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Isotopic composition and speciation of sedimentary nitrogen and carbon in the Okinawa Trough over the past 30 ka

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Abstract Total organic carbon to total nitrogen ratios (C/N) and their isotopic compositions ($\delta^{13}C_{TOC}$ and $\delta^{15}N_{TN}$) are oft-applied proxies to discern terrigenous from marine-sourced organics and to unravel ancient environmental information. In high depositional Asian marginal seas, the inclusion of N-bearing minerals in the bulk sediment dilutes or masks signals sought after in $\delta^{15}N$ and $\delta^{13}C$ analyses, thus leading to incorrect and even contradictory interpretations. We used KOH-KOBr to separate operationally defined total organic matter into oxidizable (labile) and residual fractions for content and isotope measurements. In a sediment core in the Okinawa Trough, significant amounts of carbon and nitrogen existed in the residual phase, in which the C/N ratio was ~9, resembling most documented sedimentary bulk C/N ratios in the China marginal seas. The residual carbon, which was included in operationally defined total organic carbon (TOC), displayed a $\delta^{13}C$ range (-22.7 to $-18.9‰$, mean $-20.7‰$) similar to the oft-used marine end-member. After removing the interference from the residual fraction, we found that the temporal pattern of $\delta^{13}C_{LOC}$ (LOC denotes labile organic carbon) was more variable. The residual nitrogen content was associated with illite, suggesting a terrestrial origin. Additionally, $\delta^{15}N$ in the residual fraction likely reflected the climatic controls (e.g., precipitation) on lithogenic source materials. Further studies are required to explore the controlling factors for carbon and nitrogen isotopic speciation and to retrieve the information locked in the residual fraction.

1. Introduction

The total organic carbon to total nitrogen (C/N) ratio and the isotopic compositions of total organic carbon ($\delta^{13}C_{TOC}$) and nitrogen ($\delta^{15}N_{TN}$) in terrestrial and ocean sediments are distinctive and thus, often used to infer past environmental changes and associated carbon and nitrogen dynamics [*Lamb et al.*, 2006]. Recent studies report that in certain conditions inorganic nitrogen (IN) may make up an important fraction in the total nitrogen (TN), and sometimes it has distinctive $\delta^{15}N$ values ($\delta^{15}N_{IN}$) [e.g., *Shigemitsu et al.*, 2009], which may potentially also bias the application of $\delta^{15}N_{TN}$ and C/N. For instance, reported fraction of IN in TN varies from 40% in the subtropical Atlantic sediments [*Freudenthal et al.*, 2001] to as high as 60% in the Arctic Ocean, Western Subarctic Pacific, and South China Sea sediments [*Schubert and Calvert*, 2001; *Kienast et al.*, 2005; *Shigemitsu et al.*, 2009]. Such high contribution of IN into the sedimentary total nitrogen may mislead the paleoceanographic interpretation for downcore C/N and bias $\delta^{15}N_{TN}$ values if $\delta^{15}N_{IN}$ holds distinctive values [*Freudenthal et al.*, 2001; *Schubert and Calvert*, 2001; *Shigemitsu et al.*, 2009]. Black carbon and/or graphitic black carbon, which cannot be removed from the operationally defined TOC, are widely distributed in the marginal seas [*Dickens et al.*, 2004]. The western Pacific marginal seas receive large amounts of terrestrial input via fluvial and even aeolian dust transported from continental Asia to create high temporal resolution paleoenvironmental archives. Inevitably, the bulk sediment matrix in rapid depositional environments may contain significant portions of nonlabile carbon and mineral-associated IN. Thus, the issue of speciation, including relative proportions and their isotopic compositions, is potentially important, particularly in environments with low organic content due to high mineral dilution.

The Okinawa Trough off the East China Sea, through which the Kuroshio Current flows, receives significant sediment inputs from various sources and seasonal monsoon forcing. Nevertheless, an upward decreasing trend in the C/N ratio is documented basinwide in several sediment cores taken from the south to the north of the Okinawa Trough [*Ujiié et al.*, 2001; *Kao et al.*, 2006]. Based on the concomitantly decreasing lignin phenol,
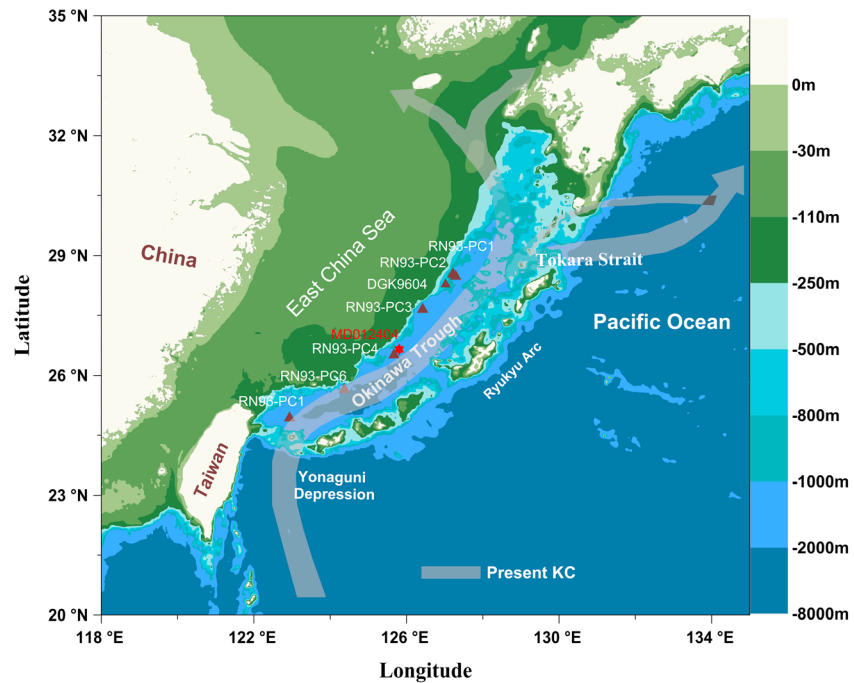
Figure 1. Map of the East China Sea and core location for IMAGES MD012404 (red star). Brown triangles stand for RN93-PC1, RN93-PC2, RN93-PC3, RN93-PC4, RN93-PC6, RN96-PC1 [from *Ujiié et al.*, 2001], and DGK9604 [from *Yu et al.*, 2009]. The flow path of the present Kuroshio Current (grey) is indicated.

the decreasing C/N ratio is attributed to progressively lower contributions of terrestrial organics induced by sea level rise and coastline retreat [*Ujiié et al.*, 2001]. However, enhanced offshore transport of materials during deglacial transgression may have opposed the reduction of terrestrial input [*Oguri et al.*, 2000; *Zhang et al.*, 2009]. Moreover, $^{13}C_{TOC}$ shifts toward terrestrial when the sea level is rising [*Kao et al.*, 2008a]. The organic signals were diluted by riverine input of clastic minerals along with the changing of environmental complexity, which seems to impede the successful application of these popular proxies in this region. Conflicts among records need to be reconciled.

