

On the sedimentological origin of down-core variations of bulk sedimentary nitrogen isotope ratios

M. Kienast,^{1,2,3} M. J. Higginson,^{4,5} G. Mollenhauer,² T. I. Eglinton,² M.-T. Chen,⁶ and S. E. Calvert¹

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[1] The bulk sedimentary nitrogen isotopic composition of two cores from nearby sites on the northern slope of the South China Sea (Site 17940 and Ocean Drilling Program (ODP) Site 1144) differs by up to >2‰ during the last glacial period. Given their close proximity, both core sites are located in the same biogeographic zone and nutrient regime, and it is thus unlikely that this offset is due to a true gradient in surface ocean conditions. In an attempt to resolve this offset, we have investigated the possible effects of two sedimentological parameters that can affect bulk sedimentary $\delta^{15}\text{N}$, namely, the variable contribution of inorganic N to bulk N in the sediment and the grain-size dependence of bulk $\delta^{15}\text{N}$. We find that neither effect, singly or in combination, is sufficient to explain the significant $\delta^{15}\text{N}$ offset between the two down-core records. By elimination the most likely explanation for the observed discrepancy is a different origin of both the organic and inorganic nitrogen at each site. This study adds to the growing body of evidence highlighting the complex nature and origin of the sedimentary components in sediment drifts, such as ODP Site 1144.

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1. Introduction

[2] The stable carbon ($\delta^{13}\text{C}_{\text{org}}$) and nitrogen ($\delta^{15}\text{N}$) isotopic compositions of sediments are widely used in palaeoceanographic studies to infer past changes in biogeochemical dynamics at a given core site and beyond [Altabet, 1996]. The isotopic signature preserved in seafloor sediments is the result of sea surface and water column processes overlying the site of a sediment sample, diagenetic processes within the sediment, as well as the delivery of sedimentary components from more remote locations, such as adjacent areas of the seafloor or the continents via surface and subsurface currents and the atmosphere. Considerable effort has been expended in attempts to unravel this complexity, and especially in the case of $\delta^{13}\text{C}$, the analytical approach has increasingly shifted toward single-compound analysis. This is because of the realization that the isotopic signal of bulk organic matter, because of its

heterogeneous multicomponent nature, is controlled by the interplay between myriad parameters (e.g., marine versus terrigenous origin of the organic matter, grain size effects, C_3 versus C_4 plant origin of the terrigenous organic matter, CO_2 and growth rate effects on the marine organic matter) and cannot, in many cases, be related to a single environmental parameter. In contrast, most studies of past changes in sedimentary $\delta^{15}\text{N}$ rely on the analysis of bulk sediments, and the few studies using a compound-specific approach interpret differences between specific components, such as diatom frustule or foraminiferal shell-bound organic matter, or compounds (e.g., chlorophyll) and bulk sediment $\delta^{15}\text{N}$ almost exclusively in terms of different susceptibility to diagenetic modification [Altabet and Curry, 1989; Nakatsuka *et al.*, 1995; Sachs and Repeta, 1999; Sigman *et al.*, 1999].

[3] Sedimentary processes such as sediment focusing and winnowing, hydrodynamic sorting and lateral particle advection have in the past been shown to exert strong controls on the geochemical composition of sediments [Pedersen *et al.*, 1992; Goni *et al.*, 1997; Freudenthal *et al.*, 2001a; Ohkouchi *et al.*, 2002]. Motivated by the significant offset (up to >2‰) that has been reported between high-resolution last glacial bulk sediment $\delta^{15}\text{N}$ records from two nearby sites in the northern South China Sea (SCS) (sites 17940 [Kienast, 2000] and ODP 1144 [Higginson *et al.*, 2003]), this study explores the potential sedimentological origin of down-core variations in bulk sediment $\delta^{15}\text{N}$. Resolution of this significant discrepancy between two $\delta^{15}\text{N}$ records from closely adjacent sites is important in view of the major conclusion of Kienast [2000] that the record from core 17940 signified no major change in whole ocean nitrate

¹Department of Earth and Ocean Sciences, University of British Columbia, Vancouver, British Columbia, Canada.

²Department of Marine Chemistry and Geochemistry, Woods Hole Oceanographic Institution, Woods Hole, Massachusetts, USA.

³Now at Department of Oceanography, Dalhousie University, Halifax, Nova Scotia, Canada.

⁴School for Marine Science and Technology, University of Massachusetts at Dartmouth, New Bedford, Massachusetts, USA.

⁵Now at Forensic Alliance Ltd., Abingdon, UK.

⁶Institute of Applied Geosciences, National Taiwan Ocean University, Keelung, Taiwan.

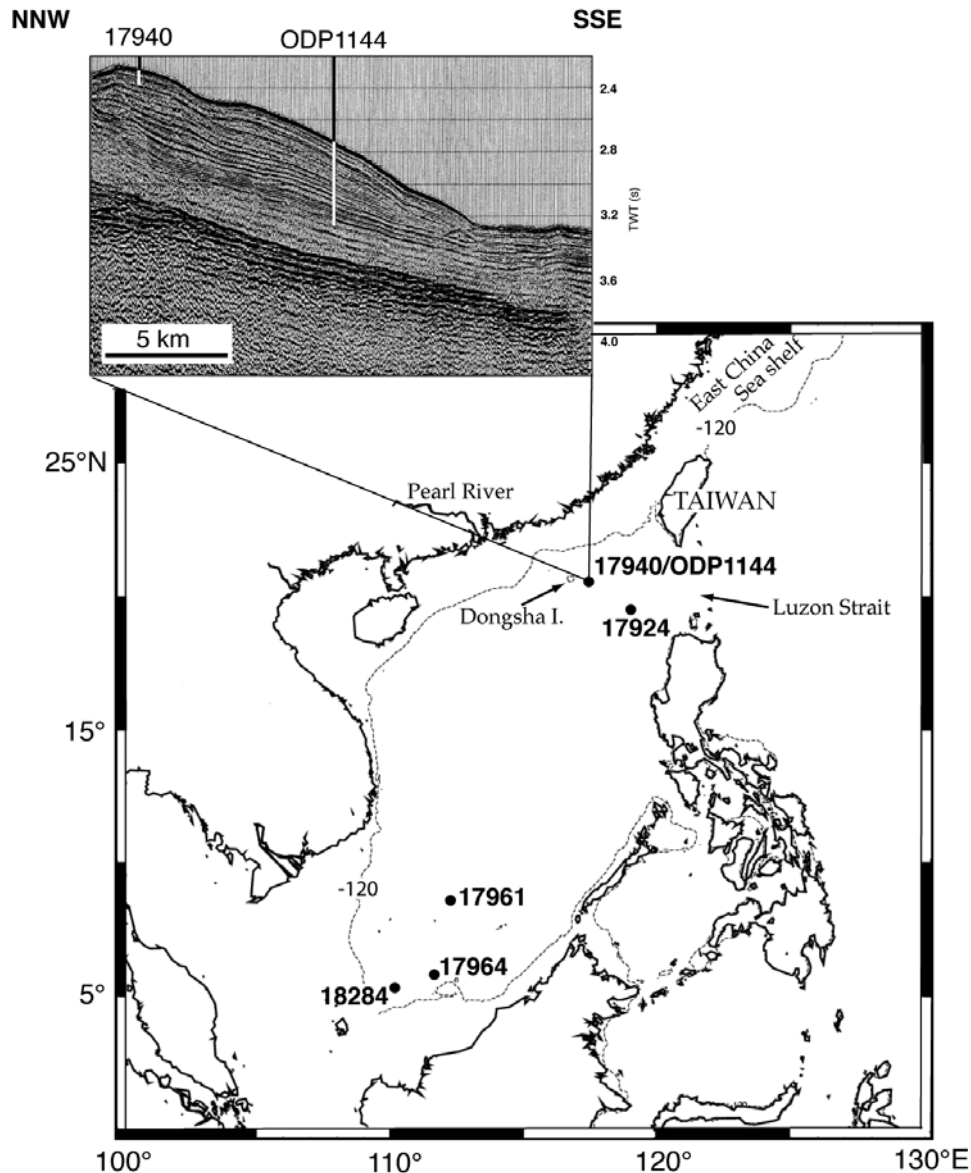


Figure 1. Map of the South China Sea and reflection seismic profile (taken from *Wang et al.* [2000]) showing the position of cores investigated in this study. The dashed -120 m isobath approximates the coastline during the glacial sea level lowstand.

inventory between the Holocene and the last glacial period and, on the other hand, that the supply of isotopically heavy nitrate to the SCS from the eastern tropical North Pacific is faithfully recorded at ODP Site 1144 [*Higginson et al.*, 2003].

