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Constraints on the sources of branched tetraether membrane lipids in distal marine sediments

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Abstract

Branched glycerol dialkyl glycerol tetraethers (brGDGTs) are membrane lipids produced by soil bacteria and occur in near coastal marine sediments as a result of soil organic matter input. Their abundance relative to marine-derived crenarchaeol, quantified in the BIT index, generally decreases off-shore. However, in distal marine sediments, low relative amounts of brGDGTs can often still be observed. Sedimentary in-situ production as well as dust input has been suggested as potential, though as yet not well constrained, sources. In this study brGDGT distributions in dust are examined and compared with those in distal marine sediments. Dust was sampled along the equatorial West African coast and brGDGTs were detected in most of the samples, albeit in low abundance. Their degree of methylation and cyclisation, expressed in the MBT' (methylation index of branched tetraethers) and DC (degree of cyclisation) indices, respectively, were comparable to those found for African soils, their presumed source. Comparison of DC indices of brGDGTS in global soils, Congo deep-sea river fan sediments and dust with those of distal marine sediments, however, clearly shows that distal marine sediments yield significantly higher DC indices. This distinctive distribution is suggestive of sedimentary in-situ production as source of brGDGTs in marine sediments, rather than dust input. The presence of in-situ produced brGDGTs in marine sediments means that caution should be exercised when applying the MBT'-CBT palaeothermometer in sediments with low BIT indices, i.e. <0.1 based on our dataset.

Keywords: Branched Tetraether; Dust; Marine Surface Sediment

1. Introduction

Marine sediments provide a unique archive to study Earth's past environment and climate. Depending on the proximity of the study location to land, a varying proportion of the organic matter (OM) input in marine sediments may be land derived. This terrigenous OM can be delivered to marine sediments by several modes of transport, i.e. eolian dust input, suspended in river water, or by means of gravity transport over the sea bed like through deep see canyons or in turbidites. Several proxies have been developed that try to distinguish between marine and terrigenous derived OM. These can be either based on bulk properties like the C:N ratio and the stable carbon isotopic ($\delta^{13}C$) composition of OM (Hedges et al., 1997 and references therein), or based on the molecular composition, e.g. the (relative) abundance of lignin phenols (e.g. Goñi et al., 1997) or other land specific biomarkers like long chain plant-wax derived *n*-alkanes (Eglinton et al., 1962) or taraxerol (Killops and Frewin, 1994; Versteegh et al., 2004).

More recently, branched Glycerol Dialkyl Glycerol Tetraether (brGDGT) membrane lipids (Fig. 1) have been used as terrigenous biomarkers in marine sediments as they derive from soil bacteria, likely belonging to the phylum of Acidobacteria (Sinninghe Damsté et al., 2000, 2011; Weijers et al., 2006b, 2009a), and since their abundance in marine sediments quickly decreases with increasing distance from the coast (Hopmans et al., 2004; Kim et al., 2006; Herfort et al., 2006). Hopmans et al. (2004) proposed the Branched vs. Isoprenoid Tetraether (BIT) index to quantify the relative abundance of these brGDGTs in marine sediments by normalising them to crenarchaeol, an isoprenoid GDGT membrane lipid derived from ubiquitous pelagic Thaumarchaeota (Sinninghe Damsté et al., 2002). It was suggested that this BIT index can be

used as proxy to trace terrigenous OM input into marine sediments (Hopmans et al., 2004). However, subsequent studies demonstrated that the BIT index actually traces soil rather than terrigenous OM input relative to marine OM input in near coastal marine sediments as brGDGTs are present in soils and not in vegetation (Huguet et al., 2007; Walsh et al., 2008; Kim et al., 2009; Weijers et al., 2009b; Smith et al., 2012).

Besides information on soil OM input, brGDGT distributions also provide information on climate conditions on land. BrGDGTs vary in the number of methyl groups at the C5 and C5' position (and recently it has been shown that methylation at the C6 and C6' position also occurs; De Jonge et al., 2013), and contain one or two cyclopentane moieties (Weijers et al., 2006a). In a set of soils obtained from across the globe, it was found that the degree of cyclisation, expressed in the Cyclisation ratio of Branched Tetraethers (CBT), shows a strong relation with soil pH, and the degree of branching, expressed in the Methylation index of Branched Tetraethers (MBT), shows a strong relation with both soil pH and annual Mean Air Temperature (MAT, Weijers et al., 2007b). Upon transport of brGDGTs to the marine environment and deposition in the marine sedimentary archive, their distribution could hence be used to reconstruct past soil pH and past annual MAT using these parameters in the so-called MBT-CBT proxy (e.g. Weijers et al., 2007a). Recently the MBT index has been slightly modified (referred to as MBT') by excluding two brGDGTs from analysis that usually occur in low abundance (i.e. <1 % of total brGDGTs) in soils (Peterse et al., 2012). That same study also provided a new calibration for the MBT'-CBT annual MAT proxy using this MBT' and based on a larger number of soils. In addition to the CBT ratio, Sinninghe Damsté et al. (2009) introduced the degree of cyclisation (DC) index in

order to define the degree of cyclisation of brGDGTs in a similar way as the degree of methylation in the MBT index, enabling a more direct comparison between the two.

Application of the BIT index and the MBT'-CBT proxy in marine sediments works under the assumption that crenarchaeol is produced in the marine realm and brGDGTs are derived from land. It has, however, been shown that Thaumarchaeota also thrive in soils, peat, lakes and river water and hence that crenarchaeol is produced in these environments as well (e.g. Weijers et al., 2004, 2006b; Powers et al., 2004; Leininger et al., 2006; Bannert et al., 2011; Zell et al., 2013). The amount of crenarchaeol in soil and peat is, however, generally low relative to brGDGTs causing soils and peat to be, on average, still characterised by a high BIT index value though rarely reaching a value of 1 (0.90 on average; Schouten et al., 2013a and references cited therein). A similar situation is observed in marine settings: although the BIT index in distal marine settings is often low, it seldom reaches a value of 0 (average 0.04; Schouten et al., 2013a) as in most distal marine sediments small amounts of brGDGTs remain detectable. The sources of these brGDGTs are uncertain. Long distance dust transport over the oceans might be a plausible mechanism for delivery of brGDGTs to remote ocean settings and brGDGTs have indeed been reported in atmospheric dust sampled off northwest Africa (Fietz et al., 2013). Alternatively, brGDGTs could be produced in-situ in marine sediments as suggested for near shore marine sediments in a Svalbard fjord (Peterse et al., 2009) and in East China Sea sediments (Zhu et al., 2011) based on differences in brGDGT distributions in marine sediments vs. soils on adjacent land. However, it remains unclear to what extent these findings represent local, near coastal in-situ production, or that marine in-situ production of brGDGTs is a more general phenomenon.

To investigate whether dust or in-situ production is responsible for the presence of brGDGTs in distal marine sediments, we analysed the distribution of brGDGTs in atmospheric dust and marine surface waters from the coast of western Africa and in globally distributed open ocean sediments. These data are compared with previously published brGDGT distributions from the western African Congo deep sea river fan sediments and with global soils in order to constrain the potential source of brGDGTs in distal marine sediments and to identify potential implications for the use of GDGT-based proxies.

2. Material and methods

2.1. Samples

Atmospheric dust was sampled along the west coast of equatorial Africa onboard the R/V Meteor cruise M41/1 in 1998. Details on sampling and extraction procedures are provided by Schefuß et al. (2003). For the present study, polar fractions of lipid extracts from 13 dust filters (Table 1; Fig. 2) were dried, redissolved in *n*-hexane:*iso*-propanol 99:1 (v/v), and filtered through a 0.45 μm mesh PTFE filter prior to analysis of their GDGT content.

