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Organic carbon and nitrogen composition in the sediment of the Kara Sea, Arctic Ocean during the Last Glacial Maximum to Holocene times

Hwa-Seong Kang,[1] Eun-Ji Won,[1] Kyung-Hoon Shin,[1] and Ho il Yoon[2]

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[1] A sharp decrease in C_{org}/N_{tot} ratios and apparently heavier stable isotope ratios of C_{org} and N_{tot} ($\delta^{13}C_{org}$ and $\delta^{15}N_{tot}$) after deglaciation were observed in sediment cores St-25 and St-34 collected from the Saint Anna Trough in the Kara Sea, exhibiting a change of sediment origin from terrestrial to marine during the LGM and Holocene times. Organic nitrogen (N_{org}) contributed about 40% to total nitrogen (N_{tot}) during the Holocene, but the N_{org} fraction was hardly observed in the lower LGM sediments (below 120 cm depth in St-25 and beneath 170 cm in St-34). This may be due to a permanent cover of sea ice in the area during the LGM. In addition, the $\delta^{13}C$ values for OC_{labile} and OC_{resi} were remarkably different between LGM and Holocene sediment. The unexpected lighter $\delta^{13}C$ values for OC_{resi} for the LGM period might be due to methanotrophic bacteria in the sediment of Kara Sea. **Citation:** Kang, H.-S., E.-J. Won, K.-H. Shin, and H. Yoon (2007), Organic carbon and nitrogen composition in the sediment of the Kara Sea, Arctic Ocean during the Last Glacial Maximum to Holocene times, *Geophys. Res. Lett.*, *34*, L12607, doi:10.1029/2007GL030068.

1. Introduction

[2] The Kara Sea is an important pathway for material transport to the Arctic Ocean [*Holmes et al.*, 2002] on account of the large pool of terrestrial organic carbon (C_{org}) and the inflow of Atlantic water mass [*Fernandes and Sicre*, 2000; *Stein et al.*, 1994]. Terrestrial organic carbon is reportedly predominant in the southern Kara Sea, which shows high C_{org}/N_{tot} ratios (9 and 14) [*Fernandes and Sicre*, 2000; *Krishnamurthy et al.*, 2001].

[3] Stable isotope ratios of carbon and nitrogen as well as C_{org}/N_{tot} ratios have been used as valuable proxies to the origin of sedimentary organic matter. In most of the studies, total nitrogen (N_{tot}) rather than organic nitrogen (N_{org}) has been available because the inorganic nitrogen content can be negligible. However, recent studies report the significant presence of inorganic nitrogen in bottom surface sediment of the Arctic Ocean and offshore from Spitsbergen [*Schubert and Calvert*, 2001; *Winkelmann and Knies*, 2005].

[4] In this study, organic carbon (KOBr-KOH oxidizable organic carbon: OC_{labile}), N_{org} removed by oxidation of organic matter using KOBr-KOH, the remaining fractions of residual organic carbon: OC_{resi} and inorganic nitrogen N_{inorg}, and the stable isotope ratios $\delta^{13}C$ of OC_{resi}, were determined for sediment core samples collected in the Saint Anna Trough of the Kara Sea. The fractions of organic carbon and nitrogen and their stable isotope ratios are first discussed in order to understand the origin of sedimentary organic matter related to paleo-ocean environmental changes during the last glacial maximum (LGM) and Holocene periods in the Kara Sea.

2. Methods and Materials

[5] Two sediment cores (St-25 and St-34) were collected in the northern Kara Sea during the 2001 Arctic cruise (Figure 1). The cores were divided into 2–4 cm length subsamples. After decalcification of the homogenized samples, total organic carbon (C_{org}) and total nitrogen (N_{tot}) contents and their stable isotope ratios were determined by using an elemental analyzer combined with a mass spectrometer (Delta Plus, Finnigan MAT). After oxidizing the organic matter with KOBr-KOH solution [*Silva and Bremner*, 1966; *Schubert and Calvert*, 2001], the stable isotope ratios of residual inorganic nitrogen (N_{inorg}) and residual organic carbon (OC_{resi}) were determined using the same instrumentation as above. The analytical precision was ±0.23 for $\delta^{13}C$ and ±0.28 for $\delta^{15}N$. The KOBr-KOH oxidizable organic carbon (OC_{labile}) was calculated by determining the difference between C_{org} and OC_{resi} [*Schubert and Calvert*, 2001]. Similar examination derived the organic nitrogen (N_{org}) content from the N_{tot} and N_{inorg} values because the organic nitrogen (N_{org}) removal efficiency was higher than 98%.

