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Chemical and isotopic alteration of organic matter during early diagenesis: Evidence from the coastal area off-shore the Pearl River estuary, south China

Fanrong Chen [a,b,*], Ling Zhang [a,c], Yongqiang Yang [a,c], Derong Zhang [a,c]

[a] Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China
[b] State Key Laboratory for Mineral Deposits Research, Department of Earth Sciences, Nanjing University, Nanjing 210093, China
[c] Graduate School of Chinese Academy of Sciences, Beijing 100049, China

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ABSTRACT

Understanding the chemical and C, N isotopic alteration of organic matter (OM) during early diagenesis is crucial to the studies of biogeochemical processes in marine and lacustrine environments. In this study, isotopic composition ($\delta^{13}C$ and $\delta^{15}N$), total organic carbon and total nitrogen content of sediment cores, plankton and particulate organic matter (POM) from the coastal area off-shore the Pearl River estuary were determined. In addition, the fractional carbon content of total hydrolysable amino acids, total carbohydrates, total lipids and acid-insoluble organic compounds and their respective $\delta^{13}C$ were analyzed. The $\delta^{13}C_{org}$ of sediment cores from geographically distinct sites (C5 and E4) is fairly constant and just slightly lower than that of the plankton, suggesting that $\delta^{13}C$ can be used as a reliable geochemical proxy indicating OM origin in the studied coastal area. Considerable diagenetic alteration of OC/N was observed, and the diagenetic alteration of $\delta^{15}N$ was significant. A rapid degradation of OM was associated with a rapid bacteria growth in the water column, which governed the diagenesis of the OM. In addition to the kinetic isotopic fractionation associated with the biodegradation of OM, formation and degradation of bacterial biomass contributed significantly to the observed change of $\delta^{13}C$ and $\delta^{15}N$ during diagenesis. Although the bacteria biomass was believed to be rich in ^{13}C relative to the substrate, bacteria biosynthesis also produced ^{13}C-rich and ^{13}C-poor fractions, and the subsequent biodegradation preferentially decomposes the ^{13}C-rich compound classes and the ^{13}C-rich compounds in a specific class as well, which made the $\delta^{13}C$ of remaining organic matter similar to the substrate in the sediment. On the other hand, the low $\delta^{15}N$ of the POM and sedimentary OM relative to the fresh plankton was resulted from the addition of ^{15}N-depleted biomass that was possibly generated by the preferential uptake of ^{15}N-depleted ammonium during bacterial growth.

1. Introduction

Carbon and nitrogen isotopes and C/N ratio have been widely used to study the sources and cycling of organic matter (OM) in estuary, coast, ocean and lacustrine systems (e.g. Altabet, 1988; Matson and Brinson, 1990; Thornton and McManus, 1994; Cifuentes et al., 1996; Nakatsuka et al., 1997; Goñi et al., 1998; Graham et al., 2001). Moreover, $\delta^{13}C_{org}$ has been used as a proxy of primary productivity and atmospheric pCO_2 levels (e.g. Hollander and McKenzie, 1991; Schelske and Hodell, 1991; Fontugne and Calvert, 1992; Meyers, 1997; Brenner et al., 1999), while nitrogen isotopic ratios have been used as a recorder of nitrate utilization (e.g., Calvert et al., 1992; Altabet and Francois, 1994; Teranes and Bernasconi, 2000) and N_2-fixation (e.g. Haug et al., 1998). However, many investigations have indicated that the chemical and isotopic composition of OM may be altered significantly during early diagenesis, probably obscuring the primary signals (e.g. Henrichs and Farrington, 1987; Macko et al., 1991; MArthur et al., 1992; Cowie and Hedges, 1994; Freudenthal et al., 2001; Lehmann et al., 2002). Thus, studies on the early diagenetic alteration of OM are necessary for a

* Corresponding author. Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China. Fax: +86 20 85290291.
E-mail address: frchen@gig.ac.cn (F. Chen).

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better understanding of the processes governing the environment evolution of aquatic systems.

Some studies have shown that early diagenesis resulted in a negative shift in $\delta^{13}C$ (e.g. Prahl et al., 1997; Böttcher et al., 1998), but many other studies indicate that the $\delta^{13}C$ of organic matter is resistant to isotopic alteration during water column or postburial diagenesis (e.g. Meyers and Eadie, 1993; Schelske and Hodell, 1995). Similarly, contradictory observations have also been reported on the diagenetic alteration of $\delta^{15}N$. In most cases, selective loss of certain organic compounds that have different isotopic compositions than the bulk OM was proposed to explain the negative shifts, because easily degradable compounds like amino acids and carbohydrates are generally enriched in ^{13}C and ^{15}N (e.g. Benner et al., 1987; Prahl et al., 1997; Böttcher et al., 1998). Alternatively, isotopic fractionation due to metabolism of the organisms that are responsible for the organic matter degradation has been proposed to be the mechanism causing the positive isotope shifts (Saino, 1992; Sigman et al., 1999). Furthermore, uptake of "light" inorganic nitrogen by bacteria attaching to the organic substrate has also been proposed to explain the negative shift in $\delta^{15}N$ during diagenesis (Altabet et al., 1991; Nakatsuka et al., 1997).