Suspended particulate matter (SPM) in marine surface waters was sampled by filtration of ca. 100 to 400 L water, provided by the ship's seawater inlet (ca. 5 m water depth), through a 0.7 μm GFF filter onboard R/V Meteor during cruise M56 in December 2002 along the west coast of equatorial Africa (Spiess and Cruise Participants, 2008). The eight sampling locations comprise a transect along the equatorial African coast and include the lower salinity (down to 28.0 ‰) Congo River outflow plume (Table 2; Fig. 2). Filters were freeze dried, cut into small pieces and extracted using a dichloromethane (DCM):methanol (MeOH) 9:1 (v/v) mixture using accelerated solvent extraction (Dionex ASE 200, 100°C, 1000 psi, 3 cycles of 5 min). The obtained total

lipid extract was saponified with 6% KOH (2 h at 85°C) and the extracted neutral fraction was dried and separated over pre-combusted silica gel columns into an apolar, a ketone, and a polar fraction using *n*-hexane, DCM, and DCM:MeOH 1:1 (v/v) solvent mixtures, respectively. Further preparation of the polar fractions was similar to that of the dust samples.

A total of 34 distal marine surface sediments (Table 3) were analysed for their brGDGT content. These sediments were selected from the core-top calibration data set used for the TEX_{86} sea surface temperature proxy, based on their low BIT index, i.e. <0.03 (Schouten et al., 2002; Kim et al., 2008, 2010). The polar fractions of the selected samples were obtained as described previously (Schouten et al., 2002; Kim et al., 2008, 2010) and analysed for their brGDGT content. The small differences in extraction techniques and clean up procedures between the sample sets are not expected to influence the GDGT distributions. Previous studies have shown that the type of extraction method and extract processing have not a large effect on the GDGT distributions (Schouten et al., 2007; Escala et al., 2009; Lengger et al., 2012) and that differences remain within repeatability limits (Schouten et al., 2013b).

2.2. GDGT analysis

Samples were analysed for their GDGT content using High Performance Liquid Chromatography / Atmospheric Pressure Chemical Ionization – Mass Spectrometry (HPLC/APCI-MS) on an Agilent 1100 series instrument equipped with Chemstation software according to Schouten et al. (2007). Separation of compounds was achieved on an analytical Alltech Prevail Cyano column (150 mm x 2.1 mm; 3μm) held at a constant 30°C and using *n*-hexane:*iso*-propanol 99:1 (v/v) as eluent, isocratically for the first 5 min, then increasing to 1.8% *iso*-propanol in 45 min. The column was rinsed in back flush mode with 10% *iso*-propanol in *n*-

hexane and re-equilibrated to starting conditions after each run. GDGTs were analysed in Selective Ion Monitoring (SIM) mode as their $[M+H]^+$ (protonated) derivatives. Relative quantification of the GDGTs was based on peak areas in the $[M+H]^+$ mass chromatograms. The BIT index was used as defined by Hopmans et al. (2004):

$$BIT = \frac{[Ia + IIa + IIIa]}{[Ia + IIa + IIIa + IV]} \quad (1)$$

The MBT' index was used as defined by Peterse et al. (2012) and differs from the original definition (Weijers et al., 2007b) in the omission of GDGTs IIIb and IIIc:

$$MBT' = \frac{[Ia + Ib + Ic]}{[Ia + Ib + Ic + IIa + IIb + IIc + IIIa]} \quad (2)$$

The degree of cyclisation (DC) of brGDGTs was used as defined by Sinninghe Damsté et al. (2009):

$$DC = \frac{[Ib + IIb]}{[Ia + Ib + IIa + IIb]} \quad (3)$$

The CBT ratio was used as defined by Weijers et al. (2007b):

$$CBT = -log\left(\frac{[Ib + IIb]}{[Ia + IIa]}\right) \quad (4)$$

158 Roman numerals refer to the structures given in Fig. 1.

159

160 *2.3. Statistical analysis*

161 An analysis of variance (ANOVA) was conducted on the DC and MBT' indices of different
162 sample groups to determine whether or not these differ significantly from each other. The
163 analysis was carried out by means of a pairwise multiple comparison test using Tamhane's T2
164 procedure, which assumes no equal variance between sample groups. Statistical analyses were
165 conducted using the SPSS 21.0 software package (IBM corp.).

166

167 **3. Results and discussion**

168 *3.1. Atmospheric dust as a potential source for brGDGTs in the marine environment*

169 HPLC-MS analysis of the dust sampled along the African coast (Fig. 2) showed the presence of
170 brGDGTs in all but one sample. However, none of the dust samples contained the full suite of
171 brGDGTs, i.e. GDGTs IIIb and IIIc were not detected in any of the dust samples. Only in 5 out
172 of the 13 dust samples all brGDGTs necessary for calculating a DC index and CBT ratio were
173 present above detection level (Table 1). In a previous study, the analysis of two dust samples
174 obtained from the same area as the dust filters analysed here did not yield any brGDGT signal
175 (Hopmans et al., 2004), making the authors to suggest that brGDGTs are barely, if at all,
176 transported by dust. The mass spectrometer in that analysis, however, was set to scan ions over
177 the range *m/z* 950 to 1450, i.e. in 'full scan' mode. The extracts of dust samples in the present
178 study were run in the more sensitive Selective Ion Monitoring (SIM) mode, scanning only for the
179 masses of interest, thereby increasing the sensitivity for GDGT detection by one to two orders of
180 magnitude (cf. Schouten et al., 2007). This likely explains why at least some brGDGTs are now

detected in dust and this implies that dust could be a potential source of brGDGTs in distal marine sediments. This corroborates a recent publication by Fietz et al. (2013) that reports brGDGTs in dust sampled off northwest Africa.

Backward trajectories for the dust samples used in our study have been computed previously (Schefuß et al., 2003) and indicate that air masses sampled on the filters mostly originate from the nearby African continent, especially from the Faya Largeau region in Chad. Therefore, it could be assumed that the brGDGTs in the dust are derived from nearby African soils and thus that their distributions, as expressed in the degrees of methylation and cyclisation (MBT' and DC), should be similar to those of African soils. The average MBT' and DC indices for brGDGTs in the dust samples are 0.80 (±0.06; n=8) and 0.11 (±0.04; n=5), respectively (Table 1). This falls within the range of African soils (from the soil database in Peterse et al., 2012), i.e. 0.76 (±0.22; n=12) and 0.13 (±0.18; n=16) for MBT' and DC, respectively, although the variation in soils is larger (Fig. 3). Furthermore, the MBT' and DC indices of the dust are similar to previously reported MBT' and DC indices of brGDGTs present in the surface sediments from the Congo deep sea river fan (Weijers et al., 2007a), i.e. 0.72 (±0.10; n=7) and 0.15 (±0.08; n=7, Table 4, Fig. 3). This indeed suggests that brGDGTs found in the dust are ultimately derived from soils on the adjacent African continent.

