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Branched glycerol dialkyl glycerol tetraethers and crenarchaeol record post-glacial sea level rise and shifts in sources of terrigenous brGDGTs in the Kara Sea (Arctic Ocean)

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ABSTRACT

This study evaluates the GDGT distribution and provenance in sediments (spanning a minimum of 13.3 ka) from the St. Anna Trough (Northern Kara Sea). The site has experienced extensive fluctuation in the delivery of river-derived organic matter (OM), caused by a eustatic change in sea level. This is in line with the record of the concentration of the isoprenoid GDGT crenarchaeol, produced by marine *Thaumarchaota*, which was low at the bottom of the core, increasing gradually in the most shallow unit. The concentration of branched (br)GDGTs showed an opposite trend and a marked shift in distribution. The deepest sediments (> 10 ka), with a distribution currently encountered in surface sediments in front of the Yenisei River, are characterized by terrigenous-derived brGDGTs, whereas the distribution in the shallowest unit (< 10 ka) is strongly influenced by marine, in-situ-produced brGDGTs. During the shift from terrigenous to marine-sourced brGDGTs, there was one horizon where a pronounced shift in the brGDGT distribution was observed and the brGDGT concentrations significantly decreased. As the brGDGTs delivered to the current Kara Sea system are derived from several sources, we postulate that a temporary change in the relative importance of the brGDGT sources happened during this interval. Both in-situ production and changing brGDGT provenance have implications for palaeoclimate reconstruction using brGDGTs. In-situ production of marine brGDGTs results in a higher reconstructed pH. However, these in-situ produced brGDGTs did not influence the reconstructed mean annual air temperature (MAT), when the MAT calibration was used. Changes in the relative contribution of brGDGT sub-pools were shown, however, to influence both soil pH reconstruction and MAT reconstruction.
1. Introduction

Branched glycerol dialkyl glycerol tetraethers (brGDGTs; Fig. 1) are ubiquitous bacterial membrane lipids produced in soils, where their distribution depends on the prevailing mean annual air temperature (MAT) applied on the soils, as well as the soil pH (Weijers et al., 2007). Based on this dependence, brGDGTs have found application as a palaeoclimate proxy for palaeo-soils (e.g. Peterse et al., 2011; Zech et al., 2012), lacustrine sediments (e.g. Niemann et al., 2012; Das et al., 2012), but initially coastal marine sediments that receive a substantial amount of soil-derived matter (Weijers et al., 2007, 2009; Bendle et al., 2010). As brGDGTs are present in high abundance in soils and decrease in concentration in the marine system, their presence in modern and down-core marine sediments was interpreted to reflect the delivery of soil-derived OM (e.g. Kim et al., 2006; Ménot et al., 2006). For this purpose, the branched and isoprenoid tetraether (BIT) index was developed, where the concentration of terrigenous brGDGTs is calculated relative to the marine thaumarchaeotal lipid crenarchaeol (Hopmans et al., 2004; Fig. 1). Additionally, soil-derived brGDGTs in coastal marine sediments may provide information on past continental climate (Weijers et al., 2007). However, several mechanisms can complicate this. Firstly, brGDGTs have been described to be produced in-situ in marine sediments (e.g. Peterse et al., 2009; Zhu et al., 2011; Zell et al., 2014a,b). These studies generally observed the production of cyclopentane-containing brGDGTs, which was explained by the relatively high pH of the pore-waters of the marine sediments. Secondly, brGDGTs are derived from a variety of watershed soils, where different soil types can carry different distributions, and erosional patterns can change through time. It is thus possible for their soil-derived brGDGT contribution to the river and the marine system to change through time (e.g. Bendle et al., 2010). BrGDGTs are also produced in river water and this has been described to influence or dominate the soil-derived brGDGTs in river systems (e.g. Zell et al., 2013, 2014; Buckles et al., 2014; De Jonge et al., 2014a). This results in a variety of brGDGT sources that can change over time and influence the brGDGT distribution and abundance in marine sediments. In the light of the diversity of the terrigenous sources of brGDGTs, De Jonge et al. (2015a) suggested to interpreting their abundance, and the derived BIT-index values, as indicative of the delivery of terrigenous organic matter (OM), including riverine OM, rather than only soil-derived OM.

Although the majority of palaeoclimate reconstruction studies has been based on a dataset of 9 brGDGTs, recent analytical developments (De Jonge et al., 2014b) now allow separation of 15 brGDGT compounds (Fig. 1), including six 5-methyl brGDGT compounds as described by Sinninghe Damsté et al. (2000) and Weijers et al. (2006), and six recently described 6-methyl compounds (De Jonge et al., 2013; 2014b) that previously co-eluted with the 5-methyl brGDGTs. The 6-methyl compounds were shown to be abundant in the Yenisei River and its outflow into the Kara Sea (De Jonge et al., 2014a, 2015a).

The Kara Sea is a shallow shelf sea connected to the Arctic Ocean. The organic matter (OM) in its sediments is influenced strongly by river-derived terrigenous material, as indicated by bulk...
elemental composition (e.g. