



# Characteristics of Organic Matter and Biomarkers in Core Sediments From the Offshore Area of Leizhou Peninsula, South China Sea

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Total organic carbon (TOC), total nitrogen (TN) and multi-biomarker indexes were analyzed for two sediment cores from the eastern coastal area of the Beibu Gulf (core 45, AMS <sup>14</sup>C dated) and Qiongzhou Strait (core 29), South China Sea. The results showed that the TOC and TN content of the samples studied were 0.32–0.62% and 0.02–0.07%, respectively. The hydrocarbons in offshore sediments of Leizhou Peninsula were consisted of biogenic hydrocarbons and petrogenic hydrocarbons. The Core 29 sediments contain more terrigenous organic matter than that of sediments in core 45 due to the difference in hydrodynamic conditions. The composition and distribution of various lipid biomarkers indicate the presence of petrogenic hydrocarbons in the sediments of the whole profile of two sediment cores. There are multiple natural sources of hydrocarbons that could potentially contribute to the petroleum background through oil seeps and erosion of carbon-rich rock outcrops or bitumen deposits. Deep sourced hydrocarbon inputs from the submarine hydrocarbon seepage cannot be excluded. Further study is needed to resolve the specific sources for the petrogenic hydrocarbons and may be significant to petroleum exploration in the study area.

**Keywords:** leizhou peninsula, sediments, organic carbon content, biomarker, beibuwan basin, *n*-alkane

## INTRODUCTION

Marine sediments act as the ultimate sink for organic carbon, incorporating organic matter (OM) into the geological carbon cycle (Dickens et al., 2004). Coastal regions are areas where active interaction between land and ocean exists. It plays a significant role in the global carbon cycle since about 80% of the global organic carbon buried in the shallow marine system, even though it only accounts for 7.6% of the total global ocean area (Hedges and Keil, 1995; Tesi et al., 2007). The sedimentary OM in the coastal area is a heterogeneous and complex mixture of organic compounds with different chemical characteristics, originating from various sources. Hydrocarbons from both natural and anthropogenic sources are very common in the marine environment (Bourbonniere and Meyers, 1996). Understanding the sources of hydrocarbons and chemical processes that affect the deposition and preservation of OM is necessary for a comprehensive examination of the global carbon cycle (Tesi et al., 2007).

There are three major hydrocarbon sources in marine sediments: 1) petrogenic hydrocarbons related to fossil organic matter (including hydrocarbons from natural oil seepage, eroded shales and coals, anthropogenic sources) and its refined products; 2) biogenic hydrocarbons generated by biologic or diagenetic process; and 3) pyrogenic hydrocarbons generated by high temperature process, including forest fires and fossil-fuel combustion (Page et al., 1996). These three different hydrocarbons have different biomarker characteristics. Much work has been done using biomarker and hydrocarbon compositional characteristics to discriminate the hydrocarbon sources in marine sediment, especially in the oil spill investigation (Page et al., 1996; Boehm et al., 2001; Yunker et al., 2014).

As one of the most critical subtropical regions of the mangrove ecosystem in China, the Leizhou Peninsula has significant marginal effects on the carbon pool of marine sediments in the offshore area (Yang et al., 2014). The Leizhou Peninsula coast is an active site because of the influence of different water masses, like the Pearl River plume and Red River plume (Bauer et al., 2013). Being the essential low latitude sea and land transition zone, the surrounding offshore region of the Leizhou Peninsula is also a typical region influenced by the East Asia monsoon. Besides, the Beibuwan Basin, located on the west margin of the Leizhou Peninsula, has been paid a lot of attention due to its abundant petroleum resources (Li et al., 2008; Zhou et al., 2019; Gan et al., 2020). The exploration, production, and transportation of crude oil may input oil pollutions into the marginal area in this region. The natural seepages can also be possible sources of the hydrocarbons which need to be taken into consideration.

There are a few studies focused on the geochemical characteristics of the surface sediments in the offshore area of the Leizhou Peninsula (Liu et al., 2012; Bauer et al., 2013; Li et al., 2014; Zhang et al., 2017). Few studies have paid attention to the origin of the OM in the studied area from the vertical perspective of time. Investigation of core sediments provides a useful tool for evaluating sediment composition and geochemistry, as well as providing information on past or ongoing environmental processes and components, both natural and human-induced (Hu et al., 2008; Bigus et al., 2014; Dong et al., 2014; Rothwell and Croudace, 2015; Jafarabadi et al., 2019). In this study, we evaluated the origins of OM using geochemical and biomarker indexes for two sediment cores from the Leizhou Peninsula's coastal zone to explore the temporal changes of sources and sinks of OM in this area.

## MATERIALS AND METHODS

### Sampling and Age Determination

The sampling sites are shown in **Figure 1**. Two sediment cores were collected in January 2018 on board the O/V Hailong of Guangdong Ocean University at the following stations: the Qiongzhou Strait (station 29; 9.1 m water depth); the eastern margin of the Beibu Gulf (station 45; 17.5 m water depth). Sediment cores were retrieved using a cylindrical box-corer (90 cm length, 60 mm diameter), and sectioned onboard at 5 cm intervals. The overall lithology of two cores is uniform, mainly belonged to clay-silt type. All sediment samples were placed into

sterile bags and stored at  $-20^{\circ}\text{C}$  until laboratory treatments. A total of twelve sediment samples including ten core sediment samples (20 cm interval) from two shallow cores and two seafloor surface sediments from the site of core samples were subjected for the bulk geochemistry and biomarker analyses in this study (**Table 1**).

Two sediment samples of core 45 was collected for accelerator mass spectrometry (AMS)  $^{14}\text{C}$  dating. The sediment sample was washed with standard hydrochloric acid to remove carbonates. Dating of bulk organic carbon sample was done at Beta Analytic Testing Laboratory. The  $^{14}\text{C}$  age was calibrated with the IntCal13 curve (Reimer et al., 2009; Reimer et al., 2013; **Table 2**).

### Analysis of Total Organic Carbon and Nitrogen

An aliquot of bulk, freeze-dried, and homogenized sediment sample was processed for elemental analyses. After the removal of inorganic carbon with 4 N HCl and being washed with deionized water, the TOC and TN values of dried treated samples were determined in German Elementar Vario MACRO Element Analyzer. Average values were reported. The analysis errors of TOC and TN were  $\pm 0.02\%$  and  $\pm 0.005\%$ , respectively.