[4] We first present new data (case studies) on some of the factors that could affect bulk sedimentary $\delta^{15}\text{N}$ records, namely the texture (grain-size distribution) of the sediments and the contribution of inorganic N (N_{inorg}) to the total N (TN) content of the sediments. In the second part of the paper, we discuss the complex interaction of these and other factors in an attempt to resolve the differences in the two bulk sedimentary $\delta^{15}\text{N}$ records from the northern

SCS, and place these findings in a (palaeo)oceanographic context.

2. Materials and Methods

2.1. Core Material

[5] Core 17940 ($20^{\circ}07.0\text{N}$, $117^{\circ}23.0\text{E}$) and ODP Site 1144 ($20^{\circ}3.18'\text{N}$, $117^{\circ}25.14'\text{E}$) are located less than 10 km apart on the continental slope of the northern SCS, in 1727 m and 2037 m water depth, respectively (Figure 1). The down-core bulk sedimentary $\delta^{15}\text{N}$ records have been published by *Kienast* [2000] and *Higginson et al.* [2003], respectively. The analytical methods used in those publica-

tions will not be repeated here. The age models of the two cores are adopted from Wang *et al.* [1999] (core 17940) and Bühring *et al.* [2004] (ODP Site 1144). Core MD97-2146 was recovered at the same site as core 17940. The age model of this core is based on seven radiocarbon dates and on matching its planktonic $\delta^{18}\text{O}$ record to that of core 17940 [Lin *et al.*, 2005]. Core 18284-3 is located at the shelf break in the southern SCS ($5^{\circ}32.5\text{N}$, $110^{\circ}32.4\text{E}$), at 226 m water depth [Steinke *et al.*, 2003], and cores 17924-3, 17961-2, and 17964-3 were recovered in the northeastern ($19^{\circ}24.7\text{N}$, $118^{\circ}50.9\text{E}$), southern central ($8^{\circ}30.4\text{N}$, $112^{\circ}19.9\text{E}$) and southern ($6^{\circ}9.5\text{N}$, $112^{\circ}12.8\text{E}$) SCS, respectively (see Figure 1 for core locations and Wang *et al.* [1999], Kienast [2000], and Kienast *et al.* [2001] for details and age models).

2.2. Analytical Methods

[6] Total nitrogen (percent TN) and total carbon (percent TC) of all samples reported here were measured on freeze-dried, ground bulk samples using a Carlo Erba NA1500 elemental analyzer, and organic carbon concentrations (percent TOC) were determined by subtracting inorganic carbon (analyzed coulometrically) from TC concentrations, following methods described by Calvert *et al.* [1993]. The analytical errors are $\pm 3.5\%$ for TN and $\pm 3\%$ for TOC analyses of bulk sediments, and up to $\pm 8\%$ and $\pm 5\%$, respectively, for small size-fractionated samples. Note that the TOC and TN values of core ODP 1144 determined for this study differ from the data published previously from the same core [Higginson *et al.*, 2003; Tamburini *et al.*, 2003]. This offset is most likely caused by the fact that TN and TOC concentrations reported in the latter two studies were determined using CHN analyzers coupled to mass spectrometers and from RockEval analyses, respectively. Both these analytical methods are generally deemed less precise for TN and TOC determinations since they are primarily designed to supply the mass spectrometer with an analyte, and to investigate the nature of TOC, respectively. Therefore, and for consistency with the down-core record of core 17940, we chose to reanalyze a low-resolution set of samples ($n = 24$) of core ODP 1144 for this study. Nitrogen isotope ratios were determined on freeze-dried, ground bulk samples using a Fisons NA1500 element analyzer coupled to a VG prism mass spectrometer in a continuous flow of helium. The $\delta^{15}\text{N}$ values are reported relative to air N_2 with an analytical precision of $\pm 0.2\text{‰}$ for bulk sediment samples, and $\pm 0.4\text{‰}$ for the (small) size-fractionated samples. The carbon isotopic composition of organic matter ($\delta^{13}\text{C}_{\text{org}}$) was measured on decalcified (10% HCl followed by oven drying without washing) samples using the instruments described above. The $\delta^{13}\text{C}_{\text{org}}$ data are reported relative to Peedee belemnite (PDB), with a precision of $\pm 0.1\text{‰}$ for bulk sediment samples, and $\pm 0.3\text{‰}$ for the size-fractionated samples. Major element (Si and Al) determinations were carried out following methods detailed by Calvert *et al.* [1985]. Briefly, 400 mg of sediment mixed with lithium tetraborate were fused at 1100°C and cast into glass beads, which were analyzed on a Philips 2400 wavelength-dispersive sequential automatic X-ray fluorescence spectrometer. Precisions of the analyses were $\pm 3\%$. Chlorin determinations were carried out following methods detailed

by Higginson *et al.* [2003]. Briefly, approximately 200 mg (dry weight) of freeze-dried and homogenized sediment were exhaustively extracted by ice cold sonication (15 min) and centrifugation (3000 rpm, 6 min) using 10% aqueous acetone (twice), followed by a single 100% acetone extraction. Extracts were combined and dried under N_2 . A methanolic solution of each extract was analyzed in duplicate by off-column HPLC employing a tunable Waters 470 scanning fluorescence detector ($\lambda_{\text{ex}} = 407\text{ nm}$, $\lambda_{\text{em}} = 662\text{ nm}$), eluting with fluorescence grade methanol. Total chlorin concentration was calculated by correlation of peak area with UV/visible light spectra absorbance measurements of standard extracts. Radiocarbon analyses of TOC were performed at the National Ocean Science AMS (NOSAMS) facility in Woods Hole following standard procedures [McNichol *et al.*, 1994]. The analytical errors range from ± 40 years for the youngest samples to ± 180 years for the oldest.

2.3. Grain Size Fractionation

[7] Sediment samples (approximately 8–10 g each) from core 18284-3 (see Figure 1 for core location) were separated into five different hydrodynamic size fractions by sedimentation in distilled water (repeated 15–20 times for each fraction) based on Stokes' law (<1 , 1–2, 2–5, 5–63 μm) and by wet sieving ($>63\text{ }\mu\text{m}$). In order to minimize coagulation and thus change in grain size composition, the sediment samples were not dried prior to grain size separation. Furthermore, because distilled water has been shown to be very effective in desorbing organic matter from mineral surfaces [Keil *et al.*, 1994], and in order to avoid as much as possible loss of organic matter during size fractionation, we dried the entire suspension of each size fraction at approximately 45°C in a laboratory oven rather than using centrifugation or ultrafiltration methods to retrieve the particles. As a result, $\delta^{15}\text{N}$ and $\delta^{13}\text{C}_{\text{org}}$ determinations on the bulk sediment agree within analytical errors with bulk $\delta^{15}\text{N}$ and $\delta^{13}\text{C}_{\text{org}}$ values calculated by adding the mass balanced isotopic composition of the different grain-size fractions (average $\Delta\delta^{15}\text{N}$ and $\Delta\delta^{13}\text{C}_{\text{org}} < 0.5\text{‰}$).

