Organic Matters and Lipid Biomarkers in Surface Sediments from the Northern South China Sea: Origins and Transport

 \mathbf{W} eihai Xu 1 , Wen Yan *1 , Zhong Chen 1 , Han Chen 1 , Weixia Huang 1 , Tian Lin 2

1. *CAS Key Laboratory of Marginal Sea Geology*, *South China Sea Institute of Oceanology*, *Chinese Academy of Sciences*, *Guangzhou* 510301, *China*

2. *Institute of Geochemistry*, *Chinese Academy of Sciences*, *Guiyang* 550002, *China*

ABSTRACT: In this study, content and distribution of organic matters (OM) and lipid biomarkers in surface sediments from northern South China Sea (SCS) were identified to reveal the sources and transport of fine-grained sediments. Organic matters and lipid biomarkers exhibited distinct spatial variation in northern SCS. Terrestrial discharge from the Pearl River and some mountainous rivers in southwestern Taiwan may contribute to the relatively high organic matters in the corresponding sea areas. The detection of unsaturated fatty acid homologues suggested the algal and/or bacterial OM contribution to surface sediments. The composites and distribution of lipid biomarkers indicate their mixed sources from terrestrial plants, marine algae and bacterial. Together with the proof of clay mineral composites in the sediments, the results suggested that the currents, including the Guangdong Coastal Current and Kuroshio Current, control the transport and distribution of terrestrial sediment and the sedimentary environment in the northern SCS.

KEY WORDS: surface sediment, lipid biomarker, South China Sea, sedimentation, transport.

1 INTRODUCTION

Organic matter (OM) in marine sediments of coastal or marginal sea is a complex mixture originating from both marine and terrestrial sources. Terrestrial OM input to ocean margins is mainly from riverine carbon and atmospheric deposition delivered by wind. Continental shelf settings are highly productive areas and characterized by high primary production represent 80% of the total carbon accumulation in the ocean (Ver et al., 1999). The organic material derived from primary marine production may be deposited in continental slop sediments. Therefore, continental shelves play a key role in the global carbon cycle (Tesi et al., 2007).

South China Sea (SCS) is the largest marginal sea of western Pacific with an average depth over 2 000 m. Previous studies have demonstrated that the river-borne terrigenous sediments compose ~80% of total SCS surface sediments and have produced high sedimentation-rate deposition in the geological past. Together with the Mekong River, the Pearl River provides the largest inflow of fresh water to the SCS. For the northern SCS, most of previous studies considered the Pearl River as the main sedimentary source with an additional volcanic source (Chen et al., 2009; Li et al., 2003; Liu et al., 2003). However, the proofs of clay mineralogy and elemental geochemistry in recent investigations had revealed that Taiwan, the

Yangtze River and the Luzon Islands also significantly contributed the terrestrial deposit to the northern SCS.

Organic biomarkers can provide abundant information about the original sedimentary source material, change in geochemical and biochemical processes, climatic changes and further for paleoenvironment records (Riboulleau et al., 2007; Winter et al., 2005). Therefore, they have been widely used to reconstruct past changes in different aquatic or deposit environment. In the last few decades, biomarkers in deep-sea sediments have been used to assess the paleoclimate changes over the Quaternary. Biomarkers in particular, can provide valuable information on OM origin and transformation processes in estuaries and marine environments. For instance, it had a long history in using stable isotope data to identify the different sources of organic matter, such as to infer C and N sources in marine sediments, although the differentiation tends to be limited to rather broad categories such as ''terrestrial" or ''marine". Clay minerals are an important and widely distributed component in soils and sediments. According to their genesis, clay minerals can be utilized to trace the surface ocean current variations and contemporaneous paleoclimatic changes prevailing in continental source areas (Liu J G et al., 2010; Wahsner et al., 1999). In the SCS, clay minerals have played a significant role in the study of the East Asian monsoon evolution (Liu et al., 2005). The primary aims of this study are to examine the abundance, distribution and sources of organic matter and lipid biomarkers in surface sediments from northern SCS. Further is to understand the transport of organic matter based on the evidences of lipid biomarkers and clay minerals.

Xu, W. H., Yan, W., Chen, Z., et al., 2014. Organic Matters and Lipid Biomarkers in Surface Sediments from the Northern South China Sea: Origins and Transport. *Journal of Earth Science*, 25(1): 189–196, doi:10.1007/s12583-014-0412-z

^{*}Corresponding author: wyan@scsio.ac.cn

[©] China University of Geosciences and Springer-Verlag Berlin Heidelberg 2014

Manuscript received April 11, 2013. Manuscript accepted August 28, 2013.

