Organic Geochemistry 60 (2013) 33–39

Contents lists available at SciVerse ScienceDirect

Organic Geochemistry

journal homepage: www.elsevier.com/locate/orggeochem

Variability of tetraether lipids in Yellow River-dominated continental margin during the past eight decades: Implications for organic matter sources and river channel shifts

Weichao Wu [a], Liang Zhao [a], Yandong Pei [b], Weihua Ding [c], Huan Yang [c], Yunping Xu [a,d,*]

[a] MOE Key Laboratory for Earth Surface Processes, College of Urban and Environmental Sciences, Peking University, Beijing 100871, PR China
[b] Tianjin Center, China Geological Survey, Tianjin 300170, PR China
[c] State Key Laboratory of Biogeology and Environmental Geology, China University of Geosciences, Wuhan 430074, PR China
[d] State Key Joint Laboratory of Environment Simulation and Pollution Control, Peking University, Beijing 100871, PR China

ARTICLE INFO

Article history:
Received 21 December 2012
Received in revised form 17 April 2013
Accepted 27 April 2013
Available online 10 May 2013

ABSTRACT

Glycerol dialkyl glycerol tetraethers (GDGTs) and bulk organic geochemical parameters were examined for a short core from the Bohai Sea, a Yellow River-dominated continental margin. A three end member mixing model using branched/isoprenoid tetraethers (BIT) index, $\delta^{13}C$ and C/N shows that the average fractions of soil, marine and plant organic matter (OM) during the period of 1933–2011 are 67.7% (38–92%), 26.1% (0–58%) and 6.2% (0–23%), respectively. Abrupt changes of sedimentary OM compositions around 1953, 1976 and 1996 are synchronous with the Yellow River mouth relocations. The BIT index values (0.33–0.80) present a stronger correlation with crenarchaeol abundance ($R^2 = 0.88$) than branched GDGTs abundance ($R^2 = 0.27$), suggesting that variations of marine Thaumarchaeota abundance rather than soil OM inputs is the first order factor controlling the BIT index values, although this proxy has been widely used for soil OM. The comparison between the BIT index, nutrient status and historical Yellow River sediment load indicates that the high sensitivity of the BIT index to the Yellow River channel shifts cannot be explained by a nutrient stimulation mechanism, but instead is likely caused by the restriction of Thaumarchaeota growth in highly turbid water due to the enormous sediment inputs from Yellow River. Our study demonstrates that local conditions should be considered when applying the BIT index as an environmental proxy.

1. Introduction

Estuaries and continental margins are key locations for the global carbon cycle since over 90% of organic carbon preserved in modern marine sediments is buried there (Hedges et al., 1997). The relative amount of allochthonous terrigenous organic matter (OM) in such environments is influenced by many factors, at least including river sediment load, distance to river mouth, relative sea level, marine primary productivity and early diagenesis (Hedges et al., 1997; Gordon and Goñi, 2004; Herfort et al., 2006). A variety of proxies based on bulk geochemical properties such as total organic carbon (TOC), stable carbon and nitrogen isotopes ($\delta^{13}C$, $\delta^{15}N$) and the organic carbon to nitrogen ratio (C/N) as well as molecular biomarkers such as long chain *n*-alkanes, lignin phenols and long chain alkenones have been proposed to distinguish OM sources (Meyers, 1997; Pancost and Boot, 2004). Since each proxy has intrinsic drawbacks, multiproxy approaches provide more accurate environmental and climatic information (Meyers, 1997).

Recently, a novel biomarker proxy, the so-called branched and isoprenoid tetraether (BIT) index, was introduced to track terrigenous (more specifically soil) OM in marine environments (Hopmans et al., 2004; Weijers et al., 2006). This index is based on the relative abundance of branched glycerol dialkyl glycerol tetraethers (GDGTs) versus isoprenoid GDGT, namely crenarchaeol (Sinninghe Damsté et al., 2002). Branched GDGTs are predominantly biosynthesized by soil/peat bacteria (Hopmans et al., 2004; Weijers et al., 2006), while crenarchaeol is specific for non-extremophilic Thaumarchaeota (previously identified as Group I Crenarchaeota) (Sinninghe Damsté et al., 2002; Spang et al., 2010). The BIT index is calculated as the following equation:

$$\text{BIT intex} = \frac{\text{I} + \text{II} + \text{III}}{\text{I} + \text{II} + \text{III} + \text{IV}}$$

where I, II, III and IV correspond to the GDGT structures in Fig. 1. The BIT index value is generally > 0.9 in soils/peats and ∼0 in marine sediments without significant fluvial inputs (Hopmans et al., 2004; Weijers et al., 2006). Since its advent, the BIT index has been

* Corresponding author at: MOE Key Laboratory for Earth Surface Processes, College of Urban and Environmental Sciences, Peking University, Beijing 100871, PR China. Tel.: +86 10 62752091; fax: +86 10 62754411.
E-mail addresses: yunpingxu@pku.edu.cn, yunpingxu@gmail.com (Y. Xu).

0146-6380/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.orggeochem.2013.04.014

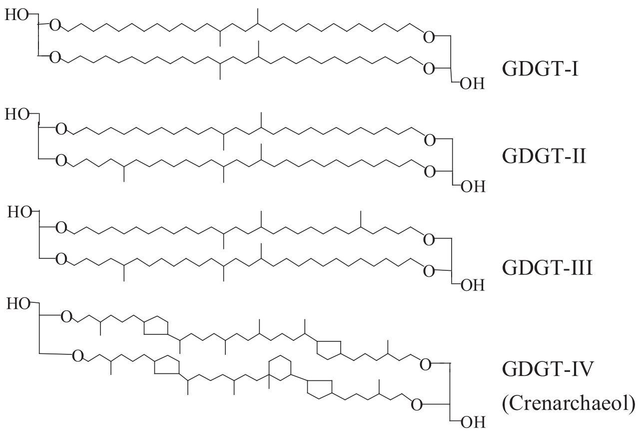

Fig. 1. Structures of branched (I–III) and isoprenoid (IV) GDGTs used for the BIT index.

increasingly used to estimate soil OM for different environments (e.g., Herfort et al., 2006; Kim et al., 2006, 2012; Schouten et al., 2007; Weijers et al., 2009; Zhao et al., 2011).