2.4. Bulk N Versus Inorganic N

[8] The isotopic composition of N_{inorg} in SCS sediments was determined on subsamples of three cores from the northeastern (core 17924-3), southern central (17961-2) and southern (17964-3) SCS treated with a KBr-KOH solution. This procedure removes in excess of 98% of the organic nitrogen (N_{org}) fraction by oxidation (see Silva and Bremner [1966] and Schubert and Calvert [2001] for details). The approach ignores any exchangeable N (in the form of ammonium), but previous studies have shown this form of N_{inorg} to be insignificant in similar sediments from the Atlantic (i.e., generally less than 1% of total N [de Lange, 1992; Freudenthal *et al.*, 2001b]).

3. Results and Discussion of the Case Studies

3.1. N Isotopic Composition of Grain-Size Fractions (Core 18284)

[9] In a seminal paper, Goni *et al.* [1997] provided compelling evidence that hydrodynamic sorting controls

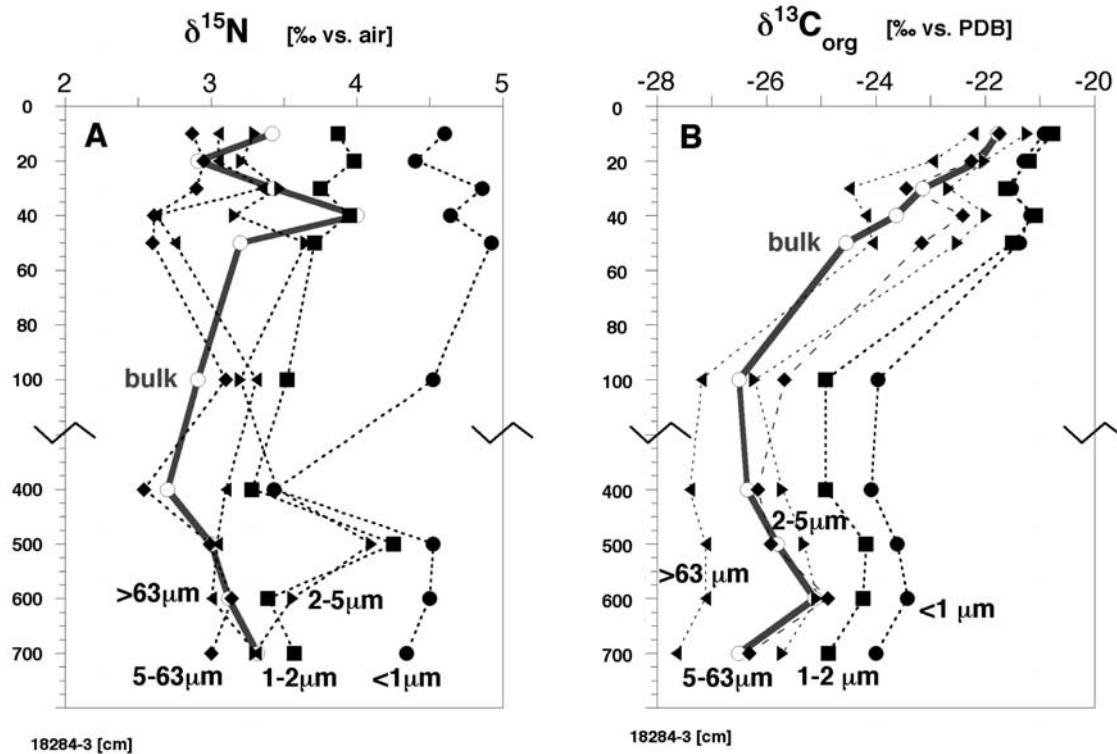


Figure 2. (a) Nitrogen and (b) carbon isotopic composition of bulk sediments (shaded line, open circles) and various grain-size fractions of core 18284 in the southern South China Sea. Uppermost samples (0–100 cm) correspond to the Holocene time interval, whereas sediments at 400–700 cm core depth were deposited ca. 15–17 (calendar years) kyr B.P. (see *Steinke et al.* [2003] for age model). Within the analytical error the isotopic composition of the bulk sediment corresponds to the weighted sum of the isotopic composition of all grain-size fractions (see text). Note change in depth scale at 150 cm core depth.

the carbon isotopic composition of bulk organic carbon in an onshore-offshore transect off the Mississippi River into the Gulf of Mexico. Thus isotopically heavy grassland soil organic matter closely associated with finer-grained detritus is transported farther into the Gulf than isotopically light terrigenous organic matter, which can lead to incorrect estimates of terrigenous organic matter contributions to marine sediments in this region. Similarly, *Bird and Pousai* [1997] demonstrated the grain-size dependence of $\delta^{13}\text{C}$ in the surface soils of a variety of Australian biomes, including forest, savannas and grasslands.

[10] We used down-core samples from core 18284-3 retrieved in the southern SCS to assess the potential effects of sediment grain size variations on bulk sedimentary $\delta^{15}\text{N}$ variability. This core was chosen because bulk sedimentary $\delta^{13}\text{C}_{\text{org}}$ analyses indicated a distinct (largest possible) difference between the organic matter in the uppermost core section compared to the lower part of the core. Thus bulk sedimentary $\delta^{13}\text{C}_{\text{org}}$ values of approximately -21‰ at the core top suggest a mostly marine origin of the organic matter, whereas bulk sedimentary $\delta^{13}\text{C}_{\text{org}}$ values of approximately -26‰ in the lower section of the core indicate the presence of significant amounts of isotopically light organic matter, presumably derived from terrestrial

C_3 plants. Both the nitrogen and carbon isotopic composition of the various grain-size fractions show a distinct trend of significantly heavier values associated with the finest fraction, and lightest values in the coarse fraction (Figure 2). The maximum difference between the finest grain-size fraction and the coarsest is larger in the $\delta^{13}\text{C}_{\text{org}}$ signal (up to 3.5‰) but also significant in the $\delta^{15}\text{N}$ signal (up to 2.5‰). Notably, the $\delta^{15}\text{N}$ signal of bulk sediments and the single fractions does not change significantly between upper and lower core sections, i.e., between time intervals dominated by marine and terrigenous organic material, respectively.

[11] Most of the sediment of this core is contained in the $>5\ \mu\text{m}$ size fraction (in excess of 80% on average), which explains why the bulk signal is weighted toward the isotopic composition of the coarse fractions. Even though this grain size distribution is coarser on average than in other cores from greater water depths in the SCS (e.g., 17924, 17940, 17961, 17964, and ODP 1144), there is still a significant and consistent spread of $\delta^{15}\text{N}$ and $\delta^{13}\text{C}_{\text{org}}$ values in the finest fractions only.

[12] The origin of this grain size dependence of the nitrogen isotopic composition is not fully understood, but on the basis of the paired $\delta^{13}\text{C}_{\text{org}}$ and $\delta^{15}\text{N}$ signatures we

offer three (not mutually exclusive) ways of explaining this trend. The increasing $\delta^{15}\text{N}$ and $\delta^{13}\text{C}_{\text{org}}$ values with decreasing grain size could be interpreted as a reflection of an increasing proportion of marine organic matter in the finer sediment fractions. The organic matter in the fraction $>63\ \mu\text{m}$, for example, is largely composed of vascular plant debris, which generally has lighter $\delta^{15}\text{N}$ and $\delta^{13}\text{C}_{\text{org}}$ values compared with marine organic matter [Peters *et al.*, 1978; Deines, 1980; Mariotti *et al.*, 1984]. Alternatively, the finest fraction could be dominated by heavily degraded, refractory terrigenous organic matter [Keil *et al.*, 1998], which has been shown to be isotopically enriched [Natelhoffer and Fry, 1988]. Finally, the distinct isotopic composition of the different grain size fractions could be related to likely variations in the contribution of N_{inorg} to TN (see discussion below) for different size fractions. However, this latter scenario is unlikely because we would expect the isotopically light N_{inorg} to be more prominent in the finest (clay size) grain-size fraction, which is opposite to the observed increase of $\delta^{15}\text{N}$ with decreasing grain size. Irrespective of the origin of the different isotopic compositions of various grain-size fractions, however, these results show that hydrodynamic sorting of particles could contribute to down-core variations in bulk sedimentary $\delta^{15}\text{N}$ and $\delta^{13}\text{C}_{\text{org}}$.