Notably, however, crenarchaeol was detected in all of the 13 dust samples and BIT indices determined for the dust are substantially lower (average 0.25±0.08, n=12; Table 1) compared to values generally found in soils, e.g. the average BIT index value in a compilation of global soil data by Schouten et al. (2013a) is 0.90 (±0.14; n=224) with only a minority of soils having BIT index values <0.5. Indeed, BIT indices for dust are also clearly lower than BIT indices for African soils reported in Peterse et al. (2012), which are on average 0.81 (±0.21; n=16). The

latter dataset only contains two soils with BIT <0.50 and none reaching as low as 0.25. These differences could be caused by two processes, i.e. selective degradation of GDGTs during atmospheric transport or addition of crenarchaeol to dust. Selective degradation of brGDGTs relative to crenarchaeol during atmospheric dust transport seems unlikely. Huguet et al. (2008) have shown that in a turbidite deposit subject to prolonged oxygen exposure, crenarchaeol is preferentially oxidized compared to brGDGTs. This was attributed, however, to the fact that the terrigenous derived brGDGTs were likely protected via close association with clay minerals in contrast to the marine-derived crenarchaeol. If derived from soils, crenarchaeol will be similarly associated with dust particles as brGDGTs and therefore no selective degradation is expected. Hence, there may be an additional source for crenarchaeol to explain the low BIT indices for dust. One likely source for additional crenarchaeol on the dust filters is sea spray. Indeed, analysis of the surface waters collected along the western African coast showed the clear presence of crenarchaeol (Table 2) pointing to sea spray as a potential source of crenarchaeol. In some of the surface waters brGDGTs were also detected, suggesting that sea spray may also be a source for the brGDGTs on the dust filters. However, only the surface waters from the lower salinity waters of the Congo River plume contain brGDGTs, likely delivered by the Congo River (cf. Hopmans et al., 2004; Weijers et al., 2007a). In contrast, surface waters taken outside the Congo River plume area barely contain brGDGTs, if at all (Table 2). Hence, the brGDGTs detected in the dust, sampled outside areas of major river influence, are suggested to be predominantly sourced by particles derived from the African continent. Notably, the dust sampled off northwest Africa by Fietz et al. (2013) reflected BIT index values of 0.84 on average. Although BIT index analyses between laboratories could differ substantially (Schouten et al., 2013b), this still is a large difference. As yet it is difficult to explain this difference, but

maybe the location of the dust samplers on the research vessel, i.e. their proximity to the sea surface, and weather conditions, might play a role here.

3.2. Sources of brGDGTs in distal marine sediments

Transport of dust from the African continent to the equatorial Atlantic oceans is a well-known phenomenon (e.g. Darwin, 1846; Chester et al., 1972; Prospero and Carlson, 1972) and for plant wax derived long chain *n*-alkanes it has been shown that they can be delivered to the marine realm via dust transport over distances of several thousand kilometres (e.g. Simoneit, 1977; Gagosian et al., 1981; Schefuß et al., 2003; Bendle et al. 2007) and recently Fietz et al. (2013) showed the presence of brGDGTs in dust far off northwest Africa. In order to see if also an important contributor to the pool of brGDGTs in distal marine sediments, we compare distributions of brGDGTs in both African soils and near shore dust with those in low latitude Atlantic Ocean surface sediments (Table 3 and Fig. 2). Analysis shows that all Atlantic Ocean surface sediments contained brGDGTs, though one sediment did not contain all brGDGTs in sufficient amounts for calculating a DC index (Table 3). The MBT' index of these Atlantic Ocean sediments is on average 0.28 (±0.10; n=9, Table 5). This is significantly different ($p<0.001$) from MBT' indices of African soils and dust, i.e. 0.76 (±0.22, n=16) and 0.80 (±0.06, n=8) on average, respectively (Tables 5 and 6). Although this could potentially indicate that brGDGTs in these sediments are not derived from the warm African continent but derived from higher and thus colder latitudes with lower MBT' values, this seems unlikely as Africa is the major source of dust in the Atlantic Ocean (e.g. Schefuß et al., 2003 and references cited therein; Fietz et al., 2013). When DC indices of African soils and dust are compared with those of low latitude Atlantic surface sediments, a similar pattern emerges as for the MBT': DC indices of

equatorial Atlantic sediments are on average 0.39 (±0.16, n=8), which is significantly different ($p<0.10$) from that of African soils and dust, i.e. 0.13 (±0.18, n=16) and 0.11 (±0.04, n=5), respectively (Tables 5 and 6, Fig. 4). Collectively, these differences in distribution strongly suggest that brGDGTs in the low latitude Atlantic sediments are not primarily sourced by African dust.

In addition to the low-latitude Atlantic Ocean sediments, a set of 25 distal marine sediments from other locations were analysed for their brGDGT distribution (Table 3). Four additional open marine sediments characterised by a low BIT index (i.e. <0.08), and for which brGDGT composition was previously reported by Peterse et al. (2009) and Zhu et al. (2011), were added to the dataset as well to make a total of 38 marine sediments, including the low latitude Atlantic Ocean sediments. Out of these 38 sediments, 35 contained sufficient amounts of brGDGTs required for calculating a DC index (Table 3). The average value of the DC indices for these distal marine sediments is 0.40 (±0.16, n=35). This is similar to the average value as found for the low-latitude Atlantic sediments, but significantly different ($p<0.10$) from DC indices of global soils (Tables 5 and 6, Fig. 4). Thus, it can be concluded that also on a more global scale the distribution of brGDGTs in distal marine sediments is significantly different from the distribution of brGDGTs in terrigenous sources and, hence, that dust input is likely not a major source for them. The alternative explanation is that brGDGTs in open marine sediments are produced in-situ. For near coastal locations, in-situ production has been suggested previously by Peterse et al. (2009) and Zhu et al. (2011) and, interestingly, these studies reported distinctively high degrees of cyclisation (i.e. low CBT ratios) for marine sediments as well. Peterse et al. (2009) found that marine and fjord sediments around Svalbard were characterised by an average CBT ratio of -0.27 (±0.09), which equals an average DC index of 0.65 (±0.03), much higher than

the average DC index of Svalbard soils of 0.17 (±0.11). Zhu et al. (2011) found increased brGDGT abundances normalised on TOC further away from the river mouth onto the shelf, which is accompanied by a trend to higher DC indices (Fig. 5, based on data reported in Zhu et al., 2011). In addition, brGDGTs have been reported in sediments at and near hydrothermal vents along the Eastern Lau Spreading Center in the South Pacific Ocean (Hu et al., 2012) and two types of brGDGTs have been reported in a carbonate chimney of Lost City Hydrothermal Field near the mid-Atlantic Ridge (Lincoln et al., 2013). Notably, based on the data provided in Hu et al. (2012), the brGDGTs in their sediment TVG8 are also characterised by a high degree of cyclisation. Our results, together with those of Peterse et al. (2009) and Zhu et al. (2011), as well as Hu et al. (2012) and Lincoln et al. (2013), form strong circumstantial evidence for the global occurrence of in-situ production of brGDGTs in marine sediments. For soils and peat it has been suggested that Acidobacteria might be the dominant producers of brGDGTs (Weijers et al., 2009a; Sinninghe Damsté et al., 2011). Although a microbial community producing brGDGTs in the marine environment might be totally different from that in soils, Acidobacteria have indeed been reported to be present in marine surface sediments as well as in hydrothermal chimneys (Barns et al., 1999; Lopez-Garcia et al., 2003, Polymenakou et al., 2005; Li et al., 2009; Brazelton et al., 2010).

3.3. Exploring factors controlling the distribution of marine brGDGTs

As discussed in section 3.2, brGDGTs present in open marine sediments are characterised by relatively high DC and low CBT values. In soils the CBT ratio of brGDGTs is related to soil pH (Weijers et al., 2007b; Peterse et al., 2010) with a higher degree of cyclisation (equals low CBT ratios) corresponding to higher pH values. When the marine CBT values are translated to pH

using the global soil calibration (Weijers et al., 2007b), reconstructed pH varies between 6.1 and 9.9. Although this includes the average ocean water pH of ca. 8, the variability is large in comparison with the relatively small variation in sea water pH. This large variation in DC indices may indicate that the brGDGTs found in marine sediments are mainly produced within these sediments, where pH values can rapidly change depending on redox conditions, rather than in the marine water column. Unfortunately, no long term pH data are available for the core top sediments used in this study to investigate the relation between the degree of cyclisation and sediment pH in more detail.

3.4. Implications for GDGT based proxies

The production of brGDGTs in marine sediments may have consequences for some of the GDGT-based proxies currently used. For example, the BIT index is used as indicator for the relative amount of soil OM in marine sediments (Hopmans et al., 2004). Due to the relatively small amounts of brGDGTs found in distal marine sediments the marine end-member of the BIT index will be slightly higher than 0. Indeed, based on a data compilation, Schouten et al. (2013a) found an average BIT index for open marine sediments of 0.04 (±0.03, n=278). However, as the end-member distributions for soils (0.90 ±0.14, n=224; Schouten et al. 2013a) and marine sediments are still substantially different, marine in-situ produced brGDGTs will not substantially influence the use of the BIT index in marine sediments as indicator of soil derived OM.