In this study, total organic carbon (TOC), total nitrogen (TN), and stable carbon and nitrogen isotopes of the bulk OM were analyzed. In addition, fractional carbon content of total hydrolysable amino acids (THAA), total carbohydrates (TCHO), total lipids and acid-insoluble organic compounds (AIOC) and their respective $\delta^{13}C$ were also determined for the plankton, particulate OM and sediments from the coastal area off-shore the Pearl River estuary. The aim of this study is to assess the extent to which the primary geochemical signals can be carried by the sediments in this area, and to provide further information on the mechanisms for the chemical and isotopic alteration of OM during early diagenesis.

2. Sampling and analytical methods

2.1. Sample collection

The sampling sites located in the coastal area off-shore the Lingding Bay are hydrographically distinctive (Fig. 1). Site C5 (21°43.0′N, 113°56.0′E) is to the south of the bay and is influenced to some extent by the Pearl River plume, while Site E4 (22°06.0′N, 114°37.0′E) is almost free of the impact of the river discharge that deflects westward due to the steering effect of the Coriolis force. For the tidal currents, seawater intrusion appears to flow largely through the eastern channel in the Lingding Bay, while the freshwater outflow uses the western channel as its main pathway (Mao et al., 2004), which minimizes the impact of freshwater ebb current at site E4.

The sediment cores were collected using a multiple corer in spring 2003. The corer was able to sample four separate and usually undisturbed sediment cores within an area of less than 0.3 m^2, each with a volume of overlying water. The plastic core tubes were 10 cm in diameter and 61 cm long, and the length of sampled sediment cores was 28–40 cm. One of the sediment cores from each site was sliced at 1 cm intervals

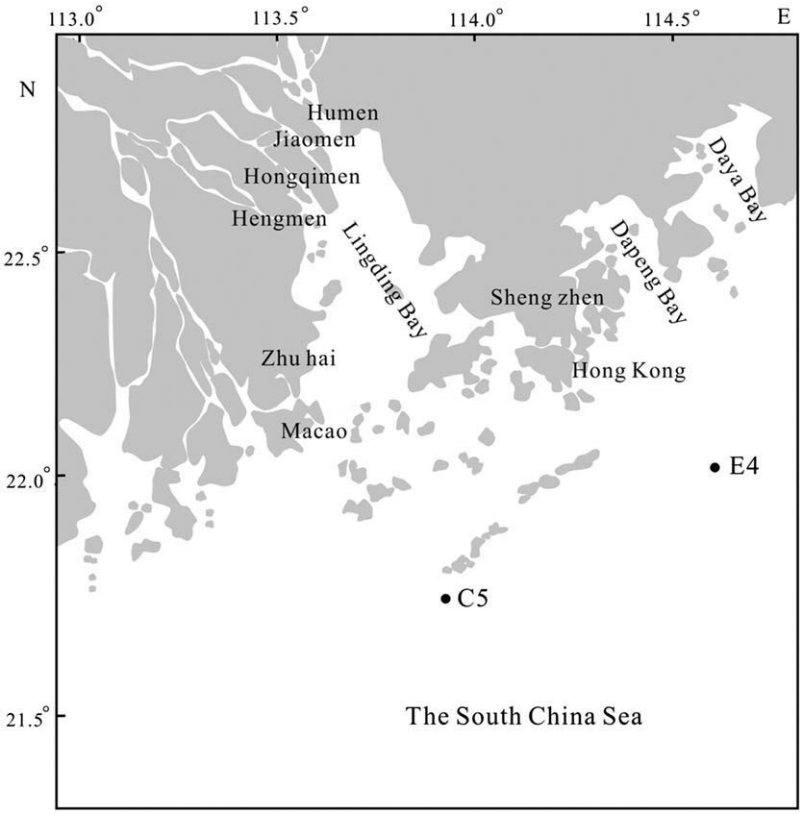

Fig. 1. A Map showing the location of the Pearl River estuaries and the sampling sites.

and stored in glass jars (acid-washed and baked at 550 °C) filled with Ar gas and frozen at −20 °C until analysis. The dissolved oxygen in the sediment cores of the studied area was measured using a Unisense (Denmark) meter and oxygen sensor, and was found to decrease rapidly to zero within a few millimeters below the sediment surface. The particulate matter was collected by centrifuging 20 l of the coastal water from 20 m below the water surface collected using a submarine pump. The plankton was collected by dragging a 20 μm pore-size net at 0–1 m water depth, and was dominated by phytoplankton.

2.2. TOC, TN content and stable carbon isotope analysis

Freeze-dried samples for TOC, TN and isotope analysis were acidified with 1.5 N HCl to remove inorganic carbon. TOC and TN contents of bulk samples were analyzed using a Vario. EL III CHN analyzer, with the combustion temperature being set at 960 °C. The precisions of duplicate analyses of samples were ±2% and ±3% of the mean values for TOC and TN, respectively. Stable carbon and nitrogen isotopic compositions were determined with a DELTA^{tlus}XL isotope ratios mass spectrometer. The precision of duplicate analyses was 0.2‰. Stable carbon and nitrogen isotope ratios were expressed in the delta notation (δ^{13}C and δ^{15}N) relative to Vienna PDB and atmospheric nitrogen, respectively.