### Analysis of Aliphatic Hydrocarbons

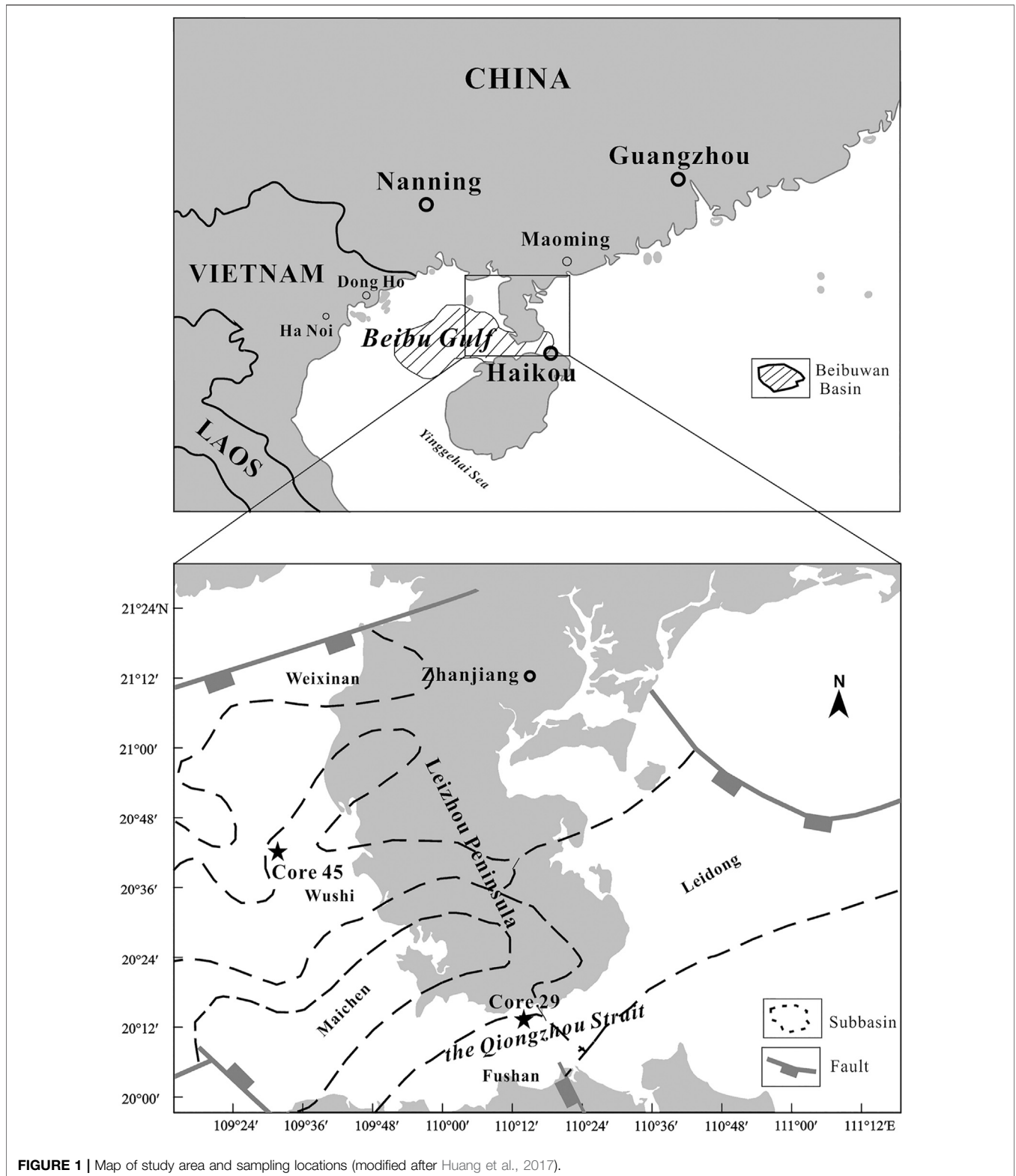
Sediment samples were freeze-dried, grounded to 100 mesh and soxhlet-extracted continuously for 72 h with dichloromethane:methanol (93:7, v/v), with activated copper added to the solvent to remove the elemental sulfur in the samples. After extraction, the solvent was evaporated, and the extract weighed. The extract was deasphalted and separated using silica gel column chromatography into saturates, aromatics, and resins. The saturated fractions were concentrated to 1 ml using a rotary evaporator.  $\text{C}_{24}\text{D}_{50}$  was added to the extract as an internal standard to instrumental analysis. The gas chromatography and mass spectrometry (GC-MS) analysis of aliphatic hydrocarbons was performed using an ISQ 7000 (Thermo Scientific, United States) interfaced to TRACE 1300 gas chromatography (GC) that was fitted with a 30 m DB-5 capillary column (0.25 mm i.d., 0.25  $\mu\text{m}$  film thickness; J&W Scientific, CA, United States). Samples were injected in the splitless mode with an injector temperature of  $280^{\circ}\text{C}$ . For GC analysis, the oven was programmed from 80 to  $300^{\circ}\text{C}$  at  $3^{\circ}\text{C}/\text{min}$  with ion source temperature of  $300^{\circ}\text{C}$ . The mass spectrum was operated in the electron ionization (EI) mode (70 eV) with the mass scanning combining selective ion monitoring (SIM) with full-scan detection between  $m/z$  50 and 650 amu. Helium was used as a carrier gas at a constant flow rate of 1 ml/min.

The steranes and terpanes were quantified in the saturated fraction of samples, and their identification was confirmed by GC-MS based on the mass spectral characteristics, peak sequence, and the previous studies.

## RESULTS

### Chronology

As shown in **Table 2**, the calculated age for core 45 at 45–50 cm depth is  $\sim 4.8$  cal ka BP, and the age for core 45 at 85–90 cm depth



is ~9.6 cal ka BP. The AMS  $^{14}\text{C}$  dates of core 45 indicated that the sediment record of core 45 covered interval from the early Holocene to the modern time.

### TOC and TN

Total organic carbon (TOC) and total nitrogen (TN) data of sediment samples from the two sediment cores are summarized

**TABLE 1** | Compositions and parameters of bulk organic matter, concentrations of *n*-alkanes and hydrocarbon parameters for core sediments.

Sampling site	Sample	Depth (cm)	Texture	TOC (%)	TN	Atomic C/N ratio	$\Sigma n$ -alkanes (ug/g dw)	CPI <sub>17-21</sub>	CPI <sub>25-35</sub>	TAR	NAR	Pr/Ph	Pr/ <i>n</i> -C <sub>17</sub>	Ph/ <i>n</i> -C <sub>18</sub>
Core 29	29-1	0-5	Clayed silt	0.45	0.04	11.68	6.03	1.14	1.15	6.58	0.042	0.64	0.52	0.80
	29-2	5-10	Clayed silt	0.5	0.04	13.17	2.65	1.11	1.60	4.48	0.144	0.62	0.77	0.94
	29-6	25-30	Clayed silt	0.51	0.05	11.36	2.50	1.21	1.71	3.08	0.181	0.66	0.73	0.91
	29-10	45-50	Clayed silt	0.45	0.05	11.43	1.54	1.08	1.79	6.05	0.165	0.52	0.69	0.97
	29-14	65-70	Clayed silt	0.32	0.02	15.30	2.09	1.11	1.71	4.77	0.167	0.60	0.77	0.97
	29-18	85-90	Clayed silt	0.39	0.03	15.30	2.60	1.09	1.59	4.70	0.134	0.57	0.71	0.88
Core 45	45-1	0-5	Clayed silt	0.62	0.07	9.92	4.14	1.02	1.34	1.48	0.120	0.70	0.81	0.92
	45-2	5-10	Clayed silt	0.6	0.07	9.57	3.58	1.06	1.51	3.30	0.126	0.52	0.71	0.76
	45-6	25-30	Clayed silt	0.5	0.06	9.77	0.37	0.65	1.39	4.89	0.091	0.53	0.62	0.40
	45-10	45-50	Clayed silt	0.36	0.04	10.65	3.25	0.76	1.28	2.79	0.079	0.60	0.64	0.58
	45-14	65-70	Clayed silt	0.48	0.05	11.37	1.40	1.04	1.41	3.33	0.115	0.59	0.66	0.75
	45-18	85-90	Clayed silt	0.33	0.03	12.09	2.07	0.86	1.25	1.74	0.100	0.67	0.61	0.60

$\Sigma n$ -alkanesv: concentration of total *n*-alkanes ( $nC_{14}$ - $nC_{37}$ ).

$CPI_{17-21} = 30 = (1/2)[(nC_{17} + nC_{19} + nC_{21})/(nC_{18} + nC_{20}) + (nC_{17} + nC_{19} + nC_{21})/(nC_{18} + nC_{20} + nC_{22})]$ .