However, several issues can complicate interpretation of the BIT index for soil OM (Walsh et al., 2008; Smith et al., 2012; Wu et al., 2012). First, as the BIT index is a ratio, its value is influenced by not only changes in the input of soil OM but also relative variations in aquatic Thaumarchaeota abundance (Fietz et al., 2011a; Smith et al., 2012). Second, selective degradation may substantially alter the BIT index values. It has been reported that degradation rates of crenarchaeol are 2-fold higher than those of soil derived branched GDGTs under long term oxygen exposure (Huguet et al., 2008, 2009). During the transport from land to sea, complex processes (e.g., hydrodynamic sorting, microbial degradation) can degrade branched GDGTs to a greater extent than other organic geochemical proxies, resulting in underestimation of soil OM based on the BIT index (Zhu et al., 2011). Third, branched GDGTs, although predominantly derived from soil/peat, may be in situ productions in lakes and rivers (Peterse et al. 2009; Zhu et al., 2011; Fietz et al., 2012; Zell et al., 2013). Therefore, more studies are needed to understand sources and distributions of GDGTs in different environments as well as their applicability as environmental proxies.

The Yellow River (YR) dominated continental margin provides an ideal venue to study the biogeochemical cycle of terrigenous OM in seas. YR is the world's second largest river in terms of sediment load and carries a long term average of 1.1×10^9 t sediment to the sea per year, strongly influencing northeast Chinese marginal seas (Milliman et al., 1987; Zhang et al., 1995). This annual sediment load, however, sharply decreased to 0.15×10^9 t after 1950 (Wang et al., 2007). One remarkable feature of YR is frequent channel shifting due to high sediment load, relatively steep river channel gradients in the lower reaches and intensive human interference (Saito et al., 2001). Since YR began flowing into Bohai Sea in 1855, its mouth has shifted more than 50 times (Qiao et al., 2011). Several studies have been carried out to reconstruct long term Holocene sediment evolution of the YR delta (Saito et al., 2001; Liu et al., 2004; Wang et al., 2007; Qiao et al., 2011). However, the effect of short term events (e.g., YR channel shift) on the dispersal and deposition of OM in the adjacent seas has rarely been reported (Yang et al., 2009). In this study, we analyzed GDGTs and bulk organic geochemical parameters in a short core from the southern Bohai Sea (Fig. 2). Our main objectives are to reconstruct high resolution variability of terrigenous and marine OM

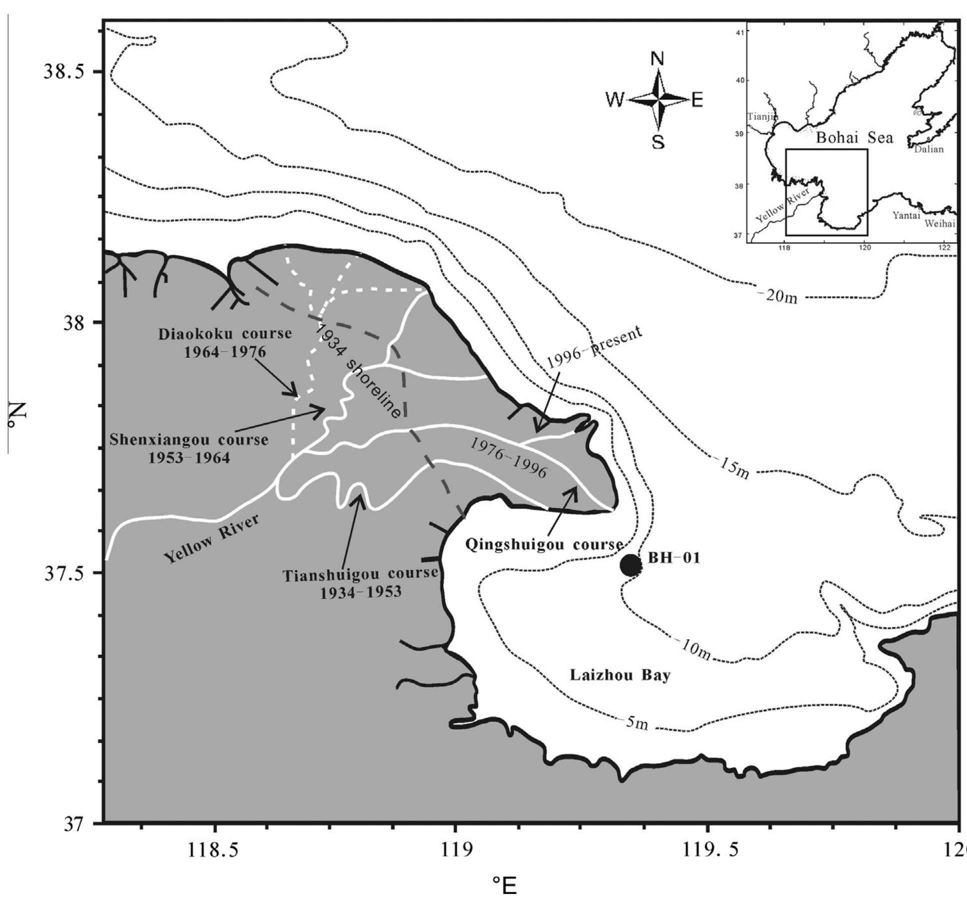

Fig. 2. Typical channel changes of the Yellow River since 1930 and the location of sampling site (black dot) in the Bohai Sea.

over the past eight decades and understand mechanisms controlling OM distributions and burial in such a dynamic continental margin.

2. Sampling and analytical methods

2.1. Study area and sampling

The Bohai Sea is a semi-enclosed shallow sea in North China with a surface area of 77,000 km^2 and an average water depth of 18 m (Sun et al., 2011). Since 1855, YR, although shifting its channel frequently, constantly drained into the Bohai Sea (Saito et al., 2001; Qiao et al., 2011). In July 2011, a 65 cm long piston core (BH-01; 119°18.999′N, 37°30.906′E) was collected in the Laizhou Bay (southern Bohai Sea) (Fig. 2). The sediments are predominantly composed of silt and clay, while sand only accounts for minor fractions. The core was sectioned at every 1 or 2 cm on the ship and transported to the lab within 48 h. All the samples were kept at −20 °C until further analyses.