The geological $\delta^{15}N$ data from the western Pacific is crucial to our understanding of whether the reactive nitrogen inventory has changed in the Pacific during glacial and interglacial stages [*Kienast*, 2000; *Deutsch et al.*, 2004; *Kao et al.*, 2008b]. Although sedimentary bulk $\delta^{15}N$, both in middle and south Okinawa cores, mimics the global temporal pattern [*Kao et al.*, 2008b], the content and $\delta^{15}N$ values of IN inherited in bulk sediment remains unclear. Clay mineral assemblages and the chemical weathering index in various sediment cores in the Okinawa Trough suggest a shift in source regime at different climate states in the last glacial cycle [*Diekmann et al.*, 2008; *Kao et al.*, 2008a; *Dou et al.*, 2010]. This is due to changes in circulation pattern and relative sediment supply from various sediment provenances. Since IN is mainly clay fixed during soil formation and less altered in the marine environment during transport or after deposition [*Schubert and Calvert*, 2001], we hypothesized that useful information about climate and sediment provenances, clay minerals, in particular, could be retrieved from $\delta^{15}N_{IN}$.

In this study, we measured the contents of C and N and their isotopic compositions separately for both organic and residual fractions in operationally defined bulk organic matter (decarbonated sediment) in core MD012404 in the Okinawa Trough. The speciation effect on the applicability of C/N was reexamined. The origin of $\delta^{15}N_{IN}$ and its potential application will be discussed. This is the first paper elaborating the relations among C/N, $\delta^{15}N$, and $\delta^{13}C$ in terms of speciation over 30 ka with multiple climate events and sea level change.

2. Materials and Methods

The studied giant piston core, IMAGES-MD012404 (total length 43 m), was recovered at 125.81°E, 26.65°N (Figure 1) at a water depth of 1397 m on the R/V *Marion Dufresne* during the cruise IMAGES VII, WEPAMA [*Bassinot et al.*, 2002]. The entire sediment core was sliced at 1 cm thick intervals immediately during the cruise.

MD012404 was retrieved from a small topographic low at the western edge of the Okinawa Trough, which is an ideal place for trapping downward settling biogenic particles in the water column, as well as suspended sediments transported from the East China Sea shelf (see Figure 1). Sediments in MD012404 are composed mainly of nearly homogenous nannofossil ooze or diatom-bearing nannofossil ooze, and no turbidites or significant tephra layers are observed [*Chang et al.*, 2005]. The accelerator mass spectrometry ^{14}C measurements were made using 20 mg of the planktonic foraminifers *Globigerinoides ruber* and *G. sacculifer* ($>$250 µm) at the Micro Analysis Laboratory, Tandem Accelerator, University of Tokyo. A detailed age model is reported in *Chang et al.* [2009] and *Kao et al.* [2008a].

To obtain δ^{13}C and δ^{15}N in different operationally defined fractions ~1 g freeze-dried sediment samples were pretreated as below. The weight of freeze-dried sample was recorded before and after each individual step of the wet chemical pretreatments so as to estimate the weight fraction. First, sediment samples were acidified with 1 N HCl to remove carbonate [*Kao et al.*, 2003]. After elimination of carbonate, the residual part of carbon is considered as TOC and nitrogen is defined as the decarbonated fraction (DCN); and their isotopic compositions are δ^{13}C$_{TOC}$ and δ^{15}N$_{DCN}$. An aliquot of the remaining acidified sediment was further treated with KOBr-KOH to remove any organic fraction of nitrogen (ON) [*Schubert and Calvert*, 2001; *Kienast et al.*, 2005] and labile organic carbon (LOC) [*Freudenthal et al.*, 2001]. According to a previous study, KOBr-KOH can eliminate ~98% of organic nitrogen [*Silva and Bremner*, 1966]. Thus, the carbon and nitrogen in the last residual portion were defined as residual carbon (RC, δ^{13}C$_{RC}$) and IN (δ^{15}N$_{IN}$).

All pretreated sediment samples were analyzed using a Carlo-Erba EA 2100 elemental analyzer coupled with a Thermo Finnigan Deltaplus Advantage isotope ratio mass spectrometer for their carbon and nitrogen contents and isotopic compositions. The precisions of carbon and nitrogen content measurements were better than 3% within the range of detection. Carbon and nitrogen isotopic compositions are presented in the standard notation with respect to Pee Dee Belemnite (PDB) carbon and atmospheric dinitrogen, respectively. U.S. Geological Survey standard 40, which has a certified δ^{13}C value of -26.24‰, acetanilide (Merck) with a δ^{13}C value of -29.76‰, and a δ^{15}N value of -1.52‰ were used as working standards. The reproducibility of both carbon and nitrogen isotopic measurements were better than 0.2‰.