2.3. Extraction of organic compounds

Samples were freeze-dried and homogeneously mixed before the extraction of organic compounds. Pure water (18 mΩ) was used in the extraction procedures that are described below.

2.3.1. Lipid extraction

Dried samples were weighed into 50 ml glass centrifuge tubes (precombusted) with Teflon-lined caps. A 2:1 v/v mixture of methylene chloride/methanol (both were high purity, Merck Co.) was added to each tube, then ultrasonicated and centrifuged (Wang et al., 1998). The supernatant was removed and the extraction was repeated four times until the supernatant was colorless. The combined solvent extracts from each sample were rotary evaporated to dryness in vacuo at 45 °C. The sample was then transferred with methylene chloride into a precombusted quartz tube and dried with water-bath. Organic carbon (OC) content of lipid was measured using a micro pressure-meter after combusting at 850 °C, then the carbon dioxide was collected and the stable carbon isotopic composition was measured using a Finnigan Model-251 isotope ratios mass spectrometer, with an overall uncertainty of <0.3‰ relative to Vienna PDB.

2.3.2. THAA extraction and isolation

Dried samples were weighed into a 50 ml glass centrifuge tube (precombusted) and hydrolyzed with 6 N HCl (G.R) under N_2 at 110 °C in an oven for 22 h to break down the combined forms, such as proteins or peptides, to free amino acids (Whelan, 1977; Lee and Cronin, 1982). After hydrolysis, the samples were centrifuged and the supernatants were transferred into 100 ml pear-shaped glass flasks. The remaining solid was rinsed twice with pure water and centrifuged. The supernatants were combined with the acid hydrolysate and dried by rotary evaporation in vacuo at 50–55 °C. The remaining HCl was removed by rinsing twice with pure water and rotary evaporation.

The dried THAA fraction was dissolved in 2 ml pure water and desalted using cation exchange column chromatography

Table 1
TOC and TN content in sediments, plankton and the constituent organic compounds

Sample and depth	TOC	TN	OC/N	THAA	TCHO	Lipid	AIOC	Yield
cm	wt.%	wt.%		% TOC	%TOC	%TOC	%TOC	(%)
Plankton	22.5	3.3	8.0	44	21	23	12	86
Suspended particulate sediment	15.3	3.8	4.7	43	5	7	47	102
Station C5								
0–1	0.48	0.097	5.8	20.7	19.3	4.6	55.4	91.0
1–2	0.53	0.101	6.1	15.5	14.1	2.7	67.7	96.7
2–3	0.47	0.119	4.6	15.3	12.5	2.7	69.5	117.1
3–4	0.50	0.089	6.6	14.8	15.6	4.3	65.3	89.1
5–6	0.56	0.125	5.2	16.3	14.7	4.5	64.5	83.6
7–8	0.40	0.092	5.1	20.8	19.3	3.9	56.0	89.3
9–10	0.40	0.110	4.2	11.3	16.8	2.8	69.1	102.1
12–13	0.35	0.085	4.8	12.4	17.1	3.1	67.4	104.2
15–16	0.45	0.114	4.6	14.4	13.4	2.9	69.3	80.5
23–24	0.39	0.101	4.5	10.6	13.4	2.0	74.2	94.6
27–28	0.36	0.102	4.1	12.2	13.8	2.7	71.3	93.5
Station E4								
0–1	0.67	0.142	5.5	16.3	14.7	4.0	64.9	94.3
1–2	0.68	0.158	5.0	17.3	17.6	3.8	61.3	82.2
2–3	0.64	0.159	4.7	19.4	15.6	3.3	61.6	84.4
5–6	0.62	0.142	5.1	17.1	18.5	3.7	60.7	79.4
7–8	0.60	0.165	4.2	11.6	18.4	4.2	65.8	81.6
9–10	0.60	0.150	4.7	15.0	16.9	4.0	64.1	88.5
12–13	0.58	0.117	5.8	15.6	17.3	3.2	63.9	90.9
15–16	0.61	0.132	5.4	13.6	15.0	2.4	69.0	87.0
19–20	0.53	0.136	4.6	11.4	13.1	4.2	71.3	111.0
23–24	0.56	0.137	4.8	10.4	15.0	3.1	71.5	90.3
27–28	0.53	0.123	5.0	9.6	13.3	2.0	75.2	107.2

(AG 50 W-X8 resin of 100–200 mesh size, analytical grade, BioRad). Free amino acids were collected in a 1.5 N NH_4OH eluate and dried by rotary evaporation. The dried sample was dissolved in pure water and the solution was scaled using a volumetric flask. An aliquot of the THAA solution was sampled for OC content analysis using a SHIMADZU TOC analyzer, and the remaining solution was transferred to a precombusted quartz tube and dried again in vacuo for carbon isotope determination as described above.

The organic compounds in the sediment residual after removal of the supernatant for THAA extraction was defined as acid-insoluble fraction. This sediment residual was transferred with purified water into a precombusted quartz tube and dried in vacuo for later combustion for OC and stable carbon isotope determination as for the lipids.