2 METHODS AND MATERIALS

2.1 Study Area and Samples Collection

The northern part of the SCS is at a typical passive continental margin, which is composed of several faulted terraces and basins. The current system is complicated in the SCS as well as in the northern SCS which controlled by several factors. The East Asian Monsoons are prevailing in the SCS, which controls the surface circulation in the SCS. The surface current flows southwestward in winter driven by the Northeast Monsoon. In contrast, it flows northeastward in summer driven by the Southwest Monsoon (Liu Z F et al., 2010; Fang et al., 1998). Therefore, the upper layer mean circulation is cyclonic in winter and anticyclonic in summer. In addition, the winter monsoon is stronger and longer in lasting period than the summer monsoon (Liu Z F et al., 2010). Guangdong Coastal Current flows on the northern shelf along the northeasterly direction of the winter monsoon winds. Studies have proved the Kuroshio Current could intrude into the SCS (Caruso et al., 2006). After entering the SCS, the Kuroshio intrusion then was separated into three parts. The dominant path of the major part was observed from northeast of Luzon to southwest of Taiwan and then westward along the northern slope of the SCS (Wang et al., 2010). The northeastward SCS warm current is a flow separated from the SCS branch of Kuroshio. In addition, the deep water current from the Luzon Strait, the only deep passage connecting the SCS with the western Pacific, can carry sedimentary materials to the northern slope of the SCS. It has been deduced that the deep water current first turns northwestward and then turns southwestward along the continental margins off southeast China after entering the SCS. Finally, it exported out of the SCS through the Luzon Strait again (Tomaru et al., 2004).

In this study, surface sediment samples $(\leq 10 \text{ cm})$ were collected with a grab sampler from August 10–30, 2007 during a Shiyan III cruise (Fig. 1). The sampling sites were mainly located in four sea areas-offshore area of Southwest Taiwan, Pearl River Mouth Basin, Shenhu area and Xisha trough, respectively. Detailed information of sampling sites was listed in Table 1. The collected sediment samples were freeze-dried at -20 ºC and ground into powder using an agate pestle and mortar.

2.2 Organic Matters Analysis

The total organic carbon (TOC) and nitrogen (TN) were measured based on the method described in Hu's study (Hu et al., 2006a). Briefly, sediment samples were treated with 4 N HCl to remove carbonate and subsequently rinsed with deionized water to remove salts before drying overnight at 60 °C. The carbonatefree samples were analyzed for TOC and TN in duplicates in a Vario EL-III Elemental Analyzer and average values were reported. Replicate analysis of one sample (*n*=6) gave a precision of ± 0.02 wt.% for TOC and ± 0.004 wt.% for TN.

The analytical extraction procedure for the organic biomarkers (aliphatic hydrocarbons and fatty acid) in the sediment samples were Soxhlet extracted by organic solvent. Detailed procedure has been reported in previous studies (Hu et al., 2009, 2006a; Lu and Zhai, 2006; Duan, 2000). Briefly, the freezedried sediment samples (about 50 g) were extracted with a chloroform-methanol (2 : 1, V/V) mixture for 48 h. Thereafter, the total extracts were fractionated by column chromatography on alumina over silica gel. The aliphatic hydrocarbons were eluted in the first fraction with hexane and fatty acids with 20% ethyl acetate in hexane. The fatty acid fraction was saponified with 0.5 M KOH in methanol and then extracted in hexane and methylated with 10% BF₃. The aliphatic hydrocarbons were analyzed and quantified using a Hewlett Packard gas chromatograph (HP 6890) with a split/splitless injector and a flame ionization detector (FID). The fatty acid was analyzed by gas chromatography-mass spectrometry (GC-MS, VG Instruments

Figure 1. Sampling locations in the northern SCS.

Table 1 Detailed information for the sampling sites

Samples	Longitude	Latitude		pH
	(°E)	$({}^\circ \mathrm{N})$	depth(m)	
S ₁	114°17.353	22°3.699	36	6.9
S ₂	114°23.163	21°50.252	52	6.9
S3	110°41.376	18°59.957	65	7.1
S4	112°0.793	18°0.341	2450	7.0
S5	114°34.477	19°43.341	1 0 5 0	5.9
S6	$115^{\circ}6.480$	19°52.267	1 3 1 2	7.0
S7	114°44.956	19°44.946	1 1 5 3	6.9
S8	115°12.976	19°54.259	1 2 2 8	6.9
S9	115°29.378	19°0.582	1 300	6.9
S ₁₀	119°30.041	$22^{\circ}0.315$	2455	6.9
S11	118°67.006	$22^{\circ}0.574$	1632	\mathbf{a}
S12	111°4.458	18°2.715	1 565	

^a. Not available.

Platform II) equipped with a DB-5 (50 m, 0.32 mm i.d., 0.25 μ m). The temperature of oven was programmed from 80 to 290 °C at 4 min, and then kept for 30 min. The carbon isotopic analyses of aliphatic hydrocarbons were performed on an HP 5890 gas chromatography combined with an Isochrom II isotope ratio mass spectrometer.

2.3 Clay Minerals Analysis

Clay minerals $(\leq 2 \mu m)$ were identified by standard X-ray diffraction (XRD) on a D8 ADVANCE diffractometer with CuKα radiation, which has been described before (Liu J G et al., 2010; Liu Z F et al., 2003). Relative percentages of each main clay mineral were measured by weighting integrated peak areas of characteristic basal reflections in the glycolated state with the empirical factors. Relative proportions of kaolinite and chlorite were obtained according to the ratio of 3.57/3.54 Å peak areas. The accuracy of semiquantitative evaluation of each clay mineral was about 5%.

