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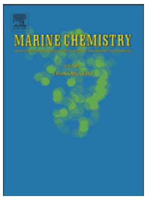

Source and distribution of glycerol dialkyl glycerol tetraethers along lower Yellow River-estuary–coast transect

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ABSTRACT

To assess the source of glycerol dialkyl glycerol tetraethers (GDGTs) and their usefulness as proxies for terrestrial organic matter inputs and temperature in the Yellow River-dominated margin, we measured isoprenoid and branched GDGT concentrations in surface sediments along a lower Yellow River-estuary–coast transect. Branched GDGTs dominated over isoprenoid GDGTs in the riverbed sediments and had similar compositions from river to coast. In contrast, isoprenoid GDGTs displayed an increasing abundance and a decreasing GDGT-0 to crenarchaeol ratio (1.6 to 0.6) toward the sea. Such distribution patterns of GDGTs, combined with the result from a principal component analysis (PCA), confirmed the different origin of branched and isoprenoid GDGTs with branched GDGTs being primarily from soil erosion of the Chinese loess plateau (CLP) whereas, in addition to allochthonous terrestrial inputs, aquatic Thaumarchaeota partially contributes to the isoprenoid GDGT pool in estuarine and coastal areas. The branched GDGT-derived temperature (avg. 11 °C) is consistent with the annual mean air temperature (MAT) of the CLP in the middle river basin, a major source region for the Yellow River sediments, whereas the isoprenoid-derived temperature (12.7 to 28.4 °C) deviated widely from the annual mean temperature in the study region. Application of a binary mixing model based on $\delta^{13}C$, the branched and isoprenoid tetraether (BIT) index and branched GDGT concentrations showed consistent decreases in the relative amount of terrestrial organic carbon toward the sea, but estimates from the latter two proxies were lower than those from the $\delta^{13}C$.

1. Introduction

Over the past decade, several geochemical proxies of organic carbon sources, temperature and soil pH based on the distribution of glycerol dialkyl glycerol tetraethers (GDGTs; Fig. 1) have been proposed and increasingly applied to biogeochemical and paleo-environmental studies (Schouten et al., 2013 and references therein). These proxies include the TEX_{86} (TetraEther indeX of 86 carbon atoms) (Schouten et al., 2002), MBT/CBT (methylation index/cyclization index of branched tetraethers) (Weijers et al., 2007a) and BIT (branched and isoprenoid tetraether) indices (Hopmans et al., 2004). The TEX_{86} proxy is based on the relative abundance of isoprenoid GDGTs (*i*GDGTs) which are membrane lipids of Thaumarchaeota, formerly assigned to Crenarchaeota (Schouten et al., 2002; Sinninghe Damsté et al., 2002). Since the number of cyclopentane groups in Thaumarchaeotal *i*GDGT is primarily controlled by growth temperature, the TEX_{86} accumulated in sediments can be used to reconstruct sea (lake) surface temperature (e.g., Kim et al., 2008, 2010; Powers et al., 2010; Schouten et al., 2002). In contrast to *i*GDGTs, branched GDGTs (*b*GDGTs) are mainly produced by as-yet unknown anaerobic bacteria thriving in soil and peat, possibly belonging to the group of Acidobacteria (Hopmans et al., 2004; Sinninghe Damsté et al., 2011). By examining 134 soil samples from 90 globally-distributed locations, Weijers et al. (2007a) found that the MBT proxy was dependent on annual mean air temperature (MAT) and to a lesser extent on soil pH, whereas the CBT proxy is correlated with soil pH. Subsequent studies extended the soil dataset to 278 globally-distributed soils, and proposed new transfer functions for the reconstruction of soil pH and MAT (Peterse et al., 2012). Because soils are more widespread than peat in the terrestrial realm, the occurrence of *b*GDGTs in aquatic environments (e.g., lakes and marginal seas) was usually attributed to allochthonous inputs of soil organic matter via runoff (Hopmans et al., 2004). A global survey shows that the BIT index is generally higher than 0.9 in soil/peat and close to 0 in marine environments devoid of terrestrial inputs (Hopmans et al., 2004; Weijers et al., 2006b),

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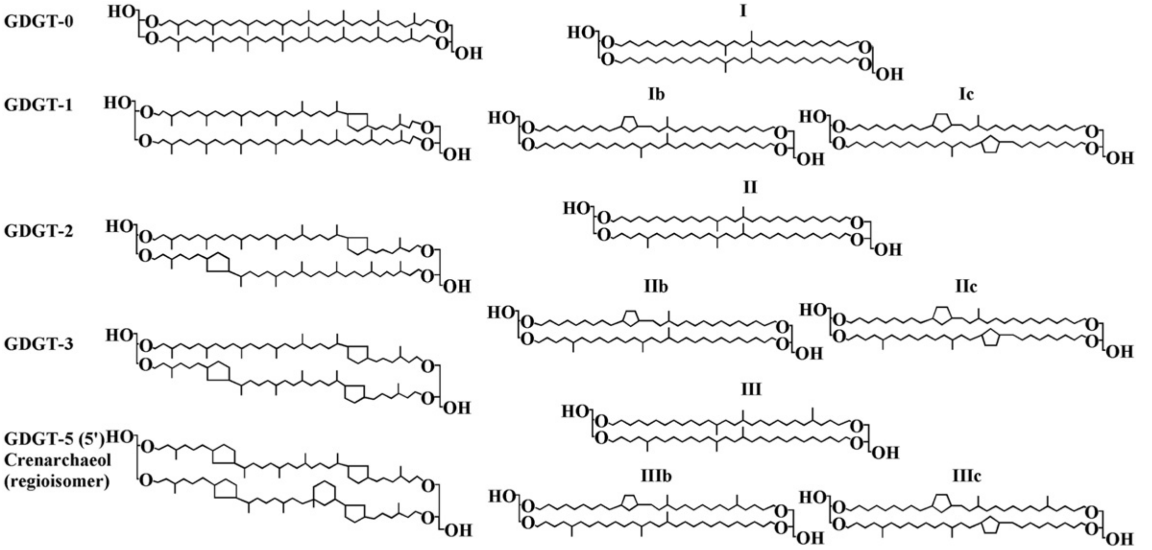

Fig. 1. Structures of isoprenoid and branched GDGTs. GDGT-5′ is a regioisomer of crenarchaeol with an anti-parallel configuration of the two glycerol moieties.

although some alkaline soils have exceptionally low BIT values (<0.3) (Yang et al., 2012).