2.3.3. TCHO extraction and isolation

The procedure used for extraction and isolation of carbohydrates was mostly derived from Sigleo (1996) and Ogier et al. (2001). Dried samples were introduced into precombusted 50 ml glass centrifuge tubes each with 1.2 N HCl, and heated under the protection of N_2 for 3 h at 100 °C in an oven. After centrifuging, the supernatant was transferred into 100 ml pear-shaped glass flask. The remaining solid was soaked with 12 N HCl for 12 h at room temperature to break down more resistant forms such as those present in vascular plant cellulose (Cowie and Hedges, 1994). Then, this concentrated acid was diluted to 1.2 N HCl for the second stage of hydrolysis. After hydrolysis, samples were centrifuged and rinsed twice. The combined hydrolysate was dried by rotary evaporation in vacuo at 50–55 °C and the remaining HCl was removed by repeated rinsing and rotary evaporation.

The hydrolysate containing free sugars was then desalted on a 20 ml mixed cation/anion exchange column packed with mixed (1:1 v/v) cation resin of AG50 W-X8 (100–200 mesh, analytical grade, BioRad) and anion resin of AG 1-X8 (100–200 mesh analytical grade, BioRad). The TCHO fraction was collected by elution with purified water. After rotary evaporating at 50 °C to about 2 ml, the TCHO was transferred to a volumetric flask and scaled to 50 ml with purified water. An aliquot of the TCHO solution was sampled for OC content analysis using a SHIMADZU TOC analyzer, and the remaining solution was transferred to a precombusted quartz tube and dried in a desiccator in vacuo for carbon isotope determination.

2.4. Control experiments

The reliability and carbon yield efficiency of organic compound extraction were tested using standards representing each organic compound. A pure cod liver oil (Sigma) and a liquid mixture of fifteen acids (Fluka) and D-glucose (Fluka) were used to test the carbon recovery of lipid, amino acid and sugar, respectively. The average carbon recovery of 4 samples for cod liver oil, amino acids and D-glucose was 87% (82–91%),

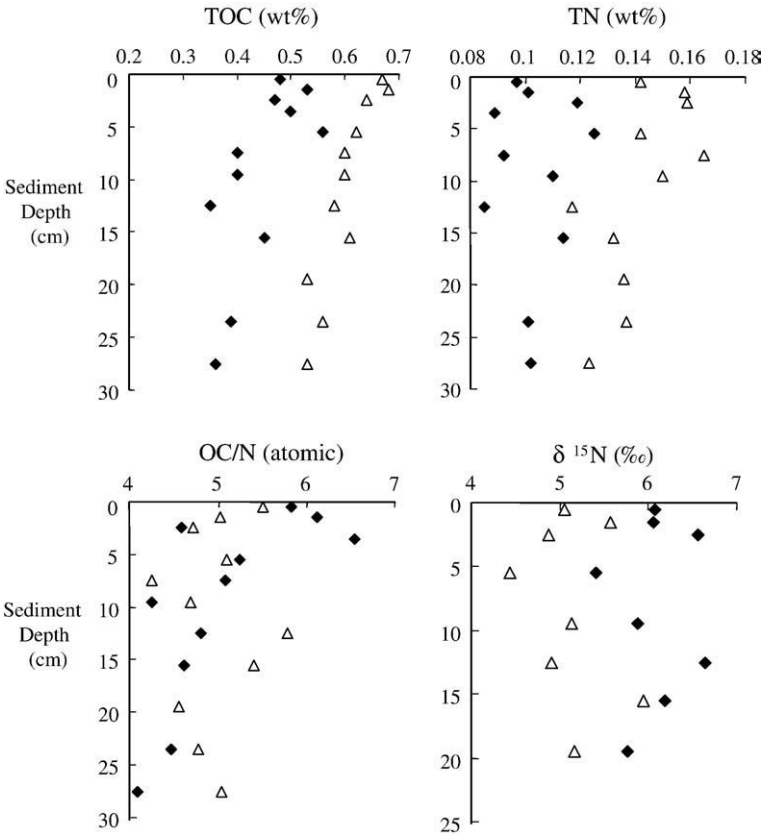

Fig. 2. Concentration profiles of TOC and TN (both as percentage of dry weight) and profiles of C/N (atomic ratio) and $\delta^{15}N$ for sediments at Sites C5 (filled diamonds) and E4 (open triangles).