The MBT'-CBT proxy is used to estimate past continental air temperatures based on the distribution of soil-derived brGDGTs (Weijers et al., 2007b; Peterse et al., 2012). It is applied in marine sediments that receive substantial soil OM input, and thus characterised by a high BIT

index, preferably near river outflows in order to obtain river-basin integrated signals (Weijers et al., 2007a). This study shows that at low BIT indices, the MBT' index and CBT ratio become skewed by the ostensibly marine in-situ produced brGDGTs and, therefore, render the MBT'-CBT proxy unsuitable. Sites characterised by low BIT indices not only include distal marine settings but also coastal settings removed from any fluvial OM input. In our dataset of Congo deep sea river fan sediments, one location with a low BIT index of 0.05 (T89-14) yields a DC index clearly higher (and consequently a CBT ratio clearly lower) than the other Congo deep sea fan sediments that are characterised by a higher BIT index (Table 4). In the East China Sea dataset of Zhu et al. (2011) the sediments with elevated DC indices, i.e. >0.35 (Fig. 5) have an average BIT index of 0.09 (±0.02, n=12). Based on these data, therefore, a BIT index threshold of >0.1 seems appropriate for MBT'-CBT applications. It needs to be emphasized, however, that at other locations this threshold might be somewhat higher, for example due to lower crenarchaeol production. Although a previous interlaboratory study highlighted concerns regarding the reproducibility of the BIT index between laboratories and instruments (Schouten et al., 2009), a recent and more extensive interlaboratory comparison showed that low BIT indices (i.e. <0.1) can be reproduced relatively precisely between laboratories (Schouten et al., 2013b). Since variations in terrigenous soil OM input also occur over time, down core MBT'-CBT applications should always be accompanied with a BIT index record.

4. Conclusions

Our study shows that brGDGTs are present in dust, albeit in low abundance. Distributions of dust-derived brGDGTs are similar to those of soils but clearly different from those of distal marine sediments. Thus, although dust input to open ocean settings might occur, it does not seem

to be an important source of brGDGTs in distal marine settings. Branched GDGT distributions in distal marine sediments are characterised by a distinctive high DC index. This strongly suggests in-situ production of brGDGTs in distal marine sediments on a global scale, and supports earlier reports of potential in-situ production in near coastal marine sediments (Peterse et al., 2009; Zhu et al., 2011). Based on the large variability of DC indices in marine sediments, it is suggested that marine derived brGDGTs are mainly produced in-situ in the sediments rather than the overlying water column. The magnitude of in-situ production of brGDGTs is low compared to pelagic marine crenarchaeol production and, therefore, not notably influencing the use of the BIT index as proxy for relative soil OM input in marine sediments. However, the MBT'-CBT proxy for continental temperatures will be biased by in-situ produced brGDGTs when the overall abundance of brGDGTs is low, i.e. at low BIT indices (based on data in this study <0.1). It should therefore only be applied to settings known to receive substantial soil OM input.

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Tables

Table 1: Fractional abundances and indices of brGDGTs and crenarchaeol present in dust sampled along the west coast of equatorial Africa. Roman numerals refer to the GDGT structures in Fig. 1, where IV is crenarchaeol; 'b.d.' = below detection limit; '-' indicates that the respective indices are not calculated due to absence of GDGTs.

Dust sample	Latitude	Longitude	GDGT fractional abundance								BIT	MBT'	DC	CBT
			f(Ia)	*f*(Ib)	*f*(Ic)	*f*(IIa)	*f*(IIb)	*f*(IIc)	*f*(IIIa)	*f*(IV)				
DO13	1.30 N	6.94 W	0.186	0.014	0.018	0.037	*b.d.*	*b.d.*	0.012	0.733	0.24	0.82	-	-
DO14	1.32 N	2.86 W	0.152	*b.d.*	*b.d.*	*b.d.*	*b.d.*	*b.d.*	*b.d.*	0.848	0.15	-	-	-
DO15	1.52 N	0.60 W	0.195	0.017	*b.d.*	0.036	0.015	*b.d.*	0.015	0.722	0.25	0.76	0.12	0.86
DO16	1.76 N	1.64 E	0.207	*b.d.*	*b.d.*	*b.d.*	*b.d.*	*b.d.*	*b.d.*	0.793	0.21	-	-	-
DO17	2.61 N	6.54 E	0.249	0.039	*b.d.*	0.067	0.020	*b.d.*	*b.d.*	0.625	0.34	0.77	0.16	0.73
DO18	1.68 N	7.97 E	0.153	*b.d.*	*b.d.*	0.063	*b.d.*	*b.d.*	*b.d.*	0.784	0.22	0.71	-	-
DO19	1.74 N	9.14 E	0.309	0.025	*b.d.*	0.062	0.017	*b.d.*	*b.d.*	0.587	0.39	0.81	0.10	0.95
DO20	1.65 N	9.11 E	0.229	*b.d.*	*b.d.*	*b.d.*	*b.d.*	*b.d.*	*b.d.*	0.771	0.23	-	-	-
DO21	1.38 S	8.54 E	0.173	0.010	0.004	0.018	0.008	0.002	0.009	0.777	0.20	0.84	0.08	1.04
DO22	2.91 S	9.21 E	0.219	*b.d.*	*b.d.*	*b.d.*	*b.d.*	*b.d.*	*b.d.*	0.781	0.22	-	-	-
DO23	6.18 S	10.05 E	0.368	0.018	0.006	0.027	0.009	*b.d.*	0.007	0.565	0.42	0.90	0.06	1.16
DO24	8.00 S	11.86 E	*b.d.*	*b.d.*	*b.d.*	*b.d.*	*b.d.*	*b.d.*	*b.d.*	1.000	-	-	-	-
DO25	10.69 S	12.50 E	0.138	0.029	b.d.	0.039	*b.d.*	*b.d.*	*b.d.*	0.794	0.18	0.81	-	-

Table 2: Fractional abundances and indices of brGDGTs and crenarchaeol present in SPM of surface waters of the Atlantic Ocean along the west coast of equatorial Africa. Volume indicates the amount of water filtered for analysis; roman numerals refer to the GDGT structures in Fig. 1; 'b.d.' = below detection limit; '-' indicates that the respective indices are not calculated due to absence of GDGTs.

SPM sample	Lati-tude	Longi-tude	Volume (L)	Tempe-rature (°C)	Salinity (‰)	GDGT fractional abundance								BIT	MBT'	DC	CBT
						f(Ia)	*f*(Ib)	*f*(Ic)	*f*(IIa)	*f*(IIb)	*f*(IIc)	*f*(IIIa)	*f*(IV)				
M56B 2	3.77 S	9.12 E	304	27.3	32.0	0.302	0.021	0.010	0.037	0.003	*b.d.*	0.004	0.623	0.38	0.88	0.07	1.14
M56B 23	4.81 S	9.91 E	244	28.1	33.5	0.233	0.025	0.014	0.027	0.003	*b.d.*	*b.d.*	0.698	0.30	0.90	0.10	0.97
M56B 34	6.28 S	10.47 E	403	27.6	28.0	0.551	0.012	0.005	0.069	0.003	*b.d.*	0.006	0.353	0.65	0.88	0.02	1.60
M56B 37	9.90 S	10.87 E	304	27.0	36.0	0.389	*b.d.*	*b.d.*	0.044	*b.d.*	*b.d.*	0.018	0.549	0.45	-	-	-
M56B 43	15.40 S	11.30 E	244	21.6	36.0	0.027	*b.d.*	*b.d.*	*b.d.*	*b.d.*	*b.d.*	*b.d.*	0.973	0.03	-	-	-
M56B 47	18.23 S	11.58 E	111	16.0	35.3	0.002	0.000	*b.d.*	0.002	*b.d.*	*b.d.*	0.001	0.995	0.00	-	-	-
M56B 53	22.99 S	13.17 E	198	18.5	35.3	0.005	*b.d.*	*b.d.*	*b.d.*	*b.d.*	*b.d.*	*b.d.*	0.995	0.01	-	-	-
M56B 57	26.10 S	14.12 E	113	16.2	35.3	0.001	*b.d.*	*b.d.*	*b.d.*	*b.d.*	*b.d.*	*b.d.*	0.999	0.00	-	-	-

Table 3: Fractional abundances and indices of brGDGTs present in distal marine surface sediments. Roman numerals refer to the GDGT structures in Fig. 1; 'b.d.' = below detection limit; '-' indicates that the respective indices are not calculated due to absence of GDGTs. Asterisks indicate sediments included in the 'equatorial Atlantic' subgroup of marine sediments (cf. Figs. 3 and 4).