3.2. Isotopic Composition of Organic N Versus Bulk N (Cores 17924, 17961, and 17964)

[13] Several studies have highlighted the contribution of N_{inorg} to the TN pool of marine sediments, particularly as it relates to the origin and nature of sedimentary organic matter based on TOC/TN ratios. For example, Müller [1977], de Lange [1992] and Schubert and Calvert [2001] report that N_{inorg} constitutes up to 94% of TN in organic-poor sediments. This large contribution of N_{inorg} to TN in sediments can also be inferred from the widely observed nonzero intercept in plots of TOC versus TN [Calvert, 2004]. Thus, for example, intercepts of approximately 0.06% TN at 0% TOC in sediments from the Santa Barbara Basin [Emmer and Thunell, 2000] and the Congo fan [Holtvoeth *et al.*, 2003] imply that approximately 13–100% and 15–50% of the TN (ranging from approximately 0.05 to 0.45% and 0.12 to 0.4%, respectively) is inorganic (see also Figure 8) at these locations.

[14] Nitrogen isotope analyses in palaeoceanographic studies are generally performed on bulk sediment samples (thus including both the isotope signal of the organic and inorganic fraction), tacitly assuming that the $\delta^{15}\text{N}$ signal primarily reflects the nitrogen isotopic composition of the (marine) organic fraction. However, Schubert and Calvert [2001] and Freudenthal *et al.* [2001b] recently demonstrated that the organic and inorganic N in sediments from the Arctic Ocean and the subtropical eastern Atlantic, respectively, have distinctly different $\delta^{15}\text{N}$ signatures, with the $\delta^{15}\text{N}$ of N_{inorg} generally being significantly isotopically lighter. In both these settings, the percentage of N_{inorg} of TN is high enough, and the $\delta^{15}\text{N}$ composition of N_{inorg} and N_{org} different enough, to bias the $\delta^{15}\text{N}$ signal of N_{org} by up to 6‰ toward lighter values in the $\delta^{15}\text{N}$ of bulk sediments.

[15] The method employed in this study successfully removed almost all N_{org} , as is illustrated by comparing the

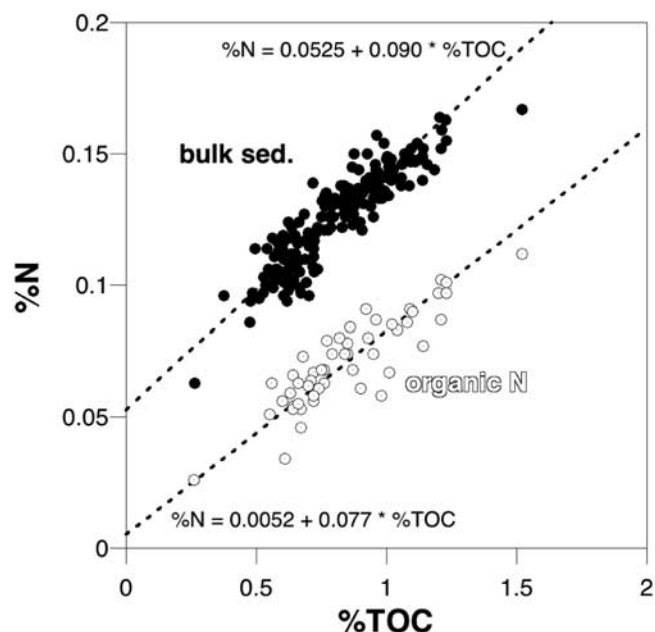


Figure 3. Relationship between nitrogen (%N) and organic carbon (%TOC) in bulk sediments (solid circles) and in the organic fraction (open circles) (operationally defined as the difference between bulk sediment and leftover after KOBBr treatment). Samples shown are from site 17924 in the northeastern South China Sea (see Kienast [2000] for details), exemplifying the success of the analytical approach used in this study to remove organic matter by oxidation of bulk sediment samples with KOBBr. Note that there is a significant (0.053%N) intercept on the N axis at 0% TOC for the bulk sediments and a negligible (0.005%N) intercept for the organic fraction. Dashed lines are geometric mean regression lines.

correlation of TOC versus TN with TOC versus N_{org} (calculated by subtracting N_{inorg} from TN) (Figure 3). Thus, whereas there is a significant nonzero intercept for TOC versus TN, this intercept is not significantly different from zero at the 95% confidence level in the TOC versus N_{org} correlation. Furthermore, the concentration of N_{inorg} determined following KOBBr-KOH treatment of samples agrees very well with the estimate of N_{inorg} based on the nonzero intercept of the regression of TOC on TN. Thus the intercept in Figure 3 suggests an N_{inorg} content of 35–62% on average for this set of samples, compared to 35–65% N_{inorg} based on TN analyses of KOBBr-oxidized samples.

[16] Isotopic analysis of this inorganic fraction reveals that N_{inorg} in the SCS has $\delta^{15}\text{N}$ values ranging from 3.1 to 4.8‰, similar to the average $\delta^{15}\text{N}$ value of 3.3‰ reported for bulk terrigenous organic matter in the SCS [Kienast, 2000] and also similar to $\delta^{15}\text{N}$ values of N_{inorg} found in the Arctic Ocean and the eastern subtropical Atlantic. The significant percentage of N_{inorg} and the distinct isotopic signature will therefore dampen any variability associated with N_{org} in the bulk $\delta^{15}\text{N}$ signal (Figure 4).

[17] In summary, our two case studies show that both variations in the grain size composition as well as the variable contribution of N_{inorg} to TN can significantly affect

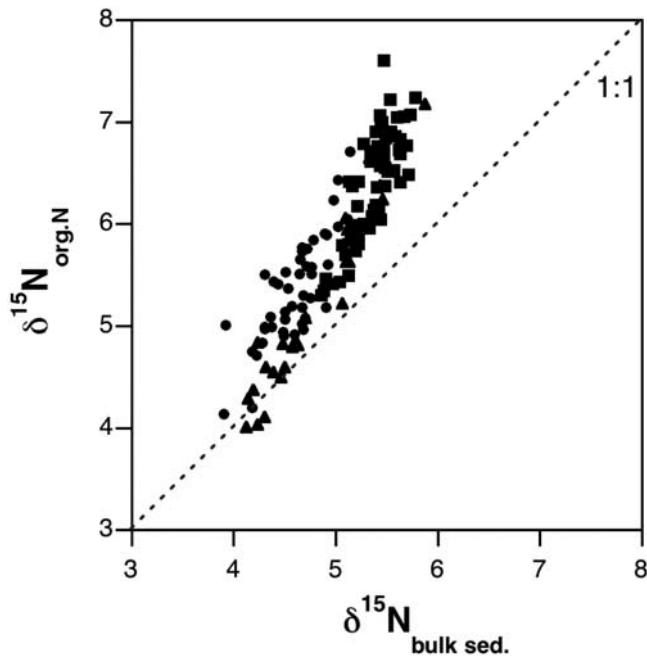


Figure 4. Relationship between the nitrogen isotopic compositions of bulk sediments ($\delta^{15}\text{N}_{\text{bulk sed.}}$) and organic nitrogen ($\delta^{15}\text{N}_{\text{org.N}}$) (calculated by mass balance from $\delta^{15}\text{N}_{\text{bulk sed.}}$, $\delta^{15}\text{N}_{\text{inorg.N}}$, and the concentrations of N_{inorg} and total nitrogen (TN) in the sediment sample) in the South China Sea. Samples are taken from three cores within the South China Sea, 17924 (circles), 17961 (squares), and 17964 (triangles). Note that the range of $\delta^{15}\text{N}$ values for the organic N only is larger than that for the bulk sediment because of the dampening effect of N_{inorg} . Dashed line is 1:1 relation.

any bulk sedimentary $\delta^{15}\text{N}$ record. With this in mind, the following sections of this paper will discuss these and other sedimentological parameters as potential causes for the significant difference between the $\delta^{15}\text{N}$ records from two closely adjacent cores in the northern SCS. We could not, unfortunately, carry out either the size fractionation or the KOBBr treatment on samples from cores 17940 or ODP 1144 because of limited sample availability. However, given the similarity in the main sedimentological parameters of the sites investigated in the case studies (see above) and sites 17940 and ODP 1144, we are confident that our extrapolation of the case studies to the sites in the northern SCS is justified. Thus all cores contain hemipelagic sediments, dominated by siliciclastic detritus, with low carbonate (<20%), low opal (<5%), low TOC (0.5–1.2%) and TN (0.08–0.16%) contents [Lin *et al.*, 1999, Kienast, 2000; Li and Wang, 2004; this study; M. Kienast, unpublished data, 2002].