Table 2
$\delta^{13}C$ and $\delta^{15}N$ of sediments, plankton and the constituent organic compounds

Sample and depth	TOC	TN	THAA	TCHO	LIPID	AIOC
	$\delta^{13}C_{org}$ (‰)	$\delta^{15}N$ (‰)	$\delta^{13}C_{org}$ (‰)	$\delta^{13}C_{org}$ (‰)	$\delta^{13}C_{org}$ (‰)	$\delta^{13}C_{org}$ (‰)
Plankton	−20.9	8.3	−20.7	−19.6	−25.7	−24.0
Suspended particulate sediment (cm)	−20.6	5.0	−20.7	−20.5	−26.1	−24.9
Site C5						
0–1	−21.7	6.1	−20.2	−20.5	−25.3	−22.9
1–2	−21.6	6.1	−19.9	−23.2	−25.0	−22.2
2–3	−21.6	6.6	−20.7	−19.7	−25.5	−23.6
5–6	−21.8	5.4	−19.9	−20.5	−25.4	−23.1
9–10	−21.7	5.9	−21.3	−19.6	−25.5	−22.5
12–13	−21.5	6.7	−20.1	−19.0	−25.6	−23.4
15–16	−21.9	6.2	−18.8	−21.9	−25.8	−21.8
19–20	−21.1	5.8	−19.6	−21.1	−25.6	−22.7
Site E4						
0–1	−21.7	5.1	−19.6	−19.5	−25.3	−22.8
1–2	−21.2	5.6	−20.1	−20.5	−24.7	−22.9
2–3	−21.5	4.9	−20.5	−18.7	−24.9	−23.2
5–6	−21.6	4.4	−19.4	−21.9	−25.4	−22.7
9–10	−21.4	5.1	−19.3	−22.7	−25.0	−23.7
12–13	−21.7	4.9	−19.8	−19.7	−25.3	−22.8
15–16	−21.7	5.9	−20.2	−22.4	−25.5	−22.6
19–20	−21.5	5.2	−19.7	−19.5	−26.1	−23.0

77% (73–81%) and 89% (85–94%), respectively. In addition, blank check was used for each extraction.

3. Results

3.1. TOC and TN content of bulk organic matter and its constituent compounds

The TOC and TN content and the TOC/TN ratio of the suspended particulate matter are lower than those of the fresh plankton (Table 1), indicating that the degradation of organic compounds in the water column resulted in a preferential release of carbon relative to nitrogen. In the sediment cores, the TOC contents are in a range between 0.35% and 0.68% with a generally down-core decreasing trend. The TOC/TN ratio exhibits a decreasing trend with depth at Site C5, while no obvious variation trend of TOC/N was observed at site E4. In general, the TOC/N ratio of the sediments displays a relatively small range (Fig. 2) with an average of 5.1, and is not significantly different from that of the POM (4.6).

Acid-insoluble organic compounds (AIOC), which are considered to be refractory, account for only 10% of the TOC in the fresh plankton. In contrast, the fractional carbon content of AIOC reaches up to 47% in the POM and is just slightly lower than that in the sediments (Table 1). This suggest that a significant part of the primary organic matter was degraded in the upper 20 m water column, which is also indicated by the low fractional content of TCHO and lipids in the POM relative to the plankton. However, this inference seems not in agreement with the high fractional content of THAA in the POM.

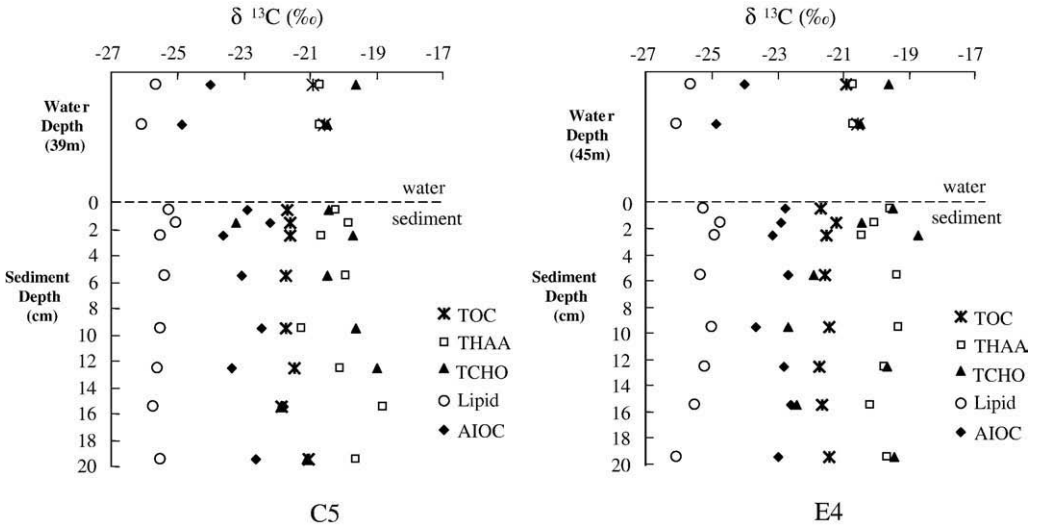

Fig. 3. $\delta^{13}C$ profiles of TOC and its constituent organic compounds (THAA, TCHO, Lipid and AIOC) in sediments of both sites. The corresponding values for the plankton and the POM were plotted for comparison.

In the sediments, AIOC accounts for 55.4% and 64.9% of the TOC in surficial sediments at Sites C5 and E4, respectively, and for more than 70% of the TOC in deep sediments (Table 1). The fractional content of THAA in the sediment is less than half of that in the POM, and exhibits a continued decrease with depth in both of the sediment cores. A similar decreasing trend from the POM into the sediment is observed for lipid. In contrast, the fractional content of TCHO in the sediment is about triple of that in the POM.