Sediment sample	Ocean/Region	Latitude	Longitude	Water depth (m)	GDGT fractional abundance							BIT	MBT'	DC	CBT
					f(Ia)	*f*(Ib)	*f*(Ic)	*f*(IIa)	*f*(IIb)	*f*(IIc)	*f*(IIIa)				
GeoB2212-1	Atlantic Ocean*	4.03 N	25.62 W	5521	0.227	b.d.	b.d.	0.144	b.d.	b.d.	0.629	0.06	0.23	-	-
GeoB2213-1	Atlantic Ocean*	1.27 N	24.15 W	4323	0.150	0.017	b.d.	0.135	0.040	b.d.	0.658	0.01	0.17	0.17	0.70
GeoB2707-4	Atlantic Ocean	41.95 S	56.32 W	3167	0.377	0.077	0.035	0.158	0.228	0.071	0.054	0.01	0.49	0.36	0.25
GeoB2722-2	Atlantic Ocean	47.33 S	58.62 W	2351	0.091	0.103	0.037	0.123	0.454	0.143	0.049	0.00	0.23	0.72	-0.41
GeoB2723-2	Atlantic Ocean	48.91 S	57.88 W	569	0.246	0.104	0.049	0.129	0.322	0.077	0.073	0.02	0.40	0.53	-0.06
GeoB2806-6	Atlantic Ocean	37.83 S	53.14 W	3542	0.159	0.160	0.073	0.149	0.292	0.079	0.089	0.01	0.39	0.59	-0.17
GeoB2809-2	Atlantic Ocean	36.33 S	51.52 W	3539	0.194	0.160	0.072	0.161	0.260	0.068	0.084	0.02	0.43	0.54	-0.07
GeoB2824-1	Atlantic Ocean	33.50 S	42.50 W	4512	0.172	0.065	0.030	0.161	0.115	0.029	0.428	0.01	0.27	0.35	0.27
GeoB6407-2	Atlantic Ocean	42.04 S	19.50 W	3384	0.147	0.026	0.010	0.143	0.135	0.035	0.505	0.01	0.18	0.36	0.26
GeoB6410-1	Atlantic Ocean	44.52 S	20.90 W	4038	0.132	0.028	0.012	0.108	0.103	0.029	0.588	0.01	0.17	0.35	0.26
GeoB8303-5	Atlantic Ocean*	34.26 S	16.78 E	3447	0.134	0.131	0.068	0.145	0.327	0.094	0.101	0.01	0.33	0.62	-0.21
GeoB8336-5	Atlantic Ocean*	29.21 S	12.34 E	3626	0.149	0.069	0.033	0.160	0.157	0.043	0.390	0.01	0.25	0.42	0.14
GeoB8342-5	Atlantic Ocean*	31.50 S	13.00 E	3521	0.143	0.053	b.d.	0.157	0.158	0.049	0.440	0.01	0.20	0.41	0.15
GeoB9526-4	Atlantic Ocean*	12.43 N	18.06 W	3223	0.175	0.107	0.044	0.131	0.351	0.120	0.072	0.02	0.33	0.60	-0.18
GeoB9529-1	Atlantic Ocean*	8.35 N	17.37 W	1234	0.326	0.080	0.047	0.198	0.220	0.064	0.065	0.02	0.45	0.36	0.24
IS-S2	Atlantic Ocean	48.18 N	9.71 W	1035	0.385	0.115	0.069	0.166	0.127	0.045	0.093	0.02	0.57	0.31	0.36
ENAM9407	Atlantic Ocean	62.96 N	4.03 W	2060	0.408	0.082	0.027	0.146	0.233	0.065	0.039	0.02	0.52	0.36	0.24
AII-GGC-22	Atlantic Ocean	54.79 S	3.33 W	2768	0.377	b.d.	b.d.	b.d.	b.d.	b.d.	0.623	0.03	-	-	-
T89-32	Atlantic Ocean*	14.97 S	10.67 E	3342	0.356	0.040	b.d.	0.190	0.130	b.d.	0.284	0.07	0.40	0.24	0.51
T89-40	Atlantic Ocean*	21.62 S	6.78 E	3060	0.173	0.034	b.d.	0.184	0.117	b.d.	0.491	0.01	0.21	0.30	0.37
NP-07-13-09 [a]	Svalbard	79.07 N	10.67 E	326	0.120	0.149	0.057	0.126	0.274	0.051	0.223	0.02	0.33	0.63	-0.24
NP-07-13-49 [a]	Svalbard	79.01 N	11.38 E	380	0.123	0.170	0.066	0.113	0.292	0.047	0.189	0.01	0.36	0.66	-0.29
HS 253	Southern Ocean	75 S	26 W	unknown	0.099	0.051	0.018	0.129	0.168	0.044	0.492	0.02	0.17	0.49	0.02
GeoB10016-2	Indian Ocean	1.60 N	96.66 E	1900	0.518	0.088	0.053	0.174	0.092	0.028	0.047	0.02	0.66	0.21	0.58
GeoB10040-3	Indian Ocean	6.48 S	102.86 E	2605	0.346	0.083	0.044	0.127	0.209	0.065	0.126	0.01	0.47	0.38	0.21
NIOP 902	Indian Ocean	10.78 N	51.58 E	459	0.241	0.118	0.077	0.273	0.091	0.031	0.170	0.03	0.44	0.29	0.39
NIOP 903	Indian Ocean	10.78 N	51.66 E	789	0.210	0.110	0.072	0.218	0.144	0.035	0.211	0.02	0.39	0.37	0.23
NIOP 904	Indian Ocean	10.79 N	51.77 E	1194	0.198	0.116	0.068	0.187	0.139	0.043	0.249	0.02	0.38	0.40	0.18
NIOP 907	Indian Ocean	10.80 N	52.25 E	2807	0.559	b.d.	b.d.	0.441	b.d.	b.d.	b.d.	0.01	-	-	-
NIOP 908	Indian Ocean	10.78 N	52.92 E	3572	0.193	0.070	0.045	0.151	0.224	0.069	0.247	0.02	0.31	0.46	0.07
Box 476	Arabian Sea	24.10 N	65.47E	1226	0.140	0.063	0.045	0.178	0.105	0.040	0.430	0.03	0.25	0.35	0.28
PM1	Peru Margin	11.98 S	77.32 W	100	0.261	0.047	0.026	0.314	0.042	0.005	0.305	0.02	0.33	0.13	0.81
PM7	Peru Margin	11.05 S	78.07 W	250	0.247	0.037	0.024	0.219	0.050	0.008	0.415	0.03	0.31	0.16	0.73
F1-3 [b]	East China Sea	30.00 N	123.99 W	63	0.169	0.135	0.111	0.255	0.123	0.050	0.156	0.07	0.42	0.38	0.22
F4-7 [b]	East China Sea	27.38 N	123.33 W	106	0.144	0.179	0.128	0.139	0.175	0.062	0.172	0.07	0.45	0.56	-0.10
Cariaco Basin	Caricaco Basin	10.67 N	65.60 W	1460	0.339	0.041	0.023	0.381	0.031	0.008	0.176	0.01	0.40	0.09	1.00
MC-1	Pacific Ocean	41.30 N	141.55 E	1002	0.177	0.143	0.062	0.182	0.194	0.049	0.194	0.02	0.38	0.48	0.03