[6] The KOBr-KOH oxidizable organic carbon isotope ($\delta^{13}C$ of OC_{labile}) value was determined by the isotope mass balance equation:

$$\delta^{13}C \text{ of } OC_{labile} = \frac{\delta^{13}C_{org} \times 100 - \delta^{13}OC_{resi} \times (100 - \text{fraction}OC_{labile})}{\text{fraction}OC_{labile}}$$

3. Results and Discussion

3.1. Corg, Ntot Contents and Stable Isotope Ratios During the LGM to Holocene Times

[7] The C_{org}/N_{tot} ratio showed an apparent decreased value of almost 10 at 64 cm depth at St-25 (Figure 2). Magnetic susceptibility (MS) was significantly high from 40–60 cm depth, where the C_{org} content also decreased rapidly. A glacial diamicton layer was found below 64 cm

[1]Department of Environmental Marine Sciences, Hanyang University, Ansan, South Korea.
[2]Korea Polar Research Institute, Korea Ocean Research and Development Institute, Incheon, South Korea.

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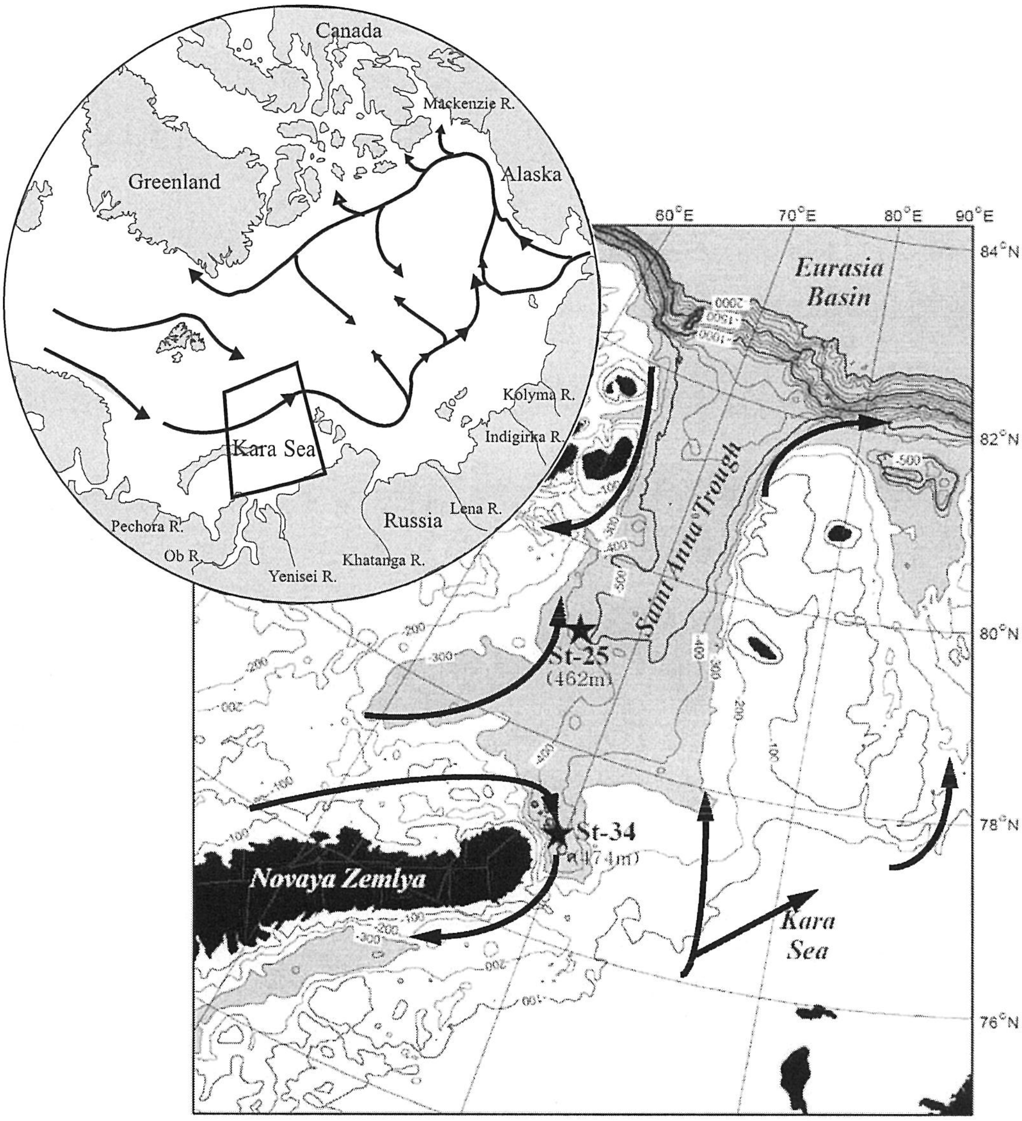