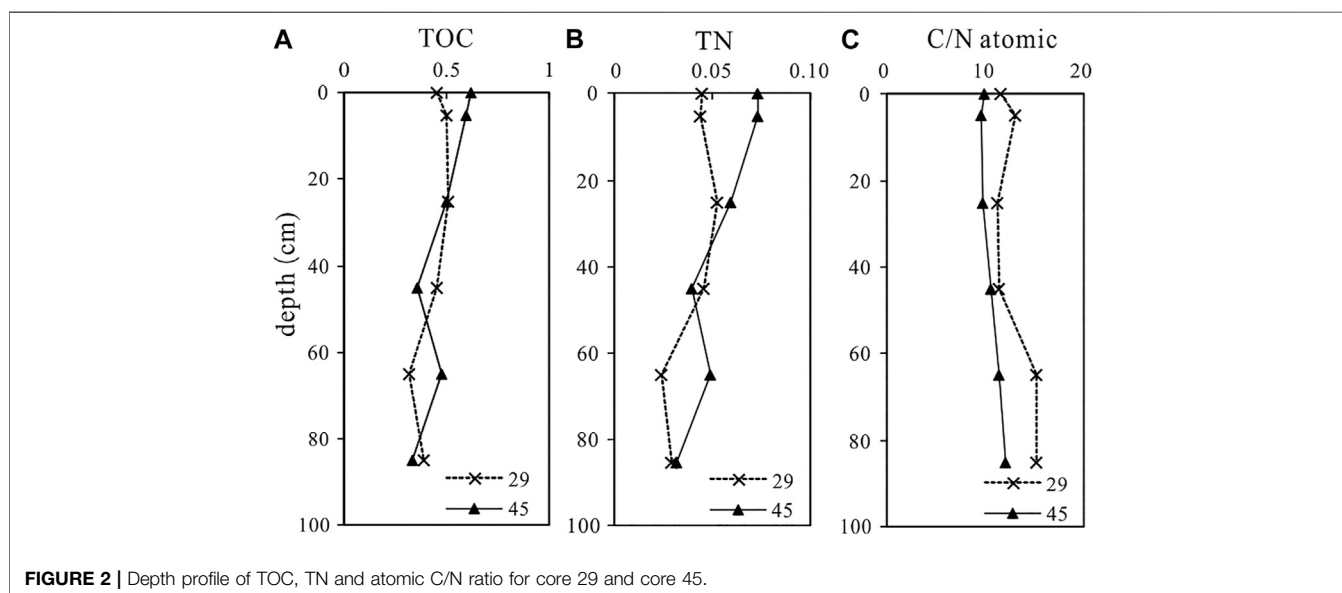
$CPI_{25-35} = (1/2)[(nC_{25} + nC_{27} + nC_{29} + nC_{31} + nC_{33} + nC_{35})/(nC_{24} + nC_{26} + nC_{28} + nC_{30} + nC_{32} + nC_{34}) + (nC_{25} + nC_{27} + nC_{29} + nC_{31} + nC_{33} + nC_{35})/(nC_{26} + nC_{28} + nC_{30} + nC_{32} + nC_{34} + nC_{36})]$ .

TAR: terrigenous/aquatic ratio =  $(nC_{27} + nC_{29} + nC_{31})/(nC_{15} + nC_{17} + nC_{19})$ .

NAR: natural *n*-alkane ratio =  $[\Sigma(C_{19}-C_{33}) - 2\Sigma(C_{20}-C_{32})_{even}] / \Sigma(C_{19}-C_{32})$ .

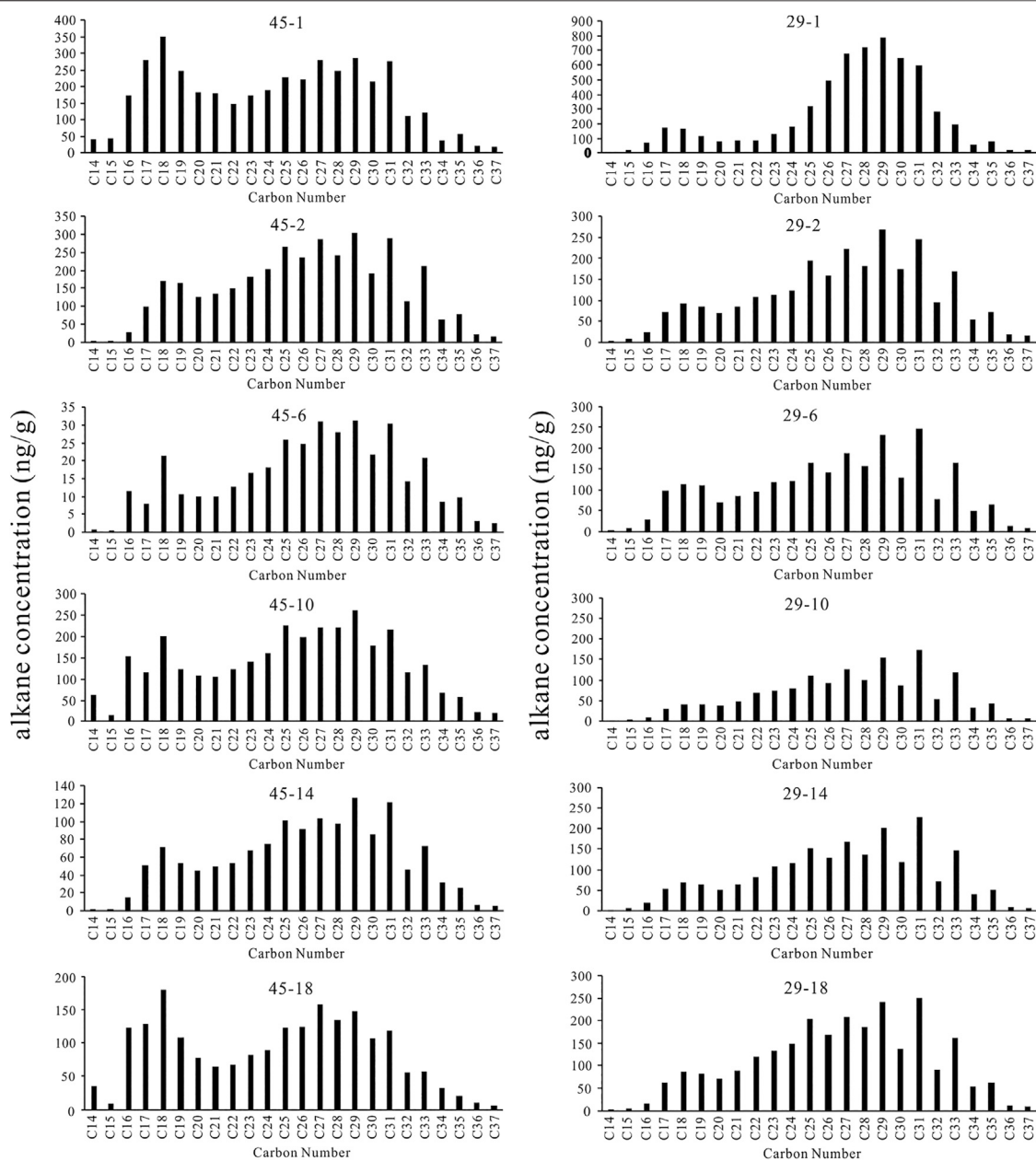
**TABLE 2** | AMS <sup>14</sup>C ages dated on core 45.

Sampling site	Sample	Depth (cm)	Material	AMS <sup>14</sup> C age (yr BP)	Calendar age (yr BP, 1σ)	Mid-point (cal yr BP)
Core 45	45-10	45-50	Organic sediment	4,120 ± 30	4,829-4,780	4,805
	45-18	85-90	Organic sediment	8,630 ± 30	9,703-9,548	9,626

**FIGURE 2** | Depth profile of TOC, TN and atomic C/N ratio for core 29 and core 45.

in Table 1. The TOC content ranges of the samples of core 29 and core 45 were 0.32–0.51% and 0.33–0.62%, respectively. The mean TOC in core 29 and core 45 samples are 0.44% and 0.48%, respectively. The TN values of core 29 and core 45 varied from

0.02 to 0.05% and between 0.03 to 0.07%, respectively. There was an increasing trend in TOC and TN from the bottom to surface in core 45 and a slight decrease in TOC and TN in core 29 from depth 25–30 cm to surface. The measured atomic C/N ratios of