In the entire pretreatment process, there were two leachable fractions, i.e., 1 N HCl leachable and KOBr-KOH leachable. The amount of exchangeable nitrogen in the total nitrogen is reported to be $<$5% elsewhere [e.g., *Müller*, 1977; *Schubert and Calvert*, 2001; *Kienast et al.*, 2005]. Based on the similarity of nitrogen isotopic compositions of bulk total and acidified sediment measured for this core [*Kao et al.*, 2008b], we suggested that the 1 N HCl leachable fraction was ignorable and will not be discussed in this paper. The second leachable fraction was KOBr-KOH leachable. The contents and isotopic compositions (δ^{15}N$_{ON}$, δ^{13}C$_{LOC}$) of this fraction could be derived using mass balance as shown in the following equations:

$$ON = DCN - N \tag{1}$$

$$\delta^{15}N_{ON} = \left(\delta^{15}N_{DCN} \times DCN - \delta^{15}N_{IN} \times IN\right)/ON \tag{2}$$

$$LOC = TOC - RC \tag{3}$$

$$\delta^{13}C_{LOC} = \left(\delta^{13}C_{TOC} \times TOC - \delta^{13}C_{RC} \times RC\right)/LOC \tag{4}$$

The error for derived ON and LOC is ±6%. Meanwhile, the propagated error through isotope mass balance calculation for δ^{13}C$_{LOC}$ and δ^{15}N$_{ON}$ are ±0.50‰ and ±0.49‰, respectively.

Note that the pretreatment procedure described above did not allow us to identify the RC as inorganic or organic; however, the residual fraction was included in TOC although this fraction might have been inorganic. Nevertheless, we still applied "TOC" since TOC is the most frequently used term, although our results revealed that the noncarbonate residual fraction was not small at all. The C/N ratio we used throughout this paper is the weight ratio.

A similar pretreatment procedure was applied to a sediment core (SK-177; 0–35 ka) taken from the Arabian Sea, where the river influence is insignificant. Core SK-177 holds low sedimentation rates and around 5–10 times higher organic carbon contents (3–6%) [see *Kao et al.*, 2015] relative to ours. We found the fraction of RC occupied 2.6 to 9.5% of TOC, with the mean value of 4.5% for the entire core (unpublished data, not shown), which was much lower than what we observed in this study. Such a low fraction of RC suggested that our KOBr-KOH pretreatment effectively removed not only organic nitrogen but also LOC buried in marine sediments.
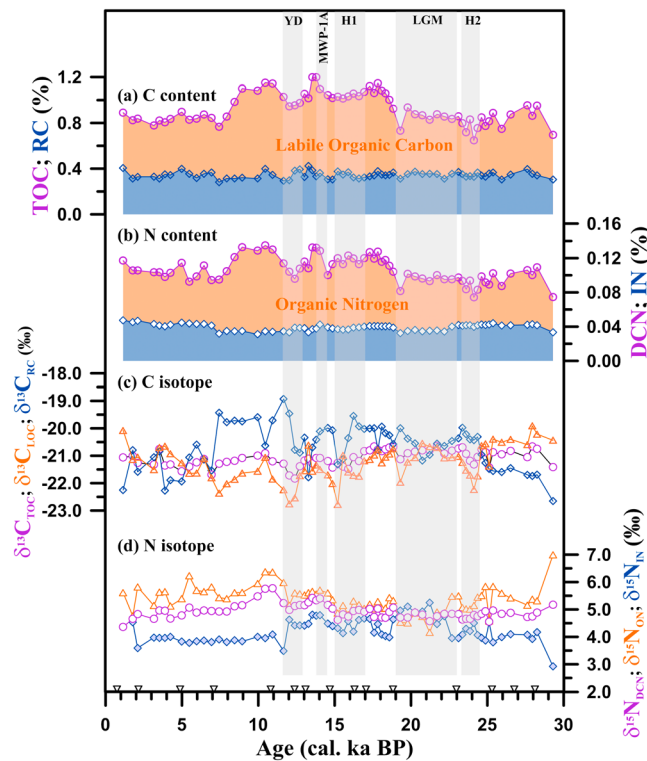
Figure 2. Temporal variations of (a) total organic carbon (TOC, purple open circles), KOH-KOBr-resistant residual carbon (RC, blue open diamonds), and labile organic carbon (LOC, shaded orange); (b) decarbonate nitrogen (DCN, purple open circles), inorganic nitrogen (IN, blue open diamonds), and organic nitrogen (ON, shaded orange); (c) isotopic composition of carbon speciation ($\delta^{13}C_{TOC}$, purple open circles; $\delta^{13}C_{LOC}$, orange open triangles; and $\delta^{13}C_{RC}$, blue open diamonds); and (d) isotopic composition of nitrogen speciation ($\delta^{15}C_{DCN}$, purple open circles; $\delta^{15}N_{ON}$, orange open triangles; and $\delta^{15}N_{IN}$, blue closed diamonds). The inverse triangles standing on the x axis indicate the dating points (taken from *Chang et al.* [2009] and *Kao et al.* [2008a]). Vertical grey bars indicate the period Younger Dryas (YD), Melt Water Pulse-1A Event (MWP-1A), Heinrich Event 1 (H1), Last Glacial Maximum (LGM), and Heinrich Event 2 (H2).

3. Results

We present the contents and isotopic compositions of different fractions of carbon and nitrogen in Figure 2. TOC ranged from 0.64 to 1.20%, with a mean value of 0.93%. The TOC values were lower and relatively constant in periods of 30–19 ka (0.65 to 0.95%, mean 0.83%) and 11–0 ka (0.77 to 1.15%, mean 0.90%), while higher values appeared during 19–11 ka (0.73 to 1.20, mean 1.04%). The contents of RC, by contrast, were relatively stable, varying in a narrow range (0.28 to 0.42%, mean 0.34%) throughout the past 30 ka regardless of significant sea level change. Unlike RC, the LOC accounted for ~60% of TOC revealing a more variable range (0.32–0.87%, mean 0.58%) in content and, obviously, governing the temporal pattern of TOC.

The temporal variation of DCN mimicked that of TOC but with much lower contents (DCN 0.07 to 0.13% mean 0.11%). Similar to RC, the IN content narrowly varied from 0.03 to 0.05%; however, such contents were higher than the reported data in Luochuan loess (0.012–0.02% [*Rao et al.* 2004]), and in subarctic ocean sediments (0.01–.03% [*Shigemitsu et al.* 2009]). The content of ON ranged from 0.03 to 0.10% with a mean value of 0.07%.