Figure 1. Bathymetric map of the study area showing sediment core locations within the Saint Anna Trough, Kara Sea (modified from *McLaughlin et al.* [1996]; *Lee et al.* [2003]).

depth [*Lee et al.*, 2003]. This layer and the MS variation are indicative of a glacial condition occurring before the Holocene period. The diamicton layer indicates a glacial environment, while the MS value is a mixed signal of river discharge and weathering conditions in the hinterland [*Stein et al.*, 2004]. The markedly increased MS value within the core sample at St-25 shows similarities to that in core obtained from the Laptev Sea continental margin [*Stein et al.*, 2001], as well as to previous results from the Saint Anna Trough [*Polyak et al.*, 1997] that have been interpreted as indicating the LGM/Holocene boundary. It is also reported that the diamicton layer is a record of glacier retreat in the Saint Anna Trough 13,000 years ago [*Hald et al.*, 1999]. In the present study, the depth horizon showing the significant decrease of C_{org}/N_{tot} ratio, therefore seems to accord with the LGM/Holocene boundary (Figure 2).

[8] In St-34, the C_{org}/N_{tot} ratio was remarkably declined at 165 cm depth, and the diamicton layer was found below 160 cm [*Lee et al.*, 2003]. Mean C_{org} content in St-34 was a relatively low 0.69% for the LGM, but shows a sharp elevation for the deglaciation and appears two times higher as 1.45% in Holocene sediments (Figure 3). AMS radiocarbon ^{14}C age dating of microshell collected from St-34 gave an age of 5641 ± 45 BP at 102 cm [*Lee et al.*, 2003]. These results are similar to the significantly increased C_{org} content observed in the southern Saint Anna Trough and the decreased C_{org}/N_{tot} ratios recorded in the northern Saint Anna Trough after deglaciation [*Stein and Fahl*, 2003; *Boucsein et al.*, 2002]. The N_{tot} content in Holocene sediment is clearly increased with respect to low values of approximately 0.05% noted in the LGM sediment of both cores, similar to the C_{org} variation. The C_{org} and N_{tot} contents