2.2. ^{137}Cs and ^{210}Pb dating

The detailed methods for ^{137}Cs and ^{210}Pb dating (half-life 22.3 years) have been described by Bao et al. (2010). Briefly, about 5 g of dried sediments were used for ^{137}Cs and ^{210}Pb measurements. The activities of ^{210}Pb, ^{226}Ra and ^{137}Cs were determined by a low background γ-ray spectrometer with a high pure Ge semiconductor (ORTEC Instruments Ltd., USA). The measurement precisions of ^{137}Cs and ^{210}Pb were ca. ± 5% and ± 10% at the 95% level of confidence, respectively. A total of 40 samples were used for the radionuclide measurement.

2.3. Elemental and stable isotope analyses

The sediments were freeze dried and ground into fine powder. After the addition of excess 1 N hydrochloric acid to completely remove inorganic carbon, TOC and TN were measured by an Elementar Vario EL element analyzer, while $\delta^{13}C$ compositions were run on a Flash EA1112HT coupled with MAT253 (Thermo Fisher Scientific, Inc). The standard deviations based on the replicate analyses were 0.02% for TOC, 0.005% for TN, and 0.15‰ for $\delta^{13}C$.

2.4. GDGTs extraction and analyses

After the addition of 600 ng C_{46} GDGT as an internal standard (Huguet et al., 2006), 10 g of freeze dried sediments were ultrasonically extracted (3×) with 20 ml dichloromethane:methanol (3:1 v:v). The combined extracts were rotary evaporated to near dryness and separated into two fractions over a silica gel column with 10 ml hexane:dichloromethane (9:1 v:v) and 10 ml dichloromethane:methanol (1:1 v:v). The second fraction containing GDGTs was dried under a mild nitrogen stream, ultrasonically dissolved in hexane:propanol (99:1 v:v) and filtered through a PTFE filter (0.45 μm pore size). An Agilent 1200 high performance liquid chromatograph-atmospheric pressure chemical ionization-Agilent 6460 triple quadrupole mass spectrometer (HPLC-APCI-MS) was used for the analyses. The injection volume was 5 μl. Separation of the compounds was achieved in normal phase on an Alltech Prevail Cyano column (150 mm; 2.1 mm; 3 μm). The GDGTs were eluted isocratically with 90% hexane (solution A) and 10% hexane:isopropanol (9:1 v:v) (solution B) for the first 5 min, and a linear gradient to 1.8% isopropanol in 45 min. After each run, the column was cleaned by 100% solution B for 10 min, and then equilibrated with solution A:B (90:10, v:v). A constant flow rate of 0.2 ml/min was used. Quantification of GDGTs was obtained by comparison of the $[M + H]^+$ peak areas of individual GDGT to the internal standard. Duplicate measurements show that the analytical reproducibility of the BIT index is better than 0.02.

3. Results

3.1. Radionuclide activity profiles and geochronology

In the BH-01 core, the $^{210}Pb_{excess}$ activities declined downward, whereas ^{226}Ra activities remained nearly constant with a mean value of 55.6 Bq/kg (Fig. 3). The plots of depth (cm) versus $^{210}Pb_{excess}$ (Bq/kg) revealed a mean sedimentation rate of 1.04 cm/yr based on a constant initial concentration (CIC) model (Kirchner, 2011).

The depth profile of ^{137}Cs activity showed maximum peaks at 41.5 cm (Fig. 3), corresponding to the maximum atomic weapon testing in 1963 (Kirchner, 2011). The first continuous appearance of detectable ^{137}Cs at 50 cm depth likely corresponds to 1952 when first atomic weapon test was conducted. Based on these two age markers, the calculated mean sedimentation rate is 0.87 cm/yr from 41.5–0 cm and 0.73 cm/yr from 65–41.5 cm.

Chronologies from the $^{210}Pb_{excess}$ and ^{137}Cs parameters are generally consistent with difference of < 5 years for the upper section (25–0 cm). The age offset increased up to 15 years for the bottom of the core. Given that the greatest YR channel shift occurred in 1976 (Fig. 2) and there is a relatively poor R^2 value (0.54) for the CIC model (Fig. 3), the sedimentation rate of the lower section is likely different from that of the upper section. Thus the age model used in this study is based on the ^{137}Cs activity, which suggests that the BH-01 core represents the period from 1933 to 2011. A total of 48 samples were analyzed and the time resolution is about 1 year/cm.

3.2. Bulk organic matter properties

The TOC content of the BH-01 core varied from 0.21–0.32%, agreeing with the previous reports for Bohai Sea sediments (Hu et al., 2009; Sun et al., 2011). The TOC content remained at relatively low values (0.21–0.26%) prior to 1964 (Fig. 4). Afterwards, this proxy increased to 0.31% in 1979 and stayed at relatively higher levels for the past three decades except for a drop in 1996. The TN content varied from 0.017–0.035% throughout the core, displaying a similar pattern to TOC ($r = 0.85$; $p < 0.001$).

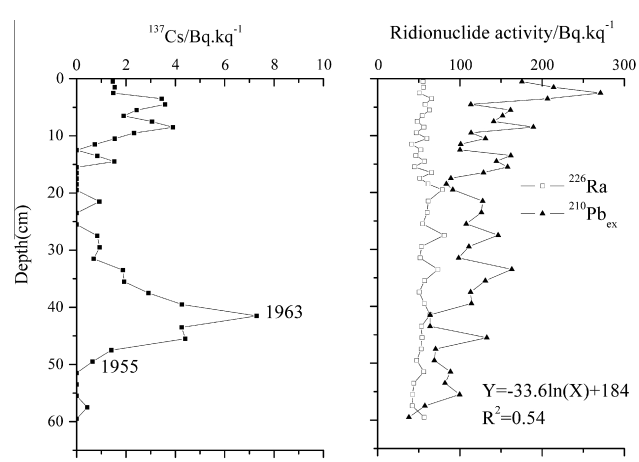

Fig. 3. Depth profiles of ^{137}Cs, ^{226}Ra and excess ^{210}Pb activities in the BH-01 core, southern Bohai Sea.