3.2. Stable carbon and Nitrogen isotopic composition of bulk sediments

$\delta^{13}C$ and $\delta^{15}N$ values of plankton and bulk sediments as well as their constituent organic compounds are listed in Table 2 and shown in Fig. 3. The $\delta^{13}C$ of the sediments falls into a narrow range from −21.8‰ to −21.0‰ (mostly between −21.8‰ and −21.4‰) with an average of −21.6‰, and is slightly lower than that of the plankton (−20.9‰). The values of $\delta^{15}N$ range between 4.4‰ and 6.6‰, with an average of 5.6‰ which is 2.3‰ below the value of the plankton.

3.3. Stable carbon isotopic composition of constituent compounds

As is shown in Fig. 3, various constituent organic compounds have quite different $\delta^{13}C$ values and variation trends with depth. For the sediments, the $\delta^{13}C$ values of THAA, lipid and AIOC vary in small ranges averaging −19.9‰, −25.4‰ and −22.9‰, respectively. Compared with the TOC, the THAA is rich in ^{13}C, while lipid and AIOC are depleted in ^{13}C. For the TCHO, however, significant carbon isotope variation was observed in both cores, and the average value of $\delta^{13}C$ (−20.7‰) is slightly higher than that of the bulk organic matter. Similar $\delta^{13}C$ variation for TCHO has also been reported in oceanic sediment cores (Macko et al., 1991; Wang and Druffel, 2001). Compared with the corresponding compounds in the plankton and POM, the AIOC in the sediment is rich in ^{13}C considerably, and the lipids in the sediments have slightly higher $\delta^{13}C$. Vertical variation of $\delta^{13}C$ in the sediment cores was not observed for THAA, TCHO and AIOC, whereas the total lipid displays an apparent ^{13}C-depleting trend downwards in the sediment cores.

4. Discussion

4.1. Geochemical indicators of organic matter origin

The $\delta^{13}C_{org}$ of the sediment cores at Sites C5 and E4 is slightly lower than that of the plankton and is significantly higher than that of the terrestrial organic matter (~−27‰, Hu et al., 2006) imported by the Pearl River. In addition, an examination of the geographical location of Sites C5 and E4 suggests that more terrestrial organic matter would be deposited at Site C5. However, the $\delta^{13}C_{org}$ values of the sediment at Sites C5 and E4 are almost the same, indicating that the sedimentary organic matter at both sites has essentially the same origin. Although the TOC and TN contents of the sediment at site E4 is generally higher than the respective values of the sediment at Site C5, all the sediment samples exhibit a similar trend in the TOC vs. TN diagram (Fig. 4), which yields an equation below by linear regression.

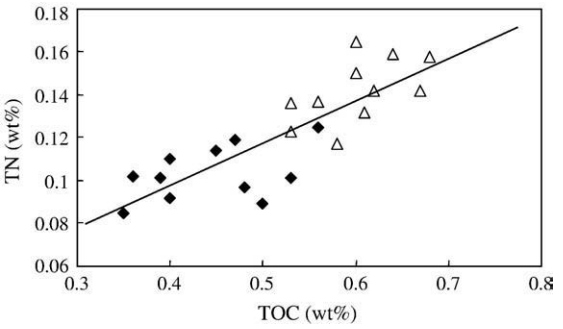

Fig. 4. TOC vs. TN diagram for sediments at Sites C5 (filled diamonds) and E4 (open triangles).

$$TN\% = 0.2*TOC\% + 0.019$$

The intercept of the regression line has been proposed to result from the fixing of NH_4^+ ion by clays, and the linear correlation was interpreted as the dilution of a relatively constant amount of inorganic N by an organic component with a relatively fixed TOC/TN ratio (Calvert, 2004). Therefore, the $\delta^{13}C_{org}$ and TOC/TN evidently indicate that the OM in the sediment of both sites is derived from aquatic biomass with little, if any, terrestrial organic mater being involved. Thus, it is likely that early diagenesis caused the differences in chemical and isotopic composition between the plankton and the sediments at Sites C5 and E4.

The observation that the $\delta^{13}C$ of sedimentary OM at the geographically distinct sites is fairly constant and close to the primary value demonstrates that $\delta^{13}C$ is a reliable geochemical proxy indicator of organic matter origin in the studied coastal area. The average value of −21.6‰ can be used as the representative value of $\delta^{13}C$ for the sediment organic carbon of aquatic origin in the studied coastal area. Because the atomic OC/N ratio of marine and terrestrial organic matters is ~5–8 and >20, respectively, with a difference of more than 10 (Meyers, 1997), and the TOC/TN ratio of the marine-derived OM is lower than that of the fresh plankton, the diagenesis induced OC/N variation (~2.5) of the sediment may be considerable but is not significant. Thus, OC/N can be used as a supplementary evidence indicating the origin of OM in the studied area. Generally, the average $\delta^{15}N$ value of terrestrial vascular plants is ~3‰ below the value of marine POC (Meyers, 1997; Maksymowska et al., 2000), whereas early diagenesis resulted in a $\delta^{15}N$ decrease of more than 2‰, with large variations (up to 2.21‰). Thus, the relatively large and irregular variation of $\delta^{15}N$ in the sediment cores indicate that it is not suitable to be used as an proxy indicating OM origin in this area. This observation is confirmed by the high $\delta^{15}N$ of the surficial sediments in the Lingding Bay as compared to the sediments in the coastal area (Hu et al., 2006).