**FIGURE 3** | The distribution of *n*-alkanes by carbon number in core sediments.

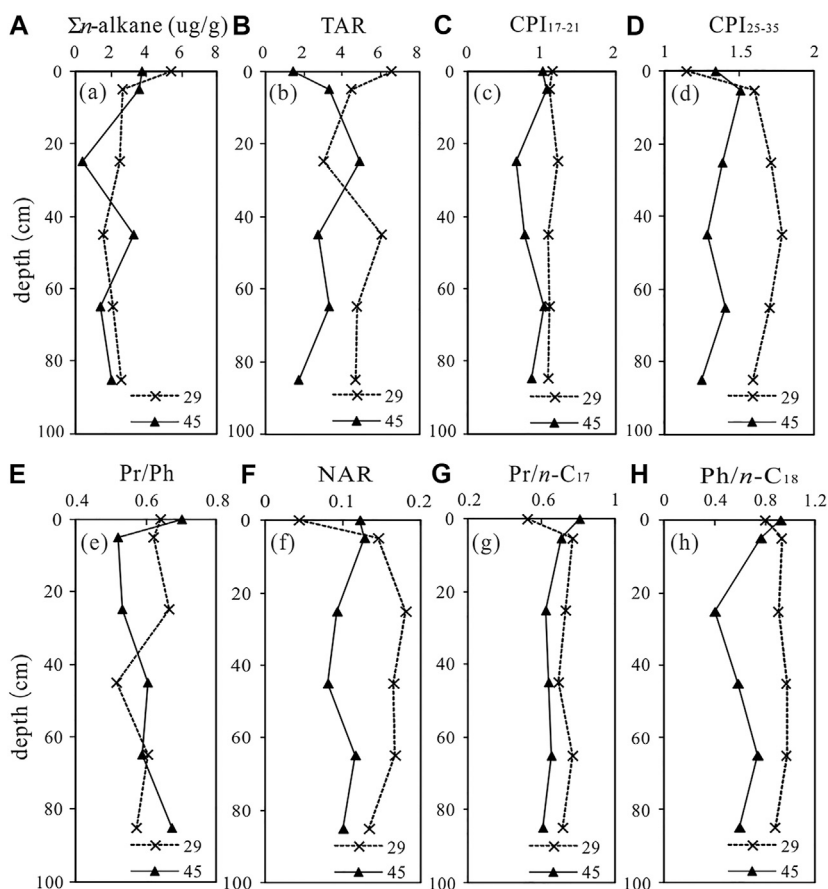
core 29 and core 45 varied from 11.43 to 15.30 and from 9.57 to 12.09, respectively, showing a downcore trend toward higher values (Figure 2).

### *n*-Alkanes and Isoprenoids

The mass of the *n*-alkanes of the samples is shown in Figure 3 and the relevant parameters are shown in Table 1. Generally, *n*-alkanes were in the range of *n*-C<sub>14</sub>~*n*-C<sub>37</sub>, showing a bimodal distribution throughout the depositional section. The dominant component in the long-chain *n*-alkanes was mainly *n*-C<sub>31</sub> for core 29, and *n*-C<sub>29</sub> for core 45. Concentrations of total *n*-alkanes in sediment cores ranged from 0.37 to 6.03 ug/g dw.

Their vertical distribution of total *n*-alkane concentration at two sampling stations is displayed in Figure 4A and listed in Table 1. The total *n*-alkane concentrations changed little in sediments from two cores, except two sections. The surface sediment in core 29 contained 6.03 ug/g *n*-alkanes, more than twice that found in lower deposits. The *n*-alkane concentration of sediment from core 45 in depth 25–30 cm was relatively low, with 0.37 ug/g.

The CPI<sub>17–21</sub> values were in the range of 1.08–1.21 and 0.65–1.06 for core 29 and 45, respectively, indicating a weak even-carbon-number predominance of short-chain *n*-alkanes for Core 45 (Figure 4C). There was a fluctuation of CPI<sub>17–21</sub> values for core 45 from the deep to the shallow sediments. The CPI<sub>25–35</sub>



**FIGURE 4** | Depth profile of parameters calculated from *n*-alkanes and isoprenoids in core 29 and core 45. **(A)** total *n*-alkanes concentration, **(B)** TAR, **(C)**  $CPI_{17-21}$ , **(D)**  $CPI_{25-35}$ , **(E)** Pr/Ph, **(F)** NAR, **(G)**  $Pr/n-C_{17}$ , and **(H)**  $Ph/n-C_{18}$ .

values were in the range of 1.59–1.79 and 1.25–1.51 for core 29 and 45, respectively, showing some odd-carbon-number predominance (**Figure 4D**). No apparent change occurred in  $CPI_{25-35}$  value for core 29 and core 45 with depth, except for the decrease in the surface sediment.

The ratio of biogenic terrestrial origins ( $n-C_{27}$ ,  $C_{29}$ , and  $C_{31}$ ) to aquatic biogenic sources ( $n-C_{15}$ ,  $C_{17}$ , and  $C_{19}$ ) was defined as TAR (Bourbonniere and Meyers, 1996; Meyers, 2003; Silliman and Schelske, 2003). For core 29 and core 45, the TAR values ranged from 3.08 to 6.58 and 1.74 to 4.89, averaging 4.94 and 2.92, respectively, indicating that higher terrestrial plants were the dominant contributor to the OM for core 29 and 45, with core 45 sediments having more aquatic biogenic material input (**Figure 4B**). As the depth changes, the TAR values changed in the opposite direction for the two sample cores, indicating different OM sources.

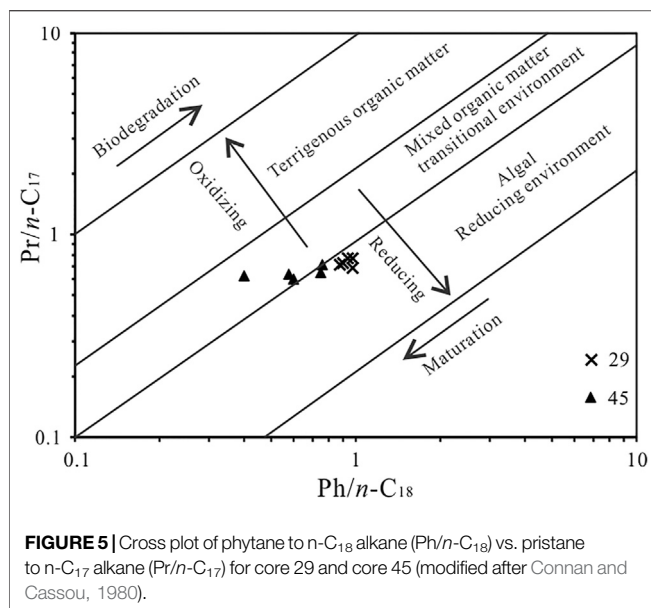
The NAR (natural *n*-alkane ratio), defined by Mille et al. (2007), is useful for identifying petrogenic and biological *n*-alkane sources. A high NAR value (close to 1) is considered as a biogenic-related input, while crude oil and petroleum hydrocarbons usually exhibited a low (close to 0) NAR value (Mille et al., 2007; Akhbarizadeh et al., 2016; Wang et al., 2018; Jafarabadi et al., 2019). Herein, the NAR values ranged from 0.042

to 0.181 and 0.120 to 0.126 for core 29 and core 45, respectively (**Figure 4F**). NAR values changed little through the whole core depth, except for the significant decrease in the surface sample of core 29 (**Table 1**). The NAR values revealed that petrogenic hydrocarbon input dominated the *n*-alkane concentration in the core sediments.

As shown in **Table 1** and **Figure 4E**, the ratio of pristane (Pr) to phytane (Ph) in all samples was within the range of 0.52–0.67. On the  $Pr/n-C_{17}$  vs.  $Ph/n-C_{18}$  plot (**Figure 5**), the samples lay within the zone of marine OM sources and reducing area. According to previous studies, the increase of  $Pr/n-C_{17}$  and  $Ph/n-C_{18}$  suggests the strong microbial activity, and the decrease of the ratios indicates the increasing maturity of the OM (González-Vila et al., 2003). In our study, the ratios of  $Pr/n-C_{17}$  and  $Ph/n-C_{18}$  indicated no apparent microbial activity in the studied sediment samples (**Figures 4G,H, 7**). Core 45 showed lower value of  $Ph/n-C_{18}$  than core 29.

## Terpanes

The typical *m/z* 191 mass chromatogram of terpane determined by GC-MS is shown in **Figure 6A** and **Figure 6B**. The terpane parameters of the sediment samples analyzed are reported in **Table 3**.