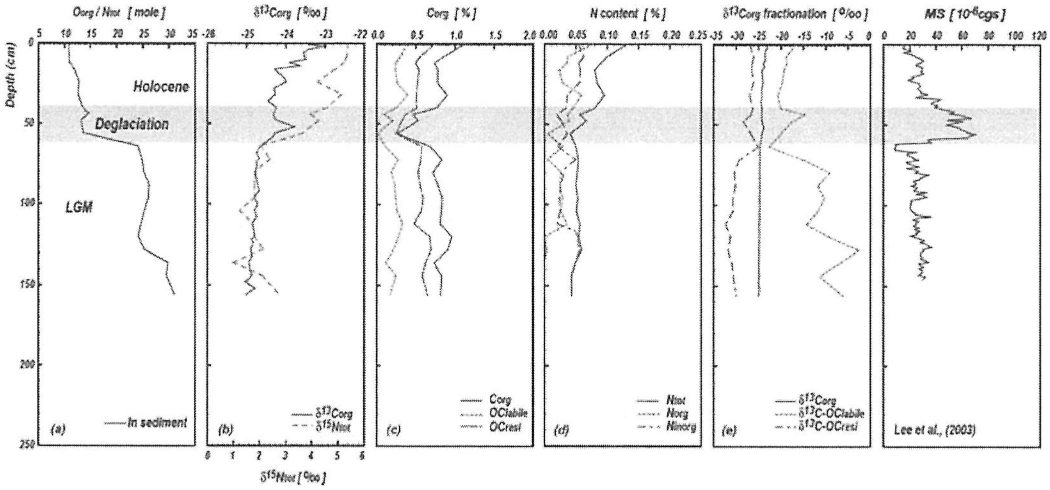

Figure 2. Vertical variation of C_{org} to N_{tot} ratio, organic carbon and nitrogen contents and stable isotope ratios, fractionated components and magnetic susceptibility (MS) within sediment core St-25 of the Saint Anna Trough.

in Holocene sediments were seen to be about twofold higher in St-34 than in St-25, indicating a greater supply of organic matter associated with higher sedimentation rate in St-34. The stable isotope ratios of organic carbon ($\delta^{13}C_{org}$) and total nitrogen ($\delta^{15}N_{tot}$) were heavier in the Holocene record than in that of the LGM at both sites, reflecting an enhanced contribution of marine organic matter (MOM) in the Kara Sea after the LGM. Marine biological production between St-25 and St-34 seem to be strongly affected by the sea ice condition as well as impact of the Atlantic water inflow during the LGM and after deglaciation.

3.2. Origin of Organic Carbon (OClabile and OCresi) and Organic and Inorganic Nitrogen (Norg and Ninorg) Fractions

[9] Total organic carbon (OC) in sediment was fractionated by KOBr-KOH oxidizable organic carbon (OC_{labile}) and KOBr-KOH residual organic carbon (OC_{resi}) (Figures 2 and 3). N_{tot} was separated into N_{org} and N_{inorg} in the same way. Around 25% and 34% of C_{org} occurred as an OC_{labile} fraction in St-25 and St-34, respectively. The contribution of terrestrial organic matter (TOM) was reportedly 75% higher in the Saint Anna Trough than elsewhere in the Kara Sea [*Boucsein et al.*, 2002], which approximately corresponds to the OC_{resi} fraction in this study (Figures 2 and 3). About 40% of the N_{tot} was N_{org}, and the large amount of N_{inorg} may reflect terrestrial discharge into the Saint Anna Trough. A notably small N_{org} fraction was observed in the lower LGM sediment below 120 cm depth in St-25 and beneath 170 cm in St-34, indicating that there was virtually no marine biological productivity. This might be due to a complete cover of sea ice in this area during the LGM period, even though 50% ~60% of N_{tot} was seen to be N_{org} in the upper LGM sediment at 80–120 cm depth in St-25. Possible earlier sea ice melting may have occurred and resulted in a seasonally ice-free condition seen in St-25,

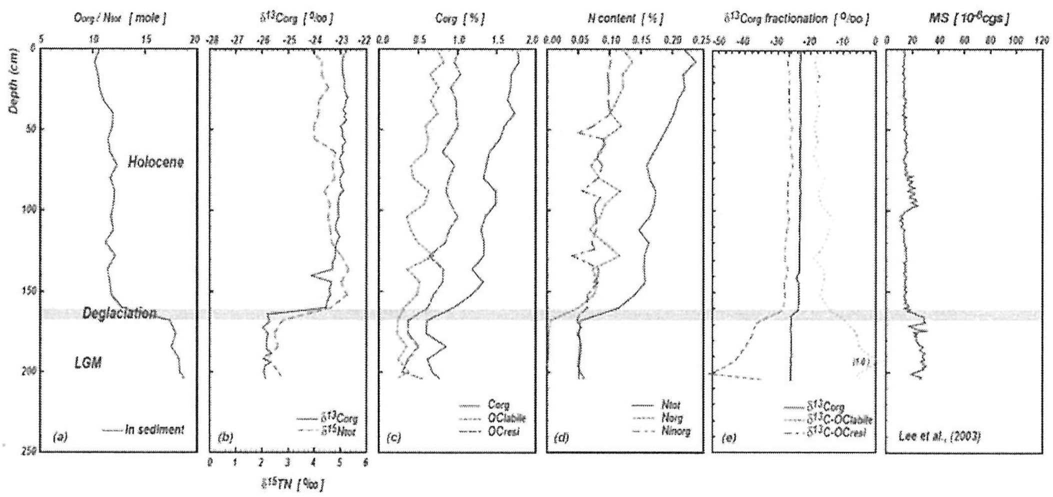

Figure 3. Vertical variation of C_{org} to N_{tot} ratio, organic carbon and nitrogen contents and stable isotope ratios, fractionated components and magnetic susceptibility (MS) within sediment core St-34 of the Saint Anna Trough.

