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Nitrogen and carbon isotopic composition of marine and terrestrial organic matter in Arctic Ocean sediments: implications for nutrient utilization and organic matter composition

Carsten J. Schubert[a,*], Stephen E. Calvert[b]

[a]Max Planck Institute for Marine Microbiology, Celsiusstrasse 1, 28359 Bremen, Germany
[b]Earth and Ocean Sciences, University of British Columbia, 6270 University Boulevard, Vancouver V6T 1Z4, Canada

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Abstract

Relationships between organic carbon, total nitrogen and organic nitrogen concentrations and variations in $\delta^{13}C_{org}$ and $\delta^{15}N_{org}$ are examined in surface sediments from the eastern central Arctic Ocean and the Yermak Plateau. Removing the organic matter from samples with KOBr/KOH and determining residual as well as total N shows that there is a significant amount of bound inorganic N in the samples, which causes TOC/N_{total} ratios to be low (4–10 depending on the organic content). TOC/N_{org} ratios are significantly higher (8–16). This correction of organic TOC/N ratios for the presence of soil-derived bound ammonium is especially important in samples with high illite concentrations, the clay mineral mainly responsible for ammonium adsorption. The isotopic composition of the organic N fraction was estimated by determining the isotopic composition of the total and inorganic nitrogen fractions and assuming mass-balance. A strong correlation between $\delta^{15}N_{org}$ values of the sediments and the nitrate concentration of surface waters indicates different relative nitrate utilization rates of the phytoplankton in various regions of the Arctic Ocean. On the Yermak Plateau, low $\delta^{15}N_{org}$ values correspond to high nitrate concentrations, whereas in the central Arctic Ocean high $\delta^{15}N_{org}$ values are found beneath low nitrate waters. Sediment $\delta^{13}C_{org}$ values are close to $-23.0‰$ in the Yermak Plateau region and approximately $-21.4‰$ in the central Arctic Ocean. Particulate organic matter collected from meltwater ponds and ice-cores are relatively enriched in ^{13}C ($\delta^{13}C_{org} = -15.3$ to $-20.6‰$) most likely due to low $CO_2(aq)$ concentrations in these environments. A maximum terrestrial contribution of 30% of the organic matter to sediments in the central Arctic Ocean is derived, based on the carbon isotope data and various assumptions about the isotopic composition of the potential endmembers. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Arctic Ocean; Carbon and nitrogen isotopes; KOBr/KOH treatment; TOC/N_{total} ratios; TOC/N_{org} ratios; Nitrate utilization; Terrestrial organic matter contribution

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* Corresponding author. Tel.: 0049-421-2028-651; fax: 0049-421-2028-690.
E-mail address: cschuber@mpi-bremen.de (C.J. Schubert).

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1. Introduction

Knowledge of the marine geology and oceanography of the permanently ice-covered Arctic Ocean remains limited in spite of the relatively recent availability of ice breaking research vessels and several expeditions to the region over the past decade (Fütterer, 1992; Fütterer, 1994; Stein and Fahl, 1997). The permanent sea ice cover strongly influences Earth's albedo, it exerts a major control over the Arctic marine ecosystem, and it strongly modulates sedimentation on the sea floor. Deep-water exchange between the Arctic and the Atlantic Oceans is a major driving force in global thermohaline circulation, controlling both global heat transfer and climate (ARCSS Workshop Steering Committee, 1990; NAD Science Committee, 1992). In addition, almost half of the area of the Arctic Ocean consists of shelves, which lie mainly off Europe and Siberia, and this leads to a strong land-ocean connection.

The goals of this study were to investigate the composition of organic material in the bottom sediments as influenced by marine and terrestrial supply and in terms of the linkages between nutrient supply and phytoplankton production. Apart from the concentrations of organic carbon and total nitrogen, we also determined the concentrations of bound and organic nitrogen in the sediments, and characterized these fractions by their stable carbon and nitrogen isotope ratios. In this way, we were able to constrain the relative contributions of marine and terrestrial organic matter in the bottom deposits.

It has been shown that the $^{15}N/^{14}N$ ratio in sedimentary organic matter may be used to track relative nutrient (NO_3^-) utilization in the overlying surface waters (Altabet and François, 1994a; Farrell et al., 1995; Francois et al., 1992). The isotope proxy is based on the observation that particulate organic matter (POM) $\delta^{15}N$ depends on the isotopic composition of the nitrogenous substrate and isotope fractionation during nitrogen uptake by phytoplankton (Wada and Hattori, 1991). In the photic zone there is preferential uptake of $^{14}NO_3^-$ by phytoplankton producing photosynthate enriched in the light isotope leaving the residual dissolved NO_3^- progressively enriched in ^{15}N. Under nutrient-replete conditions (where physical supply of NO_3^- is greater than biological assimilation), the settling organic detritus is depleted in the heavy isotope (low $\delta^{15}N$). In the eastern equatorial Pacific, for instance, where subsurface nutrients are upwelled at concentrations in excess of 5 μM (Barber and Chavez, 1991; Peña et al., 1994), bottom sediment $\delta^{15}N$ values are 5–6‰, and they increase to the north and south because of isotopic enrichment under low nutrient conditions (Farrell et al., 1995). This simple relationship can be complicated in regions of significant denitrification, which leaves subsurface waters highly enriched in ^{15}N (Liu and Kaplan, 1989), and in areas where atmospheric nitrogen fixation is important, which produces organic matter highly depleted in the heavy isotope (Wada and Hattori, 1976). The latter process also causes a low $\delta^{15}N$ value in soil organic matter. With these caveats in mind, it is possible to interpret variations of the nitrogen isotope signal in terms of changes in the source of nutrients or relative nutrient utilization.

The carbon isotope ratio of organic matter in sediments and plankton is widely used both as an indicator of the relative importance of marine vs. terrestrial input (Sackett, 1964) and of changes in the concentration of CO_2 in surface waters (Jasper and Hayes, 1990; Rau et al., 1982; Rau et al., 1992). In general, marine organic matter is isotopically heavier than terrestrial C_3 plant material (we do not consider C_4 plant sources in this paper because they are related either to sub-tropical and low-latitude temperate or to arid climates (Teeri and Stowe, 1976; Stowe and Teeri, 1978; Teeri, 1988). However, $\delta^{13}C_{org}$ values of high latitude phytoplankton can approach terrestrial values, perhaps because of the higher concentration of dissolved CO_2 at low surface water temperatures (Rau et al., 1989). Use of the isotopic carbon composition of sedimentary organic matter to determine marine/terrestrial supply ratios must therefore be carried out with caution, or applied in concert with other tracers such as certain organic compounds (biomarkers).

2. Study area

The Arctic Ocean consists of a central basin and large shelf areas, which make up about 49% of the total area. The central basin can be divided into the Amerasian Basin and the Eurasian Basin (Fig. 1a), which are further divided by large ridge systems (Gakkel, Lomonosov, and Alpha Ridge) into smaller basins (Nansen, Amundsen, Makarov, and Canada Basin).

The ocean is covered with a more or less permanent sea-ice cap. Estimates of primary production are very limited; in general, very low values characterize the central area (e.g. 0.09 gC/m^2/day, see Wheeler et al., 1996), whereas much higher values have been obtained in the marginal zones, such as the shelves and coastal fjords (Subba Rao and Platt, 1984). Values off Svalbard vary between 0.43 and 0.89 gC/m^2/day (Heimdal, 1983), whereas in the Fram Strait values show a wide range of 0.059–1.067 gC/m^2/day and are strongly correlated with the extent of sea-ice cover (Hirche et al., 1991).

The sea-ice cover has an additional effect on sedimentation by transporting sediment from the broad shelf areas into the central basins (Reimnitz and Kempema, 1987; Reimnitz and Saarso, 1991). This material, which includes lithogenic, skeletal, and organic material, is frozen into sea-ice on the shelves and released over the ocean during ice melt (Nürnberg et al., 1994). Two wind-driven surface water and sea-ice drift systems are important in the Arctic Ocean, the Beaufort Gyre, which is restricted to the Amerasian Basin and transports relatively old sea-ice (up to 13 years), and the Transpolar Drift in the Eurasian Basin, which flows from the Laptev Sea to the Fram Strait and transports ice that is one to three years old (Colony and Thorndike, 1984; Gordienko and Laktionov, 1969). The main connection between the Arctic Ocean and the other world oceans is through the Atlantic Ocean via the Fram Strait, which is up to 2600 m deep. Other connections, such as the Bering Strait (25 m) and the Barents Sea (250 m) play minor roles in water exchange (Curtin et al., 1990). The most important outflow is the East Greenland Current with cold and relatively low salinity waters (Swift, 1986), and the most important inflow is the West Spitsbergen Current, the northward continuation of the Gulf stream, with relatively warm and saline waters (Johannessen, 1986).