4.2. Diagenetic alteration of chemical composition of OM

The mechanisms of early diagenetic alteration of OM include: (1) decomposition of labile organic compounds, leaving

relatively refractory compounds in the solid phase (Henrichs and Doyle, 1986; Meyers and Eadie, 1993; Harvey et al., 1995); (2) formation and subsequent decomposition of the secondary organic compounds synthesized by heterotrophic bacteria that are responsible for the degradation of the organic matter (Meyers and Ishiwatari, 1993; Harvey et al., 1995). In general, carbohydrates and amino acids are liable compounds that are easily metabolized by heterotrophic bacteria, while lipid is less labile and acid-insoluble compounds are considered to be refractory (Hedges et al., 1988; Harvey et al., 1995).

Although the sum of the fractional carbon content of TCHO, THAA and lipid decreases as early diagenesis proceeds (from plankton→POM→sediment), a careful examination shows that the fractional carbon content of THAA is slightly higher in the POM than in the plankton, while the fractional content of TCHO and lipid in the POM is <1/3 of that in the plankton. Considering the enriching effect of intensive carbon loss due to OM degradation and the possible formation of secondary TCHO and lipids in the water column, the much lower fractional content of TCHO and lipids in the POM relative to the plankton indicates that little of the labile compounds of the primary plankton would be preserved in the POM. Sediment trap studies have shown that about three fourth of annual primary productivity would be lost in euphotic zone, and up to 70% of the remaining organic carbon would be lost in hypolimnion (Eadie et al., 1984; Meyers and Ishiwatari, 1993). Because THAA is not considered to be degraded at a lower rate than lipids, the most probable explanation for the high THAA content in the POM is the addition of secondary organic matter synthesized by microbes.

Harvey et al. (1995) showed that the greatest bacterial activity occurred during periods of high organic matter loss, and bacteria contributed more than 20% to the total biomass during microbial peak-time growth. As the bacteria grow generation after generation, labile compounds from primary organic matter will be exhausted and the newly formed organic matter will dominate the substrate. The oligotrophic nature of the studied region favors the rapid aerobic biodegradation of OM in water column. Since protein content in bacterial biomass is as high as 80% with an C/N ratio of 4–5 (Bordovskiy, 1965a,b; Müller, 1977), an addition of the secondary organic matter would partially compensate for the loss of THAA and significantly increase the fractional content of THAA relative to TCHO and lipids. This explanation is also evidenced by the much lower C/N ratio of the POM (4.6) as compared with that of the plankton (7.8).

When the sinking POM reaches the sediment/water interface and is buried in sediments, the organic matter becomes more refractory, which limits the formation of new bacterial biomass. Afterwards, decomposition of labile organic compounds is continuing at a reduced rate. Because of the fast decomposition of labile components in algae (Lehmann et al., 2002) and the low accumulation rate at Sites C5 and E4 (0.34 and 0.58 cm/a, respectively), the OM in the sediment cores should be refractory as a whole, with a small amount of newly synthesized microbe biomass.

4.3. Diagenetic alteration of stable carbon isotopic composition

Because TCHO and THAA are rich in ^{13}C and ^{15}N compared to bulk organic matter and are more labile than lipid and acid-insoluble compounds, preferential degradation of TCHO and THAA has usually been used to explain the negative shift of $\delta^{13}C$ of the residual OM during early diagenesis (e.g., Prahl et al., 1997; Böttcher et al., 1998). On the other hand, lipid also degrades along with TCHO and THAA although presumably at a lower rate, which would ease the negative shift of $\delta^{13}C$. Moreover, the formation and degradation of secondary organic compounds will largely complicate the diagenetic alteration of stable carbon isotopes of OM.

The metabolism and biosynthesis of the decomposers are expected to result in a $\delta^{13}C$ increase of remaining organic matter (Macko and Estep, 1984; Macko et al., 1987; Holmes et al., 1999), which is supposed to be comparable to the general observation in food webs of enrichment of $\delta^{13}C$ and $\delta^{15}N$ in higher trophic levels. However, no systematic increase of $\delta^{13}C$ from plankton→POM→surface sediment→buried sediment was observed in this study for TOC, THAA or any other constituent compounds. On the contrary, an apparent downward decreasing trend of $\delta^{13}C$ was observed for lipid in the sediment cores at both sites (Fig. 3). These observations suggest a preferential degradation of both ^{13}C-rich compound classes and the ^{13}C-rich compounds within a specific compound class.