which may have been strongly influenced by an increased inflow of Atlantic water in this region, as the site of St-25 is more closely located toward the Barents Sea as compared to that of St-34, which is located off Novaya Zemlya. However, N_{org} contributed more than 50% to the N_{tot} content in Holocene sediment deposited after deglaciation at both sites, demonstrating enhanced marine biological production during the Holocene period.

[10] The stable isotope ratio of KOBr-KOH oxidizable organic carbon ($\delta^{13}C$ of OC_{labile}) and KOBr-KOH residual organic carbon ($\delta^{13}C$ of OC_{resi}) showed largely different values to the organic carbon stable isotope ratio ($\delta^{13}C_{org}$), which ranged from −23‰ to −25‰ in Holocene sediment showing heavier values for OC_{labile} and lighter values for OC_{resi}. These isotopic fractionation values are consistent with the result that the isotope ratio of OC_{resi} ($\delta^{13}C$ of OC_{resi}) was less, −24 to −22‰, than $\delta^{13}OC_{labile}$, around −19‰, in subtropical Atlantic areas [*Freudenthal et al.*, 2001]. However, the OC_{resi} content seen in this study was much higher than that of subtropical Atlantic areas [*Freudenthal et al.*, 2001], implying that the Kara Sea is influenced by a large terrestrial discharge [*Holmes et al.*, 2002] and also possibly a contribution of methanotrophic bacteria during the LGM.

[11] In the Kara Sea, primary production would be extremely limited under the sea-ice covered condition at both sites (St-25 and St-34) during the LGM. So, it would be reasonable that bacterial production was much more active than marine primary production during the LGM. In previous reports, methanotrophic bacteria (including diploptene) should be dominant in the methane hydrate instability environments during the LGM [*Yamada et al.*, 1997; *Uchida et al.*, 2004]. Therefore, the unexpectedly light $\delta^{13}C$ values of OC_{resi} might be due to a significant contribution of methanotrophic bacteria, because a refractory biomarker (e.g. diploptene) of methanotrophic bacteria showed very light values which were −53‰ in the southern part of Japan Sea and −40‰ in the northwestern North Pacific, respectively [*Yamada et al.*, 1997and *Uchida et al.*, 2004]. Moreover, microbiological methane with $\delta^{13}C$ from −105 to −90‰ was observed in the sediments at depths of 40–200 m, and also autogenic carbonate material, including ikaite, was found, demonstrating the enhanced incorporation of ^{13}C-depleted CO_2 ($\delta^{13}C$ ranging from −25 to −60‰) in the sediments of Kara Sea [*Galimov et al.*, 2006].

[12] In the present study, the $\delta^{13}C$ values of OC_{labile} and OC_{resi} were significantly different between the LGM (on average at St-25, −11.3‰: OC_{labile}, −30.3‰: OC_{resi}, and on average at St-34, −4.7‰: OC_{labile}, −40.9‰: OC_{resi}) and Holocene (on average at St-25, −18.5‰: OC_{labile}, −26.2‰: OC_{resi}, and on average at St-34, −16.8‰: OC_{labile}, −26.8‰: OC_{resi}), demonstrating the unusually heavier values of OC_{labile} noted for the LGM period. This might be attributed to an extremely different organic matter source for the Saint Anna Trough during the LGM period. This result also supports the idea that a low N_{org} content in the LGM period and very high C_{org} to N_{tot} ratios could be due to permanent sea ice at that time.

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H.-S. Kang, K.-H. Shin, and E.-J. Won, Department of Environmental Marine Sciences, Hanyang University, 1271 Sa-1 dong, Sangrok-gu, Ansan, Kyeonggi-do 426-791, South Korea. (shinkh@hanyang.ac.kr)

H. Yoon, Korea Polar Research Institute, Korea Ocean Research and Development Institute, P.O. Box 32, Incheon 406-840, South Korea.