3 RESULTS AND DISCUSSION

3.1 Contents and Origins of TOC and TN in the Sediments

The TOC $(\%)$ and TN $(\%)$ values of the sediments were shown in Table 2. The TOC contents ranged from 0.28% to 0.93% with a mean value of 0.61%. Spatial distribution showed high level of TOC content in the samples located in southwest Taiwan, Pearl River Mouth Basin and Shenhu area with the highest up to 0.93% of the S11 sample. In addition, they were also much higher than the mean 0.2% identified in modern deep ocean sediments. According to previous study, terrigenous deposit from the flux of Pearl River water still play an important role in Pearl River Mouth Basin (Zhang et al., 2013). For Southwest Taiwan, mountainous rivers may contribute to the relative high organic matter. Further, it has been proved that organic matter contained in the seawater from the Bashi Channel and Taiwan Strait can deposit in this sea area (Sun et al., 1999). TN contents in the sediments range from 0.06% to 0.15%. In spatial distribution, TN contents show a positive correlation with TOC in sediment samples. It is known that C/N weight ratio has been widely used for source identification of organic matter. According to classification, the ratios 5–7 mean it is from marine organic matter and >15 from terrestrial organic matter. The measured TOC/TN ratios in this study vary from 4.5 to 8.0 with a mean of 6.3 suggesting a predominant marine origin. It should be noted that an important assumption is needed in the above identification that all of the sedimentary TN exclusively reflects N bound to organic matter. However, inorganic nitrogen (IN) often exists in marine sediment and presumably adsorbed on the clay as NH_4^+ formula in surface sediments. In addition, the presence of IN can interfere with SOM source identification especially when the TN concentrations are low. Accordingly, this identification is likely to overestimate the contribution of marine source. If the amount of IN is subtracted from each sample, the C/N ratios would range from 5.5 to 10.3. The corrected values suggest a mixed marine-terrestrial organic matter origin for some area in this study. The highest ratio was observed in the Pearl River Mouth Basin. Therefore, the conclusion can be drawn that the strong river input from the Pearl River can increase the deposition of terrigenous organic matter in the basin, which has already been proved in previous study (Hu et al., 2006a).

3.2 Composition and Distribution of Aliphatic Hydrocarbons

N-alkanes are major components of aliphatic hydrocarbons from the areas in this study. The *n*-alkanes from NSCS sediments mainly consist of $C_{13}-C_{35}$ compounds with the total absolute concentrations ranging of 0.56–1.8 μg/g. The calculated parameters of the aliphatic hydrocarbons are listed in Table 3. There was a strong odd-even carbon preference in the high molecular weight *n*-alkanes in most sediment samples. However, the *n*-alkanes in the sediments showed different molecular distributions. Such distribution of *n*-alkanes is similar to those reported in the Nansha Sea and California continental margin sediments (Mangelsdorf and Rullkotter, 2003; Duan, 2000).

In general, the distribution of the aliphatic hydrocarbons in the northern SCS can be roughly divided into three types (Fig. 2). The first distribution type is bimodal, represented by the

Table 2 Compositions and parameters of bulk organic matter in the surface sediments

Samples	TOC $(\%)$	TN(%)	C/N	C/N (R) ^a
S ₁	0.57	0.08	7.1	10.3
S ₂	0.48	0.06	8.0	9.7
S ₃	0.48	0.07	6.9	6.9
S ₄	0.38	0.08	4.5	5.5
S ₅	0.52	0.11	4.7	6.5
S ₆	0.62	0.09	6.9	7.7
S7	0.60	0.08	7.5	8.1
S ₈	0.56	0.10	5.6	7.0
S ₉	0.73	0.12	6.3	8.1
S ₁₀	0.71	0.13	5.4	8.9
S ₁₁	0.93	0.15	6.2	7.7
S ₁₂	0.81	0.14	5.8	6.7

^a. C/N (R) is the C/N values obtained after organic nitrogen (ON)-corrected for the former C/N.

samples of S1, S2 and S3. These samples have *n*-alkanes ranging from *n*-C₁₃ to *n*-C₃₃ with the maximum at *n*-C₁₆ in the short-chain and either $n-C_{29}$ or $n-C_{31}$ in the long-chain *n*-alkanes. A distinct odd-even predominance was also found in the long-chain *n*-alkanes. Short-chain *n*-alkanes ($\leq C_{21}$) have been ascribed to the sources of both marine algae and bacterial (Blumer et al., 1971). The ratios (range $0.9-1.1$) of $n-C_{21}/nC_{21+}$ obtained in the three sediment samples were lower than those in other samples, suggesting the different sources of *n*-alkanes. It has been documented that high carbon preference index (CPI) in the range of 4–10 can suggest the presence of prominent terrestrial inputs (Aboul-Kassim and Simoneit, 1996). The CPIs of $nC_{25}-nC_{35}$ obtained in the three samples were a little higher than those in other samples with the mean value of 3.0 (range 2.0–4.5). However, The CPI values were still less than the range of 4–10 reported for land plants. Besides, most of the dominant peak for the long-chain *n*-alkanes was either *n*-C₂₉ or *n*-C₃₁. Therefore, it can be concluded that the *n*-alkanes compounds from the three sampling sites mainly originated from both terrestrial plants and marine algae and bacterial. Obviously, the terrestrial parts for S1 and S2 are mainly contributed by the water flux of the Pearl River, and it has been confirmed in previous studies (Sun et al., 1999). The ratio between the sum of most abundant odd number *n*-alkanes $(C_{27}$, C_{29} , C_{31} , C_{33}) and the total *n*-alkanes can be taken as an estimation of land-derived. In this study, it is estimated that 29% of the *n*-alkanes from the S1 originated from the terrestrial plants. The figures for S2 and S3 were 28% and 30%, respectively.