3. Methods

This investigation focuses on surface sediments from the central Arctic Ocean (Eurasian Basin, Fig. 1a) as well as surface sediments and other samples (particulate organic matter (POM) from water and sea-ice, copepods) from the main exchange area between Greenland and Spitsbergen (Fig. 1b). Samples were collected during two cruises of the ice breaking research vessel *Polarstern*. Cruise ARK-VIII/3 (summer, 1991) covered the entire eastern Arctic Ocean basin from the

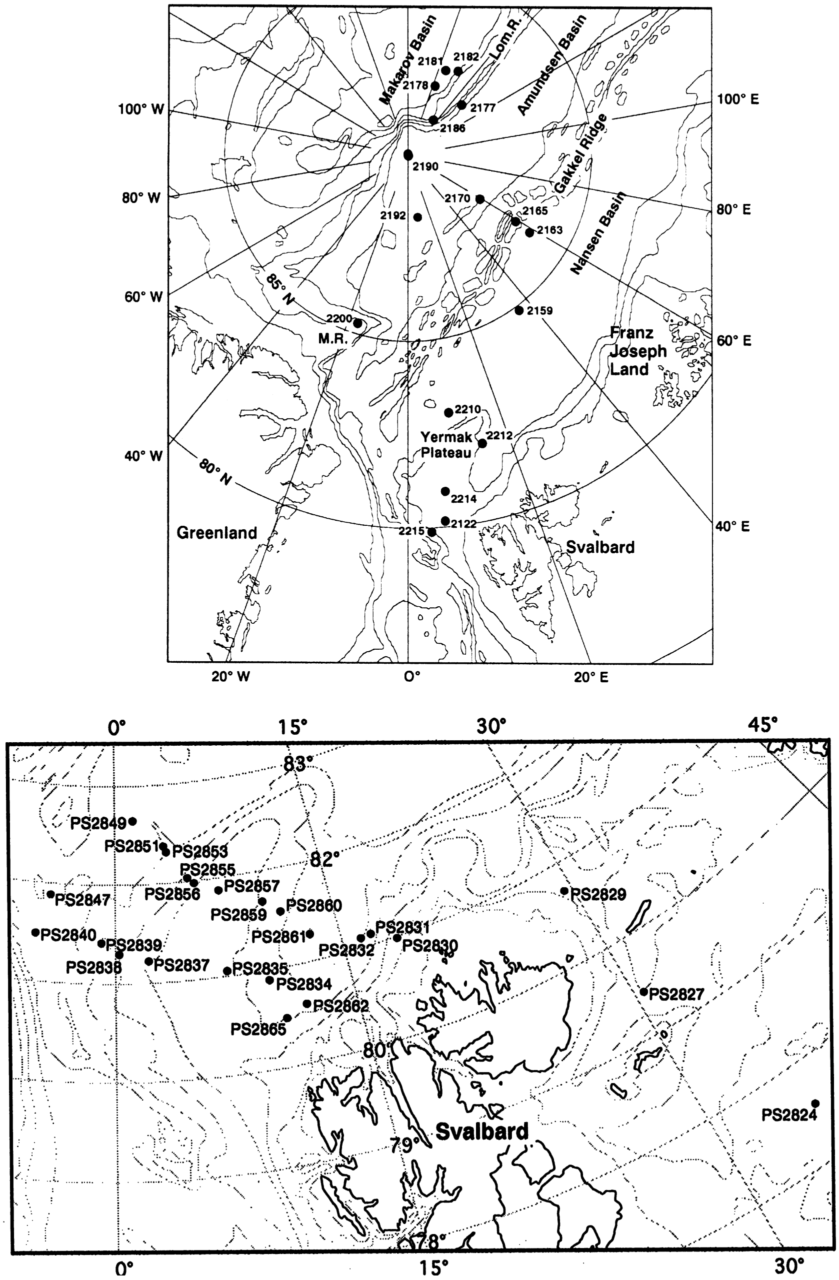

Fig. 1. (a) Sampling sites of ARK-VIII/3 expedition with RV *Polarstern*. (b) Sampling sites of ARK-XIII/2 expedition with RV *Polarstern*.

northern Fram Strait near Svalbard over the Gakkel Ridge, Amundsen Basin, Lomonosov Ridge, Makarov Basin, and Morris Yesup Rise to the Yermak Plateau. Cruise ARK-XIII/2 (summer, 1997) covered the northern Fram Strait between Greenland and Svalbard at 80–83°N, referred to here as the Yermak Plateau.

Sediment samples were recovered with either a box corer (ARK-VIII/3) or a multicorer (ARK-XIII/2). Water samples were obtained with a CTD/Rosette system, and copepods were collected with a multi-net (mesh size: 150 μm). Meltwater pond samples were recovered from the ship or by helicopter. Water samples were filtered through Whatman filters (~0.4 μm pore size). All samples were frozen immediately after recovery or filtration.

Total carbon (TC) and total nitrogen (N_{tot}) were determined on freeze-dried ground bulk samples with a Heraeus CHN-analyzer. Total organic carbon (TOC) was determined on decarbonated (HCl, 10%) sub-samples by the same technique. The carbonate content was calculated: $CaCO_3 = (TC - TOC) \times 8.33$. The precision of the total, carbonate carbon and total nitrogen determinations was ± 1.2, ± 1.2 and ± 2.7%, respectively. Bound inorganic nitrogen (N_{bnd}), which includes ammonium within clay minerals (Schachtschabel, 1961; Stevenson and Dhariwal, 1959), was determined by treating subsamples with KOBr–KOH solution to eliminate the organic nitrogen fraction following Silva and Bremner (1966). In short, 20 ml of freshly prepared KOBr–KOH (6 ml bromine added at 0.5 ml/min to 200 ml of 2 M KOH cooled with ice) was added to 500–1000 mg of finely ground sediment. The solution was swirled and allowed to stand for 2 h. 60 ml of double-distilled water (DDW) was added, and the mixture was boiled vigorously for at least 5 min. After the mixture cooled overnight, the sample was washed with 0.5 M KCl to remove the released ammonium. The high concentration of potassium in the solution during the whole process prevents the adsorption by clay minerals of ammonium formed during the oxidation process. The sample was finally washed with DDW. As shown by Silva and Bremner (1966), the efficiency of the method for removing the organic nitrogen fraction (hydrolyzable and non-hydrolyzable organic nitrogen) is higher than 98%. Additionally, we checked the efficiency of the oxidation of proteinaceous material by determining the total protein content of the sediment residues by absorbance (595 nm) after NaOH hydrolysis (Bradford, 1976). Protein values determined by this method were mostly below the detection limit (0.001% N).

Bulk samples were prepared for isotopic analysis by freeze-drying and homogenization by gentle grinding. Sub-samples were combusted in a Fisons NA1500 element analyzer, and the evolved CO_2, N_2 was passed online to a VG PRISM isotope-ratio mass spectrometer in a continuous flow of helium. Results are reported in the δ notation:

$$\delta(‰) = \{R_{\text{sample}}/R_{\text{standard}} - 1\}1000,$$

where δ(‰) is δ^{13}C(‰) or δ^{15}N(‰) and R_{sample} and R_{standard} are the $^{13}C/^{12}C$ and $^{15}N/^{14}N$ ratios of the samples and standards, respectively. VPDB and air nitrogen are the reference standards for $\delta^{13}C$ and $\delta^{15}N$, and the external measurement precision was better than ± 0.2 and ± 0.3‰ for $\delta^{13}C$ and $\delta^{15}N$, respectively. The error in determining the $\delta^{15}N_{org}$ values including processing, measurement, and calculation was estimated to be better than ± 3.3‰.