4. Site 17940 Versus ODP Site 1144: A Discussion

4.1. Down-Core Records From ODP Site 1144 Versus 17940-2

[18] Sediment cores 17940 and ODP 1144 sampled undisturbed hemipelagic terrigenous silty clay, completely

homogenized by bioturbation [Sarnthein *et al.*, 1994; Shipboard Scientific Party, 2000]. During the last approximately 12 kyr, both site 17940 and ODP Hole 1144 show comparable sedimentation rates of approximately 50 cm/kyr. Below this interval, however, sedimentation rates at both sites differ significantly (Figure 5). Thus, whereas linear sedimentation rates at site 17940 are approximately 20 cm/kyr on average [Wang *et al.*, 1999] for the interval 12–40 ka, ODP Site 1144 shows significantly higher sedimentation rates of up to 195 cm/kyr during the same time interval [Bühning *et al.*, 2004]. Even though ODP Site 1144 intentionally sampled a sediment drift site [Wang *et al.*, 2000], which is expected to have higher sedimentation rates, it remains to be determined whether the higher sedimentation rates at ODP Site 1144 compared to site 17940 prior to the Holocene are due to sediment focusing at the former (or more intense focusing there compared to site 17940) or winnowing at site 1144, or any combination thereof. It is noted, for example, that Wang *et al.* [1999] infer sediment winnowing at site 17940 prior to ca. 12 ka based on siliciclastic grain size characteristics (originally calibrated for a sediment transect off NW Africa [Koopmann, 1981], for a challenge of this interpretation see Gerbich [2001]). On the other hand, Lüdmann *et al.* [2001] propose that the elevated position of the Dongsha Islands (see Figure 1) during the last glacial period could have restricted sediment supply to upper slope stations such as site 17940. Given the very close proximity (less than 10 km apart horizontally, and approximately 300 m in water depth) of the two core sites, however, any sedimentary process envisioned to explain the significant differences between

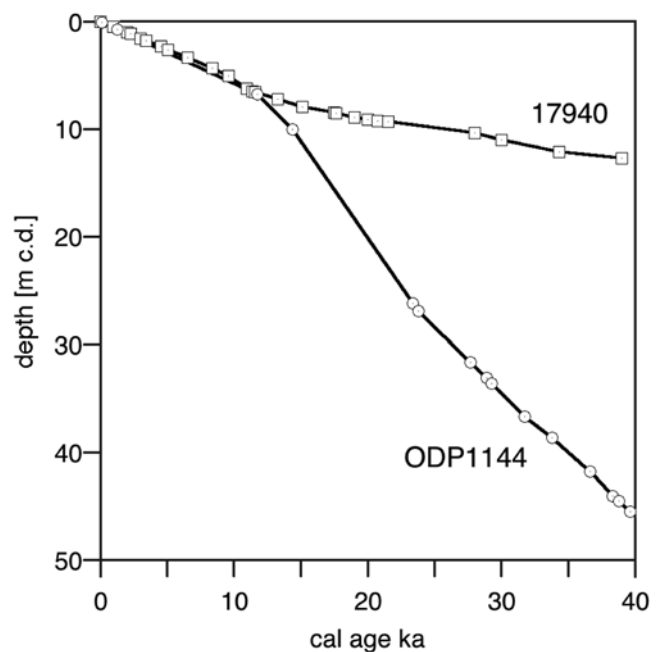


Figure 5. Age versus depth relationship for cores 17940 and ODP 1144. Age fix points are taken from Wang *et al.* [1999] and Bühning *et al.* [2004], respectively. Note the divergence in linear sedimentation rate between both sites prior to ca. 12 ka.

the sites must be able to accommodate such large gradients on rather small spatial scales (see further discussion below).

[19] The nitrogen isotope records spanning the last 40 kyr from cores 17940-2 and ODP 1144 are shown on their own timescales in Figure 6a. The main features of these records are the significantly lower degree of variability of core 17940-2 (minimum 3.85‰, maximum 5.57‰, mean $4.60 \pm 0.34\%$), with very little systematic variability on glacial-interglacial and shorter timescales, compared with ODP 1144 during the last 40 kyr (minimum 3.80‰, maximum 6.62‰, mean $5.36 \pm 0.57\%$). The greatest discrepancy between the two records is evident in core sections older than 15 ka, with ODP 1144 showing a major step-like change at 26 ka, and significant $\delta^{15}\text{N}$ variability on glacial-interglacial and millennial timescales. Five other down-core records from throughout the SCS [Kienast, 2000] and another from ODP Site 1143 in the southern central SCS [Tamburini et al., 2003] show a degree of variability comparable to or less than that shown by 17940-2. The ODP 1144 record therefore is unique in the SCS thus far.

[20] Given the proximity of core sites 17940 and ODP 1144 (see Figure 1) and the absence of any known oceanographic front in this region (both sites underlie the same nutrient regime and biogeographic zone), it is thus unlikely that the offset between the two records reflects a true gradient in surface ocean biochemistry or in the primary $\delta^{15}\text{N}$ signal. The $\delta^{15}\text{N}$ offset in the two records is not due to an analytical offset as shown by replicate analyses of ODP Site 1144 samples at UBC. These analyses yielded an average $\Delta\delta^{15}\text{N}$ of 0.07‰ ($n = 20$) and a maximal difference of 0.42‰ from the results presented by Higginson et al. [2003] (see Figure 6a), which is insignificant compared to the observed offset between the two records of up to $>2\%$. In addition, the lack of $\delta^{15}\text{N}$ variability at site 17940 is not caused by sampling artifacts or analytical or sample storage problems since we were able to reproduce a comparable record (albeit with significantly lower resolution) from core MD97-2146 (Figure 7), which was recovered at the same location as core 17940-2. Finally, the discrepancy between the $\delta^{15}\text{N}$ records cannot be the result of differing sedimentation rates or sampling intervals because (1) the records are clearly offset, particularly in the interval ca. 25–40 ka, and (2) sedimentation rates at both sites range between 15 and 195 cm/kyr throughout the records, rendering bioturbational dampening of the signal of this magnitude at one site compared to the other implausible [cf. Anderson, 2001]. Thus we must search for sedimentological origins of the $\delta^{15}\text{N}$ variability observed and the discrepancy between the two records.

4.2. Sedimentological Considerations

[21] The differing sedimentation rates at sites 17940 and ODP 1144 prior to ca. 12 ka also correspond to notable differences in the geochemical and textural composition of the sediments (Figure 6). Thus, whereas sediments at both sites show comparable concentrations of TOC, TN, and chlorins during the last 12 kyr, sediments prior to 12 ka contain significantly higher concentrations of these constituents at ODP Site 1144 compared to 17940 (Figures 6b–6d). Furthermore, sediments at both sites show distinctly

different Si/Al ratios (Figure 6e), which approximate grain size because of the negligible biogenic opal concentrations in both records [Li and Wang, 2004; Lin et al., 1999]. Thus sediments at ODP Site 1144 are finer-grained (lower Si/Al) than at site 17940 throughout the last 40 kyr, with most pronounced differences occurring prior to ca. 20 ka. As shown in Figure 2, the $\delta^{15}\text{N}$ signal of sediments in the southern SCS increases with decreasing particle size. Assuming that the same relationship also holds for sediment particles in the northern SCS, the higher proportion of finer-grained particles prior to ca. 20 ka at ODP Site 1144 is one sedimentological characteristic that could partly explain the higher $\delta^{15}\text{N}$ values there. On the other hand, the significant deglacial decrease in average grain size at both sites is not matched by an increase in $\delta^{15}\text{N}$. This could either suggest that grain size is not an overwhelming control on $\delta^{15}\text{N}$ variability in the northern SCS or that any grain-size-related deglacial increase in $\delta^{15}\text{N}$ is compensated by other, yet unexplained, effects.