The second type is also bimodal, represented by the samples of S9, S10, S11 and S12. However, the major peaks in the short-chain were far higher than those in the long-chain *n*-alkanes with the maximum at either $n-C_{15}$ or $n-C_{17}$. An odd-even predominance was also found in the long-chain *n*-alkanes. The CPI values in these four particular locations oscillate between 1.6 and 2.9, matching the CPIs observed in the deep-sea sediments from the western tropical Pacific Ocean and in the SCS (Ohkouchi et al., 1997). Obviously, these CPI values were lower than those in the samples from the first type, suggesting the weak influence from the terrestrial matter input. The ratio of $n-C_{17}/n-C_{29}$ was employed as a parameter to indicate marine or terrigenous input of *n*-alkanes.

The ratio values were in the range of 0.44–5.1 with a mean of 2.2. Similar results were found in Southeast Florida (range 0.46–6.68). However, the level examined in this study was far higher than that in Changjiang estuary, Amazon shelf or East China Sea (Elias and Cardoso, 1996; Bigot et al., 1989). The third type is represented by the samples of S4–S8. The distribution of *n*-alkanes is unimodal with *n*-C₁₅ or *n*-C₁₇ as the dominant peak. The highest nC_{21}/nC_{21+} ratio was found in these types with a range of 2.0–7.0. The high nC_{21}/nC_{21+} ratios obtained in this type suggest the dominating marine origination of these sediment samples. The long-chain *n*-alkanes exhibited a not very strong odd-even carbon number predominance, with CPI values in the range of 1.4–2.4, less than the range of 4–10 reported for land plants. Short-chain *n*-alkanes (n -C₁₄ to C₂₀) can be derived from marine plankton and/or bacteria.

3.3 Carbon Isotopic Compositions (δ13C) of Individual *n***-Alkanes**

The carbon isotopic compositions $(\delta^{13}C)$ of individual *n*-alkanes ($n-C_{13}$ to $n-C_{33}$) were measured with the range of -35.2‰– -26.3‰ for all the samples (Table 3). The mean value ranged from -31.1‰ to -28.8‰. The δ^{13} C values in the northern SCS coincide well with those in the sediments collected from the Sea of Japan and Bering Sea (Ratnayake et al., 2005; Yamada and Ishiwatari, 1999). The long-chain lipids of C_3 plants show light values (from -39% to -30%) than those of C_4 plant (from -25% to -18%). Therefore, if the contribution of C_4 plants increases, sedimentary *n*-alkanes would shift toward isotopically heavier values. In this study, the δ^{13} C values are characterized by a decreasing trend with molecular increasing, which is consistent with an increasing contribution from a terrestrial C_3 plant source. The $\delta^{13}C$ long-chain *n*-alkanes (C_{27} , C_{29} and C_{31}) suggest the organic matter at the samplings sites is a mixture of terrestrial plants and marine algae. However, the actual distribution pattern and isotopic values of *n*-alkanes depends on C₃ plant type (e.g., angiosperms vs. gymnosperms) and ocean current conditions.

3.4 Compositions and Distribution of Fatty Acid

Fatty acids are often used to identify the sources and fate

Sample	Carbon number range	$\mathbb{CPI}^{\mathsf{a}}$	$\sum n_{21} \sum n_{21+}$	$n - C_{17}/n - C_{29}$	δ^{13} C value (‰)
S ₁	$nC_{13}-nC_{33}$	2.0	1.0	0.4	$-30.5 - -26.3 (-29.9)^{b}$
S ₂	$nC_{13}-nC_{33}$	2.6	1.0	0.6	$-31.8 - -30.0$ (-31.0)
S3	$nC_{13}-nC_{33}$	4.5	1.1	1.0	$-31.0 - -26.4$ (-29.9)
S4	$nC_{13}-nC_{34}$	2.1	7.0	5.2	$-30.9 - -28.0$ (-28.8)
S5	$nC_{13}-nC_{34}$	1.4	2.6	1.9	$-30.7 - -27.3$ (-30.4)
S6	$nC_{13}-nC_{33}$	1.9	2.0	1.9	$-30.0 - -26.4(-30.1)$
S7	$nC_{13}-nC_{33}$	2.4	3.6	2.8	$-30.2 - -27.4$ (-29.9)
S8	$nC_{13}-nC_{33}$	2.3	5.6	2.7	$-30.9 - -26.6(-30.1)$
S9	$nC_{13}-nC_{35}$	2.0	1.8	1.5	$-30.8 - -26.4(-30.1)$
S ₁₀	$nC_{13}-nC_{35}$	1.8	2.6	3.0	$-31.0 - -29.2$ (-31.1)
S ₁₁	$nC_{13}-nC_{33}$	1.7	2.3	2.0	$-30.8 - -27.1$ (-29.4)
S ₁₂	$nC_{13}-nC_{33}$	2.9	2.0	1.3	$-31.8 - -26.7(-31.0)$

Table 3 Diagnostic parameters of the aliphatic hydrocarbons and δ13C value in the sediments

^a. CPI= $\sum C_{25}$ - $C_{35}/\sum C_{24}$ - C_{34} ; ^b. mean value.