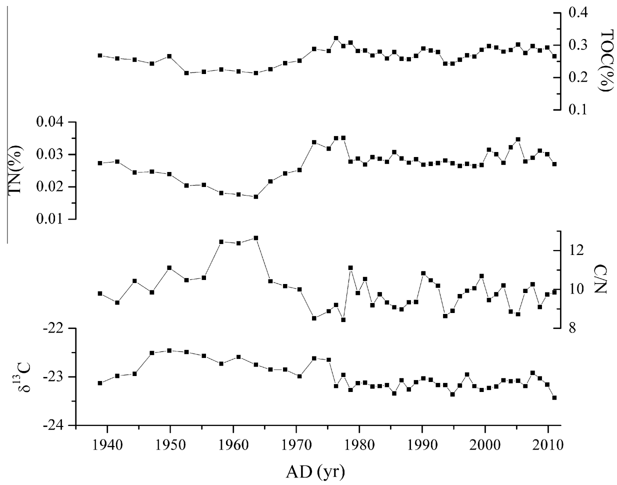

Fig. 4. Distributions of bulk organic geochemical parameters in the BH-01 core, southern Bohai Sea.

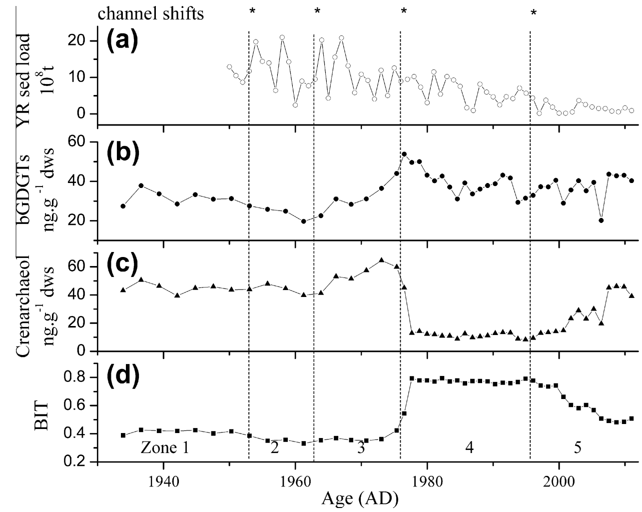

Fig. 5. Age profiles of (a) the Yellow River annual sediment load (Wang et al., 2007), (b) branched GDGTs I + II + III concentrations, (c) crenarchaeol concentrations and (d) the BIT index values in the BH-01 core, Bohai Sea. Four major Yellow River channel shifts (marked with stars) after 1950 occurred in 1953, 1964, 1976 and 1996 (see Fig. 1 for details).

The C/N ratio is an indicator for distinguishing terrigenous versus marine OM since vascular plants are abundant in cellulose and lignin and have C/N values of > 15, while protein rich algae have values of 5–8 (Meyers, 1997). In the BH-01 core, the C/N ratio ranged from 8.5–12 (Fig. 4), suggesting mixed contributions of terrigenous and marine OM. This proxy increased upwards and stayed at a relatively high level from 1958 to 1964. Afterwards, the C/N ratio decreased and reached a minimum value in 1977. The period from 1977 to 2011 is characterized by relatively low C/N values with an average of 9.7.

The organic δ^{13}C value has been widely used to estimate relative abundance of terrigenous and marine OM because C3 land plants and marine plankton have a mean δ^{13}C values of −27‰ and −20‰, respectively (Fry and Sherr, 1984). In the BH-01 core, the δ^{13}C values fell in a narrow range from −22.5‰ to −23.4‰, also reflecting mixed inputs of terrigenous and marine OM (Fig. 4).

3.3. GDGT abundances and the BIT index

Throughout the BH-01 core, the concentrations of total, branched and isoprenoid GDGTs ranged from 67–170 ng/g dry weight sediment (dws), 30.7–83.4 ng/g dws and 17.9–108 ng/g dws, respectively. Crenarchaeol, a biomarker for aquatic Thaumarchaeota (Sinninghe Damsté et al., 2002; Spang et al., 2010), varied in abundance from 8.3–64.5 ng/g dws with an average of 29.4 ng/g dws, while the concentration of branched GDGTs I + II + III (Fig. 1) ranged from 19.7–53.8 ng/g dws with an average of 35.6 ng/g dws (Fig. 5). Based on the GDGTs distributions, the BIT index values presented a wide range from 0.33–0.80.

4. Discussion

4.1. Implication of the BIT index in the YR dominated continental margin

Based on the BIT index values, the BH-01 core can be divided into five zones: Zone 1 (1933–1953): moderate BIT index values from 0.39–0.43; Zone 2 (1953–1964): lowest BIT index values from 0.33–0.36; Zone 3 (1964–1976): relatively low but increasing BIT values from 0.35–0.54; Zone 4 (1976–1997): the highest BIT index values from 0.74–0.80; and Zone 5 (1997–2011): relatively high but decreasing BIT index values from 0.76–0.48. Since the transport of soil OM to seas is mainly by rivers, the BIT index in marine sediments is usually connected to the river discharge (Kim et al., 2007). In this case, YR is the most important corridor and accounts for over 90% of the terrigenous material to the Bohai Sea (Ren, 2006; Qiao et al., 2011). The BIT index in the BH-01 core, however, presents a different pattern compared to the historical YR sediment load (Fig. 5). Since 1950, the YR annual sediment load has substantially decreased from 20×10^8 t to 0.2×10^8 t, while the BIT index values displayed an abrupt increase in 1976 and a rapid decrease around 2000 (Fig. 5). Unexpectedly, the BIT index values remained relatively constant within each zone, although the YR sediment load continuously declined (Fig. 5). These disparities demonstrate that the sediment load (or river discharge) is not the first order factor controlling the BIT index in the BH-01 core. Instead, we note that four pronounced BIT index oscillations in 1953, 1964, 1976 and 1998 are all synchronous with historical YR course shifts within the uncertainty of our dating (Fig. 5) (Pang and Si, 1979; Wang et al., 2007).

Why are the BIT index values in the BH-01 core highly sensitive to the YR channel shifts? One possible reason is that the YR mouth relocation will reduce or increase the distance to the sampling site, and thereby deposit more or less terrigenous OM there. However, since the BIT index is a ratio of branched versus isoprenoid GDGTs (Hopmans et al., 2004), its value is influenced by not only fluvial soil OM inputs but also marine Thaumarchaeota abundance (Walsh et al., 2008; Fietz et al., 2011b; Smith et al., 2012). In the BH-01 core, the BIT index shows a much stronger correlation with crenarchaeol abundance (R^2 = 0.88) than branched GDGT abundance (R^2 = 0.27) (Fig. 6). The relative magnitude of variation in crenarchaeol abundance (7.8; from 8.3-64.5 ng/g dws) is also substantially greater than the variation in branched GDGT abundance (2.7; from 19.7–53.8 ng/g dws) (Fig. 5). These facts support the proposition that large changes of marine Thaumarchaeota abundance control the BIT index values, as was similarly observed for the Louisiana Continental Shelf (Smith et al., 2012) and other marginal seas (Fietz et al., 2011a, 2012 and references therein).