Temporal patterns of TOC, LOC, DCN, and ON were similar, showing lower values in glacial and Holocene periods and higher values in the deglacial period. Note that the LOC and ON contents were relatively low during cold events, e.g., the Younger Dryas (YD), Heinrich 1 (H1), and Heinrich 2 events (H2), when compared with nearby periods.

The $\delta^{13}C_{TOC}$ values fluctuated in a narrower range from −21.8 to −20.6‰, with a mean of 21.1‰ (Figure 2c). Higher values (−21.4 to −20.6‰, mean −20.9‰) appeared during 30 ka to 19 ka and then dropped gradually from −20.5‰ at 19 ka to −21.9‰ at 11 ka. During the Holocene period, lower values (−21.7 to −20.8‰ mean −21.2‰) were observed. Such negative $\delta^{13}C_{TOC}$ transition toward the Holocene might reflect an enhancement of terrestrial-sourced organics. However, such inference was inconsistent with that derived by TOC/DCN (see below) as mentioned above.

Although $\delta^{13}C_{TOC}$ varied in a small range, a decrease of ~0.5‰ from glacial to Holocene was observed. Such an isotopic shift is observed in other IMAGES cores such as MD012403 [*Kao et al., 2008a*] and various cores in the South China Sea [*Kienast et al., 2001*]. It is noteworthy that several negative $\delta^{13}C_{TOC}$ excursions, although small in magnitude, appeared during YD, H1, and H2 events similar to these drops of LOC and ON contents. Meanwhile, $\delta^{13}C_{RC}$ ranged from −22.3 to −18.9‰ with higher values when compared with $\delta^{13}C_{TOC}$ in almost all periods except 25–30 ka, 3–5 ka, and the present day. Meanwhile, $\delta^{13}C_{RC}$ gradually increased (−23.0 to −19.5‰) from 30 ka to 16 ka. Most high $\delta^{13}C_{RC}$ values appeared during YD and the early Holocene; meanwhile, a decreasing pattern could be seen since the Holocene toward the present (−19.0 to −22.5‰).

Compared with the $\delta^{13}C_{TOC}$, the $\delta^{13}C_{LOC}$ was similar in its temporal pattern but larger in amplitude (-20.3 to -22.7‰, mean -21.3‰). Again, these low values of $\delta^{13}C_{LOC}$ appeared in cold events. Two almost identical minimum $\delta^{13}C_{LOC}$ values appeared at YD and H1. In contrast to relatively constant $\delta^{13}C_{TOC}$ in the Holocene, $\delta^{13}C_{LOC}$ increased gradually from the YD (-22.7‰) to the present (-20.0‰), and the present day had almost the highest $\delta^{13}C_{LOC}$ value over the entire 30 ka. In general, $\delta^{13}C_{LOC}$ displayed an opposite pattern when compared with $\delta^{13}C_{RC}$.

Figure 2d shows the same $\delta^{15}N_{DCN}$ values for core MD012404, which are reported by *Kao et al.* [2008b]. Although $\delta^{15}N_{DCN}$ variability was small (4.3 to 5.6‰), higher $\delta^{15}N_{DCN}$ values were found during the deglacial period (from 4.6 to 5.7‰) and a decreasing pattern from 5.7 to 4.2‰ could be seen from the Holocene toward the present. Such a temporal pattern resembled those reported for cores in the Eastern Tropical Pacific Ocean and was almost identical to the global mean pattern for the last deglaciation [*Galbraith et al.*, 2013].

Except for a few points, $\delta^{15}N_{ON}$ exhibited a similar temporal pattern of $\delta^{15}N_{DCN}$. Almost all $\delta^{15}N_{ON}$ values were higher than $\delta^{15}N_{DCN}$ values with an offset of ~0.6‰ and the positive offset amplified during the Holocene (~1.1‰). It is noteworthy that $\delta^{15}N_{IN}$ exhibited consistently lower values revealing a different temporal pattern when compared with $\delta^{15}N_{DCN}$ and $\delta^{15}N_{ON}$. Meanwhile, the values of $\delta^{15}N_{IN}$ remained low and relatively stable (3.9‰) during the entire Holocene period regardless of changes in the $\delta^{15}N_{DCN}$ and $\delta^{15}N_{ON}$ records.

4. Discussion

4.1. Scatterplot of N Content Against C Content

A sedimentary organic C-N scatterplot is widely used to judge the constant background of IN in a depositional environment [e.g., *Schubert and Calvert*, 2001; *Kienast et al.*, 2005]. The amount of IN can be derived using the linear regression of N content against C content. The regression intercept on the y axis reflects background IN, which reflects any nitrogen unassociated with carbon. Similarly, the intercept on the x axis indicates the content of background carbon not related to nitrogen.

As shown in Figure 3, the intercept of TOC-DCN was near zero (0.013 ± 0.005%; orange regression line), which suggested that the IN was not influential and TOC/DCN was a reliable proxy. However, as revealed by our measurements (Figure 2b) the residual IN contents remained relatively constant but 3 times higher (~0.048 ± 0.004%) than the intercept derived using regression. This residual IN occupied ~38% of DCN, which obviously will affect the application of TOC-DCN to interpreting organic sources.

One possibility to induce this inconsistency is the existence of a significant amount of organic nitrogen that is resistant to KOH-KOBr oxidation, i.e., the oxidation efficiency is not 100%. The poor correlation coefficient between opal and ON ($r = 0.02$, $n = 67$, $p = 0.85$, $n = 67$; not shown) rejects the possibility of organics' opal protection during KOBr-KOH oxidation. Moreover, if this is the case, residual IN may share a similar isotopic composition. However, the negative correlation ($r = -0.69$, $n = 67$, $P < 0.0001$) between $\delta^{15}N_{IN}$ and $\delta^{15}N_{ON}$ (Figure 4) suggests an incomplete oxidation unlikely.

By eliminating IN, we obtained the TOC-ON scatterplot (blue triangles in Figure 3), which revealed an intercept of 0.31 on the x axis when the nitrogen content was zero. This intercept was almost the same as the observed RC content (0.34 ± 0.03%, 37% of TOC), which indicated that a significant fraction of carbon was not associated with nitrogen. In fact, in a previous study, when NaClO is applied to remove organic carbon among a variety of samples including marine sediment from Pensacola Bay, Bayou Grande, and Bayou Chico [*Simpson and Hatcher*, 2004], they determined the black carbon in the residual fraction using nuclear magnetic resonance. Since the chemical property of NaClO ($E^0 = 0.84$ V) is similar to KOBr ($E^0 = 0.76$ V), we believed that the RC was mainly composed of black carbon and some lithogenic kerogen.