Figure 2. Distributions of *n***-alkane in the surface sediments.**

of organic matter in marine environment sediment (Hu et al., 2006b). In this study, a total of 33 fatty acids were identified in the surface sediment samples from the northern SCS. Saturated fatty acids (*n*-fatty acids) were the main compounds detected in the sediment samples. The abundance of the total saturated *n*-fatty acids ranged between 2.02 and 23.5 μg/g (Table 4). The total *n*-fatty acids show no notable trends in spatial distribution. Sampling sites S1 and S3, close to the continent, displayed a little decrease in total concentrations.

Generally, the *n*-fatty acids exhibit a bimodal distribution in all samples with maximizing at C_{16} and at C_{24} , C_{26} or C_{28} . *n*-C_{16:0}, the most abundant saturated *n*-fatty acid, contributed about 35%–59% of total fatty acids. Previous studies revealed that long chain *n*-fatty acids originated from terrestrial input, deriving from higher plant waxes (Xu et al., 2006). The ratios of short/long ranged from 5.43 to 12.3 which revealed that the *n*-fatty acids

were mainly come from marine autogenic organic matter in the northern SCS. The relatively low ratios of short/long in the S1, S2 and S3 suggest that there are several sources of organic matter in the estuarine system, such as the marine phytoplankton, bacteria and terrestrial higher plants. This indication is in agreement with that of *n*-alkanes in these surface sediments of northern SCS.

It is known that unsaturated fatty acids are easy to undergo preferential degradation relative to their saturated counterparts. However, unsaturated fatty acid homologues (e.g., $C_{16:1}$, $C_{18:1}$, $C_{18/2}$) were still detected in sediments of these samples suggesting a large algal/bacteria OM contribution to surface sediments. In this study, the unsaturated were found to be dominated by $C_{16:1}$ and $C_{18:1}$, which suggests that the main source was phytoplankton, zooplankton and bacteria. The ratios of $C_{16/1}/C_{16/0}$ are often used as evidence to assess diatom inputs in different aquatic systems (Budge and Parrish, 1998). It was

Carbon number	S ₁	S ₂	S ₃	S ₄	S ₅	S ₆	S7	S ₈	S9	S ₁₀	S ₁₁	S ₁₂
12	0.04	0.71	0.07	0.38	0.54	0.15	0.27	0.15	0.38	0.11	0.38	1.20
13	$-$ a	0.08	$\overline{}$	$\overline{}$	0.07	$\overline{}$	0.08	0.02	0.08	$\overline{}$	$\overline{}$	0.13
14	0.12	1.50	0.35	1.07	1.68	0.40	1.75	0.96	1.66	0.40	0.28	3.65
15	0.05	0.59	0.16	0.56	0.52	0.15	0.61	0.36	0.55	0.15	0.09	0.88
16	0.95	11.8	2.21	10.2	12.9	5.39	9.16	6.94	7.09	2.86	4.01	12.7
17	0.11	1.34	0.24	1.33	0.37	0.57	0.56	0.17	0.54	0.02	0.04	0.37
18	0.41	3.45	0.44	2.48	3.37	3.09	1.67	1.38	1.58	0.37	1.26	2.28
19	$\overline{}$	0.05	$\overline{}$	0.06	0.14	0.00	0.03	0.05	0.08	$\overline{}$	0.02	0.04
20	0.02	0.24	0.01	0.34	0.31	0.09	0.23	0.28	0.36	0.27	0.17	0.34
21	0.03	0.02	0.04	0.08	0.08	0.07	0.02	0.02	0.03	0.02	0.02	0.05
22	0.02	0.30	0.01	0.45	0.39	0.13	0.04	0.05	0.07	0.06	0.17	0.42
23	0.05	0.02	0.02	0.11	0.17	0.04	0.03	0.03	0.15	0.02	0.03	0.06
24	0.03	0.24	0.14	0.34	0.16	0.14	0.39	0.45	0.07	0.16	0.29	0.33
25	$\overline{}$	0.04	$\overline{}$	0.06	0.02	$\overline{}$	0.09	0.02	0.03	0.02	0.05	0.07
26	0.03	0.18	0.01	0.25	0.29	0.14	0.41	0.59	0.47	0.22	0.03	0.33
27		$\qquad \qquad -$	$\overline{}$	$\overline{}$	0.06	$\overline{}$	0.03	0.12	0.09	$\overline{}$	0.03	0.04
28	0.13	0.22	0.22	0.17	0.21	0.17	0.25	0.29	0.57	0.16	0.14	0.24
29		$\overline{}$		$\overline{}$	0.03	$\overline{}$	0.02	0.09	0.08	$\overline{}$	0.03	0.03
30	0.03	0.21	0.14	0.13	0.11	0.10	0.16	0.04	0.03	0.01	0.12	0.20
31	$\qquad \qquad -$			$\overbrace{}$	$\qquad \qquad -$	$\overline{}$		$\qquad \qquad$		$\overbrace{}$		$\overline{}$
32	$\qquad \qquad -$	0.08	$\overline{}$	$\qquad \qquad -$	0.10	0.07	$\qquad \qquad -$	$\qquad \qquad -$	0.02	$\overline{}$	0.02	0.10
Total	2.02	21.1	4.06	18.4	21.5	10.7	15.8	12.0	13.9	4.84	7.17	23.5
Short/long	5.43	15.12	6.00	10.39	12.33	11.37	9.99	6.04	7.71	6.36	6.86	11.58
$C_{16 \div 1}/C_{16 \div 0}$	0.13	0.52	0.27	0.82	0.51	0.77	0.27	0.53	0.64	0.23	0.10	1.07
$C_{18 \div 1}/C_{18 \div 0}$	3.50	4.00	7.70	2.20	3.50	3.80	5.60	6.30	5.40	4.30	6.00	3.80