In summary, multiple mechanisms evidently operated together to create the observed $\delta^{13}C$ variation of TOC and its constituent compounds during early diagenesis. In the water column where aerobic condition prevails, a rapid decomposition of amino acids, carbohydrates and lipids was associated with the growth of large quantities of heterotrophic microbes. Because the $\delta^{13}C$ of the acid-insoluble fraction of the plankton (−24.0‰) is significantly lower than that of the bulk plankton (−20.9‰), decomposition of the labile compounds is expected to decrease the $\delta^{13}C$ of the residual organic matter. However, this decrease in $\delta^{13}C$ was compensated or even outweighed by the formation of microbial biomass that is believed to be rich in ^{13}C compared to the substrate. At the sediment/water interface and in the sediment, the newly formed biomass dominated the substrate of microbes, and the biodegradation preferentially decompose the ^{13}C-rich fractions and compounds of the substrate. It was the contrasting processes that contributed to the relatively conservative nature of $\delta^{13}C_{org}$ during the early diagenesis.

4.4. Diagenetic alteration of nitrogen isotopic composition

Organic matter degradation is generally considered to cause ^{15}N-enrichment in the bulk sediment (e.g., Saino and Hattori, 1980, 1987; Altabet, 1988; Fry et al., 1991; Schaefer and Ittekkot, 1993; Altabet and Francois, 1994; Ostrom et al., 1997; Sachs and Repeta, 1999). In contrast, ^{15}N depletions in residual organic matter have been observed in other studies (e.g., Libes and Deuser, 1988; Altabet et al., 1991; Meyers and Eadie, 1993, Nakatsuka et al., 1997; Altabet et al., 1999; Lehmann et al., 2002). In this study, the $\delta^{15}N$ in the POM and the sediments is significantly lower than that of the plankton, indicating a significant ^{15}N-depletion in OM from the water column. The potential mechanisms leading to changes in the $\delta^{15}N$ of residual OM include preferential loss of isotopically distinct fractions, kinetic isotope fractionation during hydrolysis and bacterial growth. Selective decomposition of amino acids may be a possible mechanism causing the ^{15}N-depletion

of the POM relative to the plankton. However, this isotope effect cannot exceed the opposite effect associated with the hydrolysis of organic matter, which preferentially releases ^{14}N (Bada et al., 1989; Silfer et al., 1992; Lehmann et al., 2002). Therefore, the formation and degradation of bacterial biomass may have been responsible for the observed ^{15}N-depletion in the water column. Because of the general recognition that higher trophic level organisms have high $\delta^{15}N$ values, depletion in ^{15}N for biosynthesized organic matter was often attributed to the assumed preferential excretion of ^{15}N-ammonia (Macko and Estep, 1984; Lehmann et al., 2002). However, ammonia excreted by organisms is characterized by low $\delta^{15}N$ (Checkley and Miller, 1989; Holmes et al., 1999). Hence, we suggest that inorganic nitrogen, rather than the organic substrate, would be the major nitrogen source for the bacteria biosynthesis, which preferentially uses ^{14}N-rich ammonia. Because the availability and $\delta^{15}N$ of ammonia is highly variable in the water column and sediments, significant $\delta^{15}N$ variation for the bacteria biomass are expected, leading to the observed irregular variation of $\delta^{15}N$ in the sediment cores.

5. Conclusions

1. There was a rapid degradation of amino acids, carbohydrates and lipids in the water column of the coastal area off-shore the Pearl River estuary. The organic matter degradation was associated with a rapid bacteria growth and secondary biomass formation, which increased the relative content of THAA and decreased the C/N ratio in the POM. In the sediment, the organic matter is mostly refractory, and newly formed biomass should be the dominant substrate of microbes.
2. Decomposition of labile compounds (THAA, TCHO) was the major mechanism causing ^{13}C-depletion in the residual organic matter. This isotope effect would be cancelled or even be exceeded by the opposite effect due to the addition of higher trophic level organisms that are rich in ^{13}C relative to the substrate. However, bacteria biosynthesis also makes ^{13}C-rich and ^{13}C-poor fractions, and the subsequent biodegradation preferentially decomposes the ^{13}C-rich compound classes and the ^{13}C-rich compounds in a specific class, which often makes the $\delta^{13}C$ of remaining organic matter similar to that of the substrate and kept the $\delta^{13}C$ relatively constant in the sediment core.
3. Because the ^{15}N-depletion caused by preferential degradation of ^{15}N-rich compounds cannot exceed the opposite effect associated with the hydrolysis of organic matter, the addition of bacterial biomass depleted in ^{15}N contributed significantly to the $\delta^{15}N$ decline of organic matter in the water column. The inorganic pool is proposed to be an important nitrogen source for the bacterial biosynthesis, and a preferential uptake of low $\delta^{15}N$ ammonia is expected, resulting in the formation of the ^{15}N-poor bacterial biomass in water column.
4. In the studied coastal area, $\delta^{13}C$ is a reliable geochemical proxy indicating the origin of sedimentary organic matter. The average value of −21.6‰ can be used as the representative value of $\delta^{13}C$ for the sediment organic carbon of aquatic origin. The variation of C/N ratio of the sediments is not significant as compared with the C/N difference between marine and terrestrial organic matter, and can be used as a supplementary line of evidence indicating the origin of OM. However, significant alteration of $\delta^{15}N$ by early diagenesis was observed, resulting in the relatively large and irregular variation of $\delta^{15}N$ in the sediment cores.

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