Middelburg et al. [1999] conclude that black carbon accounts for around 15–30% of TOC in marine sediments from shallow estuary to abyssal plain (Atlantic Ocean, Black Sea, North Sea, Mediterranean Sea, and Madeira Abyssal Plain). As mentioned earlier, KOH-KOBr digested 95% of the organics preserved in sediment core SK-177 from the Arabian Sea. Such high digestion efficiency indicated not only the inertness of RC as defined with the KOBr method but also the regional differences in the composition of sedimentary TOC.
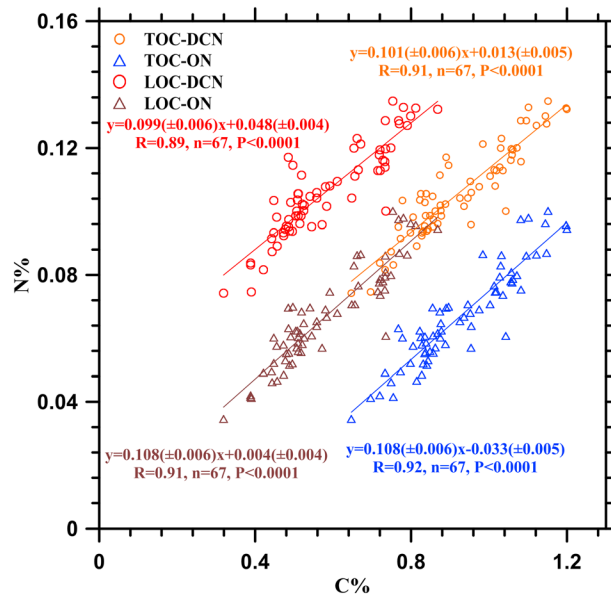
Figure 3. The scatterplot of N% against C%. Orange circles represent TOC versus DCN, blue triangles TOC versus ON, red circles LOC versus DCN, and brown triangles LOC versus ON.

Middelburg et al. [1999] also find that the contribution of black carbon increases dramatically from 25 to 47% as the TOC decreases (when the content is <1%). On the East China Sea shelf, where the TOC% is generally <1% [*Kao et al.*, 2003], black carbon contents occupy 11–55% of the TOC [*Huang et al.*, 2012; *Li et al.*, 2012]. In addition to black carbon, a previous study in the southern Okinawa Trough indicates that fossil organic carbon (lithogenic kerogen) from Taiwan occupies 29 to 63% of the sedimentary TOC [*Kao et al.*, 2008a, 2008b; *Kao et al.*, 2014]. The RC contents were high in our core (28–51%) in the middle Okinawa Trough, but still fell within the range of these reports for black carbon or fossil organic carbon in the Asian region. In fact, based on the ^{14}C age differences between sedimentary organic and black carbon, *Masiello and Druffel* [1998] conclude that widespread sedimentary black carbon must have been stored in an intermediate pool, most likely oceanic-dissolved organic carbon. Although the origin and composition of RC defined using the KOBr method remain unclear, such a high fraction of RC in the TOC definitely interfered with the usage of C/N and $^{13}C_{TOC}$ when researchers attempted to resolve the sources of recent organics and contemporary organic carbon down the core. Further studies are needed to characterize the chemical composition of RC.

TOC/ON instead of TOC/DCN is commonly used to trace the sources of organics in various environments where the IN content is significant [e.g., *Kienast et al.*, 2005; *Schubert and Calvert*, 2001; *Won et al.*, 2007]. In our case, the relatively constant RC may have canceled out the apparent IN effect, as the regression intercept displayed (orange line in Figure 3). By eliminating only RC, we could see a clear regression intercept of 0.048 in the LOC-DCN regression plot (red circles and regression line in Figure 3). This intercept was identical to the content of residual nitrogen that we measured. Once we excluded both RC and IN, the intercept of the LOC-ON regression plot returned to its origin (brown triangles in Figure 3). The above practices illustrated that the RC in operationally defined TOC concealed the existence of IN and, therefore, hampered the applicability of the TOC-DCN plot in judging the interference of IN on the C/N ratio.

The deviation among all regression slopes in Figure 3 was less than 5% (0.099–0.108). Such consistency in regression slope indicated a parallel shift among regression lines, which meant that every individual sample in the range observed contained a relatively stable amount of RC and IN. Since this amount could not be ignored,
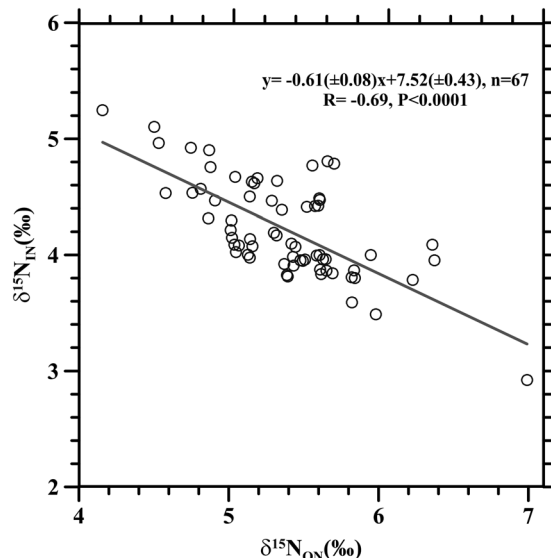