Large river dominated continental margins are areas undergoing the most intensive interaction between land and sea. Recent studies found that some of marine Thaumarchaeota are nitrifiers and their abundance is dependent on primary productivity (Wuchter et al., 2006; Sinninghe Damsté et al., 2009; Fietz et al., 2011b). Thus enhanced nutrient inputs can stimulate primary productivity in continental margins and increase Thaumarchaeota abundance.

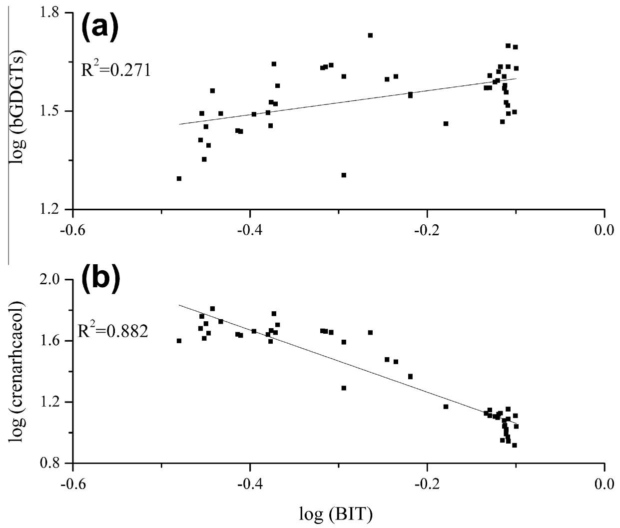

Fig. 6. Cross plots of the logarithmic values of the BIT index versus (a) branched GDGTs and (b) crenarchaeol concentrations in the BH-01 core, Bohai Sea.

Consequently, more crenarchaeol is biosynthesized and deposited in sediments, lowering the BIT index values (Walsh et al., 2008; Smith et al., 2012). In the BH-01 core, higher N contents were observed after the 1970s (Fig. 4), corresponding to recent eutrophication in the Bohai Sea due to enormous inputs of industrial wastewater and domestic sewerage (Jiang et al., 2005). However, the period from the 1970s to the 1990s is characterized by the lowest crenarchaeol abundance (even normalized to organic carbon) and the highest BIT index values (Fig. 5). This unexpected phenomenon suggests that the commonly used nutrient stimulation mechanism cannot explain the BIT index variations in the Bohai Sea. Considering that YR is the most turbid large river in the world, in which the suspended sediment concentration has an average of 25.5 kg/m^3 and may attain 220 kg/m^3 during the flood season (Ren and Shi, 1986), we propose that highly turbid flow in the estuary plays a key role in the BIT index values. When the river mouth shifts closer (further) to the study site, highly turbid flow carries more (less) sediments to the sampling site and thus reduces (increases) water transparency, providing undesirable (favorable) conditions for marine planktons (including Thaumarchaeota) growth (Turner et al., 1990). As a result, less (more) crenarchaeol accumulates in the Bohai Sea sediments. This, along with increasing (decreasing) inputs of soil derived branched GDGTs, amplifies the magnitude of variations in the BIT index values.

4.2. Estimation of organic matter sources using δ^{13}C, C/N and BIT

A two end member mixing model based on δ^{13}C or C/N has been widely used to estimate the relative amount of terrigenous and marine OM (Hedges et al., 1997 and references therein). However, this approach has considerable uncertainty due to the highly heterogeneous nature of terrigenous OM (Gordon and Goñi, 2003; Holtvoeth et al., 2005; Weijers et al., 2009). Soil OM, although mainly derived from plant litter, is distinguished from plant OM by elemental, isotopic and chemical compositions because of humification and mineralization of plant litter. Thus, a three end member (soil, plant and marine OM) mixing model is needed. Here we used the model developed by Weijers et al. (2009) to estimate the relative amount of soil, plant and marine OM in the Bohai Sea, which was expressed as follows:

$$\mathrm{BIT_{sed}} = f_{\mathrm{soil}}\mathrm{BIT_{soil}} + f_{\mathrm{mar}}\mathrm{BIT_{mar}}$$

$$(\mathrm{C/N})_{\mathrm{sed}} = f_{\mathrm{soil}}(\mathrm{C/N})_{\mathrm{soil}} + f_{\mathrm{plant}}(\mathrm{C/N})_{\mathrm{plant}} + f_{\mathrm{mar}}(\mathrm{C/N})_{\mathrm{mar}}$$

$$(\delta^{13}\mathrm{C})_{\mathrm{sed}} = f_{\mathrm{soil}}(\delta^{13}\mathrm{C})_{\mathrm{soil}} + f_{\mathrm{plant}}(\delta^{13}\mathrm{C})_{\mathrm{plant}} + f_{\mathrm{mar}}(\delta^{13}\mathrm{C})_{\mathrm{mar}}$$

With an additional mass balance equation:

$$f_{\mathrm{mar}} + f_{\mathrm{soil}} + f_{\mathrm{plant}} = 1$$

where f_{soil}, f_{plant} and f_{mar} are the fractions of soil, plant and marine OM, respectively. The marine end member values used are −20.9‰ for δ^{13}C (Fry and Sherr, 1984; Cai and Cai, 1993), 6.7 for C/N (Hu et al., 2009) and 0 for the BIT index (Hopmans et al., 2004). For plant end member values, we used 0 for BIT since no GDGTs are present in plants (Hopmans et al., 2004), 30 for C/N (Weijers et al., 2009) and −27‰ for δ^{13}C given the predominance of C3 plants in the middle to lower YR reach. The C/N ratio has a considerable range in soil from the Chinese Loess Plateau, which accounts for 90% of YR sediments (Ren, 2006). Lu and Liang (2011) analyzed C/N in three soil profiles from the central Chinese Loess Plateau, which showed C/N ratios varying from 8–12. Based on this, an average C/N value of 10 was used for the soil end member. It has been reported that particulate organic carbon in the lower YR had a mean δ^{13}C value of −24.9‰, which is close to that of modern soils in Chinese loess (Cai and Cai, 1993). Thus this value was used for the soil δ^{13}C end member. The BIT index value for the soil end member is 0.91 based on a survey of global soils (Weijers et al., 2006).