Table 4 Concentrations and geochemical proxies of fatty acids in surface sediments (μg/g)

a . Unable to determine.

documented that the ratio values higher than 1.6 have been interpreted as a predominance of diatoms (Mudge et al., 1998). In northern SCS, these ratios were usually below 1.0 except for 1.4 at sampling site S12, suggesting significant but not dominant diatom-derived OM inputs to the sediments. Thus, marine bacterium and other microorganism are considered as key contributors to fatty acids in the northern SCS.

3.5 Effects of Currents on the Transport of OM and Biomarkers

The composites and sources of the OM and lipid biomarkers both suggested that terrestrial discharge acted as an important role in the sedimentary process of the northern SCS. it was estimated that about 570 Mt/yr suspended sediments was discharged into the SCS mainly from the three large rivers (Mekong River, Pearl River, and Red River) and some mountainous rivers in southwestern Taiwan (Liu J G et al., 2010; Liu J P et al., 2008; Dadson et al., 2003). Almost a half of them were discharged into the northern SCS.

The Pearl River is the largest river surrounding the northeastern SCS, which provides 90 Mt/yr suspended matters to the SCS. Therefore, as deduced above, the terrigenous parts of the OM and biomarkers deposited in offshore of the Pearl River (Pearl River Mouth Basin) mainly come from the Pearl River discharge. This can also be confirmed by the composition and distribution of clay mineral. Figure 3 showed the composition characteristics of clay mineral in the surface sediments. Previous study revealed that the Pearl River sediments consist mainly of kaolinite (average 46%), illite (31%), and chlorite (18%) with scarce smectite (5%) (Liu Z F et al., 2009, 2008). Kaolinite is also the most abundant clay mineral (average 42%) found in the samples (S1 and S2) which located in the offshore of the Pearl River. Though smectite and chlorite showed little increase, the composition characteristics in the two samples were very similar to the Pearl River. In addition, kaolinite is also high in the S3 sample. It should be noted that among the rivers around the SCS only the Pearl River sediments consist mainly of kaolinite. Hence, it can be concluded that the suspended matter could be transferred to the southwest of Guangdong Province and even the eastern of Hainan Island under the drive of westward Guangdong Coastal Current in winter and the longshore current (Liu J G et al., 2010; Liu Z F et al., 2010). However, the major terrigenous matter from the Pearl River was limited to the offshore of the Pearl River. It was known that the vast majority of suspended matters in river discharge would deposit in the mixed zone of river and seawater due to the process of flocculation and coagulation. Consequently, kaolinite remarkably decreased in Dongsha Islands and Shenhu area.

The samples in the southwestern Taiwan provided rather similar clay mineral compositions to the mountainous rivers in

Figure 3. Composition of clay mineral in the surface sediments.

southwestern Taiwan with an average of 50% for illite and 30% for chlorite. The other two compositions were found rare in the sediments. Hence, it proved that the terrestrial discharge from Taiwan is the dominant source of organic matter and biomarkers in the sediments. In addition, due to the fact that SCS branch of the Kuroshio (SCSBK) and SCS warm current are perennially existent in SCS, Taiwan-sourced sediment is transported southwestward into Dongsha Islands and Shenhu area by their driving. The Kuroshio intrusion route had been clearly identified by the distribution of typical minerals and elements in previous literatures (Liu J G et al., 2010; Liu Z F et al., 2010). Obviously, the terrestrial matter from the Luzon Island can also be transported to the deep sea environment by the SCSBK and warm current. Smectite was dominantly detected in Luzon rivers sediments throughout the island (Liu et al., 2009). The high content of smectite and illite in the samples from the Shenhu area suggested their mixed terrestrial sources from Taiwan and Luzon Island. Smectite in the northern SCS is mainly transported from the Luzon Island via the surface current under the influence of the Kuroshio intrusion. However, it can be hardly transported to the northern shelf of the SCS due to the occurrence of eddy in the west of Luzon Island.

