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Spatial heterogeneity of sources of branched tetraethers in shelf systems: The geochemistry of tetraethers in the Berau River delta (Kalimantan, Indonesia)

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Abstract

The bulk organic matter composition (total organic carbon (TOC) content and $\delta^{13}C_{TOC}$) and composition of isoprenoid and branched glycerol dialkyl glycerol tetraethers (GDGT) in surface sediments from 43 stations in the Berau River delta (east Kalimantan, Indonesia), including two coast-shelf transects and stations within the river mouth, were examined to reveal the spatial heterogeneity in these parameters in order to assess the impact of a tropical river loaded with suspended matter on the sedimentary organic matter in the shelf system. The high-resolution study showed that, despite the extensive transport of eroded soil material by the river to the sea, terrestrial organic matter and brGDGTs are only deposited on a relatively small part of the shelf. The concentrations of brGDGTs are highest (up to 120 μg g^{-1} TOC) in sediments deposited in and close to the mouth of the Berau River and their distribution indicates that they represent a mixture of soil-derived and river in-situ produced brGDGTs. Crenarchaeol concentrations reach 700 μg g^{-1} TOC in sediments deposited on the outer shelf due to Thaumarchaeotal production in shelf waters. This results in a strong gradient (0.93–0.03) in the BIT index, with high values in the river mouth and low values on the shelf. The decline in the BIT index is caused by both decreasing concentrations of the brGDGTs and increasing concentrations of crenarchaeol. The BIT index shows a highly significant but non-linear relationship with $\delta^{13}C_{TOC}$. On the shelf, in the area not under the direct influence of the Berau River, cyclic brGDGTs become relatively dominant, most probably due to in-situ production in the alkaline pore waters of the surface sediments. The spatial heterogeneity of sources of brGDGTs on the Berau shelf complicates the use of brGDGTs as temperature proxies. Application of the global soil calibration to sedimentary mixtures of brGDGTs in the river-influenced area of the shelf results in a severe underestimation of mean annual air temperature (MAT) by 6 °C. This is due to the mixed origin of the brGDGTs, which are not only derived from soil erosion but, likely, also from riverine production, as has been observed for other river systems.

Comparison of the Berau shelf other shelf systems indicates that in-situ production of brGDGTs in shelf sediments is a widespread phenomenon that is especially pronounced at water depths of ca. 50–300 m. It is hypothesized that this is so because benthic in-situ production of heterotrophic brGDGT-producing bacteria is fueled by the higher delivery of fresh organic matter to these sediments as the consequence of higher primary productivity in shelf waters and a decreased mineralization due to the relatively short settling times of particles on the shelf. For palaeoclimatic studies of marine shelf sediments the application of brGDGTs as proxies is severely complicated by the heterogeneity of sources of brGDGTs. Comparison of

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the brGDGT composition of soils with those of shelf sediments may assist in deciding if sedimentary brGDGTs are predominantly derived from soil erosion. Several methods to do so are discussed.

Keywords: GDGT; Tetraether; Branched GDGT; Isoprenoid GDGT; BIT index; Temperature reconstruction; Shelf sea; Estuary; Soil; Riverine organic matter; Terrestrial organic matter; Surface sediments; Berau River; Svalbard fjord; South China Sea; Portuguese margin; Kara Sea

1. INTRODUCTION

Glycerol dialkyl glycerol tetraethers (GDGTs) are organic compounds occurring in membranes of archaea and bacteria and have recently raised substantial interest due to their potential as biomarkers and proxies (see Schouten et al., 2013b for a review). Specific isoprenoid GDGTs are used as tracers for (living) archaeal cells in oceans, lakes and the deep biosphere. For example, the isoprenoid GDGT crenarchaeol is specific for nitrifying archaea belonging to the Thaumarchaeota (Sinninghe Damsté et al., 2002) and ^{13}C-depleted isoprenoid GDGTs with one or two cyclopentane moieties are characteristic for archaea involved in the anaerobic oxidation of methane (Pancost et al., 2001). In contrast, the exact biological sources of branched GDGTs (brGDGTs) remain enigmatic, although there are indications that they may be sourced by Acidobacteria (Sinninghe Damsté et al., 2011, 2014).