The results from the three end member mixing model showed that the average, minimum and maximum fractions of soil, plant and marine derived OM in the BH-01 core were 67.7% (38–92%), 26.1% (0–58%) and 6.2% (0–22%), respectively (Fig. 7). The application of the three end member mixing model resulted in four negative values (−3.0% to −0.1%) for the plant or marine OM estimations, likely reflecting uncertainty of the end member values used. Since these values are close to 0, we set them as zero. Compared to other large river fans adjacent to the Congo River (Weijers et al., 2009) and the Mississippi and Atchafalaya rivers (Gordon and Goñi, 2004), the sediments in the Bohai Sea consisted of remarkably high soil OM components and exceptionally low plant OM components, which was attributed to sparse vegetation cover and severe soil erosion in the arid and semiarid Chinese loess plateau (Jiao et al., 2011). This result also agrees well with the finding of Xia and Zhang (2011) who suggested that particulate organic carbon in YR was mainly from soil erosion.

The OM composition in the BH-01 core exhibits the largest change around 1976, when the soil OM fractions sharply increased from 47% to 92% (Fig. 7). This change is synchronous with the southward shift of the YR mouth from Diaokou to Qingshuigou (Fig. 2). When the river mouth moved closer to the BH-01 site,

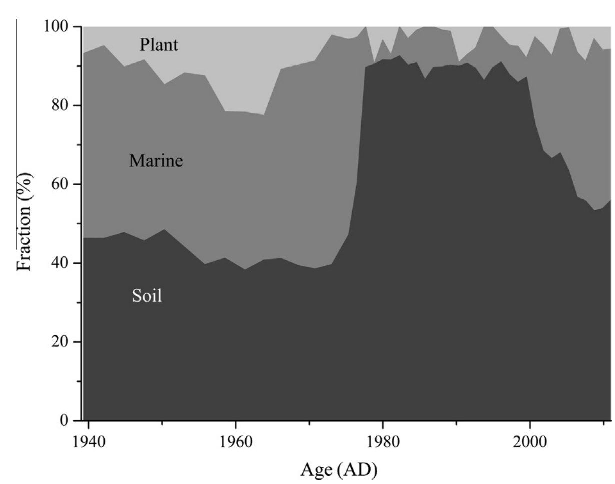

Fig. 7. Estimations of soil, marine and plant organic matter fractions in the BH-01 core based on the δ^{13}C, BIT index and C/N proxies.

enormous amounts of YR fluvial materials was transported and deposited there, resulting in an abrupt increase of terrigenous OM fractions. In contrast, a substantial decrease in the soil OM fraction from 87% to 56% occurred from 1996 to 2000, which was likely caused by the northward shift of the YR course in 1996 (Fig. 2). This northward relocation of the YR mouth increased the distance to the BH-01 site and thus decreased terrigenous influence there. Another change of the OM compositions, despite moderate, was observed in the early 1950s when the soil OM fraction decreased from 48% to 38%. This shift again coincided with the northward relocation of the YR channel in 1953 (Fig. 2). These results strongly suggest that the YR channel shift is an important driving force for redistribution of OM in the Bohai Sea.

5. Conclusions

The BIT index has been increasingly applied for tracking soil OM in different marine environments. Here we reconstruct high resolution variability of the BIT index in the Bohai Sea, a Yellow River dominated continental margin, for the past eight decades. Based on the GDGT data, bulk geochemical parameters and ^{137}Cs and ^{210}Pb activities, three conclusions can be drawn.

Soil OM represents a principal component of sedimentary OM in the core with an average of 67.7%, followed by marine OM (26.1%) and plant OM (6.2%). Such low contributions of plant OM are remarkably different from other large river fans elsewhere, likely attributed to sparse vegetation cover and severe soil erosion in the arid and semiarid Chinese Loess Plateau.

The OM compositions display abrupt changes in 1953, 1976 and 1996, all of which are synchronous with the Yellow River channel shifts. This provides evidence that the relocation of the Yellow River mouth is an important factor for redistribution of OM in this river dominated margin. Our study also suggests that the BIT index is a potential proxy for river channel shifts, although more studies are needed.

The BIT index presents a stronger correlation with crenarchaeol than branched GDGTs, demonstrating that large variation of marine Thaumarchaeota abundance is a driving forcing for the BIT index values. However, under the strong influence of high turbid Yellow River water, large oscillations of the BIT index (0.33–0.80) cannot be explained by a nutrient stimulation mechanism, suggesting that local conditions should be considered when interpreting the BIT index.

Acknowledgements

This study was financially supported by NSFC (41006042, 41176164), the State Education Ministry (SRF for ROCS, SEM) and the special fund of the State Key Joint Laboratory of Environment Simulation and Pollution Control (PKU). The authors thank Leilei Zhang, Jiaping Ruan and Su Ding for assistance in sample analyses. Dr. Antoni Rosell-Melé, Simon George and an anonymous reviewer are thanked for constructive comments.

Associate Editor – **Simon George**

References

Bao, K., Xia, W., Lu, X., Wang, G., 2010. Recent atmospheric lead deposition recorded in an ombrotrophic peat bog of Great Hinggan Mountains, Northeast China, from ^{210}Pb and ^{137}Cs dating. Journal of Environmental Radioactivity 101, 773–779.

Cai, D., Cai, A., 1993. Isotopic geochemistry investigation of organic carbon in Yellow River estuary. Science in China Series B 23, 1105–1113 (in Chinese).

Fietz, S., Martínez-Garcia, A., Huguet, C., Rueda, G., Rosell-Melé, A., 2011a. Constraints in the application of the Branched and Isoprenoid Tetraether index as a terrestrial input proxy. Journal of Geophysical Research: Oceans 116, C10032. http://dx.doi.org/10.1029/2011JC007062.

Fietz, S., Martínez-Garcia, A., Rueda, G., Peck, V.L., Huguet, C., Escala, M., Rosell-Melé, A., 2011b. Crenarchaea and phytoplankton coupling in sedimentary archives: common trigger or metabolic dependence? Limnology and Oceanography 56, 1907–1916.