4. Results and discussion

4.1. Organic and inorganic nitrogen concentrations of sediments

Nitrogen concentrations in two subsamples of each surface sediment sample, namely the bulk sample (total nitrogen, N_{tot}) and a KOBr/KOH-treated sample, which represents the inorganic nitrogen bound as ammonium in clay minerals (N_{bnd}), were determined (Tables 1 and 2). Exchangeable nitrogen concentrations account for less than 5% of total nitrogen in most sediments (Müller, 1977) and have not been considered in this study. Knowing N_{tot} and N_{bnd} we calculated the organic nitrogen concentration of each sample by difference ($N_{tot} - N_{bnd} = N_{org}$). The distinction between organic and bound inorganic nitrogen is important in the Arctic Ocean, because the sediments have a high clay content (average = 43%, range 1–80%, Stein et al., 1994) in which illite, the clay mineral species mainly responsible for ammonium binding, is dominant (average 55%, $n = 47$).

In a plot of N_{tot} versus TOC (Fig. 2), there is an intercept of 0.035% N at 0% TOC, showing that there is a significant fraction of inorganic N in the samples. Calculated TOC/N_{tot} ratios, commonly quoted as C/N values and widely used as a tool for discriminating marine from terrestrial organic matter in sediments, are low (4–8), suggesting that the organic matter in these sediments is overwhelmingly marine. However, this is an overestimation because the linear correlation between N_{org} and TOC has a very small intercept, namely at 0.003% (Fig. 2), a negligible fraction of N_{tot}. Thus, by using N_{org} rather than N_{tot} values for calculating C/N ratios, we can overcome a possible mis-interpretation of organic matter sources caused by the presence of inorganic nitrogen bound in clay minerals.

Total nitrogen values (N_{tot}) in the central Arctic Ocean vary from 0.054 to 0.153% and the organic nitrogen concentrations (N_{org}) range from 0.027 to 0.095%. Thus, the organic fraction accounts for 37–66% of N_{tot} (Table 1). TOC/N_{org} ratios lie between 8 and 15, significantly higher than TOC/N_{tot} ratios (4–8). Assuming typical values of organic matter endmembers, namely 5–7 for marine organic matter (Redfield et al., 1963), and > 20 for terrestrial organic matter (Scheffer and Schachtschnabel, 1984), the ratios shift the interpretation of the origin of the organic matter in the sediments from a mostly marine source to a mixed marine/terrestrial source.

Total nitrogen values in sediments of the Yermak Plateau area are almost double the values found in the central Arctic Ocean, and range from 0.091 to 0.209%. The organic nitrogen fraction ranges from 0.069 to 0.158%, and amounts to 40–77% of the total nitrogen, also significantly higher than in the central Arctic Ocean (Table 2). That bound inorganic nitrogen is lower in this part of the ocean can also be seen from the intercept of 0.023% N at 0% TOC in a N_{tot} versus TOC plot (not shown), which is significantly lower than the value (0.035%) observed in the central Arctic Ocean. Thus, bound inorganic nitrogen is not as important here as with the central Arctic Ocean. This may be explained by the much lower clay content (average 27%) with an average illite content of 63% ($n = 10$) of the sediments of the Yermak Plateau area.

Calculated TOC/N_{tot} and TOC/N_{org} values on the Yermak Plateau are higher than in the central Arctic Ocean, and range from 7 to 10 and 9 to 16, respectively. Thus, it is essential to use TOC/N_{org} ratios for interpreting organic matter sources in the Arctic Ocean (and maybe other areas of the world oceans) since dilution of the total nitrogen by the inorganic bound fraction is significant. On the other hand, TOC/N_{tot} ratios from other areas of the world oceans, where illite or clay contents are low, should give reasonable results.

4.2. Nitrogen isotope ratios as an indicator of nutrient utilization

$\delta^{15}N_{tot}$ values of bulk samples range from 5.4 to 8.2‰ in the central Arctic Ocean, and from 4.5 to 6.8‰ on the Yermak Plateau (Tables 1 and 2). $\delta^{15}N_{bnd}$ values, on the other hand, range between 1.8 and 3.9‰ and between 2.0 and 4.1‰, respectively. The latter values have a much narrower

Table 1
Analytical data on boxcore samples collected during the ARK-VIII/3 expedition (Central Arctic Ocean)[a]

Sample	N_{tot} (%)	N_{bnd} (%)	N_{org} (%)	% N_{org}	TOC (%)	TOC/N_{tot}	TOC/N_{org}	$^{15}N_{tot}$	$^{15}N_{inorg}$	$^{15}N_{org}$	^{13}C	Clay (%)	Illite (%)
PS2122*	0.184	0.054	0.131	71	1.31	7	10	4.5 ± 0.3	4.1 ± 0.6	4.6 ± 1.2	− 22.3	35	55
PS2159	0.118	0.050	0.068	58	0.99	8	15	5.8 ± 0.3	3.9 ± 0.6	7.1 ± 1.8	− 22.1	59	57
PS2163	0.090	0.040	0.050	56	0.47	5	9	5.4 ± 0.3	2.9 ± 0.6	7.3 ± 1.8	− 21.4	44	57
PS2165	0.054	0.027	0.027	50	0.26	5	10	6.0 ± 0.3	3.6 ± 0.6	8.3 ± 2.1	− 21.5	10	47
PS2170	0.103	0.051	0.052	50	0.61	6	12	7.1 ± 0.3	3.6 ± 0.6	10.5 ± 2.6	− 21.5	53	52
PS2174	0.127	0.056	0.071	56	0.81	6	11	7.5 ± 0.3	3.9 ± 0.6	10.3 ± 2.4	− 21.5	57	54
PS2177	0.131	0.056	0.074	57	0.71	5	10	8.2 ± 0.3	3.8 ± 0.6	11.5 ± 2.9	− 21.1	57	51
PS2178	0.091	0.057	0.034	37	0.45	5	13	7.2 ± 0.3	3.7 ± 0.6	13.1 ± 3.3	− 21.4	46	59
PS2181	0.070	0.038	0.032	45	0.36	5	11	6.9 ± 0.3	3.0 ± 0.6	11.6 ± 2.9	− 21.3	30	59
PS2182	0.067	0.035	0.032	48	0.37	6	12	7.2 ± 0.3	3.0 ± 0.6	11.8 ± 2.9	− 21.2	24	54
PS2186	0.113	0.050	0.062	55	0.67	6	11	7.7 ± 0.3	3.3 ± 0.6	11.2 ± 2.8	− 21.3	30	52
PS2190	0.153	0.066	0.087	57	1.05	7	12	7.4 ± 0.3	3.7 ± 0.6	10.1 ± 2.3	− 21.6	67	49
PS2192	0.114	0.057	0.057	50	0.56	5	10	6.8 ± 0.3	3.1 ± 0.6	10.5 ± 2.6	n.d.	70	63
PS2200	0.070	0.030	0.040	57	0.31	4	8	5.8 ± 0.3	1.8 ± 0.6	8.8 ± 2.2	− 21.1	27	67
PS2210	0.145	0.050	0.095	66	1.04	7	11	6.5 ± 0.3	3.8 ± 0.6	7.9 ± 2.0	− 21.9	45	53
PS2212*	0.160	0.050	0.110	69	1.15	7	10	6.1 ± 0.3	2.2 ± 0.6	7.8 ± 2.0	− 22.2	14	60
PS2214*	0.122	0.034	0.088	72	0.81	7	9	5.3 ± 0.3	3.1 ± 0.6	6.1 ± 1.5	− 22.5	18	56
PS2215*	0.101	0.031	0.070	69	0.69	7	10	5.4 ± 0.3	3.6 ± 0.6	6.3 ± 1.6	− 22.9	11	57

[a] Total nitrogen (N_{tot}), bound nitrogen (N_{bnd}), organic nitrogen (N_{org}), percentage organic nitrogen of total nitrogen (% N_{org}), total organic carbon (TOC), total organic carbon/total nitrogen ratio (TOC/N_{tot}), total organic carbon/organic nitrogen ratio (TOC/N_{org}), $\delta^{15}N$ measured on the total nitrogen fraction (‰ versus air), $\delta^{15}N$ measured on the bound nitrogen fraction (‰ versus air), calculated $\delta^{15}N$ of the organic nitrogen fraction (‰ versus air), $\delta^{13}C$ measured on the organic carbon fraction (‰ VPDB), total clay content of the sample in percent, values from Stein et al. (1994), percent illite of the clay fraction, values from Stein et al. (1994). Stations printed with asterisks are in the text mentioned under Yermak Plateau samples.