[22] The second effect that could explain the differing $\delta^{15}\text{N}$ records at sites ODP 1144 and 17940 is related to the different nitrogen isotopic composition of organic versus inorganic N, as we have demonstrated, whereby smaller relative contributions of isotopically light N_{inorg} to TN would result in higher bulk $\delta^{15}\text{N}$ values (compare Figure 4). In the absence of N_{inorg} determinations from both cores, we approximate the contribution of N_{inorg} to TN from the relationship of TOC versus TN. Thus the TOC versus TN relationship for both down-core records shows a slightly larger intercept on the TN axis for ODP Site 1144 (0.038 ± 0.007 compared to 0.029 ± 0.006 for core 17940, Figure 8). However, because of the higher TN concentrations on average at ODP Site 1144 compared to 17940 (see Figures 6c and 8), the intercept on the TN axis is more significant at the latter site, suggesting that, by proportion, there are comparable amounts of N_{inorg} (20–32% in core 17940 and 23–34% in core ODP 1144) on average contributing to the $\delta^{15}\text{N}$ signal at sites 17940 and ODP 1144. Applying the same method to core sections older than 15 ka only, where the offset between the $\delta^{15}\text{N}$ records is most evident, yields slightly lower N_{inorg} contributions at site 17940 compared to ODP Site 1144 (15–23% and 23–29%, respectively). Thus, assuming $\delta^{15}\text{N}$ values of N_{inorg} within the range of values presented for the SCS (this study; see above) and the Arctic [Schubert and Calvert, 2001] and eastern subtropical Atlantic [Freudenthal et al., 2001b], respectively, the N_{inorg} contribution to TN should, in fact, lower glacial $\delta^{15}\text{N}$ values at ODP Site 1144 compared to site 17940. This effect is opposite to the observed offset between both records. Overall, however, the difference in N_{inorg} contribution to both down-core records is too small to cause any significant offset in the $\delta^{15}\text{N}$ records.

4.3. Sediment Transport and/or Reworking

[23] In addition to grain size effects and the variable contribution of N_{inorg} to TN discussed above, advection of organic and/or inorganic N with a different $\delta^{15}\text{N}$ signature is possible and even likely, as previously shown by [Freudenthal et al., 2001a] for a site off NW Africa. This assertion of an allochthonous origin of some or most of the organic and/or inorganic N, at least at ODP Site 1144 is

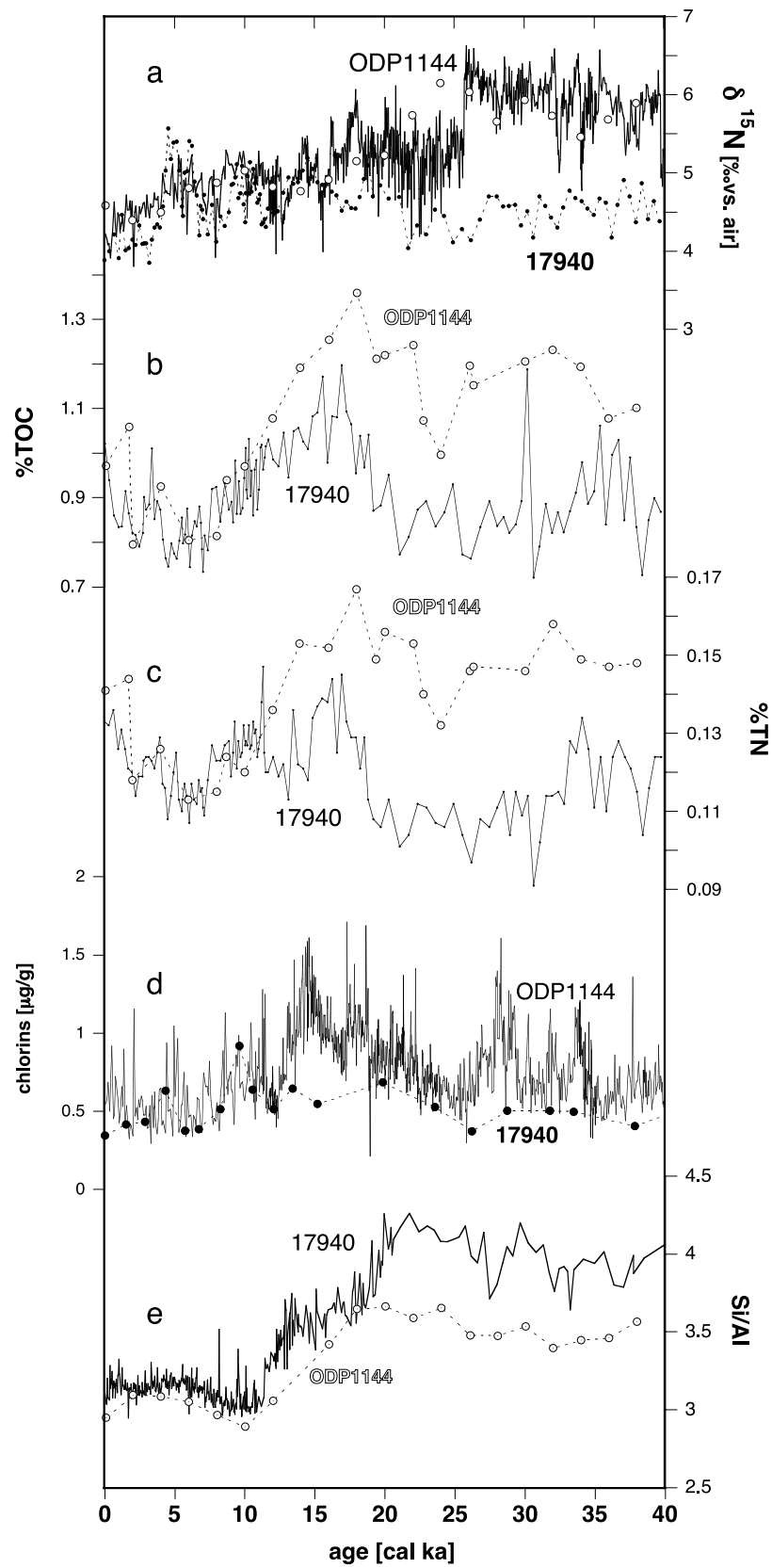


Figure 6

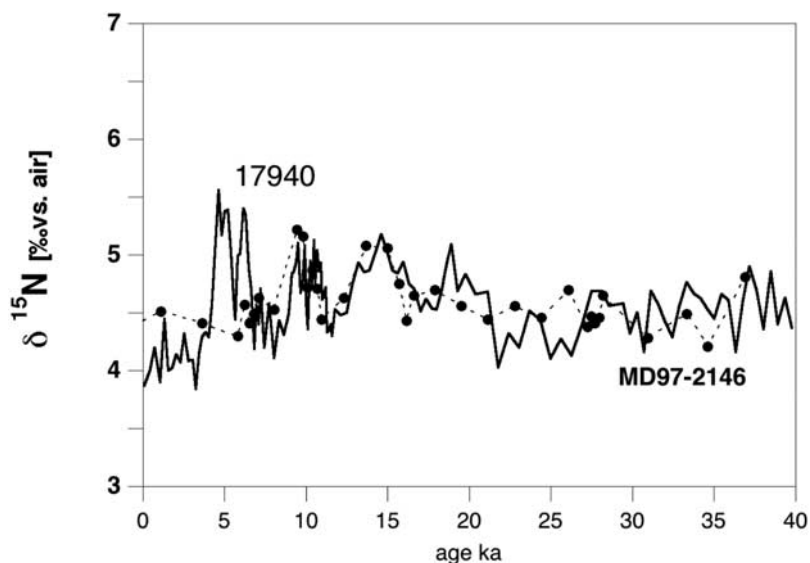


Figure 7. Comparison of down-core $\delta^{15}\text{N}$ records from sites 17940 (solid line) [Kienast, 2000] and MD97-2146 (dashed line) in the northern South China Sea on their independent timescales. Core MD97-2146 was recovered at the same position as core 17940.

