Ubiquitous production of branched glycerol dialkyl glycerol tetraethers (brGDGTs) in global marine environments: a new source indicator for brGDGTs

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Abstract. Presumed source specificity of branched glycerol dialkyl glycerol tetraethers (brGDGTs) from bacteria thriving in soil/peat and isoprenoid GDGTs (iGDGTs) from aquatic organisms led to the development of several biomarker proxies for biogeochemical cycle and paleoenvironment. However, recent studies reveal that brGDGTs are also produced in aquatic environments besides soils and peat. Here we examined three cores from the Bohai Sea and found distinct difference in brGDGT compositions varying with the distance from the Yellow River mouth. We thus propose an abundance ratio of hexamethylated to pentamethylated brGDGT (IIIa/IIa) to evaluate brGDGT sources. The compiling of globally distributed 1354 marine sediments and 589 soils shows that the IIIa/IIa ratio is generally <0.59 for soils, 0.59–0.92 and >0.92 for marine sediments with and without significant terrestrial inputs, respectively. Such disparity confirms the existence of two sources for brGDGTs, a terrestrial origin with lower IIIa/IIa and a marine origin with higher IIIa/IIa, likely attributed to generally higher pH and the production of brGDGTs in cold deep water in

sea. The application of the IIIa/IIa ratio to the East Siberian Arctic Shelf proves it a sensitive source indicator for brGDGTs, which is helpful for accurate estimation of organic carbon source and paleoclimates in marine settings.

1 Introduction

Glycerol dialkyl glycerol tetraethers (GDGTs), membrane lipids of archaea and certain bacteria, are widely distributed in marine and terrestrial environments (Reviewed by Schouten et al., 2013). These lipids have been a focus of attention of organic geochemists for more than ten years because they can provide useful environmental and climatic information such as temperature, soil pH, organic carbon source and microbial community structure (e.g., Schouten et al., 2002; Hopmans et al., 2004; Weijers et al., 2006; Lipp et al., 2008; Kim et al., 2010; Peterse et al., 2012; Zhu et al., 2016). There are generally two types of GDGTs, isoprenoid (iGDGTs) and non-isoprenoid, branched GDGTs (brGDGTs; Fig. 1). The former group is more abundant in aquatic settings and generally thought to be produced by Thaumarchaeota, a specific genetic cluster of the archaea domain (Sinninghe Damsté et al., 2002; Schouten et al., 2008), although Euryarchaeota may be a significant source of iGDGTs in the ocean (e.g., Lincoln et al., 2014). In contrast, the 1,2-di-*O*-alkyl-*sn*-glycerol configuration of brGDGTs was interpreted as an evidence for a bacterial rather than archaeal origin for brGDGTs (Sinninghe Damsté et al., 2000; Weijers et al., 2006). So far, only two species of Acidobacteria were identified to contain one brGDGT with two 13,16-dimethyl octacosanyl moieties (Sinninghe Damsté et al., 2011), which hardly explains high diversity and ubiquitous occurrence of up to 15 brGDGT isomers in environments (Weijers et al., 2007b; De Jonge et al., 2014). Therefore, other biological sources of brGDGTs, although not yet identified, are likely.

The source difference between brGDGTs and iGDGTs led researchers to developing a branched and isoprenoid tetraether (BIT) index, expressed as relative abundance of terrestrial-derived brGDGTs to aquatic-derived Thaumarchaeota (Hopmans et al., 2004). Subsequent studies found that the BIT index is specific for soil organic carbon because GDGTs are absent in vegetation (e.g., Walsh et al., 2008; Sparkes et al., 2015). The BIT index is generally higher than 0.9 in soils, but close to 0 in marine sediments devoid of terrestrial inputs (Weijers et al., 2006; Weijers et al., 2014). Since its advent, the BIT index has been increasingly used in different environments (e.g., Herfort et al., 2006; Kim et al., 2006; Blaga et al., 2011; Loomis et al., 2011; Wu et al., 2013). Besides the BIT index, Weijers et al. (2007b) found that the number of cyclopentane moieties of brGDGTs, expressed as Cyclization of Branched Tetraethers (CBT), correlated negatively with soil pH, while the number of methyl branches of brGDGTs, expressed as Methylation of Branched Tetraethers (MBT), was dependent on annual mean air temperature (MAT) and to a lesser extent on soil pH. The MBT/CBT proxies were further corroborated by subsequent studies (e.g., Sinninghe Damsté et al., 2008; Peterse et al., 2012; Yang et al., 2014a). Assuming that brGDGTs preserved in marine sediments close to the Congo River outflow were derived from soils in the river catchment, Weijers et al. (2007a) reconstructed large-scale continental temperature changes in tropical Africa that span the past 25,000 years by using the MBT/CBT proxy. Recently, De Jonge et al. (2013) used a tandem high performance liquid chromatography-mass spectrometry (2D HPLC-MS) and identified a series of novel 6-methyl brGDGTs which were previously coeluted with 5-methyl brGDGTs. This finding resulted in the redefinition and recalibration of brGDGTs' indexes (e.g., De Jonge et al., 2014; Xiao et al., 2015).

The premise of all brGDGT-based parameters is their source specificity, i.e., brGDGTs is only biosynthesized by bacteria thriving in soils and peat. Several studies, however, observed different brGDGT compositions between marine sediments and soils on adjacent lands, supporting in situ production of brGDGTs in marine environments (e.g., Peterse et al., 2009a; Zhu et al., 2011; Liu et al., 2014; Weijers et al., 2014; Zell et al., 2014), analogous to lacustrine settings (e.g., Sinninghe Damsté et al., 2009; Tierney & Russell, 2009; Tierney et al., 2012) and rivers (e.g., Zhu et al., 2011; De Jonge et al., 2015; French et al., 2015; Zell et al., 2015). Peterse et al. (2009) compared the brGDGT distribution in Svalbard soils and nearby fjord sediments, and found that concentrations of brGDGTs (0.01–0.20 μg/g dw) in fjord sediments increased towards the open ocean and the distribution was strikingly different from that in soil. Zhu et al. (2011) examined distributions of GDGTs in surface sediments across a Yangtze River-dominated continental margin, and found evidence for production of brGDGTs in the oxic East China Sea shelf water column and the anoxic sediments/waters of the Lower Yangtze River. At the global scale, Fietz et al. (2012) reported a significant correlation between concentrations of brGDGTs and crenarchaeol ($p < 0.01$; $R^2 = 0.57–0.99$), suggesting that a common or mixed source for brGDGTs and iGDGTs are actually commonplace in lacustrine and marine settings. More recently, Sinninghe Damsté (2016) reported tetraethers in surface sediments from 43 stations in the Berau River delta (Kalimantan, Indonesia), and this result, combined with data from other shelf systems, supported a widespread biosynthesis of brGDGTs in shelf sediments especially at water depth of 50–300 m.

