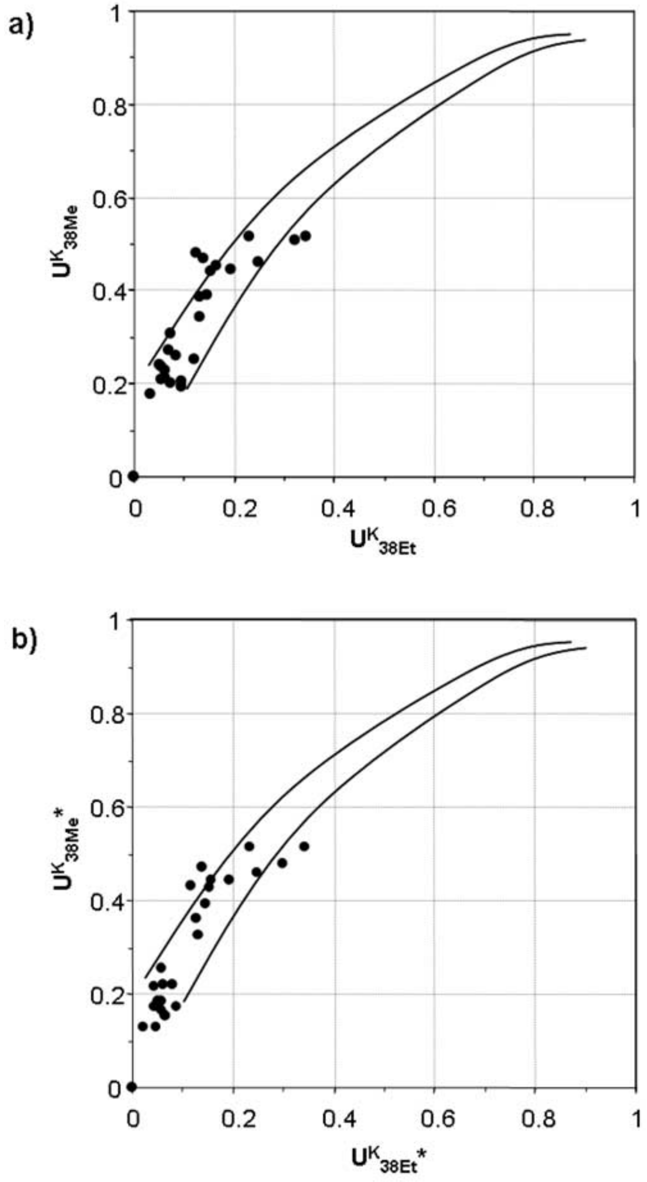

Figure 7. Distributions of (a) U^{K}_{38Me} versus U^{K}_{38Et} and (b) U^{K}_{38Me*} versus U^{K}_{38Et*} for Nordic seas POM samples. Solid lines are for comparison only and delimit distribution of U^{K}_{38Me} versus U^{K}_{38Et} data derived from *E. huxleyi* cultures by *Conte et al.* [1998] Equations are as follows: $U^{K}_{38Me} = C_{38:2}$ Me/($C_{38:2}$ Me + $C_{38:3}$ Me); $U^{K}_{38Et} = C_{38:2}$ Et/($C_{38:2}$ Et + $C_{38:3}$ Et); $U^{K}_{38Me*} = C_{38:2}$ Me/($C_{38:2}$ Me + $C_{38:3}$ Me + $C_{38:4}$ Me); $U^{K}_{38Et*} = C_{38:2}$ Et/($C_{38:2}$ Et + $C_{38:3}$ Et + $C_{38:4}$ Et).

(e.g., subtropical gyres; *Ohkouchi et al.* [1999]) environments between 0 and 200 m, and by laboratory experiments [*Prahl et al.*, 2003]. Therefore *E. huxleyi* could be capable of surviving and of producing alkenones in an environment as extreme as the EGC and be the source of the high percent $C_{37:4}$ alkenones in the polar waters. It cannot be ruled out that naked nonmotile "N cells" [*Klaveness*, 1972] of *E. huxleyi* were a source of alkenones in our samples. However, due to sampling technique (high pressure vacuum pump) we were unable to identify naked cells.