corroborated by rare earth element analyses [Shao *et al.*, 2001] of the siliciclastic material. These measurements indicate that a significant part of the detrital material at this site originates from a continental island arc such as Taiwan, transported through the Penghu channel to the coring site in the northern SCS [Shao *et al.*, 2001], and is not representative of the vertical particle flux to the seafloor. An allochthonous origin of sedimentary components at ODP Site 1144 is further corroborated by seismic reflection profiles which show a geometry/morphology of the deposit and a surface and internal structure characteristic of sediment drift [see Wang *et al.*, 2000].

[24] In order to investigate this assertion further and to assess whether there are significant differences in the proportion of terrigenous to marine organic nitrogen between both sites, ^{14}C analyses of TOC were performed on sediments from sites 17940 and ODP 1144, based on the simplistic premise that autochthonously produced marine organic matter is younger than redeposited terrigenous (or marine) material. Thus, at both sites ^{14}C ages of TOC increase with increasing sediment age, and there is no significant difference in the age offset between foraminiferal and TOC ^{14}C ages between the glacial and interglacial sections of the records (Figure 9). The minor offset in ages of TOC at ODP Site 1144 compared to 17940 indicates that

comparable amounts of terrigenous organic carbon contribute to bulk organic matter at both sites, assuming that all terrigenous organic material is radiocarbon dead and all marine organic matter of modern age at the time of deposition. This insignificant difference in the admixture of terrigenous organic matter between the sites is also corroborated by the $\delta^{13}\text{C}_{\text{org}}$ values (ranging between -19 and -21 ‰ at both sites, not shown) that indicate the absence of significant amounts of terrigenous organic carbon derived from C_3 plants at both sites. The slightly older TOC at ODP Site 1144 compared to site 17940, however, is entirely consistent with the assertion of a larger proportion of redeposited marine organic matter at the former site. Both the variable offset between the $\delta^{15}\text{N}$ records at both sites in the northern SCS as well as the $\delta^{15}\text{N}$ variations during the last 40 kyr at ODP Site 1144 itself can thus be explained either as changes in the source region of the allochthonous N or as a reflection of glacial-interglacial variations in $\delta^{15}\text{N}$ in the source region itself or a combination of both. Given the lack of $\delta^{15}\text{N}$ records from potential source regions, however, it is not possible to further assess these scenarios. The only data set available to date is a compilation of the nitrogen isotopic composition of surface sediments from the East China Sea shelf. These sediments have $\delta^{15}\text{N}$ values between 4 and 5‰ on average [Kao *et al.*, 2003], indistin-

Figure 6. Comparison of the geochemical and textural composition of sediments at sites 17940 and ODP 1144 in the northern South China Sea on their independent timescales. (a) The $\delta^{15}\text{N}$ records from sites 17940 [Kienast, 2000] and ODP 1144 [Higginson *et al.*, 2003]. Open circles are replicate analyses of ODP 1144 samples (see text). Down-core records of (b) percent total organic carbon (%TOC), (c) percent total nitrogen (%TN), and (d) sedimentary chlorins (in $\mu\text{g/g}$ sediment) (the record at site ODP 1144 is taken from Higginson *et al.* [2003]). Note that the TOC and TN records of site ODP 1144 differ from records presented previously from the same core [Tamburini *et al.*, 2003; Higginson *et al.*, 2003] because of a different analytical approach (see section 2). (e) Down-core records of the Si/Al ratio for cores 17940 and ODP 1144. Lower Si/Al values approximate finer-grained sediment texture.

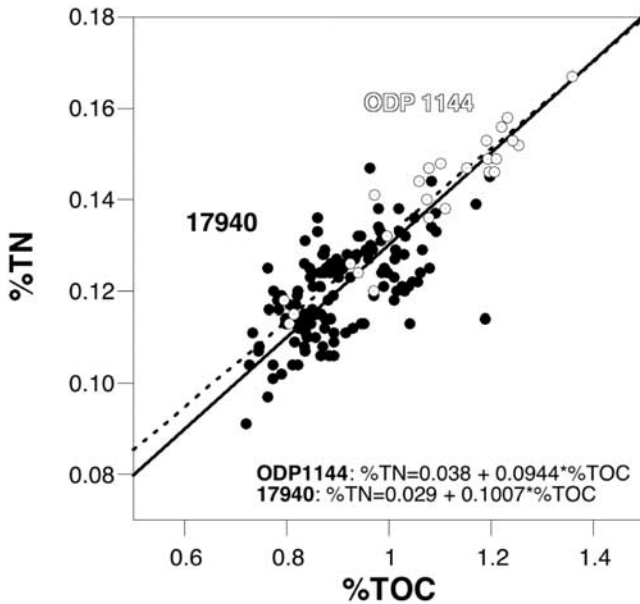


Figure 8. Relationship of total nitrogen (TN) versus organic carbon (TOC) in bulk sediments from sites 17940 (solid circles) and ODP 1144 (open circles) in the northern South China Sea. Note that the relationship of TOC versus TN records of ODP Site 1144 differs from data presented previously from the same core [Tamburini *et al.*, 2003] because of a different analytical approach (see section 2). Dashed and solid lines are geometric mean regression lines for ODP 1144 and 17940, respectively.

guishable from the $\delta^{15}\text{N}$ of surface sediments in the northern SCS [Kienast, 2000].

4.4. Oceanographic Considerations

[25] The sedimentological considerations discussed here call for circulation in the northern SCS that is capable of transporting siliciclastic material from Taiwan to the core site(s). In the literature on SCS oceanography, both surface and subsurface currents have been reported that could act as transport media. Thus the northeasterly winter-monsoon-driven surface current through the Taiwan Strait [Chern and Wang, 1992; Chen, 2003] could transport sediments from Taiwan to the northern SCS both in suspension as well as along the seabed. However, the glacial emergence of the shelf between southeastern China and Taiwan (see Figure 1) would restrict the presence of this current to interglacial sea level highstands, thereby undermining this scenario. Given the better agreement between both sedimentary records during the Holocene interglacial compared to the glacial section it is unlikely that surface currents exert an important control on the spatial variations of sedimentation in the northern SCS.

[26] The circulation of the deeper waters in the northern SCS is constrained by only few observations. Temperature/salinity, oxygen, and nutrient profiles across the Luzon Strait (sill depth approximately 2000 m, see Figure 1 for location) suggest a sandwiched structure: Pacific water enters the SCS in the upper (<700 m, North Pacific Tropical

Water and North Pacific Intermediate Water) and deeper (>1500 m, Pacific deep water) layers, and exits in between, corresponding to Antarctic Intermediate Water depths [Wyrki, 1961; Nitani, 1972; Shaw, 1991; Gong *et al.*, 1992; Chen and Wang, 1998; Chen *et al.*, 2001; Qu, 2002; Higginson *et al.*, 2003; Qu and Lindstrom, 2004]. The exact depths of these flows are debated [e.g., Chen and Wang, 1998; Qu, 2002], but Chen and Wang [1998] suggest that the water exiting the SCS eventually contributes to the Kuroshio Intermediate Water, and subsequently wells up onto the East China Sea shelf [Chen *et al.*, 2001]. Thus the layered water exchange through the Luzon Strait provides a possible link between the SCS subsurface and the global overturning circulation [Qu, 2002; Qu *et al.*, 2004]. According to one ocean model, this exchange (and, indeed, current patterns in the western Pacific in general) is also highly sensitive to the basin configuration and opening/closing of passages in the Indonesian archipelago [Metzger and Hurlburt, 1996], and thus to sea level variations.