Figure 4. The scatterplot of $\delta^{15}N_{ON}$ versus $\delta^{15}N_{IN}$ of sediment core MD012404.
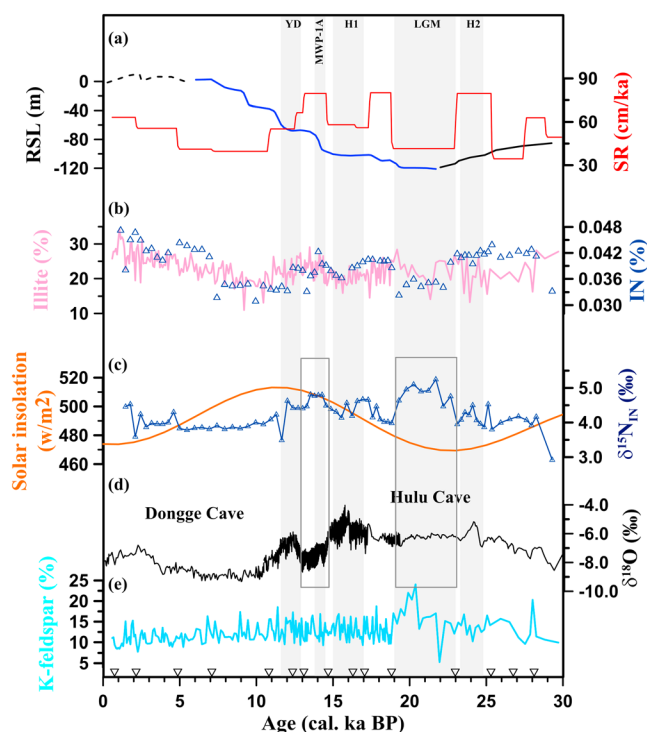
Figure 5. Temporal variations of (a) linear sedimentation rates of MD012404 (red line) and the relative sea level (RSL, black solid curved derived from *Cutler et al.* [2003], blue solid curve from *Liu et al.* [2004], and black dashed curve from *Saito et al.* [1998]); (b) illite content (pink curve, data from *Chen et al.* [2011]) and inorganic nitrogen (blue triangles); (c) summer solar insolation at 30°N (orange line) and stable isotope of inorganic nitrogen ($\delta^{15}N_{IN}$, blue triangles); (d) stable oxygen isotope of stalagmites in Dongge and Hulu Caves; and (e) the K feldspar content in MD012404 redrawn from *Chen et al.* [2011]. For explanation of the inverse triangles standing on the x axis and the vertical grey bars, see Figure 2.

the effect of RC and IN could only be neglected when sedimentary organic matter reached a sufficiently high content (e.g., TOC > 3%, thus RC can be <10% of TOC). Unfortunately, sediments with TOC contents >2% are sparse in the entire China marginal seas [*Kao et al.*, 2003; *Li et al.*, 2012; *Liu et al.*, 2006]. Since both RC and IN are refractory and resistant to oxidation, high contents of IN (38% of TN, this study; 30–59% of TN in the Western Subarctic Pacific [*Shigemitsu et al.*, 2009]; and 20–45% of TN in Pacific deep-sea sediments [*Müller*, 1977]) and black carbon are widely observed even in the deep ocean (12–31% of TOC [*Masiello and Druffel*, 1998]). Obviously, the issue of residual C/N impact on the operationally defined TOC/TN ratio is important not only for nearshore but also for offshore and pelagic sedimentary studies as well as for modern and paleoenvironment reconstructions.

4.2. Source and Isotopic Compositions of Residual Nitrogen

Sea level has risen stepwise since the Last Glacial Maximum (LGM) (Figure 5a). Accompanying the rising sea level, the sedimentation rate peaked during H2, the very first stage of sea level rise and Melt Water Pulse-1A (MWP-1A). Following these three peaks, a gradual increase in the sedimentation rate was also observed when the sea level was steady in the Holocene. Note that illite, which serves as an important component of major minerals (including feldspar, quartz, and kaolinite), displayed a similar pattern in content (the pink line in Figure 5b; data from *Chen et al.* [2011]) to the variation of the sedimentation rate. A relatively higher illite proportion appeared in the H2 event, the beginning of deglaciation, MWP-1A, and the late Holocene. On top of the illite proportion, we added the IN content (blue triangles in Figure 5b) for comparison, which revealed consistent patterns between IN and illite contents, suggesting that illite was the dominant carrier of IN.

In fact, the IN in marine sediments may come from allogenic and authigenic origins (the latter meaning the IN formed during the post-depositional organic degradation process). If authigenic fixation were significant, the correlation between $\delta^{15}N_{IN}$ and $\delta^{15}N_{ON}$ is positive [*Kendall*, 1998]. However, the negative correlation between the $\delta^{15}N_{IN}$ and $\delta^{15}N_{ON}$ that we observed excluded the authigenic mechanism (Figure 4). *Shigemitsu et al.* [2009] also tried to construct a correlation between $\delta^{15}N_{IN}$ and $\delta^{15}N_{ON}$ for sediments at subarctic western Pacific, but do not find any significant correlation even though their sediment had been buried for over 145 ka. Since the lattice-associated NH_4^+ would hardly be altered during transport and deposition in the ocean because there are no chemical gradients of NH_4^+ or K^+ between the clay minerals and seawater because of the high K^+ content of seawater [*Müller*, 1977; *Schubert and Calvert*, 2001], the lattice-associated NH_4^+ in sedimentary IN is often suggested to be allogenic [e.g., *Freudenthal et al.*, 2001; *Shigemitsu et al.*, 2009].

Based on the similarity in the ionic radius between K^+ and NH_4^+, the K^+ in the lattice structures of 2:1 type clay minerals (such as illite and vermiculite) are usually substituted by the ambient NH_4^+ in soils [*Young and Aldag*, 1982]. The major factor known to affect $\delta^{15}N_{IN}$ in soil is the fractionation between NH_4^+ in soil solutions and IN

[*Hübner*, 1986], which is governed by climate parameters, such as temperature and precipitation. The temporal variation of $\delta^{15}N_{IN}$, which revealed its own pattern and did not follow the sedimentation rate or IN content (the blue triangles in Figure 5c), suggests that the $\delta^{15}N_{IN}$ might carry extra information to be deciphered. Since the IN was sourced from the land, we speculated that the nitrogen isotopic composition locked in illite might provide information regarding the climate conditions during its formation.