River and wind are the most important pathways for transporting terrestrial material into sea. In continental shelf, fluvial discharge is more important because brGDGTs in atmospheric dust are either below the detection level (Hopmans et al., 2004) or present at low abundance (Fietz et al., 2013; Weijers et al., 2014). In the remote ocean where no direct impact from land erosion via rivers takes place, eolian transport and in situ production are major contributors for brGDGTs. Weijers et al. (2014) found that distributions of African dust-derived brGDGTs were similar to those of soils but different from those of distal marine sediments, providing a possibility to distinguish terrestrial vs. marine brGDGTs based on molecular compositions. However, so far no robust molecular indicator is available for estimating source of brGDGTs in marine environments. Considering this, we conduct a detailed study about GDGTs in three cores from the Bohai Sea which are subject to the Yellow River influence to different degree. Our purpose is to evaluate the source discerning capability of different brGDGT parameters, from which the most sensitive parameter is selected and applied for globally distributed marine sediments and soils to test whether it is valid at the global scale. Our study supplies an important step for improving accuracy of brGDGT-derived proxies and better understanding the marine carbon cycle and paleoenvironments.

2 Material and methods

2.1 Study area and sampling

The Bohai Sea is a semi-enclosed shallow sea in northern China, extending about 550 km from north to south and about 350 km from east to west. Its area is 77,000 km^2 and the mean depth is 18 m (Hu et al., 2009). The Bohai Strait at the eastern portion is the only passage connecting the Bohai Sea to the outer Yellow Sea. Several rivers, including Yellow River, the second largest river in the world in terms of sediment load (Milliman & Meade, 1983), drain into the Bohai Sea with a total annual runoff of 890×10^8 m^3. One gravity core of 64 cm long (M1; 37.52°N, 119.32°E) was collected in July 2011, while other two cores were collected in July 2013, namely M3 (38.66°N, 119.54°E; 53 cm long) and M7 (39.53°N, 120.46°E; 60 cm long) (Fig. 2). The sites M1, M3 and M7 are located in the south, the center and the north of the Bohai Sea, respectively. The cores were transported to the lab where they were sectioned at 1 or 2 cm interval. The age model was established on basis of ^{210}Pb and ^{137}Cs activity, showing that these cores cover the sedimentation period of less than 100 years (Wu et al., 2013 and unpublished data).

2.2 Lipid extraction and analyses

The detailed procedures for lipid extraction and GDGT analyses were described in previous studies (Ding et al., 2015; Xiao et al., 2015). Briefly, the homogenous freeze-dried samples were ultrasonically extracted with dichloromethane (DCM)/methanol (3:1 v:v). The extracts were separated into nonpolar and polar fraction over silica gel columns. The latter fraction containing GDGTs was analyzed using an Agilent 1200 HPLC-atmospheric pressure chemical ionization-triple quadruple mass spectrometry (HPLC-APCI-MS) system. The separation of 5- and 6-methyl brGDGTs was achieved with two silica columns in sequence (150 mm×2.1 mm; 1.9 µm, Thermo Finnigan; USA). The quantification was achieved by comparison of the respective protonated ion peak areas of each GDGT to the internal standard (C_{46} GDGT) in selected ion monitoring (SIM) mode. The protonated ions were m/z 1050, 1048, 1046, 1036, 1034, 1032, 1022, 1020, 1018 for brGDGTs, 1302, 1300, 1298, 1296, 1292 for iGDGTs and 744 for C_{46} GDGT.

2.3 Parameter calculation and statistics

The BIT, MBT, Methyl Index (MI), Degree of Cyclization (DC) of brGDGTs and weighted average number of cyclopentane moieties for tetramethylated brGDGTs (#$Rings_{tetra}$) were calculated according to the definitions of Hopmans et al. (2004), Weijers et al. (2007b), Zhang et al. (2011), Sinninghe Damsté et al. (2009) and Sinninghe Damsté (2016), respectively.

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

$$\mathrm{MBT} = \frac{\mathrm{Ia + Ib + Ic}}{\mathrm{Ia + IIa + IIIa + Ib + IIb + IIIb + Ic + IIc + IIIc}} \quad (2)$$

$$\mathrm{MI} = 4 \times (\mathrm{Ia + Ib + Ic}) + 5 \times (\mathrm{IIa + IIb + IIb}) + 6 \times (\mathrm{IIIa + IIIb + IIIc}) \quad (3)$$

$$\mathrm{DC} = \frac{\mathrm{Ib + IIb}}{\mathrm{Ia + IIa + Ib + IIb}} \quad (4)$$

$$\#\mathrm{Rings}_{\mathrm{tetra}} = \frac{\mathrm{Ib} + 2 \times \mathrm{Ic}}{\mathrm{Ia + Ib + Ic}} \quad (5)$$

where roman numbers denote relative abundance of compounds depicted in Fig. 1. In this study, we used two silica LC columns in tandem and successfully separated 5- and 6-methyl brGDGTs. However, many previous studies (e.g., Weijers et al., 2006) used one LC column and did not separate 5- and 6-methyl brGDGTs. Considering this, we combined 5-methyl and 6-methyl brGDGT as one compound in this study, for example, IIIa denotes the total abundance of brGDGT IIIa and IIIa' in figure 1.

An analysis of variance (ANOVA) was conducted for different types of samples to determine if they differ significantly from each other. The SPSS 16.0 software package (IBM, USA) was used for the statistical analysis. Squared Pearson correlation coefficients (R^2) were reported and a significance level is $p < 0.05$.

2.4 Data compilation of global soils and marine sediments

The dataset in this study are composed of GDGTs from 1354 globally distributed soils and 589 marine sediments (Fig. 2 and supplementary data). These samples span a wide area from 75.00ºS to 79.28ºN and 168.08ºW to 174.40ºE and have water depth of 1.0 to 5521 m. The marine samples are from the South China Sea (Hu et al., 2012; Jia et al., 2012; O'Brien et al., 2014; Dong et al., 2015), Caribbean Sea (O'Brien et al., 2014), western equatorial Pacific Ocean (O'Brien et al., 2014), southeast Pacific Ocean (Kaiser et al., 2015), the Chukchi and Alaskan Beaufort Seas (Belicka & Harvey, 2009), eastern Indian Ocean (Chen et al., 2014), East Siberian Arctic Shelf (Sparkes et al., 2015), Kara Sea (De Jonge et al., 2015; De Jonge et al., 2016), Svalbard fjord (Peterse et al., 2009a), Red Sea (Trommer et al., 2009), the southern Adriatic Sea (Leider et al., 2010), Columbia estuary (French et al., 2015), globally distributed distal marine sediments (Weijers et al., 2014) and the Bohai Sea (this study). Soil samples are from the Svalbard (Peterse et al., 2009b), Columbia (French et al., 2015), China (Yang et al., 2013; Yang et al., 2014a; Yang et al., 2014b; Ding et al., 2015; Xiao et al., 2015; Hu et al., 2016), globally distributed soils (Weijers et al., 2006; Peterse et al., 2012; De Jonge et al., 2014), California geothermal (Peterse et al., 2009b), France and Brazil (Huguet et al., 2010), western Uganda (Loomis et al., 2011), the USA (Tierney et al., 2012), Tanzania (Coffinet et al., 2014), Indonesian, Vietnamese, Philippine, China and Italia (Mueller-Niggemann et al., 2016).