Table 2
Analytical data on multicorer surface samples collected during the ARK-XIII/2 expedition (Yermak Plateau)[a]

Sample	N_{tot} (%)	N_{bnd} (%)	N_{org} (%)	% N_{org}	TOC (%)	TOC/N_{tot}	TOC/N_{org}	$^{15}N_{tot}$	$^{15}N_{inorg}$	$^{15}N_{org}$	^{13}C
PS2824	0.222	0.044	0.178	80	1.80	9	10	6.5 ± 0.3	3.1 ± 0.6	7.4 ± 1.8	– 24.2
PS2827	0.212	0.041	0.171	81	1.60	8	9	6.1 ± 0.3	2.7 ± 0.6	7.0 ± 1.8	– 23.8
PS2831	0.091	0.022	0.069	76	0.69	8	10	5.1 ± 0.3	3.4 ± 0.6	5.6 ± 1.4	n.d.
PS2832	0.112	0.028	0.084	75	0.78	8	9	6.3 ± 0.3	2.5 ± 0.6	7.6 ± 1.9	– 23.3
PS2834	0.153	0.043	0.110	72	1.26	9	11	5.4 ± 0.3	2.8 ± 0.6	6.4 ± 1.6	– 23.3
PS2835	0.135	0.039	0.096	71	1.13	8	12	5.8 ± 0.3	2.8 ± 0.6	7.0 ± 1.8	– 23.5
PS2837	0.209	0.051	0.158	76	1.90	10	12	5.2 ± 0.3	2.3 ± 0.6	6.2 ± 1.5	– 23.2
PS2839	0.151	0.045	0.106	70	1.37	10	13	5.8 ± 0.3	2.6 ± 0.6	7.2 ± 1.8	– 23.5
PS2840	0.053	0.032	0.021	40	0.34	7	16	5.7 ± 0.3	2.4 ± 0.6	10.7 ± 2.6	– 23.5
PS2847	0.110	0.037	0.073	66	0.92	9	13	6.2 ± 0.3	2.0 ± 0.6	8.3 ± 2.1	– 23.6
PS2849	0.091	0.038	0.053	58	1.37	8	13	6.8 ± 0.3	2.2 ± 0.6	10.2 ± 2.4	– 22.0
PS2851	0.161	0.042	0.119	74	0.34	10	11	5.7 ± 0.3	3.0 ± 0.6	6.7 ± 1.7	– 23.2
PS2853	0.096	0.024	0.072	75	0.90	10	13	5.5 ± 0.3	2.4 ± 0.6	6.6 ± 1.7	– 23.5
PS2855	0.174	0.045	0.129	74	1.54	10	12	5.2 ± 0.3	3.0 ± 0.6	6.0 ± 1.5	– 23.0
PS2856	0.160	0.049	0.111	69	1.45	10	13	5.8 ± 0.3	3.0 ± 0.6	7.0 ± 1.8	– 24.1
PS2857	0.150	0.042	0.108	72	1.21	8	11	5.7 ± 0.3	2.7 ± 0.6	6.9 ± 1.8	– 23.5
PS2860	0.160	0.044	0.116	73	1.50	10	13	5.7 ± 0.3	2.6 ± 0.6	6.8 ± 1.8	– 22.9
PS2862	0.199	0.046	0.153	77	1.44	8	9	5.6 ± 0.3	3.2 ± 0.6	6.3 ± 1.6	– 23.1
PS2865	0.193	0.062	0.131	68	1.74	9	13	4.6 ± 0.3	3.7 ± 0.6	5.0 ± 1.3	– 24.2

[a] Total nitrogen (N_{tot}), bound nitrogen (N_{bnd}), organic nitrogen (N_{org}), percentage organic nitrogen of total nitrogen (% N_{org}), total organic carbon (TOC), total organic carbon/total nitrogen ratio (TOC/N_{tot}), total organic carbon/organic nitrogen ratio (TOC/N_{org}), δ^{15}N measured on the total nitrogen fraction (‰ versus air), δ^{15}N measured on the bound nitrogen fraction (‰ versus air), calculated δ^{15}N of the organic nitrogen fraction (‰ versus air, all including measurement error), δ^{13}C measured on the organic carbon fraction (‰ VPDB).

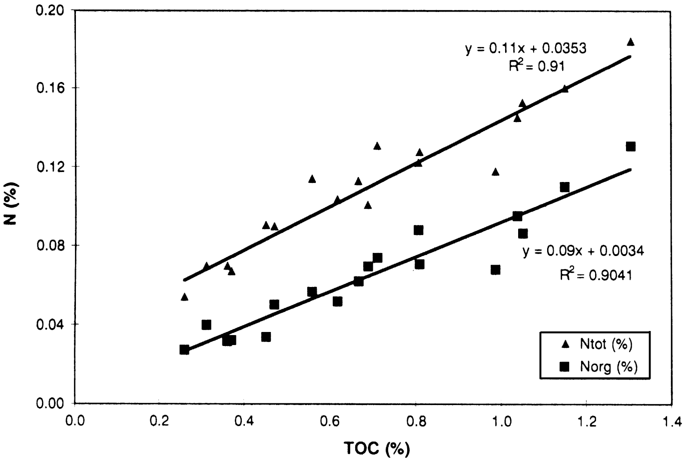

Fig. 2. Correlation between total nitrogen (N_{tot}) and organic carbon (TOC%) and between organic nitrogen (N_{org}) and organic carbon for the central Arctic Ocean (ARK-VIII/3) samples.

range than the N_{tot} values in both areas, indicating that bound ammonium in the clay minerals has a relatively well-defined $\delta^{15}N$ value. It is well known that ammonium substitutes for K^+ in the interlayer exchange sites of illite (Scheffer and Schachtschnabel, 1984). Once incorporated in the illite structure, NH_4^+ will be released only if the concentrations of NH_4^+ and K^+ in the porewaters are extremely low (e.g. if there is active uptake of NH_4^+ by plants). If NH_4^+ loss does occur, it takes place only at positions at the periphery of the mineral; NH_4^+ included in the inner part of an illite crystal is not affected by this process (Scheffer and Schachtschnabel, 1984). However, potassium always occurs in relatively high concentrations in soil porewaters, so that there is no chemical gradient forcing the NH_4^+ or K^+ out of the illite. It seems reasonable to assume, therefore, that once ammonium is bound in illites on land, there will be no leakage of this ion out of the mineral once it is delivered to the ocean because of the high potassium content of seawater. For this reason, the $\delta^{15}N$ signal of bound inorganic nitrogen should represent a signal obtained on land. This suggestion is strongly supported by the fact that the $\delta^{15}N_{bnd}$ values (average 3.0 ± 1.2‰) are close to the atmospheric $\delta^{15}N$ value (~0‰), indicating only minor fractionation by land plants. This is consistent with a study reported by Wada et al. (1987b), who showed that land plants had $\delta^{15}N$ values of − 1.8 ± 0.8‰ ($n = 7$), detrital organic matter in a river had values of 2.8 ± 0.1‰ ($n = 3$), and soil organic matter had values of 4.1 ± 0.4‰ ($n = 4$).

Knowing the concentrations of the N_{org} and N_{bnd} we can calculate the $\delta^{15}N_{org}$ value by mass balance:

$$\delta^{15}N_{org} = (\delta^{15}N_{tot}100 - \delta^{15}N_{bnd}(100 - \text{fraction}\,N_{org}))/\text{fraction}\,N_{org}, \qquad (1)$$

where 'fraction N_{org}' is the percent organic nitrogen of the total nitrogen in a sample. The results of these calculations show that $\delta^{15}N_{org}$ values for both areas investigated are much heavier than $\delta^{15}N_{tot}$ values, ranging between 7.1 and 13.1‰ in the central Arctic Ocean, and between 4.6 and 10.7‰ in the Yermak Plateau region (Table 1 and 2).