Despite successful applications of GDGT-proxies (Schouten et al., 2013 and references therein), caution still should be taken. In-situ production of *b*GDGTs in lakes and rivers complicates the interpretation of the MBT/CBT and BIT indices as continental environmental proxies (Bechtel et al., 2010; Blaga et al., 2010; Tierney et al., 2012; Zell et al., 2013; Zhu et al., 2011). On the other hand, significant inputs of terrestrial *i*GDGTs can bias the TEX_{86}-derived temperature signal in marginal seas or small lakes (Powers et al., 2010; Weijers et al., 2006a). Thus, it is crucial to elucidate the origins of *b*GDGTs and *i*GDGTs before they can be confidently used as environmental proxies.

River-dominated continental margins are subject to the intensive land–ocean interactions. Because of large terrestrial inputs and relatively high primary productivity, river-dominated continental margins play a key role in the global carbon cycle, and their sediments contain abundant information about marine and continental environments (Pancost and Boot, 2004). Previous studies of the Amazon (Kim et al., 2012; Zell et al., 2013), the Yangtze (Yang et al., 2013; Zhu et al., 2011) and the Mississippi Rivers (Smith et al., 2012) have identified multiple sources of GDGTs and complex processes in river systems. Compared to other large rivers, the Yellow River (YR) is distinguished by its extremely high turbidity with suspended particle loads of up to 220 kg m^{-3} (Ren and Shi, 1986), and may have unique microbial community and biogeochemical behaviors. Nevertheless, so far no data is available for GDGTs in the YR, although limited studies have focused on the BIT index in its adjacent seas (Wu et al., 2013; Zhao et al., 2011).

Here, we present a comprehensive study about the distributions and compositions of GDGTs in surface sediments along a lower YR-estuary–coast transect. Our main aims are to: (1) constrain sources of *b*GDGTs and *i*GDGTs by comparing soils in the Chinese loess plateau (CLP), a principal contributor to the YR sediments (Ren, 2006); and (2) evaluate the applicability of the GDGT-based proxies in the YR-dominated continental margin.

2. Materials and methods

2.1. Study area and sampling

The YR with a total length of 5464 km drains a wide basin that covers over 750,000 km^2 of China (Wang et al., 2007). It originates in the Bayankala Mountains of the Tibet Plateau (western China), flows through nine provinces and discharges into the Bohai Sea (northeastern China). The upper, middle and lower YR basins have distinct climates with MATs of 1 to 4 °C, 8 to 14 °C, and 12 to 14 °C, respectively (Chen et al., 2005) and mean annual precipitations of 368 mm, 530 mm and 670 mm, respectively (IRTCES, 2004). Due to severe soil erosion in the CLP in the middle river basin, the YR has an annual sediment load of 1.1×10^9 ton, ranking as the world's second largest river in terms of sediment load (Milliman et al., 1987). The pattern of a sediment dispersal off the YR mouth is mainly controlled by the tidal shear fronts and the tidal currents (Bi et al., 2010). Because of the barrier effect of the tidal shear front and the weak river flow, most sediment from the YR is deposited near the estuary and in the adjacent sea, causing the YR delta to grow at a rate of approximately 1.29 km per year (Li et al., 2001; Wang et al., 2007). The modern YR delta, with an area of 5400 km^2, formed after 1855 when the YR started to drain into the Bohai Sea (Pang and Si, 1979).

In July 2011, a total of forty surface sediments (0–10 cm) were collected by a grab sampler. These samples can be divided into four groups, namely the lower YR, the modern YR estuary (1996–present), the old YR estuary (1976–1996) and the coast (Fig. 2). They are dominated by silt (avg. 61.1%), fine sand (avg. 28.9%) and clay (avg. 9.9%). In addition, fifty surface soil samples (0–2 cm) were collected over an extensive area of the CLP (latitude from 32°N to 42°N; longitude from 100°E to 120°E) in order to compare their geochemical properties to those of the sediments in the YR-dominated continental margin. The soils in the CLP developed on clastic, predominantly silt-sized wind-blown sediment and include various soil types such as cultivated loessial soil and dark loessial soil. After collection, all samples were stored at −20 °C until analysis.

2.2. Grain size, elemental and stable isotope analyses

For grain size analysis, freeze-dried sediments were reacted with excess 1 N hydrochloric acid and hydrogen peroxide to remove carbonates and decompose the organic matter, respectively (Sun et al., 2011). After that, sodium hexametaphosphate $[Na(PO_3)_6]$ was added, and the sediments were allowed to settle for 24 h. After ultrasonication for 1 min, the sediment grain size was measured by a Mastersizer 2000 Laser Particle Size Analyzer. The scan range was from 0.02 to 2000 μm, and categorized into three fractions: sand (64–2000 μm), silt (4–64 μm) and clay (<4 μm).

The elemental and stable isotopic analyses were described in detail by Sun et al. (2011). Briefly, excess 1 N hydrochloric acid was added