BS 07E	Black Sea	43.0 N	34.0 E	1288	0.216	0.117	0.071	0.186	0.177	0.028	0.204	0.02	0.40	0.42	0.13

[a] data from Peterse et al. (2009); [b] data from Zhu et al. (2011)

Table 4: Fractional abundances and indices of brGDGTs and crenarchaeol present in surface sediments of the Congo deep sea river fan (from Weijers et al., 2007a). The two anker samples represent grab samples taken from the Congo River estuary (cf. Schefuß et al., 2004). Roman numerals refer to the GDGT structures in Fig. 1; 'b.d.' = below detection limit; '-' indicates that the respective indices are not calculated due to absence of GDGTs.

Sample ID	Latitude	Longitude	Water depth (m)	GDGT fractional abundance								BIT	MBT'	DC	CBT
				f(Ia)	*f*(Ib)	*f*(Ic)	*f*(IIa)	*f*(IIb)	*f*(IIc)	*f*(IIIa)	*f*(IV)				
Anker 24	6.03 S	12.57 E	5	0.712	0.054	0.016	0.140	0.019	0.003	0.015	0.041	0.95	0.82	0.08	1.06
Anker 26	6.05 S	12.48 E	6	0.584	0.062	0.038	0.192	0.026	0.008	0.033	0.056	0.94	0.72	0.11	0.94
T89-12	5.20 S	7.97 E	4068	0.193	0.034	0.009	0.080	0.028	0.003	0.050	0.604	0.35	0.59	0.20	0.64
T89-14	3.51 S	9.69 E	868	0.029	0.004	0.002	0.007	0.007	0.002	0.009	0.939	0.05	0.58	0.29	0.50
T89-15	4.21 S	10.02 E	1930	0.128	0.010	*b.d.*	0.019	0.018	*b.d.*	0.015	0.809	0.17	0.73	0.18	0.72
T89-16	5.71 S	11.23 E	826	0.280	0.014	0.005	0.037	0.009	*b.d.*	0.016	0.638	0.34	0.83	0.07	1.15
T89-19	6.04 S	9.96 E	3140	0.413	*b.d.*	*b.d.*	0.047	*b.d.*	*b.d.*	*b.d.*	0.540	0.46	-	-	-
T89-20	7.31 S	11.54 E	1080	0.102	0.005	0.002	0.013	0.007	0.002	0.008	0.861	0.12	0.79	0.10	0.96

Table 5: Average BIT, MBT' and DC indices and CBT ratios of the different sample groups discussed in the text. Numbers in parentheses are standard deviations; 'n.a.' = not applicable since samples were selected based on their BIT index values.

Sample group	BIT	MBT'	DC	CBT
Global soils[a]	0.90 *(0.15)*	0.49 *(0.23)*	0.16 *(0.15)*	0.96 *(0.59)*
African soils[a]	0.85 *(0.20)*	0.76 *(0.22)*	0.13 *(0.18)*	1.28 *(0.79)*
Dust filters	0.25 *(0.08)*	0.80 *(0.06)*	0.11 *(0.04)*	0.95 *(0.17)*
Surface water	0.23 *(0.25)*	0.89 *(0.01)*	0.06 *(0.04)*	1.24 *(0.33)*
Congo fan	0.42 *(0.35)*	0.72 *(0.10)*	0.15 *(0.08)*	0.85 *(0.24)*
African Atlantic	*n.a.*	0.28 *(0.10)*	0.39 *(0.16)*	0.21 *(0.31)*
Global marine	*n.a.*	0.35 *(0.12)*	0.40 *(0.16)*	0.20 *(0.32)*

[a] soils from database in Peterse et al. (2012)

Table 6: Results of the ANOVA pairwise multiple comparison test. Values in bold indicate that the mean difference between the respective sample groups is significant at the 90 % confidence level. Group numbers correspond to the following sample groups (cf. Fig. 4): 1 = global soils, 2 = African soils, 3 = dust, 4 = surface water SPM, 5 = Congo deep sea fan sediments, 6 = low latitude Atlantic Ocean sediments with BIT values <0.08, 7 = global marine sediments with BIT <0.08.

Group	1	2	3	4	5	6
2	1.000	-	-	-	-	-
3	0.465	1.000	-	-	-	-
4	0.525	0.957	0.996	-	-	-
5	1.000	1.000	0.997	0.740	-	-
6	**0.086**	**0.062**	**0.024**	**0.011**	**0.065**	-
7	**0.000**	**0.000**	**0.000**	**0.000**	**0.000**	1.000

Figure captions

Figure 1: Structures of glycerol dialkyl glycerol tetraethers (GDGTs) referred to in the text

Figure 2: Sample location map: A) sample locations of marine surface sediments; B) sample locations of dust, surface waters and Congo deep sea fan sediments along the equatorial African coast.

Figure 3: Cross plot of the degree of cyclisation (DC) and the methylation index (MBT') of brGDGTs of the different sample groups discussed in the text.

Figure 4: Box plots of DC indices for the different sample groups discussed in the text. Horizontal solid line within the boxes represents the median, gray boxes comprise 50 % of samples and dots beyond the whiskers represent upper- and lowermost 10 % of samples. No whiskers plotted if n<10. The soil data used are those from Peterse et al. (2012). African soils and low latitude Atlantic sediments are subsets of global soils and global marine sediments, respectively. Groups that are statistically significantly different from each other (at 90 % confidence level) are assigned different letters.

Figure 5: Degree of cyclisation (DC index) of brGDGTs in coastal and shelf sediments from the East China Sea (ECS) shelf plotted against water depth, which in the ECS is in general equivalent to distance from the coast. Red triangles indicate sediments shallower than 10 m;

these shallow sediments are generally characterised by high BIT indices (average = 0.86). Data from Zhu et al. (2011).