Several proxies based on GDGTs have been developed such as the TEX_{86} for sea surface temperature reconstruction and the BIT index for soil organic matter input (Schouten et al., 2013b). One of the interesting applications for palaeoclimatology is the use of brGDGTs in shallow marine sediments to reconstruct continental climate (Weijers et al., 2007a) based on the premise that brGDGTs produced in soil are brought by rivers to coastal regions. Since the distribution of the brGDGTs reflects the temperature and pH of the soil at the time of the production of the bacterial membranes, expressed in the MBT/CBT indices (Weijers et al., 2007b), the fossilized brGDGTs in coastal marine sediments may provide a record of past variations in the temperature of the catchment of the river system, enabling continental climate reconstructions. By reconstructing both continental and sea temperature using one marine core inferences about the contrast in temperature between sea and land may be made and its impact on the hydrology (e.g., Weijers et al., 2007a). In the last years, however, various complications with this approach, such as the provenance of soil-derived brGDGTs (Bendle et al., 2010) and potential in-situ production in the river (Zell et al., 2013a,b; De Jonge et al., 2014b), the oxic (Zell et al., 2014a,b; De Jonge et al., 2015) and anoxic (Liu et al., 2014; Xie et al., 2014) marine water column, and in marine sediments (e.g. Peterse et al., 2009a; Zhu et al., 2011), have been recognized.

Here, GDGT proxies in the delta of a river system draining a tropical rain forest are evaluated. The Berau River delta is located in NE Kalimantan (Indonesia), where the river enters into the Sulawesi Sea. The delta has an area of ca. 800 km^2, varies in depth from a few to 100 m, and is shielded from the open ocean by coral reefs, resulting in calm waters. We analyzed surface sediments from 43 stations (Fig. 1) for bulk parameters (TOC content, $\delta^{13}C_{TOC}$) and GDGTs using LC-MS techniques enabling the separation of the 5- and 6-methyl brGDGTs (cf. De Jonge et al., 2014a; Hopmans et al., 2016). These results are discussed in comparison with data from other river delta systems and global soils to evaluate the consequences for the application of GDGT proxies in palaeoclimate studies.

2. MATERIALS AND METHODS

2.1. Setting

The Berau shelf (Fig. 1) is approximately 50 km wide and separated from the Makassar Strait by a steep slope. The steep edge of the shelf is topped by extensive barrier reefs in the north (Pulau Panjang to Pulau Semama complex) and south (Karang Besar complex), but in the central part the shelf break is at 100–120 m water depth (Fig. 1b). A large river, the Berau River, discharges over the shelf area. Yearly precipitation in the Berau region is ca. 2900 mm y^{-1} with only moderate changes in monthly precipitation. The Berau River discharges a plume extending up to 15 km over the shelf, but in the wet season it might reach as far as the barrier islands in the North, about 30 km off shore (Renema, 2006). The catchment of the river is ca. 100 km^2 and consists for the major part of rainforest, although forest clearing in recent years is affecting this, resulting, in combination with the high rainfall, to a high suspended matter load in the river (2 Mt y^{-1}; Buschman et al., 2012) and high sedimentation rates in the delta (up to 3 cm y^{-1}).

2.2. Sampling

Surface sediments (usually 0–1 cm, in other cases 1–2 cm) from 26 stations (see Table 1) in the Berau River delta on two coast-shelf transects (Fig. 1; Transects A and B) were retrieved by sub-sampling of box cores obtained during a cruise of the R/V Geomarin I in July 2003. Surface sediments (0–5 cm) from 17 stations closer to the river mouth (Fig. 1) were collected in April 2007 using a Smith-McIntyre grab sampler as described by Booij et al. (2012).

During the 2007 expedition also a 100 cm long sediment core was obtained at station 11B by a scuba diver. Nine selected 3 cm-slices of this core were also studied. Appreciable excess ^{210}Pb activity (Table 2) was detected over the entire depth of the measured profile, indicating that there is a layer of at least 1 m of relatively recent sediment of 100–150 years old present at the coring location. In the upper 50 cm of the core no downcore decrease in ^{210}Pb