3 Results and discussion

3.1 Distribution and source of brGDGTs in Bohai Sea

A series of iGDGTs including crenarchaea and brGDGTs including 5-methyl and 6-methyl isomers were detected in Bohai Sea sediments. For brGDGTs, a total of 15 compounds were identified including three tetramethylated brGDGTs (Ia, Ib and Ic), six pentamethylated brGDGTs (IIa, IIb, IIc, IIa', IIb' and IIc') and six hexamethylated brGDGTs (IIIa, IIIb, IIIc, IIIa', IIIb' and IIIc'). In order to evaluate provenances of brGDGTs, we calculated various parameters including the BIT index, percentages of tetra-, penta- and hexa-methylated brGDGTs, #rings for tetramethylated brGDGTs, DC, MI, MBT, brGDGTs IIIa/IIa and Ia/IIa (Table 1). The values of the BIT index ranged from 0.27 to 0.76 in the core M1, which are much higher than that in the core M3 (0.04–0.25) and the core M7 (0.04–0.18). Such difference is expectable since the site M1 is closest to the Yellow River outflow, and receives more terrestrial organic carbon than other two sites (Fig. 2). However, the BIT index itself has no ability to distinguish terrestrial vs. aquatic brGDGTs because brGDGTs and crenarchaea used in this index are thought to be specific for soil organic carbon and marine organic carbon, respectively (Hopmans et al., 2004). For individual brGDGTs, the core M1 is characterized by significantly higher percentage of brGDGT IIa (28±1%) than the core M2 (18±1%) and the core M3 (18±0%; Fig. 3). We performed ANOVA for a variety of brGDGTs' parameters, and the results (Table 1) show that all parameters except MI can distinguish Chinese soils from Bohai Sea sediments, but only the IIIa/IIa ratio can completely separate Chinese soils (0.39±0.25; Mean±SD; same hereafter), M1 sediments (0.63±0.06), M3 sediments (1.16±0.12) and M7 sediments (0.93±0.07) into four groups.

Three factors may account for the occurrence of higher IIIa/IIa ratio in the Bohai Sea sediments than Chinese soils: selective degradation during land to sea transport, admixture of river produced brGDGTs and in situ production of brGDGTs in sea. Huguet et al. (2008; 2009) reported that iGDGTs (i.e., crenarchaea) was degraded at a rate of 2-fold higher than soil derived brGDGTs under long term oxygen exposure in the Madeira Abyssal Plain, leading to increase of the BIT index. Such selective degradation, however, cannot explain significant different IIIa/IIa ratio between the Chinese soils and Bohai Sea sediments because unlike crenarchaea, both IIIa and IIa belong to brGDGTs with similar chemical structures and thus have similar degradation rates. In situ production of brGDGTs in rivers is a widespread phenomenon, and can change brGDGTs' composition in sea when they were transported there (e.g., Zhu et al., 2011; De Jonge et al., 2015; Zell et al., 2015). However, this effect is minor in the Yellow River because extremely high turbidity (up to 220 kg/m^3 during the flood season; Ren & Shi, 1986) greatly constrain the growth of aquatic organisms. The studies along lower Yellow River-estuary-coast transect suggested that brGDGTs in surface sediments were primarily a land origin (Wu et al., 2014). Therefore, the enhanced IIIa/IIa values in the Bohai Sea sediments is most likely caused by in situ production of brGDGTs, which is supported by the spatial distributional pattern of IIIa/IIa in the

Bohai Sea. The site M1 is adjacent to the Yellow River mouth and receives the largest amount of terrestrial organic matter, causing lower IIIa/IIa values. In contrast, the site M3 located in central Bohai Sea comprises of the least amount of terrestrial organic matter, resulting in higher IIIa/IIa values. The intermediate IIIa/IIa values at the site M7 is attributed to moderate land erosion nearby northern Bohai Sea (Fig. 2). These GDGTs' results, consistent with other terrestrial biomarkers such as C_{29} and C_{31} *n*-alkanes and C_{29} sterol (data not showed here), strongly suggest that the IIIa/IIa ratio is a sensitive indicator for assessing source of brGDGTs in the Bohai Sea.

3.2 Regional and global validation of brGDGT IIIa/IIa

To test whether the IIIa/IIa ratio is valid in other environments, we apply it to the Svalbard (Peterse et al., 2009a), the Yenisei River outflow (De Jonge et al., 2015) and the East Siberian Arctic Shelf (Sparkes et al., 2015). By comparing the compositions of brGDGTs in Svalbard soils and nearby fjord sediments, Peterse et al. (2009a) indicated that sedimentary organic matter in fjords was predominantly a marine origin. A plot of BIT vs. IIIa/IIa (Fig. 4a) clearly grouped the samples into two groups which correspond to soils (>0.75 for BIT and <1.0 for IIIa/IIa) and marine sediments (<0.3 for BIT and >1.0 for IIIa/IIa). Another line of evidence is from De Jonge et al. (2015) who examined brGDGTs in core lipids (CLs) and intact polar lipids (IPLs) in the Yenisei River outflow. As the IPLs are rapidly degraded in the environment, they can be used to trace living or recently living material, while the CLs are generated via degradation of the IPLs after cell death (White et al., 1979; Lipp et al., 2008). The compiling of brGDGTs from De Jonge et al. (2015) shows significant difference of the IIIa/IIa ratio between the IPL fractions (>1.0) and CL fractions (<0.8; Fig. 4b). Such disparity supports that brGDGTs produced in marine environments have higher IIIa/IIa values because labile intact polar brGDGTs are mainly produced in situ, whereas recalcitrant core brGDGTs are composed of more allochthonous terrestrial components. Sparkes et al. (2015) examined brGDGTs in surface sediments across the East Siberian Arctic Shelf (ESAS) including the Dmitry-Laptev Strait, Buor-Khaya Bay, ESAS nearshore and ESAS offshore. The plot of BIT vs. IIIa/IIa again results into two groups, one group with lower BIT values (<0.3) and higher IIIa/IIa values (0.8–2.3) mainly from ESAS offshore, and another group with higher BIT values (0.3–1.0) and lower IIIa/IIa values (0.4–0.9) from the Dmitry-Laptev Strait, Buor-Khaya Bay and ESAS nearshore (Fig. 4c). A strong linear correlation was observed between the IIIa/IIa ratio and the distance from river mouth (R^2=0.58; p<0.05; Fig. 4d), in accord with the data of the BIT index and $\delta^{13}C_{org}$ (Sparkes et al., 2015). All lines of evidence support that marine-derived brGDGTs have higher IIIa/IIa values than terrestrial derived brGDGTs.