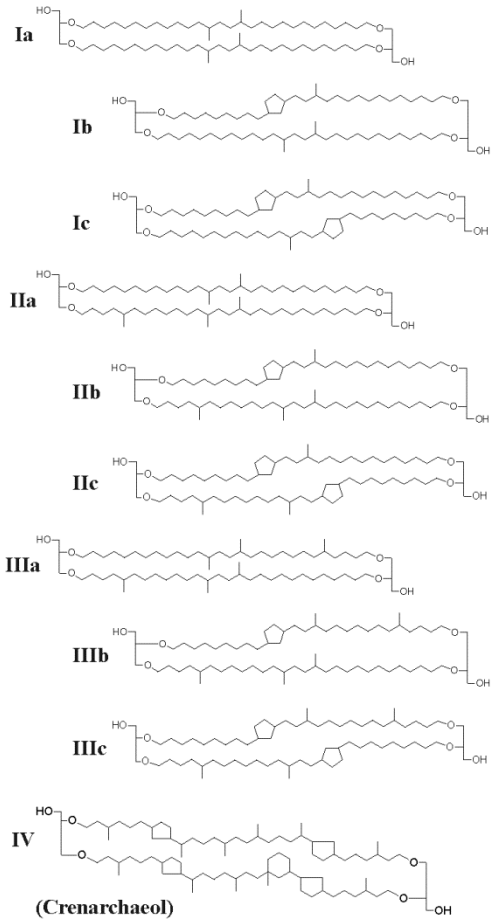

Figure 1

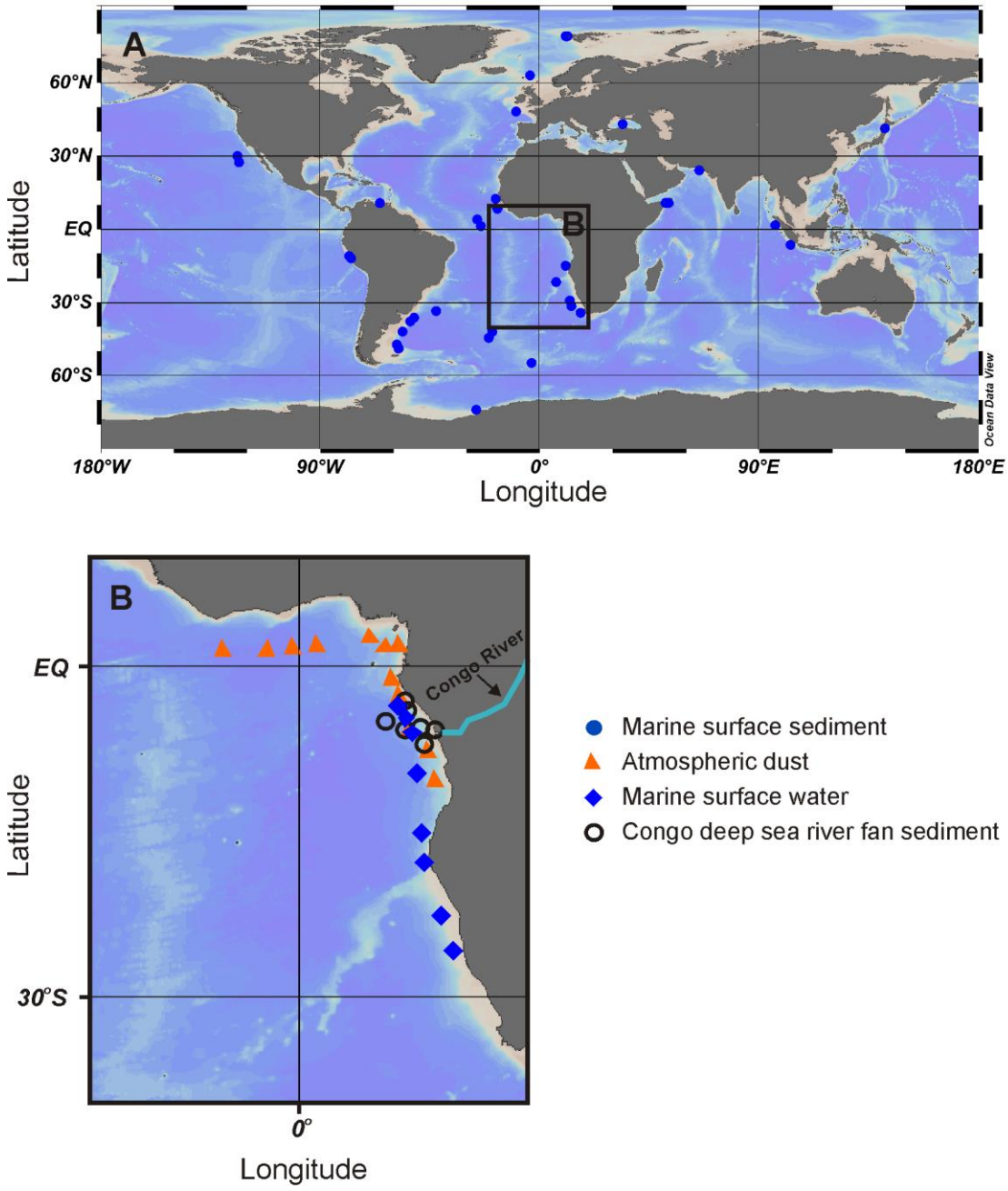
A
60°N
30°N
EQ
30°S
60°S
Latitude
180°W
90°W
0°
90°E
180°E
Longitude
Ocean Data View
B
EQ
30°S
0°
Latitude
Longitude
Congo River
Marine surface sediment
Atmospheric dust
Marine surface water
Congo deep sea river fan sediment

Figure 2

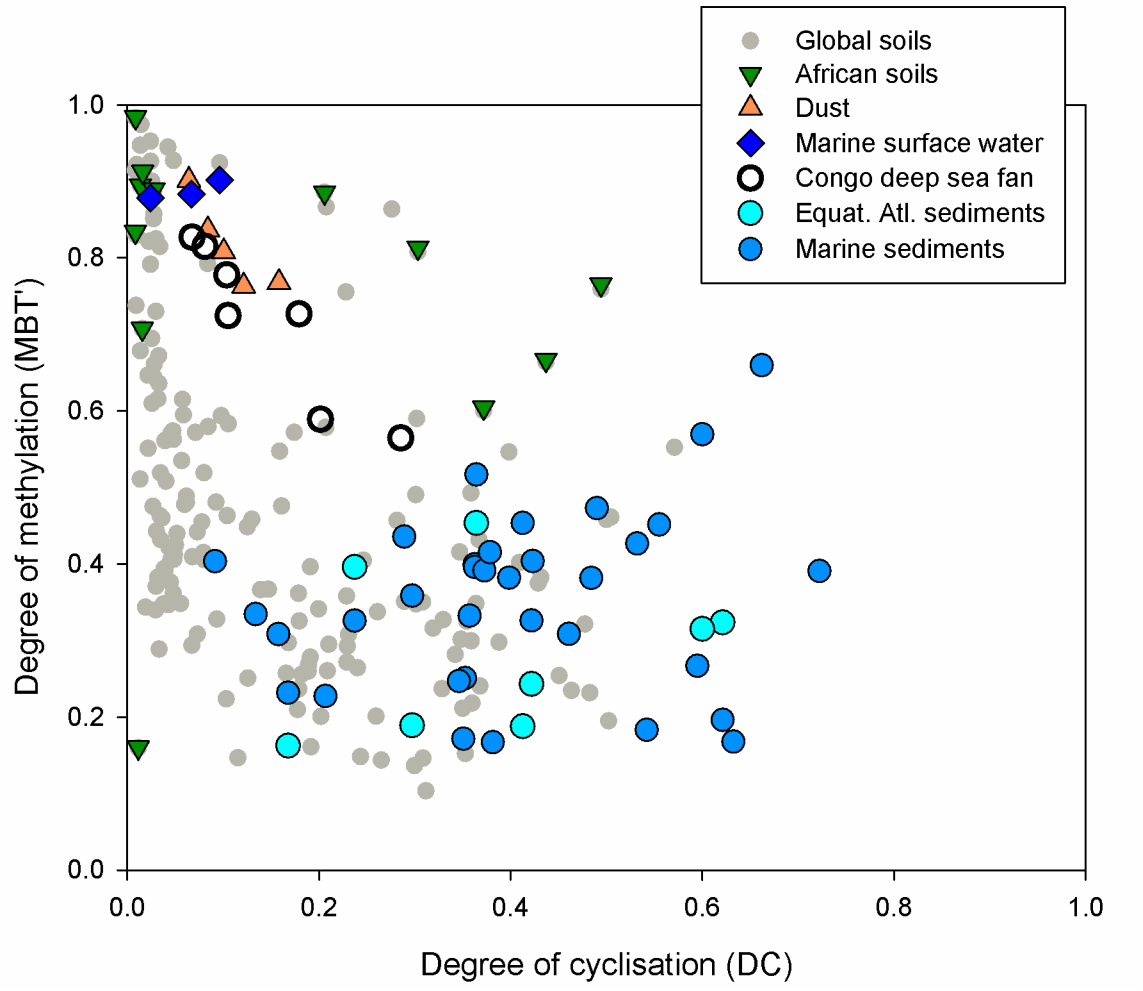
Global soils
African soils
Dust
Marine surface water
Congo deep sea fan
Equat. Atl. sediments
Marine sediments
Degree of methylation (MBT')
Degree of cyclisation (DC)
0.0
0.2
0.4
0.6
0.8
1.0