Fietz, S., Huguet, C., Bendle, J., Escala, M., Gallacher, C., Herfort, L., Jamieson, R., Martínez-Garcia, A., McClymont, E.L., Peck, V.L., Prahl, F.G., Rossi, S., Rueda, G., Sanson-Barrera, A., Rosell-Melé, A., 2012. Co-variation of crenarchaeol and branched GDGTs in globally-distributed marine and freshwater sedimentary archives. Global and Planetary Change 92–93, 275–285.

Fry, B., Sherr, E.B., 1984. Δ^{13}C measurements as indicators of carbon flow in marine and freshwater ecosystems. Contributions in Marine Science 27, 13–47.

Gordon, E.S., Goñi, M.A., 2003. Sources and distribution of terrigenous organic matter delivered by the Atchafalaya River to sediments in the northern Gulf of Mexico. Geochimica et Cosmochimica Acta 67, 2359–2375.

Gordon, E.S., Goñi, M.A., 2004. Controls on the distribution and accumulation of terrigenous organic matter in sediments from the Mississippi and Atchafalaya river margin. Marine Chemistry 92, 331–352.

Hedges, J., Keil, R., Benner, R., 1997. What happens to terrestrial organic matter in the ocean? Organic Geochemistry 27, 195–212.

Herfort, L., Schouten, S., Boon, J.P., Woltering, M., Baas, M., Weijers, J.W.H., Damste, J.S.S., 2006. Characterization of transport and deposition of terrestrial organic matter in the southern North Sea using the BIT index. Limnology and Oceanography 51, 2196–2205.

Holtvoeth, J., Kolonic, S., Wagner, T., 2005. Soil organic matter as an important contributor to late Quaternary sediments of the tropical West African continental margin. Geochimica et Cosmochimica Acta 69, 2031–2041.

Hopmans, E.C., Weijers, J.W.H., Schefu, E., Herfort, L., Sinninghe Damst, J.S., Schouten, S., 2004. A novel proxy for terrestrial organic matter in sediments based on branched and isoprenoid tetraether lipids. Earth and Planetary Science Letters 224, 107–116.

Hu, L., Guo, Z., Feng, J., Yang, Z., Fang, M., 2009. Distributions and sources of bulk organic matter and aliphatic hydrocarbons in surface sediments of the Bohai Sea, China. Marine Chemistry 113, 197–211.

Huguet, C., Hopmans, E.C., Febo-Ayala, W., Thompson, D.H., Damste, J.S.S., Schouten, S., 2006. An improved method to determine the absolute abundance of glycerol dibiphytanyl glycerol tetraether lipids. Organic Geochemistry 37, 1036–1041.

Huguet, C., de Lange, G.J., Gustafsson, Ö., Middelburg, J.J., Sinninghe Damsté, J.S., Schouten, S., 2008. Selective preservation of soil organic matter in oxidized marine sediments (Madeira Abyssal Plain). Geochimica et Cosmochimica Acta 72, 6061–6068.

Huguet, C., Kim, J.-H., de Lange, G.J., Sinninghe Damsté, J.S., Schouten, S., 2009. Effects of long term oxic degradation on the *UK'37*, and BIT organic proxies. Organic Geochemistry 40, 1188–1194.

Jiang, H., Cui, Y., Chen, B., Chen, J., Song, Y., 2005. The variation trend of nutrient salts in the Bohai Sea. Marine Fisheries Research 26, 61–67 (in Chinese).

Jiao, J., Han, L., Jia, Y., Wang, N., Lei, D., Li, L., 2011. Can seed removal through soil erosion explain the scarcity of vegetation in the Chinese Loess Plateau? Geomorphology 132, 35–40.

Kim, J.-H., Schouten, S., Buscail, R., Ludwig, W., Bonnin, J., Damste, J.S.S., Bourrin, F., 2006. Origin and distribution of terrestrial organic matter in the NW Mediterranean (Gulf of Lions): Exploring the newly developed BIT index. Geochemistry Geophysics Geosystems 7, Q11017, 11010.11029/12006GC001306.

Kim, J.-H., Ludwig, W., Schouten, S., Kerhervé, P., Herfort, L., Bonnin, J., Sinninghe Damsté, J.S., 2007. Impact of flood events on the transport of terrestrial organic matter to the ocean: a study of the Têt River (SW France) using the BIT index. Organic Geochemistry 38, 1593–1606.

Kim, J.-H., Zell, C., Moreira-Turcq, P., Pérez, M.A.P., Abril, G., Mortillaro, J.-M., Weijers, J.W.H., Meziane, T., Sinninghe Damsté, J.S., 2012. Tracing soil organic carbon in the lower Amazon River and its tributaries using GDGT distributions and bulk organic matter properties. Geochimica et Cosmochimica Acta 90, 163–180.

Kirchner, G., 2011. ^{210}Pb as a tool for establishing sediment chronologies: examples of potentials and limitations of conventional dating models. Journal of Environmental Radioactivity 102, 490–494.

Liu, J.P., Milliman, J.D., Gao, S., Cheng, P., 2004. Holocene development of the Yellow River's subaqueous delta, North Yellow Sea. Marine Geology 209, 45–67.

Lu, H., Liang, Z., 2011. Preliminary analysis on abnormal granularity layers of soil profile and the response of relative factors in Loess Plateau. Agricultural Science & Technology 12, 1671–1673.

Meyers, P., 1997. Organic geochemical proxies of paleoceanographic, paleolimnologic, and paleoclimatic processes. Organic Geochemistry 27, 213–250.

Milliman, J.D., Yun-Shan, Q., Mei-e, R., Saito, Y., 1987. Man's influence on the erosion and transport of sediment by Asian rivers: the Yellow River (Huanghe) example. The Journal of Geology, 751–762.

Pancost, R.D., Boot, C.S., 2004. The palaeoclimatic utility of terrestrial biomarkers in marine sediments. Marine Chemistry 92, 239–261.

Pang, J., Si, S., 1979. The estuary changes of Huanghe River I. changes in modern time. Oceanologia Et Limnologia Sinica 19, 136–141 (in Chinese).

Peterse, F., Kim, J.-H., Schouten, S., Kristensen, D.K., Koç, N., Sinninghe Damsté, J.S., 2009. Constraints on the application of the MBT/CBT palaeothermometer at high latitude environments (Svalbard, Norway). Organic Geochemistry 40, 692–699.