The derivation of $\delta^{15}N_{org}$ values for the surface sediments of the Arctic Ocean by correcting for the presence of soil-inherited nitrogen allows us to interpret more securely the variations in $\delta^{15}N_{org}$ in terms of relative nutrient utilization in the surface waters. Dissolved nitrate concentrations in the upper 30 m of the water column (unpublished data of Leif Andersen, University of Göteborg, 1997) are higher in lower latitudes (in the Svalbard area) compared with those at higher latitudes (in the central Arctic Ocean, Fig. 3a). This simply reflects the fact that Atlantic water with relatively high nitrate is intruding into the Arctic through the Fram Strait and the Barents Sea; nitrate then becomes progressively lower in concentration because of utilization by phytoplankton as the surface waters flow northward. In the region of the Lomonosov Ridge and Makarov Basin at about 88°N, nitrate values vary between 3 and 4 μmol/kg, reflecting the mixing of surface waters of the Eurasian and Amerasian Basins. Surface sediment $\delta^{15}N_{tot}$ and $\delta^{15}N_{org}$ values increase with latitude (Fig. 3b), and decrease with increasing surface nitrate concentration (Fig. 3c). This reflects the progressive isotopic enrichment of the residual nitrate pool in the surface waters as it is drawn down by phytoplankton growth; where nutrient levels are relatively high, relative nitrate utilization is low and there is a larger fractionation of the N isotopes in favor of ^{14}N. Scatter of the data points around the regressions in Fig. 3c probably reflects the fact that we are comparing instantaneous surface water nitrate concentrations with an integrated isotopic signal in bottom sediments.

Since $\delta^{15}N$ in organic material is not directly related to nitrate concentration per se but rather to the degree of nitrate utilization, we can examine the degree of isotope fractionation from the relationship between the fraction of unutilized nitrate (f) and the $\delta^{15}N_{org}$ and $\delta^{15}N_{tot}$ values. f was determined from the ratio of $[NO_3^-]$ in the surface water of each sample location to $[NO_3^-]$ of the inflowing water to the Arctic Ocean (5.9 μmol/kg). r^2 for the logarithmic regression is 0.5 ($n = 13$) for $\delta^{15}N_{org}$ and 0.3 ($n = 13$) for $\delta^{15}N_{tot}$, confirming that a significant fraction of the variance in $\delta^{15}N_{org}$ values is accounted for by changes in $[NO_3^-]$. The regressions also show that $\delta^{15}N_{org}$ rather than the $\delta^{15}N_{tot}$ values represent a much better means for monitoring nitrate utilization in the Arctic Ocean. The fractionation factor ε_u, given by the slope of the regressions of $\delta^{15}N_{org}$ on ln $[NO_3^-]$ (Fig. 4), is 7.2‰, lying in the range of previously published values of 0.3–23‰ (Montoya, 1994) and comparing well with values of 8 and 9‰ from the Weddell Sea and Subarctic Pacific, respectively (Biggs et al., 1988; Altabet and Francois, 1994b).

In the Svalbard region, $\delta^{15}N_{org}$ values lie, with three exceptions, between 4.6 and 7.4‰ and reflect the inflow of warm and relatively nitrate-rich surface waters from the West Spitsbergen current inflow. Surface nitrate is replenished by this inflow and does not become significantly depleted, which leads to relatively light $\delta^{15}N_{org}$ values in the sediments. On the other hand, at stations 2840, 2847, and 2849, $\delta^{15}N_{org}$ values are 10.7, 8.3, and 10.2‰, respectively, much heavier than at the more eastern stations. These three stations in the westernmost part of the sampling area lie beneath the East Greenland Current (Perry, 1986; Perry et al., 1980), a low salinity, cold current with low nitrate concentrations. The $\delta^{15}N_{org}$ values of the sediments in this area therefore reflect the cumulative effect of NO_3^- uptake with the remaining substrate enriched in $^{15}NO_3^-$.

The regional pattern of $\delta^{15}N_{org}$ values in the central Arctic Ocean surface sediments therefore monitors the extent of nutrient utilization by phytoplankton. Light $\delta^{15}N_{org}$ values in the Svalbard area with the inflow of relatively nitrate-rich surface waters contrast with heavier values in the central Arctic Ocean and in the East Greenland Current, where nitrate-depleted waters occur. Although the distribution of $\delta^{15}N_{tot}$ values also shows higher values in the central Arctic Ocean and lower values in the Svalbard area, this pattern is much better resolved with $\delta^{15}N_{org}$ values.

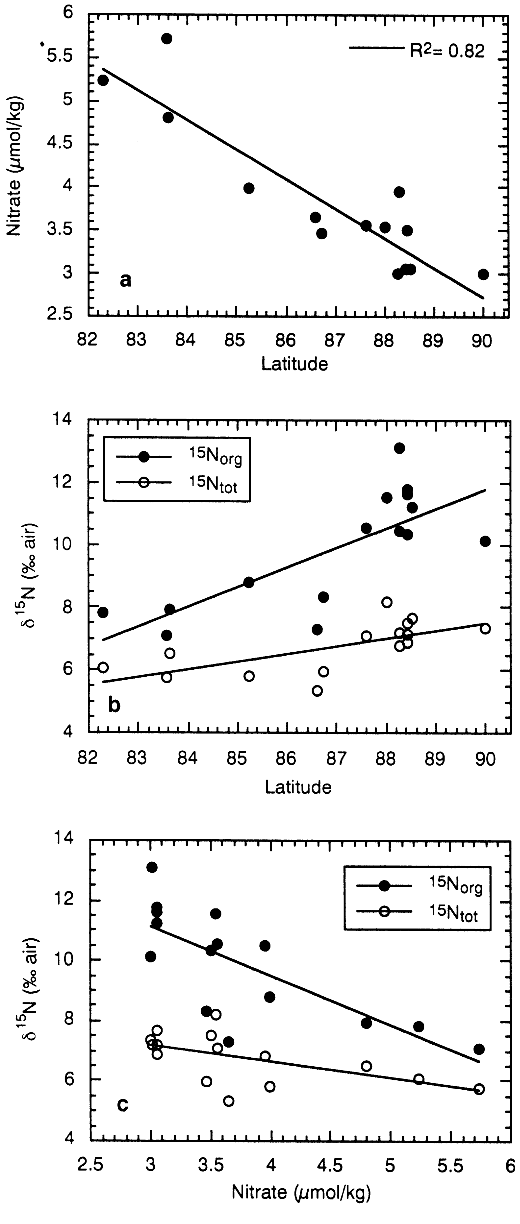

Fig. 3. (a) Nitrate concentration of surface waters (0–30 m depth) from the ARK-VIII/3 expedition plotted versus latitude. Nitrate data kindly provided by Leif G. Anderson, University of Göteborg. (b) $\delta^{15}N$ values of sediments from the ARK-VIII/3 expedition plotted versus latitude. (c) $\delta^{15}N$ values of sediments from the ARK-VIII/3 expedition plotted versus nitrate concentrations of surface waters (0–30 m depth; nitrate).

Interpretation of variations in the nitrogen isotopic composition of sedimentary organic matter must take into account changes in the isotopic signal brought about by diagenesis, that is, changes in the water column during particle settling and in the sediment after burial. Possible diagenetic

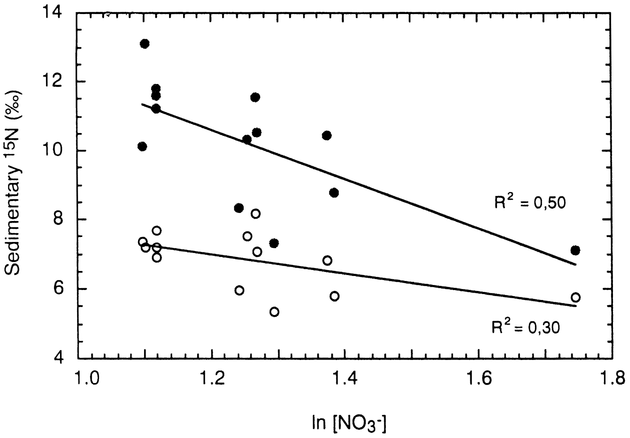

Fig. 4. $\delta^{15}N_{tot}$ (open circles) and $\delta^{15}N_{org}$ (closed circles) values of sediments from the central Arctic Ocean (ARK-VIII/3) plotted versus ln $[NO_3^-]$. See text for explanation.

alterations are discussed in detail by Altabet and François (1994a,b) and Altabet et al. (1999). In the Equatorial Pacific and in the high latitude Southern Ocean, bottom sediments appear to be significantly enriched in $\delta^{15}N_{tot}$ compared to the surface-generated signal (Altabet and Francois, 1994b; Biggs et al., 1988), although the contrast in isotopic values between nutrient-replete and nutrient-depleted regions appears to be maintained. Thereafter, isotopic changes during burial appear to be small. Alteration during settling may also occur in the Arctic Ocean, although we do not have an adequate set of plankton samples nor sediment trap samples to determine if this is so. We therefore assume, based on the work of Altabet and Francois (1994a, b, although done on $\delta^{15}N_{tot}$ and not $\delta^{15}N_{org}$), that the range of $\delta^{15}N_{org}$ values reflects a similar range of surface-generated organic matter values; this must, of course, be checked in future studies of the Arctic and other world oceans.