To compare climate and $\delta^{15}N$, we used the summer solar insolation at 30°N to represent air temperature (the orange curve in Figure 5c), but no correlation was revealed. We studied the $\delta^{18}O$ of stalagmite records in the Dongge and Hulu caves, to represent precipitation [e.g., *Cheng et al.*, 2012; *Wang et al.*, 2001] and found that the temporal pattern of $\delta^{15}N_{IN}$ broadly followed the $\delta^{18}O$ pattern, where higher $\delta^{15}N_{IN}$ values corresponded to lower precipitation (the black curve in Figure 5d) except for the LGM and MWP-1A periods. A previous study indicates that K feldspar content (Molecular formula: $K_2O \cdot Al_2O_3 \cdot 6SiO_2$, Figure 5e) peaks during LGM [*Chen et al.*, 2011] to dilute illite (Figure 5b), and thus, the deviation in $\delta^{15}N_{IN}$ values (Figure 5c) during LGM were attributable to the change of IN origin, likely to be aeolian. As for the deviation during MWP-1A, we suggested that this was influenced by offshore transport induced by strong sediment reworking during that period [*Dou et al.*, 2010].

The negative correlation between $\delta^{15}N_{IN}$ and precipitation in our case differed from that reported in the global pattern, where mean annual air temperature exerts the major control on nitrogen isotope ratios in soil organic matter [*Amundson et al.*, 2003]. Nevertheless, the soil nitrogen isotope is related to regional climate variations and the sensitivity of the soil nitrogen isotope's response to climate factors may vary across regions [*Liu and Wang*, 2009]. On the Loess Plateau, where the climate was subject to the control of the East Asian Monsoon, the negative correlation between mean annual precipitation and soil $\delta^{15}N$ is also observed [*Liu and Wang*, 2009].

Superimposed on the changing mineral provenance, the temporal variation of $\delta^{15}N_{IN}$ in the Okinawa Trough suggests its utility to infer changes in climate on land, although elusive. To promote the applicability of $\delta^{15}N_{IN}$ in paleoenvironment studies, a fundamental data set is needed to explore the linkage between the governing parameters and $\delta^{15}N$ during soil formation.

4.3. Influence of the Residual Fraction on Proxies

In the East China Sea, the lowest $\delta^{13}C_{TOC}$ is reported to be −23.5‰ within 100 km of the Changjiang Estuary [*Kao et al.*, 2003; *Li et al.*, 2012] and almost all other surface sediments in the East China Sea hold higher values from −22.5 to −19.6‰. The influence of RC on $\delta^{13}C_{TOC}$ is not ignorable since RC occupies a significant fraction in TOC and its isotopic compositions (−23.98 to −20.50‰, according to our study and to *Li et al.* [2012]), just falling between the marine and terrestrial end-members. Based on our results, we suggested eliminating RC to minimize the uncertainty while estimating burials of organic carbon from different sources by applying $\delta^{13}C_{TOC}$ in the East China Sea. However, the removal of RC from operationally defined TOC might directly challenge the end-member-derived distributions and estimates for marine/terrestrial TOC and their burial in high sedimentation regions, e.g., the East China Sea [*Kao et al.*, 2003; *Deng et al.*, 2006] and the Gaoping Canyon southwest of Taiwan. Thus, the issue of TOC burial requires reevaluation.

As mentioned in section 1, a decreasing pattern in C/N ratio since 15 ka (see Figure 6a) is found trough-wide in the Okinawa Trough [*Kao et al.*, 2008a; *Ujiié et al.*, 2001]. The decreasing pattern in the Holocene inferred reduction of a terrestrial influence; however, this mismatched the decreasing $\delta^{13}C_{TOC}$ (Figure 6b) that suggested an increase in the terrestrial fraction. The inconsistency also appeared prior to the Holocene, during which C/N ratios were high (more terrestrial) and $\delta^{13}C_{TOC}$ values were also high (more marine). In fact, similar decreasing patterns of $\delta^{13}C_{TOC}$ during deglaciation are observed in various cores in the South China Sea [*Kienast et al.*, 2001] and in the Arabian Sea [*Kao et al.*, 2015], although *Kienast et al.* [2001] rule out many possibilities, such as terrigenous input, direct temperature effects, diagenetic alteration, and other biological factors. However, the cause for the negative shift of $\delta^{13}C_{TOC}$ in the western Pacific marginal and Indian Ocean during transgression has not yet been answered.

After eliminating the residual fraction, the LOC/ON values (Figure 6c) became more variable when compared with TOC/DCN; meanwhile, the temporal variation of $\delta^{13}C_{LOC}$ exhibited a larger variability (Figure 6d). A synchronous variation of LOC/ON and $\delta^{13}C_{LOC}$ can be seen since 14 ka BP; however, an inconsistent pattern
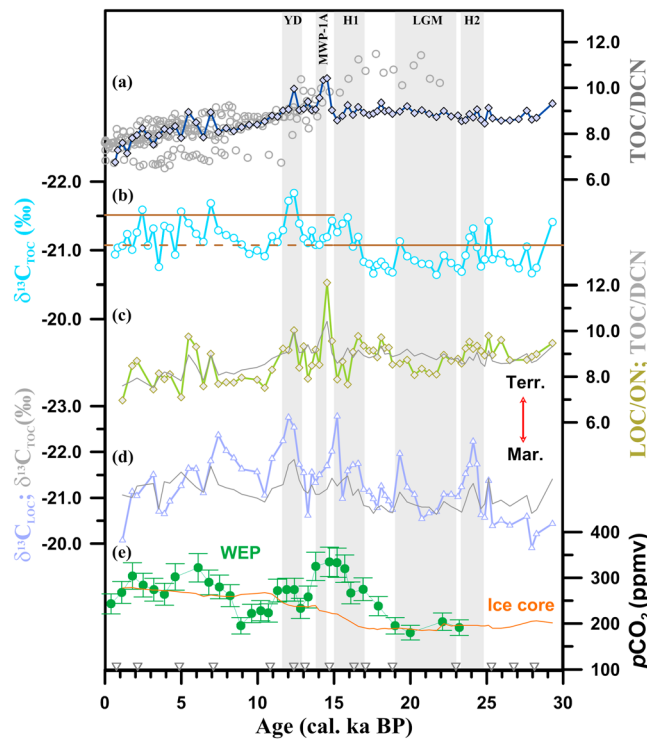
Figure 6. The temporal variations of (a) TOC/DCN ratios from Okinawa Trough sediment cores (grey circles for RN93-PC1, RN93-PC2, RN93-PC3, RN93-PC4, RN93-PC6, and RN96-PC1 sourced from *Ujiié et al.* [2001] and blue diamonds for MD012404 by *Kao et al.* [2006]); (b) stable isotope of total organic carbon ($\delta^{13}C_{TOC}$ (blue circles, from *Kao et al.* [2006])). The two horizontal lines in brown are the mean values, for 30 ka to 15 ka and 15 ka to the present; (c) ratios of labile organic carbon to organic nitrogen (LOC/ON, grey diamonds), the grey line is TOC/DCN in Figure 6a for comparison; (d) stable isotope composition of labile organic carbon ($\delta^{13}C_{LOC}$, blue triangles); the grey line is for $\delta^{13}C_{TOC}$ in Figure 6b; and (e) atmospheric CO_2 record in Taylor Dome Ice Core (orange line [*Indermühle et al.*, 1999]) and pCO_2 in surface ocean in the Western Equatorial Pacific (WEP, green dots, from *Palmer and Pearson* [2003]). Double-headed arrows indicate organic source contributions. For explanation of the inverse triangles standing on the *x* axis and the vertical grey bars, see Figure 2.