A series of hopanes consisting of C<sub>27</sub> to C<sub>34</sub> (without C<sub>28</sub>) were identified in the samples. C<sub>30</sub> 17 $\alpha$  (H)-hopane (C<sub>30</sub>H) was the dominant triterpane in all samples, with  $\beta\alpha$  hopanes in much lower abundance. In addition to hopanes, tricyclic and tetracyclic terpanes were also observed in m/z 191 mass chromatograms of the marine sediment samples analyzed. The sediment samples had a low content of oleanane. The homohopanes distribution exhibited a decreasing pattern from C<sub>31</sub> to C<sub>34</sub> in all the samples.

The ratio of 17 $\beta$ , 21 $\alpha$  (H)-moretanes to their corresponding 17 $\alpha$ , 21 $\beta$  (H)-hopanes decreases with thermal maturity from ~0.8 in immature bitumens to < 0.15 in mature source rocks and oils to a minimum of 0.05 (Mackenzie et al., 1980; Seifert and Moldowan, 1980). For the sediment samples in our study, the ratio of C<sub>30</sub> $\beta\alpha$  (C<sub>30</sub> moretane)/C<sub>30</sub> $\alpha\beta$  (C<sub>30</sub> hopane) ranged from 0.15 to 0.23 (Figure 7B), suggesting that the hydrocarbons in our marine sediments are in the immature to mature thermal evolution stage, and thus pointing to petrogenic hydrocarbon inputs.

The isomerization ratio of 22S/(22S+22R) for C<sub>31</sub> homohopane is often used as maturity index in petroleum geochemistry and increases (0 to ~0.6) with thermal maturity, reaching the equilibrium value at 0.57–0.62 (Seifert and Moldowan, 1980; Peters et al., 2005). In this study, this ratio for sediment samples ranged from 0.33 to 0.54 and 0.45–0.52 for core 29 and core 45, respectively (Figure 7C).

The ratio of 18 $\alpha$  (H)-22,29,30-trisnorhopane (Ts)/17 $\alpha$  (H)-22,29,30-trisnorhopane (Tm) is also an index of maturity (Seifert et al., 1978). As shown in Table 3 and Figure 7D, the Ts/Tm ratios ranged from 0.83 to 1.13 and 0.72 to 1.00, respectively, for core 29 and core 45, suggesting the low-mature to mature OM across the whole sediment cores.

The tricyclic terpane series extended from the C<sub>19</sub> up to C<sub>29</sub> (Figures 6A,B) and were dominated by C<sub>23</sub> tricyclic terpane (abbreviated C<sub>23</sub>TT). Samples from core 29 and 45 displayed C<sub>19</sub>TT/C<sub>23</sub>TT between 0.06–0.14 and 0.06–0.12, respectively

(Figure 7E). This indicated the petrogenic hydrocarbon input generated from the marine environment because C<sub>23</sub>TT is often the dominant homolog in crude oils of saline lacustrine and marine sources (Peters et al., 2005; Tao et al., 2015). The C<sub>24</sub> Tet (C<sub>24</sub> tetracyclic terpane)/(C<sub>24</sub> Tet + C<sub>26</sub> TT) ratios ranged narrowly from 0.29 to 0.35 and 0.30 to 0.34, respectively for core 29 and core 45. The C<sub>23</sub> TT/(C<sub>23</sub> TT + C<sub>30</sub> H) ratios ranged from 0.37 to 1.57 and 0.80 to 1.50, respectively for core 29 and core 45 (Figure 8).

## Steranes

The typical sterane (m/z 217) fingerprints of the sediment samples are displayed in Figures 6C,D. All samples from section 29 and core 45 possessed similar biomarker compositions and were dominated by regular steranes and pregnane, with a moderate abundance of diasteranes and low content of C<sub>30</sub> 4-methylsteranes.

The regular C<sub>27</sub>–C<sub>29</sub> steranes in the core sediment samples were dominated by the C<sub>27</sub> series (C<sub>27</sub> > C<sub>29</sub> > C<sub>28</sub>) (Figures 6C,D, 7F). The enhanced occurrence of the C<sub>27</sub> homolog is a typical characteristic of marine petrogenic hydrocarbons (Huang and Meinschein, 1979; Moldowan et al., 1985; Shanmugam, 1985; Bouloubassi et al., 2001).

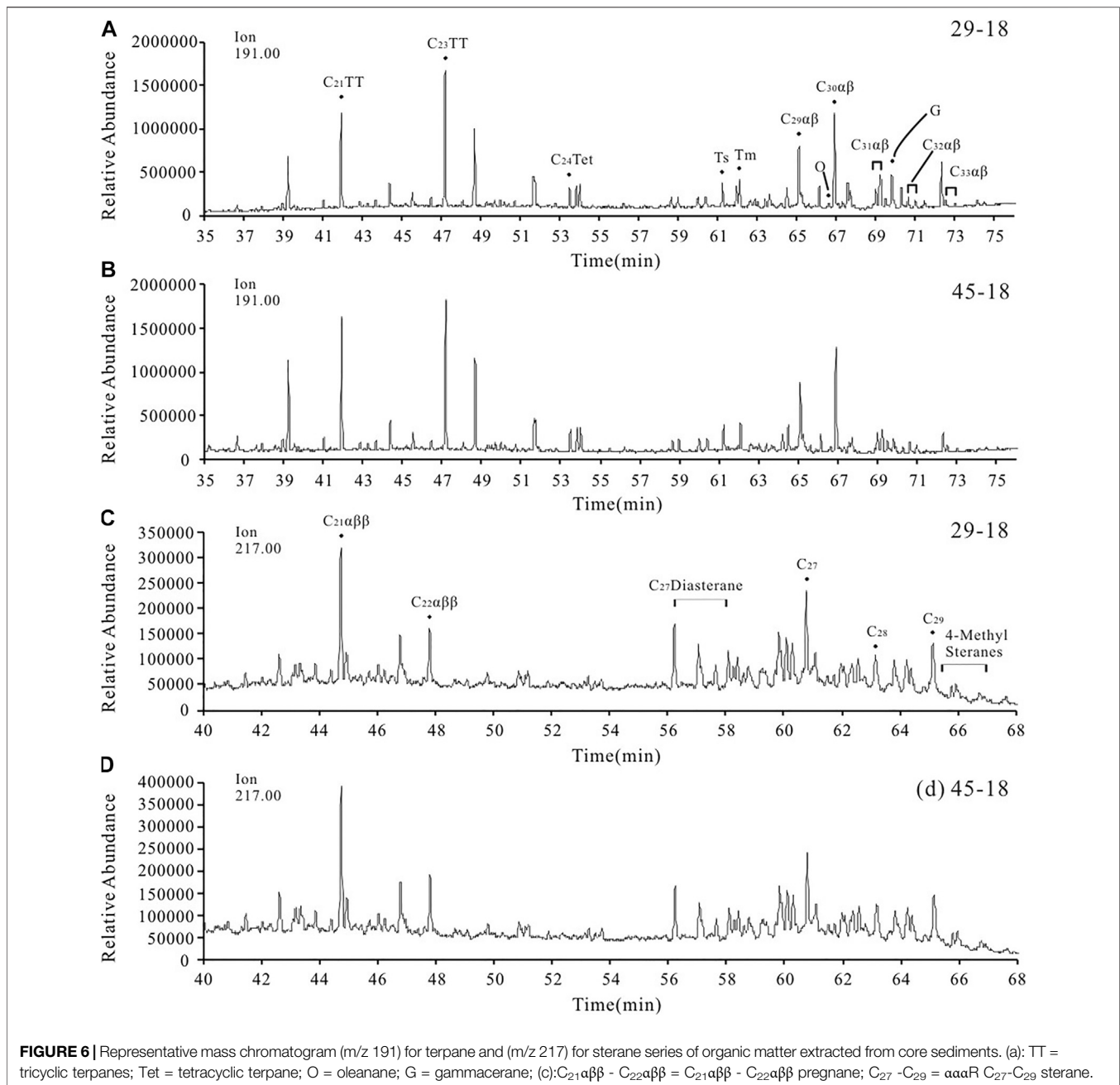
For C<sub>29</sub> steranes, the isomerization ratios S/(S + R) and  $\alpha\beta\beta/(\alpha\alpha\alpha+\alpha\beta\beta)$  are the two most commonly used sterane maturity parameters. Both ratios increase with maturity and reach equilibrium values of approximately 0.55 (equivalent to vitrinite reflectance about 0.8–0.9%) and ~0.70 (equivalent to vitrinite reflectance about 0.90–1.0%), respectively (Mackenzie et al., 1984; Seifert and Moldwan, 1986; Aboul-Kassim and Simoneit, 1996; Peters et al., 2005). Values of  $\alpha\alpha\alpha$  C<sub>29</sub> sterane S/(S + R) ratios in our study ranged from 0.39 to 0.50 and from 0.41 to 0.50, respectively, for core 29 and core 45 (Figure 7G). Values of  $\alpha\beta\beta/(\alpha\alpha\alpha+\alpha\beta\beta)$  for C<sub>29</sub> sterane ranged from 0.40 to 0.49 and from 0.44 to 0.48 for the two core sections, respectively (Figure 7H). Both ratios changed little in two cores. The values of both two sterane maturity parameters indicated the maturity stage of early oil generation, suggesting the presence of petrogenic hydrocarbons in all sediment samples.