Denitrification, as observed in some continental margin regimes (Ganeshram et al., 1995; Altabet et al., 1999), is another factor that may lead to large changes (8–12‰) in sedimentary nitrogen isotopic composition. Denitrification in the well-oxygenated water column of the Arctic Ocean, however, is very unlikely and should not have affected the nitrogen isotopic signal.

4.3. Elemental and isotopic composition of POM

During the 1997 expedition, we collected filtered samples of POM from meltwater ponds, surface waters, ice cores and copepods. Organic carbon and nitrogen concentrations, C/N ratios and the isotopic compositions are reported in Table 3. In ice samples, organic C and total N concentrations ranged from 35 to 79 μmol/l and 4 to 10 μmol/l, respectively. The lowest values came from an internal piece of an ice core, whereas the other samples represent the lowermost portion of the ice cores. Relatively high accumulation of organic material in the form of algae in the lowermost part (sea-ice/surface water interface) of ice cores compared to the interior of the ice had been shown earlier by Gradinger (1998). C/N weight ratios range from 6.4 to 8.4, and $\delta^{15}N$ values range between 3.5 and 5.6‰. A sample of surface sea-ice that was collected approximately 5 m from the

Table 3
Carbon isotope data on meltwater pond, surface water, ice core, sea ice and copepods samples. Meltwater ponds in which water with sediment contamination was recovered are marked with sediment. The lowermost 10 cm of ice cores were sampled since here the highest biomass is located. Copepods were sampled with a multinet from the uppermost 30 m water depth

Sample name	PON (μmol/l)	POC (μmol/l)	C/N weight	^{15}N (‰ versus air)	^{13}C (‰ versus VPDB)	Sample type
2853	8.2	79.4	8.4	5.6	− 19.2	Ice core
2834	9.6	71.3	6.4	5.4	− 20.6	Ice core
2861					− 18.3	Ice core
2829					− 23.6	Ice core
2837	4.1	35.1	7.3	3.5	− 19.9	Ice core (internal)
2860	10.0	90.0	7.7	9.0	− 20.4	Sea ice
2834	65.6	n.d.	n.d.	4.5	− 18.6	Meltwater pond
2830	21.4	n.d.	n.d.	− 4.2	− 15.3	Meltwater pond
2859	3.1	32.3	8.9	3.0	− 22.3	Meltwater pond (sediment)
2851	1.7	19.9	9.8	4.9	− 24.9	Meltwater pond (sediment)
2833	16.4	126.8	6.6	− 0.69	− 25.9	Meltwater pond (sediment)
2839					− 23.8	Meltwater pond (sediment)
2838					− 25.3	Meltwater pond (sediment)
2860					− 26.1	Meltwater pond (sediment)
2829					− 23.4	Meltwater pond (sediment)
2824					− 27.6	Surface water (0–30 m)
2830					− 22.9	Surface water (0–30 m)
2822					− 24.2	Surface water (0–10 m)
2832					− 23.8	Copepods
2861					− 25.2	Copepods
2838					− 24.2	Copepods
2849					− 26.2	Copepods
2824					− 26.6	Copepods

vessel with the ship's crane showed values of 10 μmol/l PON and 90 μmol/l POC, a C/N ratio of 7.7, and a δ^{15}N value of 5.9‰. Samples from sediment-free meltwater ponds showed very high values of 21 and 66 μmol/l PON compared to the sea-ice samples. This is consistent with extremely high productivity in under-ice ponds as described earlier (Gradinger, 1996). δ^{15}N values are highly variable: − 4.2 and 4.5‰. Three samples of meltwater ponds of which two were heavily 'contaminated' with sediment and one contained only minor amounts of sediment showed PON values of 0.8, 0.4, and 4.1 μmol/l, and POC values of 8.1, 5.0, and 31.7 μmol/l, respectively. Thus, the sample containing only minor amounts of sediment has a much higher nitrogen content, leading to a lower C/N ratio (6.6 compared with 8.9 and 9.8) indicative of a higher contribution of protein-rich planktonic material relative to terrestrial material. δ^{15}N values vary from − 0.7‰ for the meltwater pond sample with a low amount of sediment to 3.0 and 4.9‰ for the sediment 'contaminated' meltwater pond samples.

POM from the lowermost part (10 cm) of ice cores has δ^{13}C values ranging from − 18.3 to − 20.6‰ ($\bar{x} = -19.7$‰, $n = 5$). These values are in agreement with data from sea-ice samples from the Weddell Sea (Fischer, 1991). Both Fischer (1991) and Wada et al. (1987b) proposed that such heavy $\delta^{13}C_{org}$ values are due to sea-ice algae growing under CO_2-limited conditions. Biological production in sea-ice leads to a relatively rapid and intense depletion in CO_2(aq), since the exchange of CO_2 with the atmosphere is limited (Gleitz et al., 1995). Such reduced CO_2 availability results in reduced photosynthetic ^{13}C discrimination, elevating the $\delta^{13}C$ of the organic fraction (Kerby and Raven, 1985). An even stronger enrichment of ^{13}C is seen in phytoplankton samples recovered from sediment free meltwater ponds (− 15.3 and − 18.6‰). In this case, the productivity in the meltwater ponds might have been even greater than in sea-ice, since the light influx through a thin ice cover over the pond is much larger than under a 1–3 m thick sea-ice cover. However, the thin ice cover effectively hinders carbon dioxide exchange with the atmosphere, leading to extreme CO_2(aq) depletion and relatively high phytoplankton $\delta^{13}C$ values.

POM from ponds that contained sediment has values significantly lighter, with an average of − 24.5‰. This could be due to a mixture of isotopically heavy algal material and light terrestrial organic matter. POM filtered from ice-free surface water has values between − 23.0 and − 27.6‰ (Ø = − 25.0‰, $n = 3$). Copepods collected from open waters have $\delta^{13}C_{org}$ values of − 23.8 to − 26.6‰ (average − 25.2 ± 1.4‰, $n = 5$), a range similar to that obtained by Saupe et al. (1989) and Schell et al. (1998). If we assume that the isotopic signal of zooplankton reflects the isotopic value of its diet with a small food-chain enrichment (Wada et al., 1987a), it appears that copepods feed either on ^{13}C-depleted phytoplankton or on terrestrial organic detritus, the first being more plausible.

Our results show that meltwater ponds as well as ice cores are highly variable regimes in which the production of phytoplankton, probably the grazing influence of zooplankton, the amount of terrestrial organic matter input, and also bacterial activities determine the distribution of the measured parameters. However, there is no clear trend from one regime to the other. The very light nitrogen isotope ratios determined in two of the meltwater pond samples might indicate a contribution of nitrogen-fixing bacteria, which are known to fractionate atmospheric nitrogen to a very small extent (Hoering and Ford, 1960), but are normally restricted to warm areas. On the other hand, Wada et al. (1987a) obtained values of − 3 to 1‰ in sinking particles in the Southern Ocean (60°S), which they explained by high fractionation by diatoms as the main contributors to the sinking material. In the same area, Rau et al. (1991) measured $\delta^{15}N$ of POM as low as − 5.4‰. Since diatoms and flagellates are the dominant phytoplankton groups in sea-ice (Gradinger, 1998), diatoms might be responsible for the very light $\delta^{15}N$ values observed in this study. C/N ratios show small changes from environments with some more terrestrial influence (meltwater pond with sediments), with an average value of 9.4, to a solely marine regime (ice core or meltwater pond without sediments), with an average value of 7.3.