Qiao, S., Shi, X., Saito, Y., Li, X., Yu, Y., Bai, Y., Liu, Y., Wang, K., Yang, G., 2011. Sedimentary records of natural and artificial Huanghe (Yellow River) channel

shifts during the Holocene in the southern Bohai Sea. Continental Shelf Research 31, 1336–1342.
Ren, M., Shi, Y., 1986. Sediment discharge of the Yellow River (China) and its effect on the sedimentation of the Bohai and the Yellow Sea. Continental Shelf Research 6, 785–810.
Ren, M., 2006. Sediment discharge of the Yellow River, China: past, present and future-a synthesis. Advances in Earth Science 6, 551–563 (in Chinese).
Saito, Y., Yang, Z., Hori, K., 2001. The Huanghe (Yellow River) and Changjiang (Yangtze River) deltas: a review on their characteristics, evolution and sediment discharge during the Holocene. Geomorphology 41, 219–231.
Schouten, S., Ossebaar, J., Brummer, G.J., Elderfield, H., Sinninghe Damsté, J.S., 2007. Transport of terrestrial organic matter to the deep North Atlantic Ocean by ice rafting. Organic Geochemistry 38, 1161–1168.
Sinninghe Damsté, J.S., Schouten, S., Hopmans, E.C., van Duin, A.C.T., Geenevasen, J.A.J., 2002. Crenarchaeol: the characteristic core glycerol dibiphytanyl glycerol tetraether membrane lipid of cosmopolitan pelagic crenarchaeota. Journal of Lipid Research 43, 1641–1651.
Sinninghe Damsté, J.S., Ossebaar, J., Abbas, B., Schouten, S., Verschuren, D., 2009. Fluxes and distribution of tetraether lipids in an equatorial African lake: constraints on the application of the TEX_{86} palaeothermometer and BIT index in lacustrine settings. Geochimica et Cosmochimica Acta 73, 4232–4249.
Smith, R.W., Bianchi, T.S., Li, X., 2012. A re-evaluation of the use of branched GDGTs as terrestrial biomarkers: implications for the BIT Index. Geochimica et Cosmochimica Acta 80, 14–29.
Spang, A., Hatzenpichler, R., Brochier-Armanet, C., Rattei, T., Tischler, P., Spieck, E., Streit, W., Stahl, D.A., Wagner, M., Schleper, C., 2010. Distinct gene set in two different lineages of ammonia-oxidizing archaea supports the phylum Thaumarchaeota. Trends Microbiol 18, 331–340.
Sun, D., Tan, W., Pei, Y., Zhou, L., Wang, H., Yang, H., Xu, Y., 2011. Late Quaternary environmental change of Yellow River Basin: an organic geochemical record in Bohai Sea (North China). Organic Geochemistry 42, 575–585.
Turner, R.E., Rabalais, N.N., Nan, Z.Z., 1990. Phytoplankton biomass production and growth limitations on the Huanghe (Yellow River) continental shelf. Continental Shelf Research 10, 545–571.
Walsh, E.M., Ingalls, A.E., Keil, R.G., 2008. Sources and transport of terrestrial organic matter in Vancouver Island fjords and the Vancouver-Washington Margin: a multiproxy approach using $\delta^{13}C_{org}$, lignin phenols, and the ether lipid BIT index. Limnology and Oceanography 53, 1054–1063.
Wang, H., Yang, Z., Saito, Y., Liu, J.P., Sun, X., Wang, Y., 2007. Stepwise decreases of the Huanghe (Yellow River) sediment load (1950–2005): impacts of climate change and human activities. Global and Planetary Change 57, 331–354.
Weijers, J.W.H., Schouten, S., Spaargaren, O.C., Sinninghe Damsté, J.S., 2006. Occurrence and distribution of tetraether membrane lipids in soils: implications for the use of the TEX86 proxy and the BIT index. Organic Geochemistry 37, 1680–1693.
Weijers, J.W.H., Schouten, S., Schefuß, E., Schneider, R.R., Sinninghe Damsté, J.S., 2009. Disentangling marine, soil and plant organic carbon contributions to continental margin sediments: a multi-proxy approach in a 20,000 year sediment record from the Congo deep-sea fan. Geochimica et Cosmochimica Acta 73, 119–132.
Wu, W., Tan, W., Zhou, L., Yang, H., Xu, Y., 2012. Sea surface temperature variability in southern Okinawa Trough during last 2700 years. Geophysical Research Letters 39, L14705. http://dx.doi.org/10.1029/2012GL052749.
Wuchter, C., Abbas, B., Coolen, M.J., Herfort, L., van Bleijswijk, J., Timmers, P., Strous, M., Teira, E., Herndl, G.J., Middelburg, J.J., Schouten, S., Sinninghe Damsté, J.S., 2006. Archaeal nitrification in the ocean. Proceedings of the National Academy of Sciences of the United States of America 103, 12317–12322.
Xia, B., Zhang, L., 2011. Carbon distribution and fluxes of 16 rivers discharging into the Bohai Sea in summer. Acta Oceanologica Sinica 30, 43–54.
Yang, W., Chen, M., Li, G., Cao, J., Guo, Z., Ma, Q., Liu, J., Yang, J., 2009. Relocation of the Yellow River as revealed by sedimentary isotopic and elemental signals in the East China Sea. Marine Pollution Bulletin 58, 923–927.
Zell, C., Kim, J.-H., Moreira-Turcq, P., Abril, G., Hopmans, E.C., Bonnet, M.-P., Sobrinho, R.L., Damsté, J.S.S., 2013. Disentangling the origins of branched tetraether lipids and crenarchaeol in the lower Amazon River: implications for GDGT-based proxies. Limnology and Oceanography 58, 343–353.
Zhang, J., Huang, W., Letolle, R., Jusserand, C., 1995. Major element chemistry of the Huanghe (Yellow River), China-weathering processes and chemical fluxes. Journal of Hydrology 168, 173–203.
Zhao, M., Gao, W., Xing, L., Zhang, Y., Li, L., Liu, J., 2011. Estimates of the origins of organic matter in the Old-Huanghe estuary using the BIT index. Marine Geology & Quaternary Geology 31, 29–37 (in Chinese).
Zhu, C., Weijers, J.W.H., Wagner, T., Pan, J.-M., Chen, J.-F., Pancost, R.D., 2011. Sources and distributions of tetraether lipids in surface sediments across a large river-dominated continental margin. Organic Geochemistry 42, 376–386.