4 CONCLUSION

TOC and TN in the samples from the northern SCS correlated well and indicated mixed sources for organic matters. The results show that there are great spatial variations in terms of organic matter abundance and hydrocarbon composition from northern SCS. The profiles of both *n*-alkanes and fatty acids indicated the mixed sources in the northern SCS. Pearl River and some mountainous rivers in southwestern Taiwan were dominant terrigenous sources to the northern SCS. A relatively abundant short-chain of fatty acids were found at the sampling sites indicating that fatty acids in northern SCS surface sediments predominantly derived from marine bacteria with subordinate abundance of higher terrestrial plants. Clay mineral composites partly proved that the transport and distribution of terrestrial sediments and the sedimentary environment in northern SCS can be controlled by Guangdong Coastal Current and Kuroshio Current.

ACKNOWLEDGMENTS

We thank the open cruise of Shiyan-III organized by South China Sea Institute of Oceanology, CAS, for providing the opportunity to sample in the SCS. This study was supported by the Innovative Program of CAS (No. KZCX2-YW-GJ03) and 973 Project (No. 2009CB219502-04). This study was also founded by the Natural Science Foundation of Guangdong Province (No. S2013010013744) and Scientific Frontier Program for Young Talents of the South China Sea Institute of Oceanology, CAS (No. SQ200909).

REFERENCES CITED

- Aboul-Kassim, T. A. T., Simoneit, B. R. T., 1996. Lipid Geochemistry of Surficial Sediments from the Coastal Environment of Egypt І. Aliphatic Hydrocarbons—Characterization and Sources. *Marine Chemistry*, 54(1–2): 135–158
- Bigot, M., Saliot, A., Cui, X., et al., 1989. Organic Geochemistry of Surface Sediments from the Huanghe Estuary and Adjacent Bohai Sea (China). *Chemical Geology*, 75(4): 339–350
- Blumer, M., Guillard, R. R. L., Chase, T., 1971. Hydrocarbons of Marine Phytoplankton. *Marine Biology*, 8(3): 183–189
- Budge, S. M., Parrish, C. C., 1998. Lipid Biogeochemistry of Plankton, Settling Matter and Sediments in Trinity Bay, Newfoundland. II. Fatty Acids. *Organic Geochemistry*, 29(5–7): 1547–1559
- Caruso, M. J., Gawarkiewicz, G. G., Beardsley, R. C., 2006. Interannual Variability of the Kuroshio Intrusion in the South China Sea. *Journal of Oceanography*, 62(4): 559–575
- Chen, Z., Yan, W., Tang, X. Z., et al., 2009. Magnetic Susceptibility in Surface Sediments in the Southern South China Sea and Its Implication for Sub-Sea Methane Venting. *Journal of Earth Science*, 20(1): 193–204
- Dadson, S. J., Hovius, N., Chen, H. G., et al., 2003. Links between Erosion, Runoff Variability and Seismicity in the Taiwan Orogen. *Nature*, 426(6967): 648–651
- Duan, Y., 2000. Organic Geochemistry of Recent Marine Sediments from the Nansha Sea, China. *Organic Geochemistry*, 31(2–3): 159–167
- Elias, V. O., Cardoso, J. N., 1996. Sources and Transport of Lipids

on Amazon Continental Shelf. *Geo-Marine Letters*, 16(1): 11–16

- Fang, W. D., Guo, Z. X., Huang, Y. T., 1998. Observational Study of the Circulation in the Southern South China Sea. *Chinese Science Bulletin*, 43(11): 898–905
- Hu, J. F., Peng, P. A., Chivas, A. R., 2009. Molecular Biomarke Evidence of Origins and Transport of Organic Matter in Sediments of the Pearl River Estuary and Adjacent South China Sea. *Applied Geochemistry*, 24(9): 1666–1676
- Hu, J. F., Peng, P. A., Jia, G. D., et al., 2006a. Distribution and Sources of Organic Carbon, Nitrogen and Their Isotopes in Sediments of the Subtropical Pearl River Estuary and Adjacent Shelf, Southern China. *Marine Chemistry*, 98(2–4): 274–285
- Hu, J. F., Zhang, H. B., Peng, P. A., 2006b. Fatty Acid Composition of Surface Sediments in the Subtropical Pearl River Estuary and Adjacent Shelf, Southern China. *Estuarine Coastal and Shelf Science*, 66(1–2): 346–356
- Li, X. H., Wei, G. J., Shao, L., et al., 2003. Geochemical and Nd Isotopic Variations in Sediments of the South China Sea: A Response to Cenozoic Tectonism in SE Asia. *Earth and Planetary Science Letters*, 211(3–4): 207–220
- Liu, J. G., Chen, M. H., Chen, Z., et al., 2010. Clay Mineral Distribution in Surface Sediments of the South China Sea and Its Significance for in Sediment Sources and Transport. *Chinese Journal of Oceanology and Limnology*, 28(2): 407–415
- Liu, J. P., Liu, C. S., Xu, K. H., et al., 2008. Flux and Fate of Small Mountainous Rivers Derived Sediments into the Taiwan Strait. *Marine Geology*, 256(1–4): 65–76
- Liu, Z. F., Colin, C., Li, X. J., et al., 2010. Clay Mineral Distribution in Surface Sediments of the Northeastern South China Sea and Surrounding Fluvial Drainage Basins: Source and Transport. *Marine Geology*, 277(1–4): 48–60
- Liu, Z. F., Tuo, S. T., Colin, C., et al., 2008. Detrital Fine-Grained Sediment Contribution from Taiwan to the Northern South China Sea and Its Relation to Regional Ocean Circulation. *Marine Geology*, 255(3–4): 149–155
- Liu, Z. F., Zhao, Y. L., Colin, C., et al., 2009. Chemical Weathering in Luzon, Philippines from Clay Mineralogy and Major-Element Geochemistry of River Sediments. *Applied Geochemistry*, 24(11): 2195–2205
- Liu, Z. F., Colin, C., Trentesaux, A., et al., 2005. Clay Mineral Records of East Asian Monsoon Evolution during Late Quaternary in the Southern South China Sea. *Science in China Series D*: *Earth Sciences*, 48(1): 84–92
- Liu, Z. F., Trentesaux, A., Clemens, S. C., et al., 2003. Clay Mineral Assemblages in the Northern South China Sea: Implications for East Asian Monsoon Evolution over the Past 2 Million Years. *Marine Geology*, 201(1–3): 133–146
- Lu, X. X., Zhai, S. K., 2006. Distributions and Sources of Organic Biomarkers in Surface Sediments from the Changiiang (Yangtze River) Estuary, China. *Continental Shelf Research*, 26(6): 823–823
- Mangelsdorf, K., Rullkotter, J., 2003. Natural Supply of Oil-Derived Hydrocarbons into Marine Sediments along the California Continental Margin during the Late Quaternary.