4.4. Compositional and isotopic indicators of the source of organic material in Arctic Ocean sediments

The distribution of $\delta^{13}C_{org}$ values for the ARK-VIII/3 and the ARK-XIII/2 expeditions shows lower values (− 22.0 to − 24.2‰) in the Svalbard area increasing to values of − 21.1‰ in the central Arctic Ocean (Tables 1 and 2). It is known that the $^{13}C:^{12}C$ ratio in phytoplankton in higher latitudes is significantly lower than in lower latitudes (Fischer, 1991; Rau et al., 1982; Rau et al., 1991), the range being from − 16.7 to − 30.4‰. This was originally attributed to the effects of variations in molecular CO_2 concentrations in surface waters, which ranged between 8 and 26 μM over a temperature range of 2 – 28°C (Rau, 1994). More recent work (Laws et al., 1995; Rau et al., 1997) has shown that the fractionation of the carbon isotopes by phytoplankton is related to cell growth rate, cell size and cell membrane CO_2 permeability as well as $[CO_{2aq}]$. This variability in the marine "endmember" leads to some uncertainty in the application of sedimentary $\delta^{13}C_{org}$ values for determining organic matter sources in the ocean.

Our results for the Arctic Ocean show that there is significant variability and a consistent trend in $\delta^{13}C_{org}$ values from the marginal area around Svalbard (-22.0 to -24.2 ‰) to the central Arctic (-21.1 to -22.1‰). The lighter values around Svalbard most likely reflect a mixture of planktonic organic matter that is depleted in ^{13}C, as has been shown by Rau et al. (1982, 1991) for plankton from high latitudes, and isotopically light terrestrial organic material with $\delta^{13}C_{org}$ values (C_3 plants) of approx. -26 to -28‰. This would be consistent with results of biomarker and microscopic investigations on sediment trap samples (Fahl, personal. communication, 1998) and the distribution of terrestrial biomarkers in sediments, which are enriched in this area compared to the central Arctic Ocean (Schubert and Stein, 1997).

The significantly heavier $\delta^{13}C_{org}$ values in central Arctic Ocean sediments are somewhat surprising in view of the suggestion that there is a high terrestrial organic matter contribution to the sediments (Schubert and Stein, 1997; Stein et al., 1994), and the fact that low surface temperatures should lead to high $[CO_{2aq}]$, which in turn should lead to a larger fractionation of the isotopes. However, the very light plankton $\delta^{13}C_{org}$ values (-24.0 to -30.0‰) observed in the Southern Ocean (Fischer, 1991; Rau et al., 1992) were not found so far in high northern latitudes (up to 72°N), where values ranged from -18.4 to -23.3‰ ($\bar{x} = -20.9$‰, $n = 14$) (Rau et al., 1982) and from -22.0 to -23.2‰ in POC from surface waters in the East Greenland current (Notholt, 1998). Only in our study, $\delta^{13}C_{org}$ values of POC from surface waters (-23.0 and -27.6‰) are almost in the range as observed in the Southern Ocean. But in contrast to the Southern Ocean, a significant fraction of this material could be from a terrestrial source.

Nitrogen isotope ratios have also been used to distinguish between marine and terrestrial organic material, with marine organic matter being isotopically heavier due to fractionation during nutrient uptake and terrestrial organic matter being relatively lighter since fractionation here is low or even absent (e.g. Wada et al., 1987b). We have therefore examined the relationship between $\delta^{15}N_{tot}$ and $\delta^{13}C_{org}$ and between $\delta^{15}N_{org}$ and $\delta^{13}C_{org}$. In Fig. 5 we have plotted the sediment data together with our measured or assumed endmembers. For river POC we have included an average $\delta^{13}C_{org}$ value of -27.1‰ (Rachold and Hubberten, 1999). The $\delta^{13}C_{org}$ of POM from the Lena River (with the second largest water discharge into the Arctic Ocean) is reported to range from -25.7 to -28.8‰ ($\bar{x} = -27.1$‰, $n = 19$), whereas POM from the Yana, Omoloy, and Khatanga Rivers has values of -25.7, -27.2, and -27.7‰, respectively (Rachold and Hubberten, 1999). We have used the average value of the Lena river (-27.1‰) here as the terrestrial end member since the Lena carries about 1.2×10^6 t/yr POC into the Laptev Sea, a load that is 20 and 30 times more than the Yana and the Khatanga, respectively (Rachold and Hubberten, 1999). Furthermore, we used an estimated value for $\delta^{15}N_{tot}$ of 3.5‰, an average of detrital river material and soil organic matter (cf. Wada et al., 1987b). For plankton in the surface water we used our measured $\delta^{13}C_{org}$ values and values by Notholt (1998). $\delta^{15}N_{tot}$ and $\delta^{15}N_{org}$ values have been assumed to be between 11 and 15‰ (similar to the heavier $\delta^{15}N_{org}$ sediment values); however, there might be significant deviation from this assumption. As expected by assuming a mixture of three components, the regression of the sediment $\delta^{13}C_{org}$ and $\delta^{15}N_{tot}$ correlation is rather weak

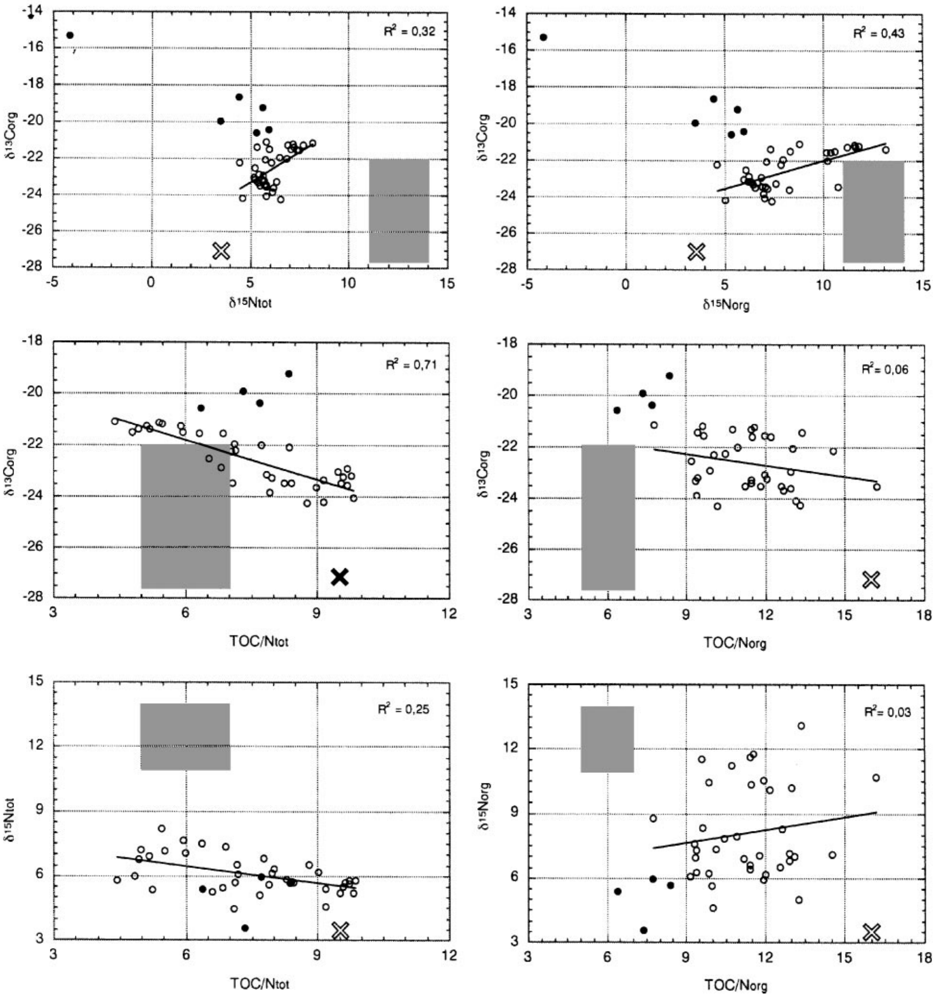

Fig. 5. $\delta^{15}N_{tot}$, $\delta^{15}N_{org}$, TOC/N_{org}, and TOC/N_{tot} of Arctic Ocean sediments (both regions) versus each other and $\delta^{13}C_{org}$. The open circles indicate sediment data. Closed circles indicate ice algae in ice cores or meltwater ponds. The open cross is the terrestrial endmember (river input) with an estimated nitrogen isotope value and TOC/N_{org} ratio. The closed cross is the terrestrial endmember (river input) with indicated values being measured. The gray bar is the phytoplankton endmember derived by carbon isotope measurement and an assumed TOC/N_{org} ratio and nitrogen isotope value (see text for explanation). Regression line and coefficient is plotted for sediment data.