We further compile all available data in literatures representing globally distributed soils and marine sediments (Fig. 5). The statistical analysis clearly showed that at the global scale, the IIIa/IIa ratio is significantly higher in marine sediments than soils (p<0.01). An exception was observed for Red Sea sediments which have unusually low IIIa/IIa values (0.39±0.21). The Red Sea has a restricted connection to the Indian Ocean via the Bab el Mandeb. This, combined with high insolation, litter precipitation and strong winds result in surface water salinity up to 41 PSU in the south and 36 PSU in the north of the Red Sea (Sofianos et al., 2002). Under such extreme environment, distinct microbial populations may be developed and produced GDGTs different from that in other marine settings (Trommer et al., 2009).

Overall, the global distribution of IIIa/IIa presents the highest level in many deep sea sediments (2.6–5.1), the lowest level in soils (<1.0), and an intermediate level in sediments from bays, coastal areas or marginal seas (0.87–2.62; Fig. 5). These results are consistent with our data from the Bohai Sea, and confirm that the IIIa/IIa ratio is a useful proxy for tracing the source of brGDGTs in marine sediments at regional and global scales.

Why do marine sediments have higher IIIa/IIa values than soils? It has been reported that relative number of methyl groups positively correlates with soil pH and negatively correlates with MAT (Weijers et al., 2007b; Peterse et al., 2012). The IIIa/IIa ratio is actually an abundance ratio of hexamethylated to pentamethylated brGDGT, and thus is also affected by ambient temperature and pH. Unlike iGDGTs which is well known to be mainly produced by Thaumarchaeota (Sinninghe Damsté et al., 2002; Schouten et al., 2008), the marine source of brGDGTs remains elusive. Here, we assume that marine organisms producing brGDGTs response to ambient temperature in the same way as those soil bacteria producing brGDGTs, i.e., a negative correlation between relative number of methyl group of brGDGTs and ambient temperature. Because a large temperature gradient exists from surface to bottom water in ocean, we need consider the locale where brGDGTs are produced. If brGDGTs in marine environments are predominantly produced in euphotic zone, we would not observe a significant difference for the IIIa/IIa ratio between land and sea because both soils and marine sediments are globally distributed, leading to no systematic difference between soil temperature and sea surface temperature. Alternatively, if brGDGTs in marine sediments are partially derived from deep-water dwelling or benthic organisms, cold deep water (generally 1–2 ºC) would cause higher IIIa/IIa values in marine sediments, as we observed in this study. Although to the best of our knowledge, there is no study reporting in situ production of brGDGTs throughout water column in ocean. Recent studies (Taylor et al., 2013; Kim et al., 2015) have suggested that Thaumarchaeota thriving in the deeper, bathypelagic water-column (>1000 m water depth) biosynthesized iGDGTs with different compositions as surface dwelling Thaumarchaeota, and thereby alter signals of TEX_{86} in sediments. Besides temperature, pH can also alter compositions of brGDGTs (Weijers et al., 2007). Based on global soil data, the IIIa/IIa ratio shows a strong positive correlation with soil pH (R^2=0.51; Fig. 6). In our study, the majority of soils are acidic or neutral (pH<7.3) and only 8% of soil samples mainly from semi-arid and arid regions have pH of >8.0 (e.g., Yang et al., 2014a). In contrast, seawater is constantly alkaline with a mean pH of 8.2. With this systematic difference, bacteria living in soils tend to produce higher proportions of brGDGT IIa, whereas unknown marine organisms tend to biosynthesize higher proportions of brGDGT IIIa if they response to ambient pH in a similar way as soil bacteria in term of biosynthesis of brGDGTs. It should be pointed out that unlike fairly stable pH of overlying sea water, the pH of pore waters in marine sediments can vary significantly, which may influence compositions of brGDGTs. Nevertheless, at current stage, the occurrence of higher IIIa/IIa values in marine sediments is most likely attributed to relatively higher pH and lower deep water temperature. Further studies are needed to disentangle relative importance of these two factors.

3.3 Implication of IIIa/IIa on other brGDGT proxies

Because brGDGTs can be produced in marine settings, they are no longer specific for soil organic matter, which inevitably affects brGDGT proxies (e.g., BIT, MBT/CBT). The plot of BIT vs. IIIa/IIa on basis of global dataset shows that the IIIa/IIa ratio has the value of <0.59 for 90% of soil samples and >0.92 for 90% of marine sediments (Fig. 7). Considering this fact, we propose that the IIIa/IIa ratio of <0.59 and >0.92 represents terrestrial (or soil) and marine endmembers, respectively. The BIT index has the value of >0.67 for 90% of soils and <0.16 for 90% of marine sediments (Fig. 7). Overall, the BIT index decreased with increasing IIIa/IIa values ($\mathrm{BIT} = 1.08 \times 0.28^{\frac{\mathrm{IIIa}}{\mathrm{IIa}}} - 0.03$; $R^2 = 0.77$; Fig. 7), suggesting that both the IIIa/IIa and BIT are useful indexes for assessing soil organic carbon in marine settings. However, when the BIT index has an intermediate value (i.e., 0.16 to 0.67), it is not valid to determine the provenance of brGDGTs. For example, several marine samples having BIT values of ~0.35 show a large range of IIIa/IIa (0.4 to 2.4; Fig. 7), suggesting that the source of brGDGTs can vary case by case. Under this situation, the measurement of the IIIa/IIa ratio is strongly recommended.

The different IIIa/IIa values between land and marine endmembers may supply an approach to quantify the contribution of soil organic carbon in marine sediments. Similar to the BIT index, we used a binary mixing model to calculate percentage of soil organic carbon ($\%OC_{soil}$) as follow:

$$\%\mathrm{OC}_{\mathrm{soil}} = \left[\frac{[\mathrm{IIIa/IIa}]_{\mathrm{sample}} - [\mathrm{IIIa/IIa}]_{\mathrm{marine}}}{[\mathrm{IIIa/IIa}]_{\mathrm{soil}} - [\mathrm{IIIa/IIa}]_{\mathrm{marine}}}\right] * 100 \qquad (6)$$

Where $[\mathrm{IIIa/IIa}]_{\mathrm{sample}}$, $[\mathrm{IIIa/IIa}]_{\mathrm{soil}}$ and $[\mathrm{IIIa/IIa}]_{\mathrm{marine}}$ are the abundance ratio of brGDGT IIIa/IIa for samples, soils and marine sediments devoid of terrestrial influences, respectively.

We applied this binary mixing model to the East Siberian Arctic Shelf because the data of BIT, $\delta^{13}C_{org}$ and distance from river mouth are all available (Sparkes et al., 2015).