Organic Geochemistry, 34(8): 1145–1159

- Mudge, S. M., East, J. A., Bebianno, M. J., et al., 1998. Fatty Acids in the Ria Formosa Lagoon, Portugal. *Organic Geochemistry*, 29(4): 963–977
- Ohkouchi, N., Kawamura, K., Kawahata, H., et al., 1997. Latitudinal Distributions of Terrestrial Biomarkers in the Sediments from the Central Pacific. *Geochimica et Cosmochimica Acta*, 61(9): 1911–1918
- Ratnayake, N. P., Suzuki, N., Matsubara, M., 2005. Sources of Long Chain Fatty Acids in Deep Sea Sediments from the Bering Sea and the North Pacific Ocean. *Organic Geochemistry*, 36(4): 531–541
- Riboulleau, A., Schnyder, J., Riquier, L., et al., 2007. Environmental Change during the Early Cretaceous in the Purbeck-Type Durlston Bay Section (Dorset, Southern England): A Biomarker Approach. *Organic Geochemistry*, 38(11): 1804–1823
- Sun, X. J., Li, X., Beug, H. J., 1999. Pollen Distribution in Hemipelagic Surface Sediments of the South China Sea and Its Relation to Modern Vegetation Distribution. *Marine Geology*, 156(1–4): 211–226
- Tesi, T., Miserocchi, S., Goni, M. A., et al., 2007. Organic Matter Origin and Distribution in Suspended Particulate Materials and Surficial Sediments from the Western Adriatic Sea (Italy). *Estuarine Coastal and Shelf Science*, 73(3–4): 431–446
- Tomaru, H., Matsumoto, R., Lu, H. L., et al., 2004. Geochemical Process of Gas Hydrate Formation in the Nankai Trough Based on Chloride and Isotopic Anomalies in Interstitial Water. *Resource Geology*, 54(1): 45–51
- Ver, L. M. B., Mackenzie, F. T., Lerman, A., 1999. Carbon Cycle in the Coastal Zone: Effects of Global Perturbations and Change in the Past Three Centuries. *Chemical Geology*, 159(1–4): 283–304
- Wahsner, M., Muller, C., Stein, R., et al., 1999. Clay-Mineral Distribution in Surface Sediments of the Eurasian Arctic Ocean and Continental Margin as Indicator for Source Areas and Transport Pathways—A Synthesis. *Boreas*, 28(1): 215–233
- Wang, X., Wu, S., Yuan, S., et al., 2010. Geophysical Signatures Associated with Fluid Flow and Gas Hydrate Occurrence in a Tectonically Quiescent Sequence, Qiongdongnan Basin, South China Sea. *Geofluids*, 10(3): 351–368
- Winter, M. J., Verweij, F., Garofalo, E., et al., 2005. Tissue Levels and Biomarkers of Organic Contaminants in Feral and Caged Chub (Leuciscus Cephalus) from Rivers in the West Midlands, UK. *Aquatic Toxicology*, 73(4): 394–405
- Xu, Y. P., Mead, R. N., Jaffe, R., 2006. A Molecular Marker-Based Assessment of Sedimentary Organic Matter Sources and Distributions in Florida Bay. *Hydrobiologia*, 569: 179–192
- Yamada, K., Ishiwatari, R., 1999. Carbon Isotopic Compositions of Long-Chain N-Alkanes in the Japan Sea Sediments: Implications for Paleoenvironmental Changes over the Past 85 kyr. *Organic Geochemistry*, 30(5): 367–377
- Zhang, L., Yin, K. D., Yang, Y. Q., et al., 2013. Distribution Characteristics and Sources of Sedimentary Organic Matter in the Pearl River Estuary and Adjacent Coastal Waters, Southern China. *Journal of Earth Science*, 24(2): 262–273