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

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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

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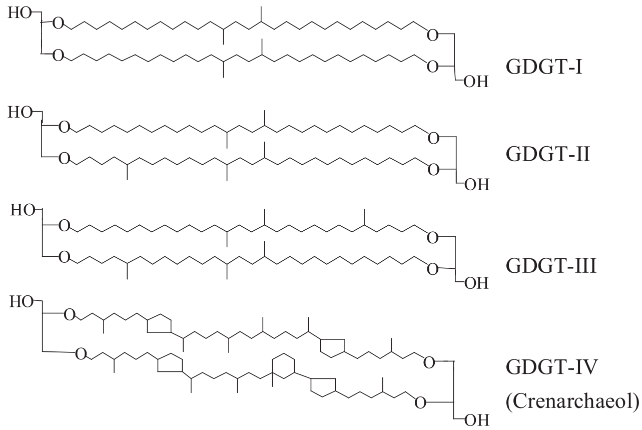

Fig. 1. Structures of branched (I–III) and isoprenoid (IV) GDGTs used for the BIT index.

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

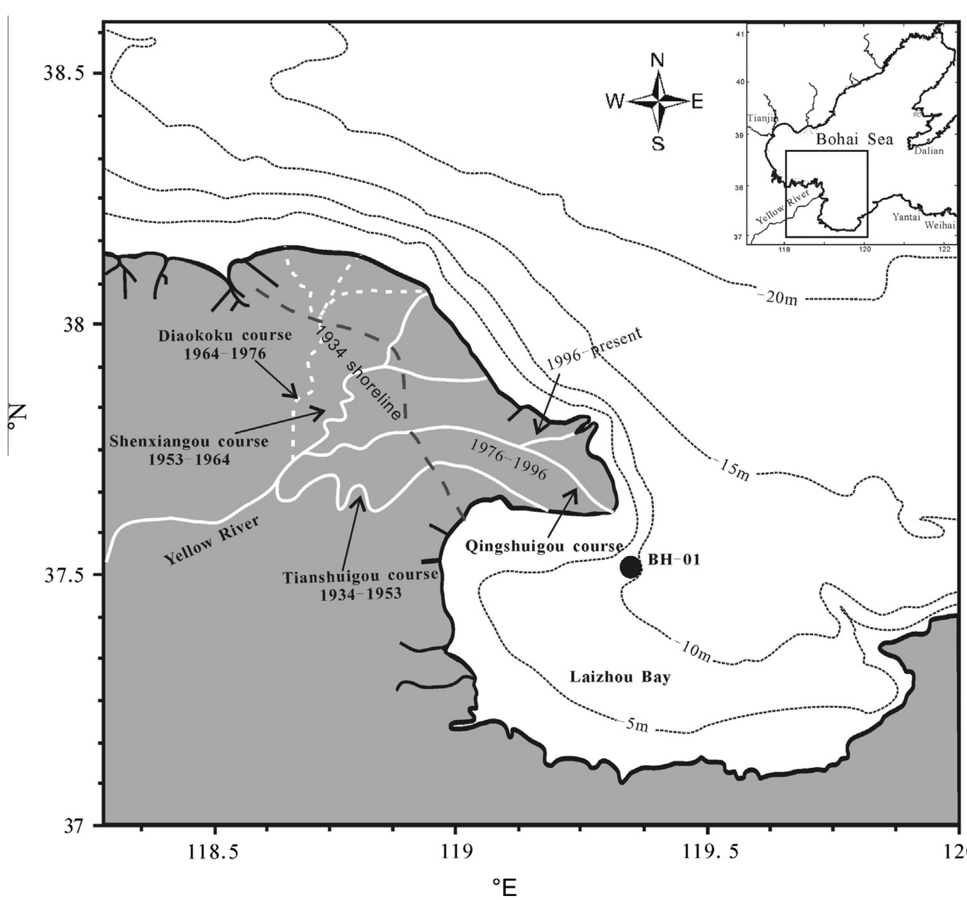

Fig. 2. Typical channel changes of the Yellow River since 1930 and the location of sampling site (black dot) in the Bohai Sea.