($r^2 = 0.32$), whereas we obtain a regression of $r^2 = 0.43$ between $\delta^{13}C_{org}$ and $\delta^{15}N_{org}$. A higher regression coefficient ($r^2 = 0.59$, not shown) is obtained using samples only from the central Arctic Ocean, possibly due to the greater influence of CO_2 and nutrient dependence on the isotopic composition of C and N. High phytoplankton productivity leading to a drawdown of nutrients and, therefore, higher nutrient utilization (i.e. higher $\delta^{15}N$ values) would also lead to a drawdown in CO_2 (at least in a closed system like an ice core or meltwater pond) leading to heavier $\delta^{13}C_{org}$ values as observed here.

TOC/N_{tot} ratios and $\delta^{13}C_{org}$ values of all sediment samples included in this study appear to show a high degree of covariance ($r^2 = 0.71$, Fig. 5). However, the high regression coefficient is based mainly on the fact that we have two data sets, one plotting in the lower right quadrant (Yermak Plateau samples, with light $\delta^{13}C_{org}$ and high TOC/N_{tot} values) and one plotting in the higher left quadrant of the plot (central Arctic Ocean, with heavy $\delta^{13}C_{org}$ and low TOC/N_{tot} values). The lower TOC/N_{tot} values in the central Arctic Ocean are mainly due to high inorganic ammonium contents as discussed above and therefore cannot be used for interpreting the composition of the organic material. Surface water plankton TOC/N_{tot} and TOC/N_{org} ratios were assumed to be 5–7 (Redfield et al., 1963), the measured river TOC/N_{tot} was 9.5 (Rachold and Hubberten, 1999), and the river TOC/N_{org} ratio was assumed to be 16 including a correction for 40% of inorganic nitrogen. On the other hand, correlation between $\delta^{13}C_{org}$ values and TOC/N_{org} ratios is extremely low ($r^2 = 0.06$, Fig. 5), again a result of a three component mixing.

Having discussed the elemental and isotopic composition of sediments and corresponding endmembers, we now try to model the marine and terrestrial organic matter contributions to Arctic Ocean sediments. There are two different sources of primary organic matter in the Arctic Ocean: sea-ice phytoplankton and surface water phytoplankton, and additionally, terrestrial organic matter which might by itself have different sources such as soils, ancient sedimentary rocks or coals. However, since we do not have any specific information on the terrestrial source we have to model these components as one uniform source.

First we have to distinguish between the two types of phytoplankton, sea-ice versus open water phytoplankton. Estimates of the ratio of within- and under-ice production are highly variable (e.g. between 1:10 and 2:1, Markus Gleitz unpublished data). Gradinger (1996) reported very high values of 11 g Chl a/m^3 in an algal bloom in an under-ice meltwater pond compared with ice covered surface water (0.2 g Chl a/m^3) or open water (1.5 g Chl a/m^3) values in the Arctic Ocean. It is difficult, therefore, to estimate the relative roles of these two sources of phytoplanktonic organic material.

We approach this problem by considering three different scenarios and their corresponding isotopic signals: (1) 50:50 contribution of sea-ice to surface water plankton, (2) 20:80 contribution of sea-ice to surface water plankton, (3) 80:20 contribution of sea-ice to surface water plankton. The resulting isotopic compositions are obtained from the following mass balance:

$$\delta^{13}C_{\text{marine}} = a(\delta^{13}C_{\text{surface water plankton}}) + (1 - a)(\delta^{13}C_{\text{sea-ice plankton}}).$$

Using a $\delta^{13}C$ value of − 17.0‰ for meltwater pond samples and − 19.7‰ for ice-core samples, we obtain an average value for ice-related plankton of − 18.3‰. POM in surface waters has values ranging from − 22.0 to − 27.6‰ (Table 3, and Notholt, 1998). Since we do not know how the input of terrestrial POM has influenced these values, we use the heaviest composition, assuming that to be closer to the marine value (− 22.0‰). This leads to the following results for the three scenarios: (1) $\delta^{13}C_{\text{marine}} = -20.2$‰, (2) $\delta^{13}C_{\text{marine}} = -21.3$‰, and (3) $\delta^{13}C_{\text{marine}} = -19.0$‰. The terrestrial endmember $\delta^{13}C_{\text{terrestrial}}$ is, as discussed above, − 27.1‰.

To calculate the isotopic composition of total organic matter in terms of marine versus terrestrial contributions we use the measured average $\delta^{13}C$ value (− 21.4 ‰) for the central Arctic Ocean and the following mass balance, where TOM is the total organic matter:

$$\delta^{13}C_{\text{TOM}} = a(\delta^{13}C_{\text{marine}}) + (1 - a)(\delta^{13}C_{\text{terrestrial}}).$$

This suggests that there is a contribution of 17, 2, and 30% of terrestrial organic matter in the central Arctic Ocean sediments for scenarios (1), (2), and (3), respectively. The same calculations for the elemental compositions (TOC/N_{org} ratios) assuming a ratio of 6 for surface water plankton, 7.5 for sea-ice plankton, and 16 for river transported POC lead to a contribution of 43–48% of terrestrial organic matter. However, we have to take into account that changes in the isotopic/elemental composition of the different endmembers (sea-ice plankton, surface water plankton, and terrestrial organic matter) as well as the variation in the contribution of the different marine endmembers might significantly affect the modelled proportions of marine and terrestrial input. We have not calculated a terrestrial contribution using nitrogen isotope ratios since we have only very roughly estimated values for the marine and terrestrial endmembers.

The results of this study, especially the low terrestrial contribution calculated by the carbon isotopic signals, are at variance with the conclusions of Schubert (1995) and Schubert and Stein (1997), who found evidence for a much higher amount of terrestrial organic carbon based on biomarker investigations in central Arctic Ocean sediments. Schubert and Stein (1997) used the abundance of long-chain *n*-alkanes for estimating terrestrial organic matter input to the total organic matter in Arctic Ocean sediments. However, it is possible that plant wax long-chain *n*-alkanes may not be representative for the bulk terrestrial organic matter or that the delivery and transport in the sediments may differ as described earlier (Prahl et al., 1994). Low lignin concentrations (Schubert, unpublished results) might support the lower input of terrestrial organic matter into central Arctic Ocean sediments; however, without a constraint on the difference in the lignin content of the inputs and the effect of transport this remains an open question.

5. Summary and conclusions

This study shows that a more reliable interpretation of the factors controlling the C/N ratio of Arctic Ocean sediments is made possible by correcting bulk N determinations for the presence of inorganic (bound) nitrogen using an established KOBr–KOH leach, which removes the organic matter almost quantitatively. This is especially true in sediments with low organic carbon and high illite contents, where adsorption of ammonium onto clays can account for up to 63% of total sedimentary nitrogen.

Nitrogen isotope ratios in Arctic Ocean sediments reflect the surface water nitrate content and the utilization of this nitrate by phytoplankton. Low δ^{15}N values in sediments near Svalbard reflect the inflow of relatively nitrate-rich waters with the West Spitsbergen Current, while high values in the central Arctic Ocean are a response to the low surface nitrate concentrations. By applying the KOBr–KOH leach technique to our sediment samples, we show that the calculated $\delta^{15}N_{org}$ values are significantly higher than $\delta^{15}N_{tot}$ values and they have a much clearer relationship to surface nitrate concentrations.

Ice algae are relatively enriched in $^{13}C_{org}$ due to the low $CO_{2(aq)}$ in either the underside of sea-ice or ice-covered meltwater ponds.

Contributions of terrestrial organic matter estimated from the carbon isotope data on central Arctic Ocean sediments (not including the shelf and slope areas, such as the Barents and Laptev Sea) could be as high as 30% depending on assumptions about the composition of different phytoplankton endmembers. Using TOC/N_{org} ratios the terrestrial contribution was estimated to be as high as 48%. The interpretation of the carbon isotope data presented here contradicts earlier conclusions about the relative abundance of terrestrial organic matter in Arctic Ocean sediments. However, it must be remembered that the carbon isotopic composition of phytoplankton in the Arctic Ocean, whether it be in surface waters, sea-ice, or meltwater ponds, is highly variable, which hinders its use as a marine/terrestrial source indicator.

Further investigations, including both comprehensive biomarker and isotopic studies on surface water plankton, sediment trap materials, and sedimentary organic material are necessary to understand organic sedimentation in the Arctic Ocean better.

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