With the distance from river mouth increasing from 25 to >700 km, the BIT, IIIa/IIa and $\delta^{13}C_{org}$ change from 0.95 to 0, 0.53 to 2.21 and –27.4‰ to –21.2‰, respectively, reflecting spatial variability of sedimentary organic carbon sources. For the BIT index, we used 0.97 and 0.01 as terrestrial and marine endmember values based on previous studies for Arctic surrounding regions (De Jonge et al., 2014; Peterse et al., 2014), which are similar to global average values (Hopmans et al., 2004). For $\delta^{13}C_{org}$, we chose –27‰ and –20‰ as C3 terrestrial and marine organic carbon endmembers (Meyers, 1997). For the IIIa/IIa ratio, we used a global average value of marine sediments (1.6) and soils (0.24), respectively, based on this study. By applying these endmember values into Eq. 6, we calculated percentage of soil organic carbon ($\%OC_{soil}$). We removed a few data points if their calculated $\%OC_{soil}$ were greater than 100% or below 0%. It should be noted that the endmember value will affect quantitative results, but does not change a general trend of $\%OC_{soil}$. The results based on all three parameters show a decreasing trend seawards (Fig. 8). However, the $\%OC_{soil}$ based on $\delta^{13}C_{org}$ is the highest (75±18%), followed by that from the IIIa/IIa ratio (58±15%) and then that from the BIT index (43±27%). This difference have been explained by that $\delta^{13}C_{org}$ is a bulk proxy for marine vs. terrestrial influence of sedimentary organic carbon (SOC), whereas the BIT index is for a portion of the bulk SOC, i.e., soil OC (Walsh et al., 2008) or fluvial OC (Sparkes et al., 2015). For the estimated $\%OC_{soil}$, $\delta^{13}C_{org}$ presents a stronger positive correlation with the IIIa/IIa ratio (R^2=0.49) than the BIT index (R^2=0.45), suggesting that the IIIa/IIa ratio may serve a better proxy for quantifying soil organic carbon than the BIT index because it is less affected by selective degradation of branched vs. isoprenoid GDGTs and high production of crenarchaea in marine environments (Smith et al., 2012).

4 Conclusions

Based on a detailed study on GDGTs for three cores in the Bohai Sea and a compiling of GDGT data from globally distributed soils and marine sediments, we have reached several important conclusions. Firstly, the ratio of brGDGTs IIIa/IIa is generally lower than 0.59 in soils, but higher than 0.92 in marine sediments devoid of significant terrestrial inputs, making it a sensitive proxy for assessing soil vs. marine derived brGDGTs at regional and global scales. Secondly, in situ production of brGDGTs in marine environments is a ubiquitous phenomenon, which is particularly important for those marine sediments with low BIT index (<0.16) where brGDGTs are exclusively of a marine origin. Thirdly, a systemic difference of the IIIa/IIa value between soils and marine sediments reflects an influence of pH rather than temperature on the biosynthesis of brGDGTs by source organisms. Given these facts, we strongly recommend to calculate the IIIa/IIa ratio before estimating organic carbon source, paleo-soil pH and MAT based on the BIT and MBT/CBT proxies. We also note a relatively large scatter of the IIIa/IIa ratio within both terrestrial and marine realms, and different environmental responses of 5-methyl and 6-methyl brGDGTs (e.g., De Jonge et al., 2014, 2016; Xiao et al., 2015). As a result, the separation of these two types of isomers is needed in future studies to develop more accurate brGDGTs-based proxies.

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Fig.1. Chemical structures of branched GDGTs and crenarchaeol.

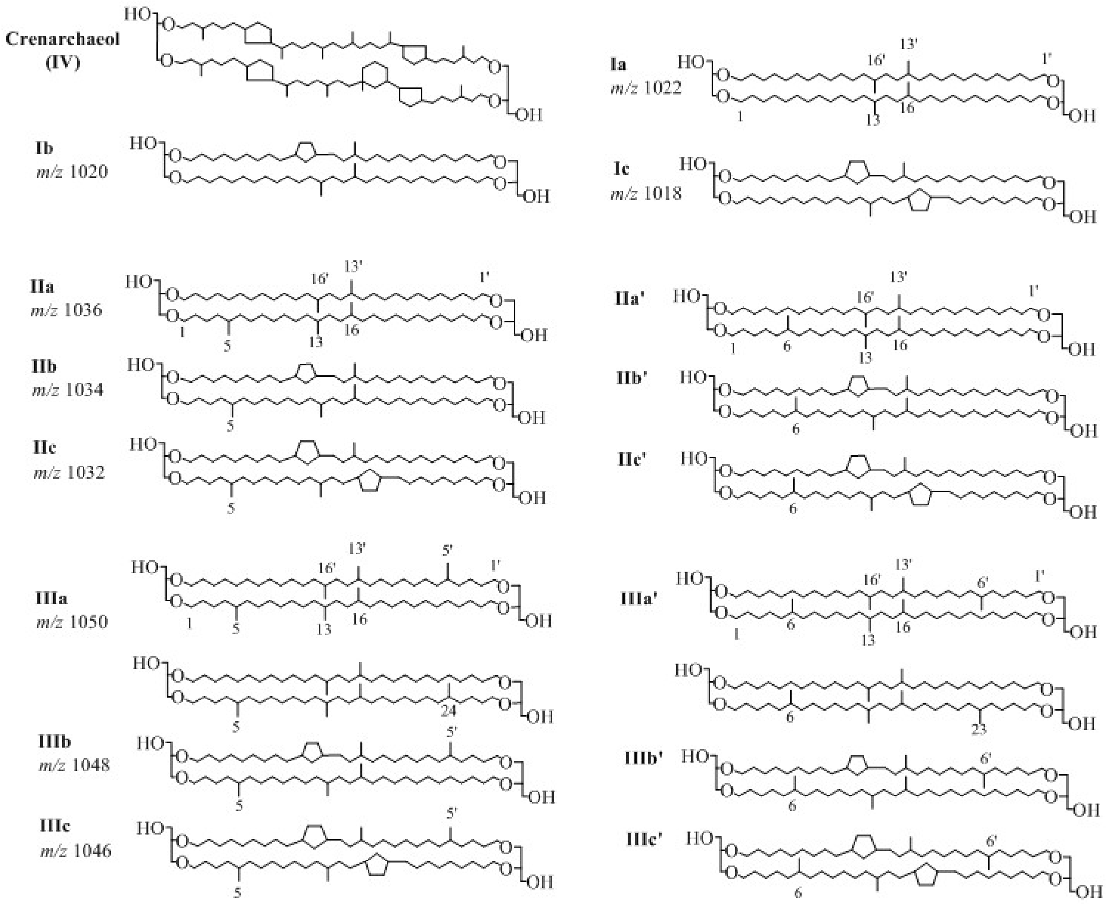

Fig.2. Location of the samples used in this study. White circles and black circles indicate the soils and marine sediments, respectively. Red crosses denote three sediment cores (M1, M3 and M7) in the Bohai Sea. YR is the Yellow River.