between LOC/ON and $\delta^{13}C_{LOC}$ remained for the glacial period. Likely, there were other controls superimposed on the process of marine-terrestrial mixing. Since the $\delta^{13}C_{org}$ of the phytoplankton was a function of sea water $[CO_2(aq)]$ [e.g., *Popp et al.*, 1989; *Rau et al.*, 1989, 1991], the marine end-member might change as the atmospheric pCO_2 varies during transgression. Combining the empirical equation proposed by *Rau et al.* [1989] with alkenone U^K_{37} sea surface temperature versus sea surface salinity (data from *Yu et al.* [2009]) in the Okinawa Trough, the 80 ppm atmospheric pCO_2 increase (the orange curve in Figure 6e; data from Taylor Dome Ice Core by *Indermühle et al.* [1999]) during transgression may cause a negative shift of around 1.3‰ in marine $\delta^{13}C_{org}$. Such a negative shift could mask the increasing relative contribution of marine organics if we applied a fixed marine $\delta^{13}C_{org}$ end-member. In addition, for the tropical western Pacific area, where the Kuroshio Current originates, sea surface pCO_2 (green curve with dots in Figure 6e) over the last 23 ka was not in equilibrium with atmospheric pCO_2 [*Palmer and Pearson*, 2003]. Moreover, the phytoplankton growth rate and the relative contributions of passive and active carbon uptake by phytoplankton were also known to impact the $\delta^{13}C$ values [e.g., *Laws et al.*, 1995; *Keller and Morel*, 1999]. Besides the marine, the terrestrial $\delta^{13}C_{org}$ end-member may also vary and the pCO_2-dependent fractionation factor has been successfully used to

reconcile the marine and terrestrial carbon isotope excursion [*Schubert and Jahren*, 2013]. Thus, before the $\delta^{13}C_{org}$ end-member issue is resolved, any evaluation of the sedimentary history of the relative contribution from terrestrial- and marine-sourced organics will be problematic.

As for the residual nitrogen influence on $\delta^{15}N$, using the same core as in this study, *Kao et al.* [2008b] report a synchronous increase of $\delta^{15}N_{DCN}$ during the deglacial period when denitrification in the eastern tropical Pacific Ocean was enhanced. Here we found that although IN accounted for 38% of the DCN, the high proportion of IN did not bias the $\delta^{15}N_{DCN}$ significantly (a similar temporal pattern of $\delta^{15}N_{ON}$ can be seen in Figure 2c after eliminating residual nitrogen). That is because the $\delta^{15}N_{IN}$ varied within a narrow range (3.0–5.0‰), which was very close to the range of $\delta^{15}N_{DCN}$ (4.0–7.0‰), particularly during 30–11 ka. During 30–11 ka, the mean value of $\delta^{15}N_{DCN}$ (4.9‰) was only 0.6‰ higher than the mean of $\delta^{15}N_{IN}$ (4.3‰). Although the IN occupied 38% of the DCN, its isotope similarity resulted in a small difference between $\delta^{15}N_{DCN}$ and $\delta^{15}N_{ON}$ (0.2‰); while in the Holocene, the decreasing trend remained as compared with previous reports for the Holocene even though the isotope difference was amplified to 1.1‰ (Figure 2d). Overall, the report by *Kao et al.* [2008b] was not changed after eliminating the IN interference. As mentioned earlier by *Kienast et al.* [2005], the sedimentary IN effect has received less attention in the low latitude especially

in the regions with high fluvial input, and more studies are needed to explore the IN effect on surface sediments. Nevertheless, caution should be taken in interpretation unless the organic nitrogen content is high enough.

5. Conclusions

Our results illustrated that caution should be taken while applying C/N, $\delta^{13}C_{TOC}$, and $\delta^{15}N_{TN}$ in the study of modern and past oceanographic changes, particularly in those regions with high temporal resolution archives resulting from fluvial inputs. Our major conclusions were the following:

1. The C-N scatterplot, which is often used to discern the content of IN, might not be useful in China's marginal seas owing to the masking effect by RC.
2. Illite was the major carrier of IN in the middle Okinawa Trough.
3. The proportions of IN were high in the Okinawa Trough sediment, yet the difference between $\delta^{15}N_{ON}$ and $\delta^{15}N_{DCN}$ was small, and hence, the isotopic compositions of bulk nitrogen were not influenced significantly by IN.
4. $\delta^{15}N_{IN}$ likely reflects the climatic control on lithogenic materials sourced from land.
5. The LOC/ON versus $\delta^{13}C_{LOC}$ instead of TOC/DCN versus $\delta^{13}C_{TOC}$ was more suitable to decipher the organic sources.
6. And when applying $\delta^{13}C_{LOC}$ into an end-member mixing model over geological timescales, one should consider the shift in the marine end-member value induced by the atmospheric CO_2 variations.

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