## DISCUSSION

### Origins of Organic Matter in Sediments

The C/N ratio is frequently used to identify the biological origins of OM (Meyers, 1994; Meyers, 1997; Jia and Peng, 2003; Hu et al., 2009). It has been reported that marine algae has C/N ratios between 4 to 10 due to richness in protein and cellulose absence. In contrast, vascular plants have atomic C/N ratios >20 due to the abundance of cellulose (Meyers, 1997). TAR value is another index commonly used to identify OM origin. Both C/N ratio and TAR value indicated that both sites' biogenic OM origin included marine phytoplankton and terrestrial higher plants, with the latter dominated.

The dominant peak for long-chain n-alkanes was n-C<sub>31</sub> for core 29, whereas, in core 45, n-C<sub>29</sub> dominated (Figure 3). This suggested different types of terrestrial plant inputs for two sites,



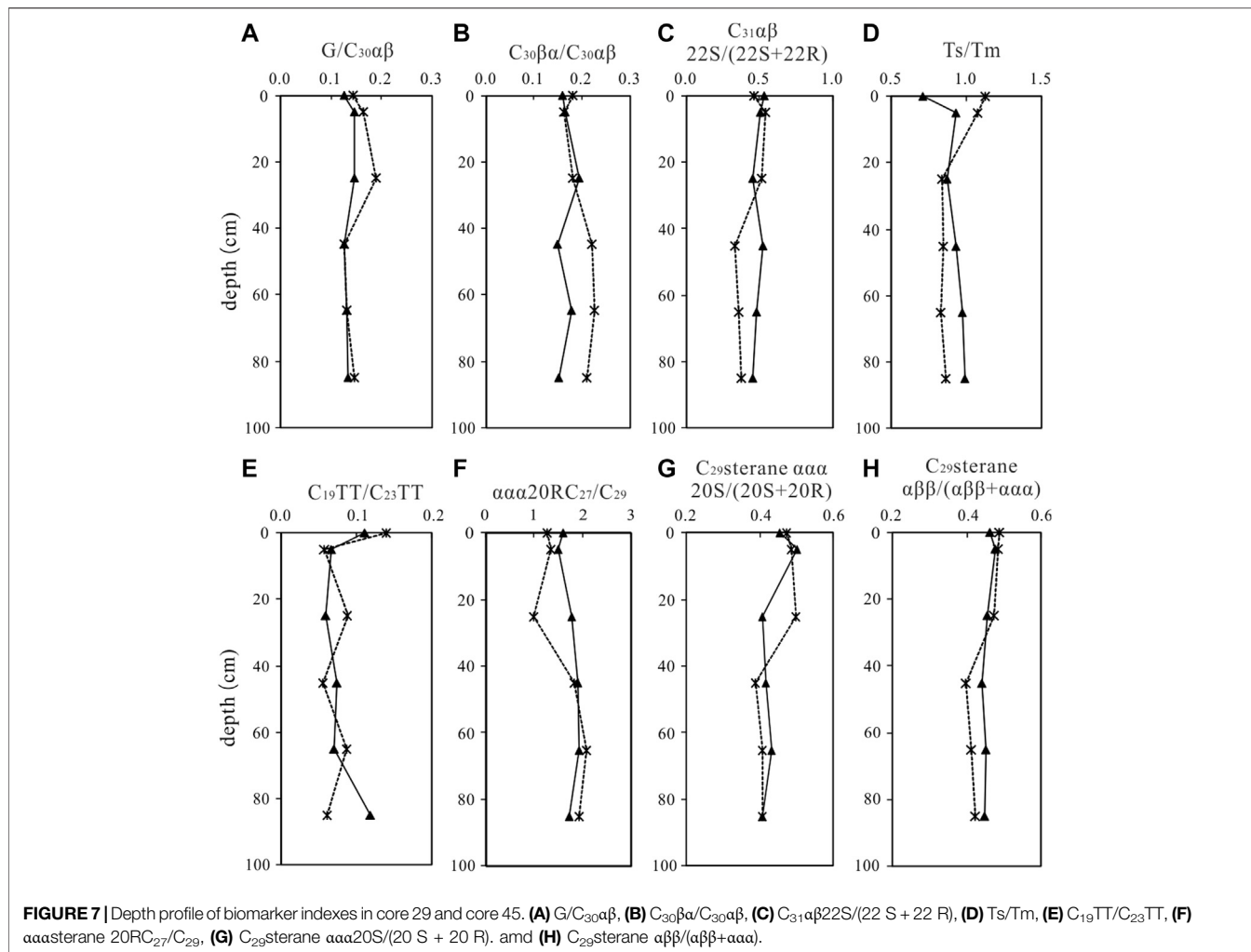
consistent with the palynological research of the surface sediment from the Beibu Gulf (Tong et al., 2012). Besides, TAR value was higher in core 29. The value of atomic C/N ratio was also higher in core 29 sediments. This suggested more terrestrial biogenic material input in core 29 than core 45. The TAR values changed in the opposite direction within depth for the two cores. TAR values increased upward in 30 cm upmost sediments in core 29 and decreased upward in 30 cm upmost sediments in core 45 (Figure 2), showing that more terrestrial OM deposited in Qiongzhou Strait, whereas more marine algae inputted on the west coast of the Leizhou Peninsula in the latest

sedimentation period. Core 45 is farther away from the shore than core 29. Besides, core 29 is located near the port of Haian, an essential passage from the Chinese mainland to Hainan island. In addition to the Leizhou Peninsula's material sources, Hainan Island also contributes to the OM deposits in Qiongzhou Strait through river runoff. As a result, terrestrial OM accumulates more at the site of core 29. In addition to the supply of coastal area, core 29, located in Qiongzhou Strait, can also get the material from the eastern region of Qiongzhou strait or even Taiwan Island, and having more contribution of terrestrial provenance brought by Huanan nearshore current (Zhang



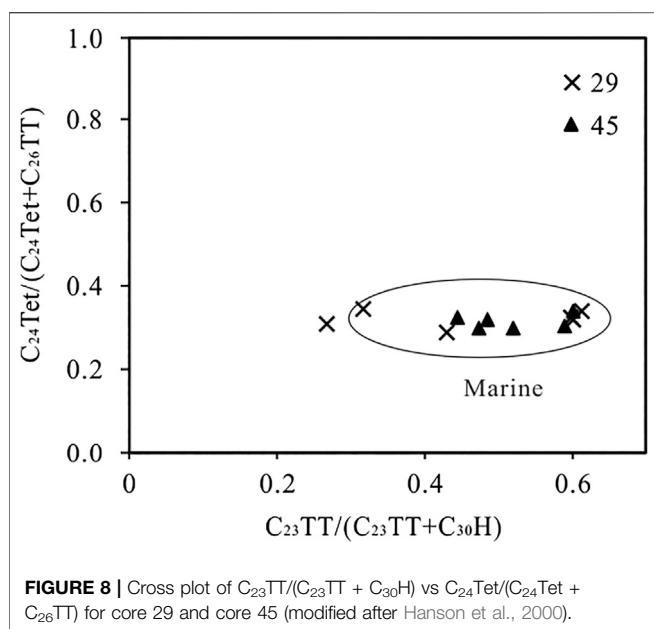
**TABLE 3** | Terpane and sterane parameters for core sediments.