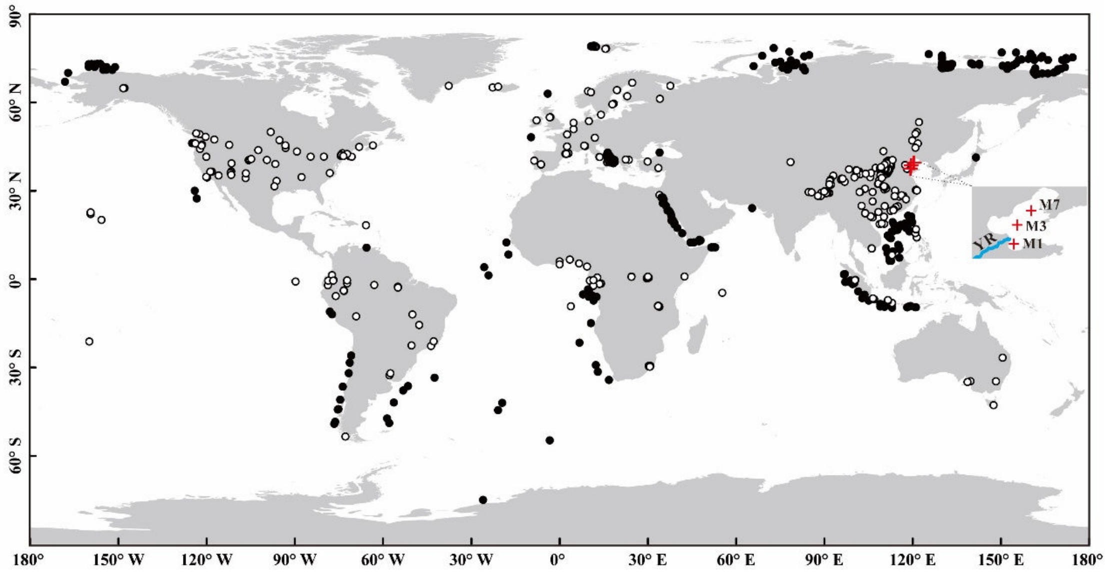

Fig.3. Averaged percentages of individual brGDGTs in soils (a), core M1 (b), M3 (c) and M7 (d). The soil data are from Yang et al. (2014a).

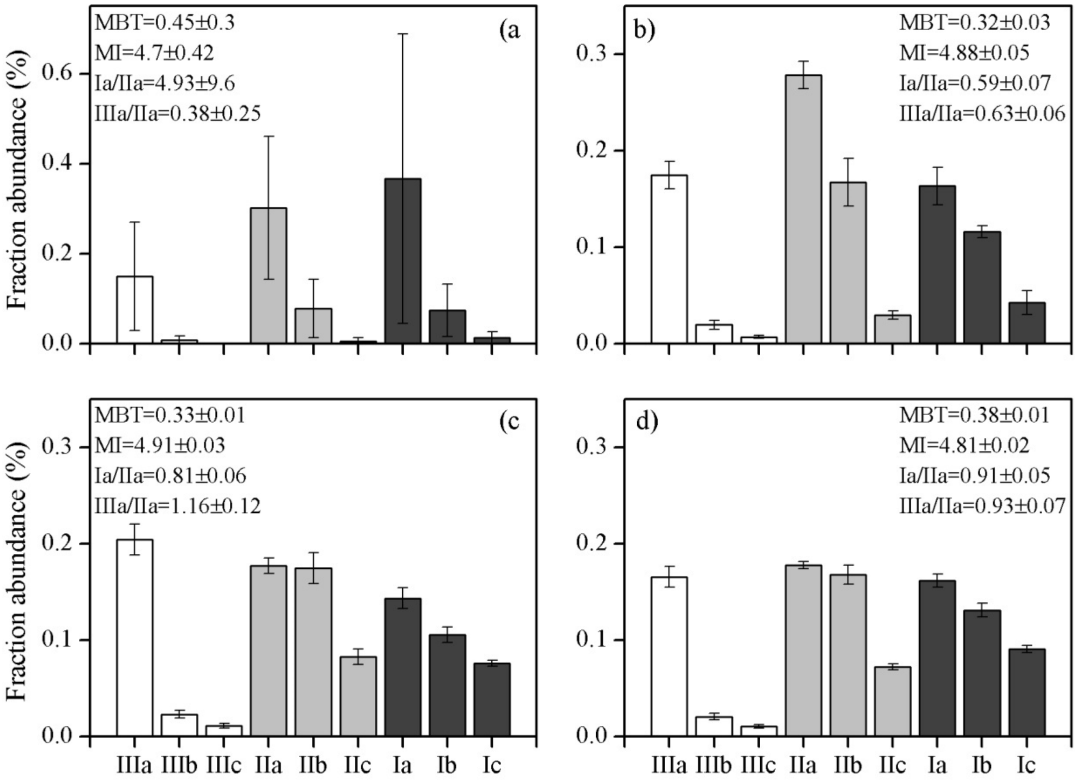

Fig. 4. a) The relationship between brGDGT IIIa/IIa ratio and the BIT index of samples from Peterse et al. (2009a); b) histograms of brGDGT IIIa/IIa ratio of the core lipids (CLs) and intact polar lipids (IPLs) in samples from De Jonge et al. (2015); c) the relationship between brGDGT IIIa/IIa ratio and the BIT index in samples from Sparkes et al. (2015); d) the relationship between brGDGT IIIa/IIa ratio and distance from river mouth in samples from Sparkes et al. (2015).