[27] According to this picture of subsurface circulation in the northern SCS, both core sites today are affected by Pacific deep water entering through the Luzon Strait. However, both the similarity between the sedimentary

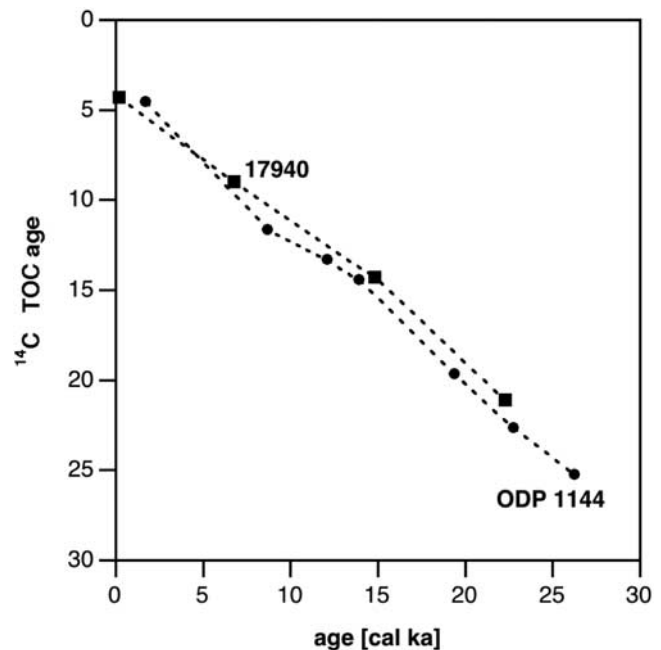


Figure 9. Comparison of radiocarbon ages of total organic carbon (^{14}C TOC) versus calendar age of the sediment at sites 17940 and ODP 1144. Note that, apart from the uppermost section, TOC is consistently older by 500–1000 years at ODP Site 1144. This offset is deemed significant because of both the low analytical error of the ^{14}C analyses (see text) and the high quality of the age models of both cores, which are not only based on a large number of ^{14}C ages [Wang *et al.*, 1999; Bühring *et al.*, 2004] but also on a close matching of both high-resolution planktonic foraminiferal $\delta^{18}\text{O}$ records to the Greenland Ice Sheet Project 2 oxygen isotope record [Wang *et al.*, 1999; Bühring *et al.*, 2004].

records of sites 17940 and ODP 1144 (this study) as well as the grain size distribution at site 17940 (in the sense of *Koopmann* [1981] as noted by *Wang et al.* [1999]) suggest that this current today does not significantly affect sedimentation at either site through sediment focusing or winnowing. It is noted, however, that *Bühring et al.* [2004] observed hiatuses during peak interglacials (MIS 15.3, 11.3, 9.1, lower 7.5, and 5.5) at ODP Site 1144, which they ascribe to erosional boundary current activity. Today, evidence of this erosional regime is restricted to water depths below ODP Site 1144 (2037 m), where PARASOUND echo characters (microfurrows) have been interpreted as evidence for strong bottom current activity [*Lehmann*, 1996]. Taken at face value, the winnowed (in the sense of *Wang et al.* [1999], see discussion above) glacial sediments at site 17940 and the high glacial sedimentation rates (sediment focusing) at ODP Site 1144 could be reconciled by invoking a deepening of the outflow of water from the SCS to depths around the core site of 17940, which could winnow sediments there, and a possible invigoration of the focusing activity of the current entering the SCS below. Alternatively, the inflow of Pacific deep water to the SCS would need to change such as to allow for focusing at the depth of ODP Site 1144 and winnowing above.

[28] The major step-like changes in the differences between the isotopic and geochemical composition at sites 17940 and ODP 1144 occur at ca. 25 ka and at ca. 12 ka. Both time intervals are not related to any known major event in the deglacial rise of sea level, paleoclimate in this region or the Pacific Ocean circulation. Thus the main forcing of deglacial variations in sediment provenance remains elusive. The step-like changes in bulk sedimentary $\delta^{15}\text{N}$, particularly at ca. 25 ka at ODP Site 1144, however, suggest that threshold behavior plays a crucial role in governing the sedimentary dynamics of the northern SCS. Furthermore, it is conceivable that the convergence of both records at 12 ka is related to the attainment of the Holocene sea level highstand [*Wang*, 1999].

5. Conclusions and Implications

[29] In an attempt to resolve the observed offset of up to $>2\%$ between the nitrogen isotopic composition of two closely adjacent down-core records in the northern SCS (17940 and ODP 1144), we examined several sedimentological parameters that can potentially affect the $\delta^{15}\text{N}$ signature of bulk sediments. Our results show that, in fact, the sediments from both sites from the northern SCS contain very similar amounts of N_{inorg} on average, and the finer-grained nature of glacial sediments at ODP Site 1144 compared to 17940 can only partly explain the higher glacial $\delta^{15}\text{N}$ signature of the former record. In addition,

there is no indication that the offset is related to variable admixture of terrigenous organic matter. Thus the most likely explanation for the observed offset between the two $\delta^{15}\text{N}$ records older than 15 ka is a different origin of both the organic and inorganic N at both sites. This assertion is not only supported by the distinctly different geochemical and textural composition of glacial sediments (this study) and the significantly different pollen abundances/assemblages [*Sun and Li*, 1999; *Sun et al.*, 2003] at both sites, but also by several lines of evidence that suggest a very substantial contribution of allochthonous sediments to ODP Site 1144 during the last glacial period. Thus rare earth element analyses of core ODP 1144 indicate the derivation of the siliciclastic material from an island arc setting in Taiwan, to the northeast of the core site [*Shao et al.*, 2001], seismic reflection profiles attest to the drift nature of the sediments at ODP Site 1144 [*Wang et al.*, 2000], and, finally, glacial sedimentation rates at ODP Site 1144 exceed regional sedimentation rates (including sedimentation rates at site 17940) by up to an order of magnitude.

[30] This study highlights the complex nature and origin of the sedimentary components in sediment drifts, expanding on the study by *Ohkouchi et al.* [2002], who, on the basis of compound-specific ^{14}C analyses, suggested a long-range transport of fine-grained sediment constituents (alkenones) to a drift deposit in the North Atlantic. Thus sediment redeposition such as at sediment drift sites can cause significant biases of down-core proxy records, not just by affecting sediment accumulation rates [*François et al.*, 2004] and potentially distorting the phase relation between different grain-size fractions [*Ohkouchi et al.*, 2002; *Mollenhauer et al.*, 2003, 2005] but also by importing sediments whose isotopic and geochemical signature is reflective of the vertical flux distal from the actual core site [*Freudenthal et al.*, 2001a]. Such sedimentological issues need to be fully understood prior to quantitative reconstruction and modeling [*Deutsch et al.*, 2004] of past changes in the marine nitrogen cycle. For example, records of past changes in the intensity of denitrification could be amplified/dampened by the sedimentological effects described here.

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- S. E. Calvert, Department of Earth and Ocean Sciences, University of British Columbia, Vancouver, B. C., Canada V6T 1Z4.
- M.-T. Chen, Institute of Applied Geosciences, National Taiwan Ocean University, Keelung 20224, Taiwan.
- T. I. Eglinton and G. Mollenhauer, Department of Marine Chemistry and Geochemistry, Woods Hole Oceanographic Institution, Woods Hole, MA 02543, USA.
- M. J. Higginson, Forensic Alliance Ltd., F5 Culham Science Park, Abingdon, Oxfordshire, OX14 3ED, UK.
- M. Kienast, Department of Oceanography, Dalhousie University, Halifax, N. S., Canada B3H 4J1. (markus.kienast@dal.ca)