Sampling site	Sample	Depth (cm)	$C_{30}\beta\alpha/C_{30}\alpha\beta$	$C_{31}\alpha\beta$ 22S/ (22 S + 22 R)	Ts/ Tm	$C_{19}TT/C_{23}TT$	$C_{23}TT/C_{30}H$	$C_{24}Tet/$ ( $C_{24}Tet +$ $C_{26}TT$ )	$C_{23}TT/$ ( $C_{23}TT+C_{30}H$ )	$C_{29}sterane$ $\alpha\beta\beta/\alpha\beta\beta+\alpha\alpha\alpha$	$C_{29}Sterane$ $\alpha\alpha\alpha 20S/$ (20 S + 20 R)	$\alpha\alpha\alpha 20RC_{27}/$ $C_{29}$
ST29	29-1	0-5	0.18	0.46	1.13	0.14	0.47	0.35	0.32	0.49	0.47	1.28
	29-2	5-10	0.16	0.54	1.08	0.06	0.37	0.31	0.27	0.48	0.49	1.35
	29-6	25-30	0.18	0.51	0.84	0.09	0.75	0.29	0.43	0.47	0.50	0.98
	29-10	45-50	0.22	0.33	0.85	0.06	1.51	0.32	0.60	0.40	0.39	1.81
	29-14	65-70	0.23	0.36	0.83	0.09	1.57	0.34	0.61	0.41	0.41	2.08
	29-18	85-90	0.21	0.37	0.87	0.06	1.48	0.32	0.60	0.42	0.41	1.91
ST45	45-1	0-5	0.16	0.53	0.72	0.11	1.08	0.30	0.52	0.46	0.45	1.59
	45-2	5-10	0.17	0.51	0.93	0.07	0.90	0.30	0.47	0.48	0.50	1.50
	45-6	25-30	0.19	0.45	0.87	0.06	1.50	0.34	0.60	0.45	0.41	1.78
	45-10	45-50	0.15	0.52	0.93	0.07	0.80	0.32	0.44	0.44	0.42	1.90
	45-14	65-70	0.18	0.48	0.98	0.07	0.94	0.32	0.49	0.45	0.43	1.93
	45-18	85-90	0.15	0.45	1.00	0.12	1.43	0.30	0.59	0.45	0.41	1.73



et al., 2018). Therefore, more higher terrestrial OM in core 29 than core 45 reflects the different hydrodynamic conditions between two sites.

There was a mild odd-even carbon preference in the higher-molecular-weight *n*-alkanes ( $n \geq 25$ ) in the two core samples, and the carbon preference indices  $CPI_{25-35}$  ranged from 1.15 to 1.79.



The CPI value can be influenced by both source input and maturity. According to the previous studies, the  $n-C_{24}\sim n-C_{35}$  alkanes derived from marine OM tend to have little or no carbon-number preference (Peters et al., 2005). In addition to this, the CPI value decreases with increasing maturity. The high CPI in modern sediment indicates low maturity and land-plant input, and the recent sediments with CPI  $\sim 1$  may arise from a predominance of marine input and/or petroleum input (Tolosa et al., 2004; Seki et al., 2006). Based on the TAR and C/N value, the origins of OM included marine phytoplankton and terrestrial plants with terrestrial plants dominating. Therefore, the low CPI<sub>25-35</sub> in the sediment samples from two core sites indicated the petrogenic hydrocarbon input.

The CPI<sub>17-21</sub> ranged from 0.65 to 1.21, and even-to-odd predominance was observed at three depth in core 45. It has been reported that the even carbon number preference in the low molecular weight in sediment mainly indicates microbial activities (Nishimura and baker, 1986; Grimalt and Albaiges, 1987; Wang et al., 2012) or possible petroleum-derived inputs (Harji et al., 2008). The Ph/ $n-C_{18}$  and Pr/ $n-C_{17}$  ratio did not indicate obvious biodegradation (Figure 5). Given this, the even carbon number preference should be due to petrogenic hydrocarbon input. From the whole section, the CPI<sub>17-21</sub> and CPI<sub>25-35</sub> of core 45 was lower than core 29, indicating a higher proportion of petrogenic hydrocarbon in core 45 sediment than core 29. Figure 5 showed that the Ph/ $n-C_{18}$  of core 45 sediments (sediment 45-6, 45-10, 45-14 and 45-18) was lower than core 29 samples, showing slightly higher maturity. This difference was consistent with the higher values of  $C_{31}$  homohopane 22S/(22S+22R) and lower values of  $C_{30}\beta\alpha/C_{30}\alpha\beta$  for these four samples than core 29 samples (Figure 7). This can be caused by more petrogenic hydrocarbon inputs in core 45 or is simply reflection of variable maturity for the petrogenic hydrocarbon sources.

The isoprenoids pristane and phytane are often found in petroleum products. Pristane is also found biogenically, while phytane rarely occurs in biogenic material (Shaw and Baker, 1978; Venkatesan and Kaplan, 1982; Broman et al., 1987). In addition to indicating a reductive sedimentary environment, pristane/phytane ratio close to or smaller than 1 in our sediment samples can indicate petrogenic hydrocarbons (Shaw et al., 1985; Broman et al., 1987; Commendatore and Estevesa, 2004).

Hopanes and steranes are derived from bacteria, algae, and vascular plants (biogenic sources) and are also constituents of crude oil and derived products (petrogenic sources) (Huang et al., 1992). The biological  $\beta\beta$ -configuration of hopanoids in the organism is unstable and readily convert to  $\beta\alpha$ -(moretane) and  $\alpha\beta$ -hopane configurations during burial, and  $\alpha\beta$ -hopane is thermodynamically stable and dominates in petroleum (Seifert et al., 1980; Peters et al., 2005; Huang et al., 2014). The predominance of 17 $\alpha$  (H), 21 $\beta$  (H)-hopane, maximizing at  $C_{30}$  and  $C_{29}$  homologous in all core samples in our study demonstrated a pivotal hydrocarbon contribution from petrogenic sources. No  $\beta\beta$ -isomers were identified in core sediment samples, and the contribution of biogenic hopanes can be excluded. Sediment samples in our study were buried less than 1 m, during the very early diagenesis stage of OM evolution. The biomarker ratios, including  $C_{31}$  homohopane 22S/(22S+22R), Ts/Tm,  $C_{30}\beta\alpha/C_{30}\alpha\beta$ ,  $C_{29}$  sterane  $\alpha\beta\beta/(\alpha\alpha\alpha+\alpha\beta\beta)$  and  $\alpha\alpha\alpha$   $C_{29}$  sterane S/(S + R), all suggested that the maturity of OM was in the early oil generation stage. The maturity of the OM indicated the allochthonous petrogenic hydrocarbons.

The NAR value of sediments from both cores were all smaller than 0.2, with a mean of 0.139 and 0.105 for core 29 and core 45, respectively. This low NAR values indicated a predominant petrogenic hydrocarbon input, and a minor role of biogenic hydrocarbons. NAR values lower in core 45 than core 29 indicates more petroleum input in core 45 than core 29, consistent with the CPI indication.

## Possible Origin of Petrogenic Hydrocarbons in Sediment Cores

Liquid petroleum and gas are essential industrial materials and necessities of people living in modern society. The worldwide extraction, transportation, and use of petroleum inevitably result in its release to the environment. Most of the spilled oil entering the sea comes from land-based sources and tankers, and so on.