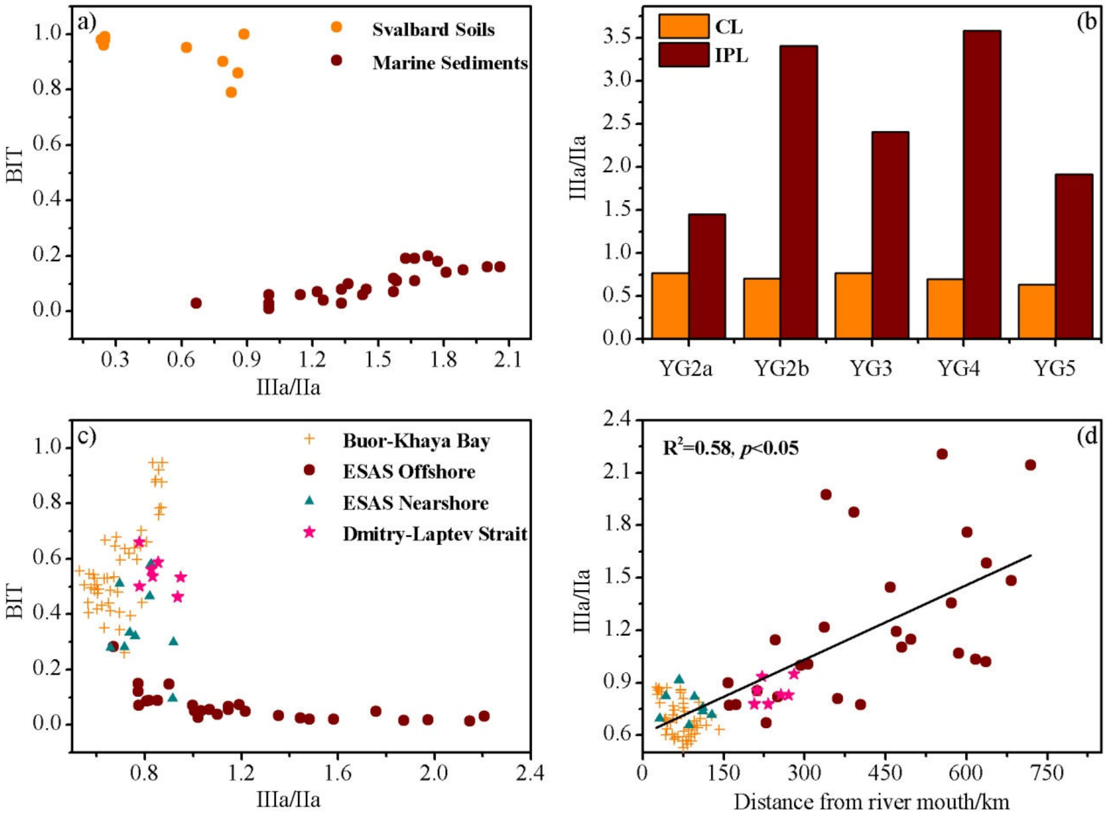

Fig. 5. Global distribution pattern of brGDGT IIIa/IIa ratio in soils and marine sediments.

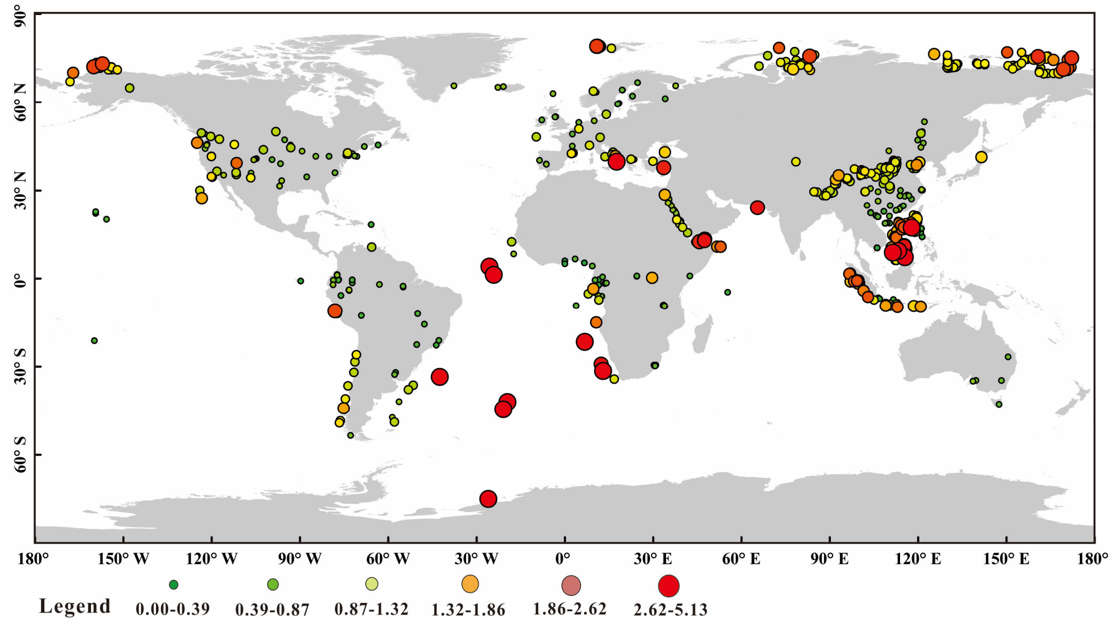

Fig. 6 a plot showing a positive correlation between soil pH and IIIa/IIa. The data are from Peterse et al. (2012) and this study.

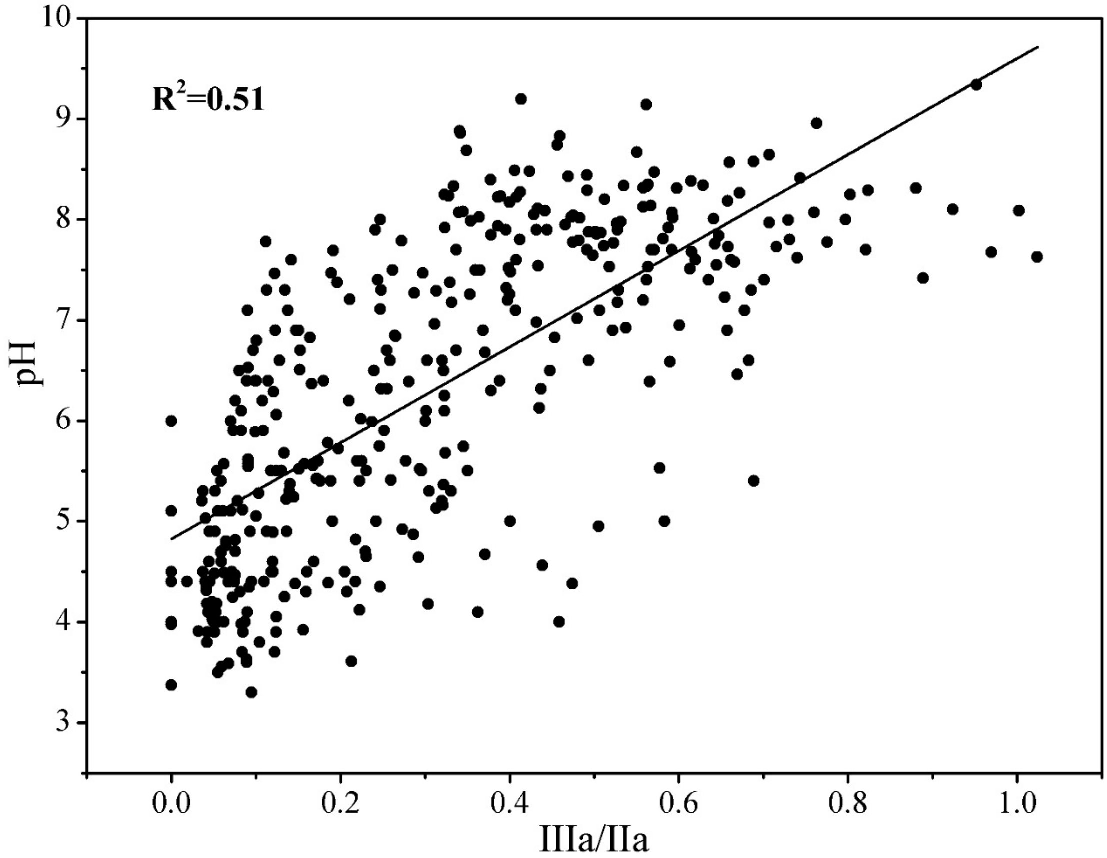

Fig. 7. Relationship between the IIIa/IIa ratio and the BIT index of globally distributed samples: soils (orange circle) and marine sediments (red circle). Dashed lines represent lower or upper threshold values for 90% of soils/sediments.