[42] Some further insight into the origins of the unusual alkenone distributions may be gained from considering the full suite of C_{37} and C_{38} alkenones. Thus some studies have shown that the relative distributions of some of the alkenones are characteristic of different species. Figure 1c illustrates how the large changes in the relative abundances of the C_{37} alkenones are also mirrored by changes in the C_{38} alkenones. The general correlation between the degree of unsaturation of the C_{37} and C_{38} alkenones is demonstrated quantitatively by comparison of C_{37} and C_{38} alkenone indices, and has been reported by a number of previous workers [*Marlowe et al.*, 1984; *Rosell-Melé et al.*, 1994; *Yendle*, 1989]. Extremely high values of percent $C_{37:4}$ (up to 77%) are reported from polar waters in this study. High values of percent $C_{37:4}$ have also been previously reported in brackish and lacustrine environments (up to ~60%) [*Cranwell*, 1985; *Ficken and Farrimond*, 1995; *Schulz et al.*, 2000; *Zink et al.*, 2001]. In sediments from these environments, the C_{38} methyl alkenones in particular became reduced in abundance relative to the other alkenones, often to the point of being below detection limit [*Schulz et al.*, 2000]. However, in our study no such pattern is observed. Plotting the C_{38} ethyl versus C_{38} methyl unsaturation ratios ($U^{K}_{38}Et$ and $U^{K}_{38}Me$ respectively, see legend in Figure 7) has been suggested as method to confirm if *E. huxleyi* is the main source of alkenones [*Conte et al.*, 1998], when other coccolithophoral species may be also potential contributors. Figure 7 shows that the alkenones from this study fall within, or close to, the range of values attributed to *E. huxleyi* as determined by *Conte et al.* [1998] on the basis of culture work. Therefore, based on the relative abundance of C_{38} alkenones, there is no compelling evidence to advocate for a non-*E. huxleyi* source for the polar water alkenones, and taking all the evidence we have in consideration we think that *E. huxleyi* cannot be discarded as the producer of the polar water alkenones.

4. Conclusions

[43] Alkenones were measured in POM collected in the mixed layer from across the spectrum of water mass types in the Nordic seas, and for the first time in polar waters under conditions of up to 80% sea ice cover and salinities <34.4 psu. Values of percent $C_{37:4}$ across the Nordic seas showed a strong association with water mass type, with clustering of high percent $C_{37:4}$ values (40–77%) within polar waters, low values (0–3%) in Atlantic waters and low to intermediate values (0–28%) in arctic and Norwegian coastal waters. Absolute amounts of alkenones in polar waters were, however, very low in comparison to concentrations in arctic and Atlantic water masses. Comparison of alkenone distributions with coccolithophore assemblage data suggests that *E. huxleyi* cannot be ruled out as the producer of the polar alkenones with extremely high percent $C_{37:4}$ values. An *E. huxleyi* source is supported by the C_{38} alkenone within-class distributions.

[44] The values of percent $C_{37:4}$ in POM were found to be linearly correlated to both SST (R^2 = 0.75) and SSS (R^2 = 0.79). When combined with previous sea surface POM data from the Nordic seas and north Atlantic [*Sicre et al.*, 2002]

the data set showed a stronger correlation to SSS (R^2 = 0.72) than to SST (R^2 = 0.5). Comparison with a global data set confirms that percent $C_{37:4}$ has no consistent global relationship to either SST or SSS. The relative abundances of $C_{37:4}$ in sea surface POM and surficial sediments of the Nordic seas in areas influenced by polar and arctic water masses are substantially different, being much lower in the sediments in a given location. The magnitude of the difference can not be attributed to just the preferential degradation of the $C_{37:4}$ alkenone versus the triunsaturated and diunsaturated components. We propose that the percent $C_{37:4}$ sedimentary contents may reflect the mixing in the water column of authochthonous and allochthonous inputs, the latter containing relatively higher abundances of $C_{37:3}$ and $C_{37:2}$ alkenones to $C_{37:4}$. This is supported by previous observations of resuspension and mixing of coccolithophore assemblages, particularly in the Greenland Sea.

[45] Our results do not support the use of percent $C_{37:4}$ to estimate, quantitatively, past variations in SSS or SST. However, as suggested in previous publications, the data obtained support the use of percent $C_{37:4}$ as a proxy to estimate the relative influence of arctic/polar versus Atlantic water masses in the North Atlantic and to infer local variations in the salinity budget of the surface ocean in arctic and polar water masses.

[46] **Acknowledgments.** We would like to thank The Natural Environment Research Council for a studentship to J.B., funding through the ARCICE thematic program for cruise participation, and for granting access to the Organic Mass Spectrometry facility at Bristol. Ian Bull and Jim Carter are thanked for assistance with GC-CI-MS at said facility; Marie Russell, Frank Davies, Paul Andrews, and Pau Comes are thanked for assistance in the laboratory and sampling collection; and Saskia Kaar is thanked for operating the SEM and making photographs and Bianca de Bernardi for coccolith quantification. Anne de Vernal, Eystein Jansen, and Michael Sarnthein are thanked for providing sediment samples from the N Atlantic. Arnim Flügge and Elizabeth Sikes are thanked for providing copies of a thesis and data set, respectively. Reiner Schlitzer is thanked for the free software program "Ocean Data View" available from www.awi-bramerhaven.de/GEO/ODV. We thank the SeaWiFS Project (code 970.2) and the Goddard Earth Sciences Data and Information Services Center/Distributed Active Archive Center (code 902) at the Goddard Space Flight Center, Greenbelt, MD 20771, USA, for the production and distribution of satellite images, respectively. These activities are sponsored by NASA's Earth Science Enterprise, and data are available at http://seawifs.gsfc. nasa.gov/SEAWIFS.html.

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