Shaw et al. (1985) investigated the hydrocarbons in the sediments of Ports Valdez, Alaska, after three to five years of oil terminal operation with a routine daily discharge of 170 kg of petroleum residue in an otherwise undeveloped sea. They found the petroleum contamination occurs in the 0–5 cm sediments near the terminal. Jafarabadi et al. (2019) studied the levels and vertical distribution of hydrocarbons in sediment cores from the coral islands of the Persian Gulf. They found that the highest levels recorded at 10–20 cm depth in the industrial sites, and the  $n$ -alkanes concentration is as high as 5,000  $\mu\text{g/g dw}$ , and down to a tenth of the highest at 40 cm depth. We can conclude from the

above instances that the concentration of *n*-alkanes is highest near the benthic surface and decreases downward in sediment cores polluted by anthropogenic petroleum discharge.

In our study, the concentration of *n*-alkanes ranged from 0.37 to 6.03 ug/g dw, with a mean of 2.68 ug/g dw. The *n*-alkanes concentrations in the core sediment in the coastal region of the Leizhou Peninsula were similar to those in surface sediments and short marine core sediments (50 cm length) from Bohai Sea, where the spilled oil in sediments was identified (Hu et al., 2009; Li et al., 2015; Wang et al., 2018). The concentrations of *n*-alkanes changed little from the surface to the bottom in our study, showing different characteristics with sediment profile contaminated by human. The dating of the sediment core was conducted using the AMS <sup>14</sup>C method. The results showed that the age of the bottom sample of core 45 is ~9.6 cal ka BP (Table 2). Petroleum has not been large-scaled until the middle period of the 19<sup>th</sup> century. The anthropogenic petroleum pollution input is excluded for the petrogenic hydrocarbon input to the sediment samples predate industrial activity in this study.

The identical distribution of terpanes and steranes and similar values of derived parameters in two cores suggested the consistency of sources for the petrogenic hydrocarbon input during different sedimentation period (Figures 6, 7). The tricyclic terpane series are ubiquitous in source rock extracts and petroleum samples (De Grande et al., 1993), and are commonly used to relate oil and source rocks (Peters et al., 2005; Bennett and Olsen., 2007; Hao et al., 2009; Tao et al., 2015). C<sub>19</sub> or C<sub>20</sub> tricyclic terpanes are often the dominant homologs in terrigenous petrogenic hydrocarbons, while C<sub>23</sub> tricyclic terpane is abundant in marine petroleum and source rocks (Peters and Moldowan, 1993; Preston and Edwards, 2000; Volk et al., 2005). Low C<sub>19</sub>/C<sub>23</sub> TT ratios of core sediment samples in this study indicated the occurrence of petrogenic hydrocarbons generated from marine OM. The cross plot of C<sub>24</sub> Tet/(C<sub>24</sub> Tet + C<sub>26</sub> TT) vs. C<sub>23</sub> TT/(C<sub>23</sub> TT + C<sub>30</sub> H) ratios have been successfully used to distinguish between marine oils and non-marine oils (Hanson et al., 2000; Duan et al., 2008; Tao et al., 2015). It is clear from Figure 8 that core 29 and core 45 have the similar marine origins for the petrogenic hydrocarbon input (Figure 8).

There are multiple natural sources of hydrocarbons that contribute to the petroleum background in marine area through oil seeps or erosion of carbon-rich rock formations. Residual oil stains, asphaltic sandstones and organic-rich mudstones are present in exposures in Hanoi and Dong Ho, Vietnam. Oil seeps occur onshore and offshore of Vietnam (Traynor and Sladen, 1997). Organic rich mudstones are exposed on island in Beibu Gulf (Nytoft et al., 2020). Oil and gas seepage are also present offshore in the Yinggehai Sea, on the southwest coast of Hainan Island. Oil and bitumen from these sources could be picked up and transported by ocean circulation of Beibu Gulf. Two oil shale horizons outcrop in the vicinity of Maoming in Guangdong Province, some 100 km to the northeast of Leizhou Peninsula (Brassell et al., 1986; Figure 1). The weathered and eroded oil shale could be transported by the Huanan nearshore current and the water masses flowing westward through the Qiongzhou Strait into the gulf.

The Beibuwan Basin (Figure 1) is a Cenozoic sedimentary basin that includes Paleogene lacustrine and Neogene Quaternary littoral sea-neritic sea facies in the northern South China Sea (Huang et al., 2013). It has been paid a lot of attention due to its petroleum resources since some oil fields and numerous oil-bearing structures have been discovered on Weixinan, Wushi, and Fushan subbasins (Figure 1; Huang et al., 2017). Abundant oil and gas have been discovered in the Beibuwan Basin. Wushi and Fushan subbasin are located under the seafloor of core 45 and core 29, respectively. Although no natural oil seepages in the study area have been reported, this source of background petrogenic hydrocarbons could be potentially a very important contributor to Leizhou Peninsula offshore sediment.

The biomarker component characteristics in the core sediments, such as the high ratio of C<sub>23</sub> tricyclic terpane/hopane (C<sub>23</sub>TT/C<sub>30</sub>H), low content of oleanane and 4-methyl steranes, and the coexistence of pregnane and diasteranes illustrated that the OM in sediments could be linked to a mixture of sources (Bao et al., 2007; Li et al., 2008; Huang et al., 2011; Huang et al., 2017; Zhou et al., 2019; Gan et al., 2020). Further research is needed to resolve the specific origin of the petrogenic hydrocarbon background in offshore area of Leizhou Peninsula.

The surface sediment in core 29 and core 45 contained more *n*-alkanes than those found in deeper deposits. Besides, the CPI value of surface sediments from two cores was obviously smaller than the subsurface core sediments. NAR value decreased significantly in the surface sample of core 29. The maturity of the OM in uppermost sediment samples of two cores was higher than deeper sediment samples according to the isomerization of C<sub>31</sub> homohopane and C<sub>29</sub> sterane (Figures 7G,F). All of these indicated more petrogenic hydrocarbon inputs in the surface sediment for core 29. However, the terpane and sterane indexes showed no obvious difference for the surface sediment with the subsurface core sediments. This suggested a common organic source for all the samples. The increasing input of petrogenic hydrocarbons may be induced by the petroleum exploitation in Beibuwan Basin in the last century.

## CONCLUSION

Sedimentary organic matter from two separate sites under different hydrodynamic conditions in the coastal areas of the Leizhou Peninsula are studied in term of atomic C/N ratios, *n*-alkane concentrations, and biomarker indexes. Overall, atomic C/N ratios and TAR values demonstrate a mixed terrestrial and marine source for the sedimented organic matter for the two sites. The lower atomic C/N ratio and TAR value in core 45 imply that aquatic organic matter contributed more to site 45 than site 29. The consistent in the difference of the maximum carbon number of long-chain *n*-alkanes through the whole core length is interpreted to represent different terrestrial vegetation source types between two sites. The NAR value and compositional characteristics of

terpane and sterane revealed major proportion of low mature petrogenic hydrocarbon. The compositional characteristics of terpane and sterane also suggest the occurrence of petroleum hydrocarbons generated from marine organic matter. The anthropogenic petroleum pollution input cannot account for the petroleum input to the deep sediments. The similar biomarker characteristics showed no significant source variation for the petrogenic hydrocarbon in two cores through the whole depth. The biomarker component characteristics in the core sediments also illustrated that the organic matter in sediments indicated mixed petrogenic hydrocarbon sources. Further research is needed to resolve the specific origin of the petrogenic hydrocarbon background in offshore area of Leizhou Peninsula.

## DATA AVAILABILITY STATEMENT

The original contributions presented in the study are included in the article/Supplementary Material, further inquiries can be directed to the corresponding author.

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## AUTHOR CONTRIBUTIONS

YG: Methodology, Investigation, Formal analysis, Conceptualization, Writing - Review and Editing, Funding acquisition JT: Investigation, Visualization JX: Resources, Investigation, Methodology, Software, Conceptualization, Visualization Y-PW: Writing - Review and Editing SW: Project administration YH: Investigation JH: Investigation ZS: Writing - Review and Editing, Fundingacquisition, Methodology.

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**Conflict of Interest:** The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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