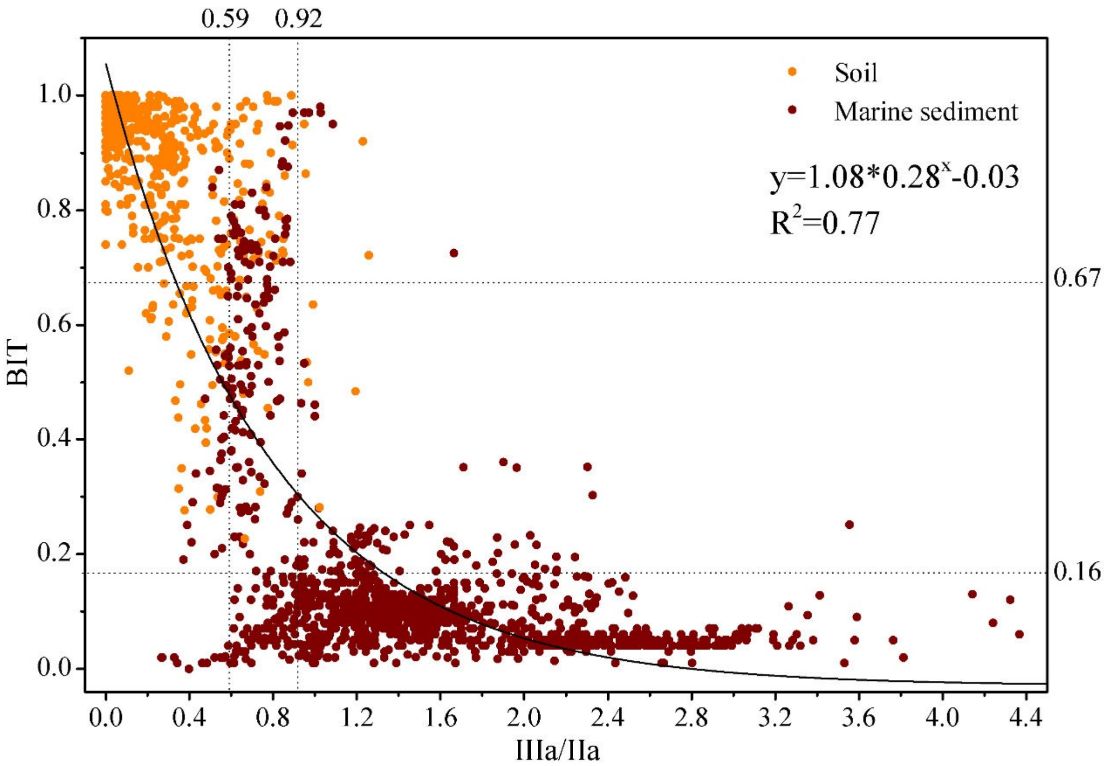

Fig. 8. Percentage of soil organic carbon (%OC_{soil}) or terrestrial organic carbon (%OC_{terr}) based on a binary mixing model of BIT (a), $\delta^{13}C_{org}$ (b) and IIIa/IIa (c) for the East Siberian Arctic Shelf (Sparkes et al., 2015).

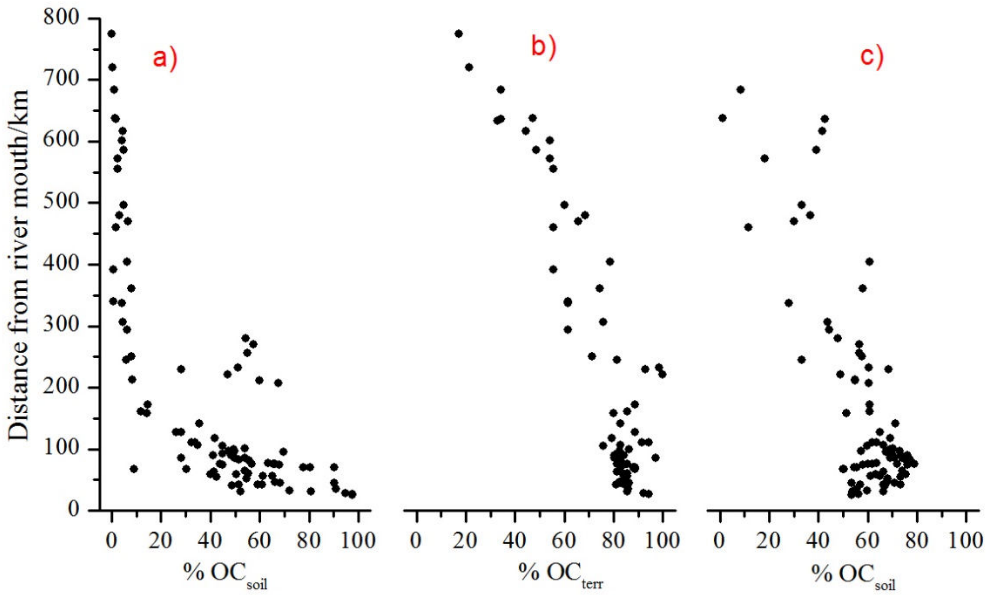

Table 1: Parameters including brGDGTs IIIa/IIa, Ia/IIa, the BIT index, MBT, MI, DC, percentages of tetra-, penta- and hexa-methylated brGDGTs, and the weighted average number of cyclopentane moieties (#rings for tetramethylated brGDGTs) based on the GDGTs from three cores (M1, M3 and M7) in the Bohai Sea. Different letters (a, b, c, d) represent significant difference at the level of $p<0.05$.

Indexes	Soil	M1	M3	M7
IIIa/IIa	0.39±0.25 (a)	0.63±0.06 (b)	1.16±0.12 (c)	0.93±0.07 (d)
Ia/IIa	4.93±9.60 (a)	0.59±0.07 (b)	0.81±0.06 (b)	0.91±0.05 (b)
BIT	0.75±0.22 (a)	0.50±0.19 (b)	0.14±0.06 (c)	0.11±0.03 (c)
MBT	0.45±0.30 (a)	0.32±0.03 (b)	0.33±0.01 (b)	0.38±0.01 (ab)
MI	4.70±0.42 (a)	4.88±0.05 (b)	4.91±0.03 (b)	4.81±0.02 (ab)
DC	0.31±0.21 (a)	0.62±0.03 (b)	0.79±0.03 (c)	0.82±0.02 (c)
%tetra	0.45±0.30 (a)	0.32±0.03 (b)	0.33±0.01 (c)	0.38±0.01 (c)
%hexa	0.16±0.12 (a)	0.20±0.02 (b)	0.24±0.02 (b)	0.20±0.01 (b)
%penta	0.39±0.20 (a)	0.48±0.02 (b)	0.44±0.02 (b)	0.42±0.01 (b)
#Rings$_{tera}$	0.20±0.15 (a)	0.39±0.03 (b)	0.47±0.02 (c)	0.47±0.02 (c)