Figure 3

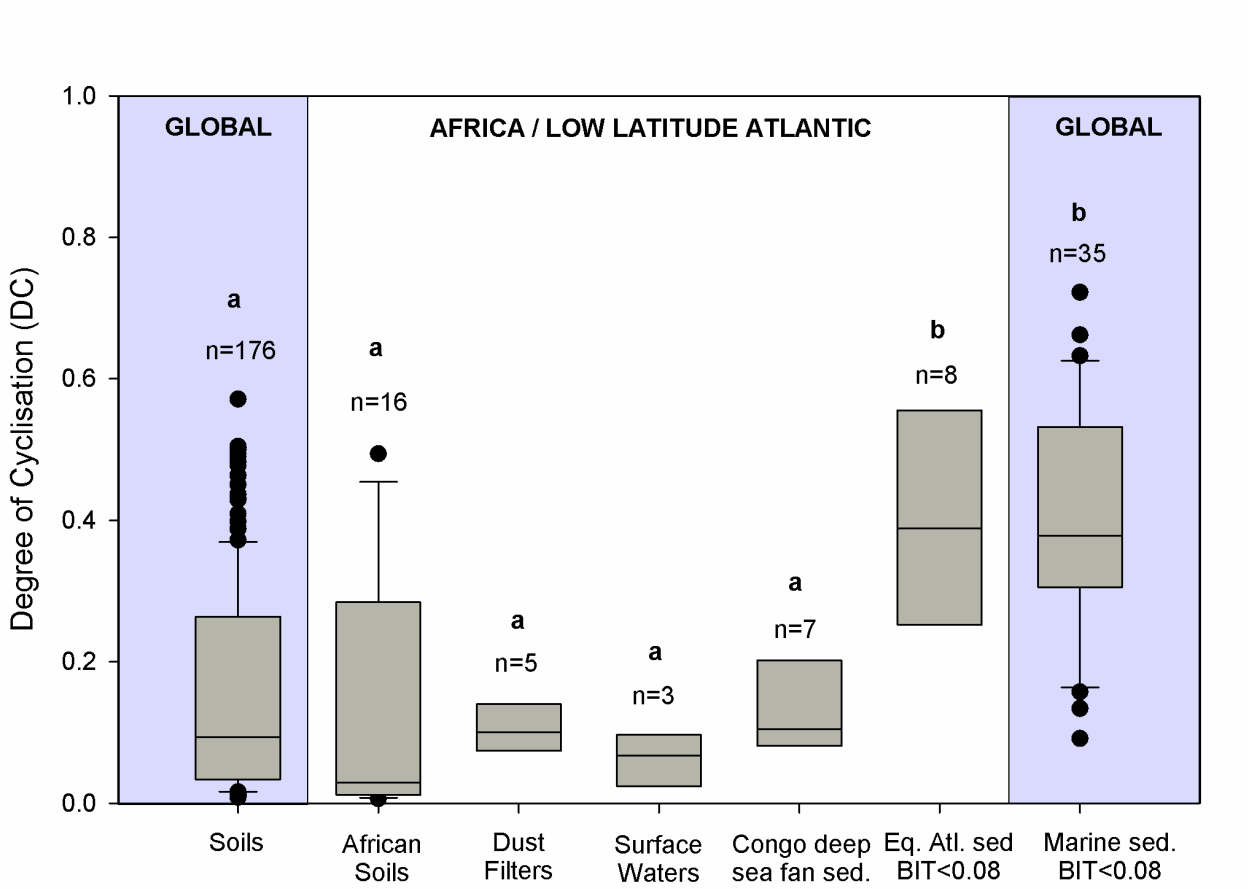
GLOBAL
AFRICA / LOW LATITUDE ATLANTIC
GLOBAL
Degree of Cyclisation (DC)
1.0
0.8
0.6
0.4
0.2
0.0
a
n=176
a
n=16
a
n=5
a
n=3
a
n=7
b
n=8
b
n=35
Soils
African Soils
Dust Filters
Surface Waters
Congo deep sea fan sed.
Eq. Atl. sed BIT<0.08
Marine sed. BIT<0.08

Figure 4

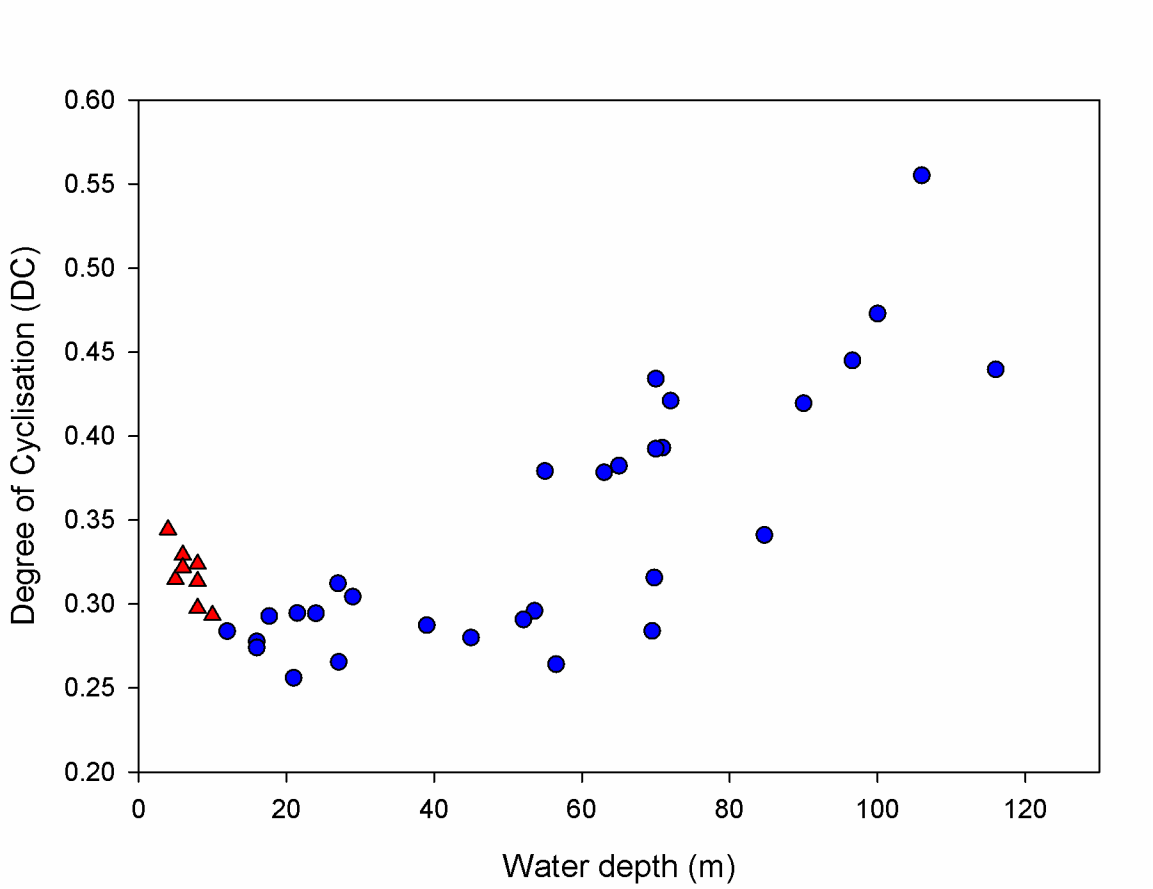
Degree of Cyclisation (DC)
0.60
0.55
0.50
0.45
0.40
0.35
0.30
0.25
0.20
0
20
40
60
80
100
120
Water depth (m)

Figure 5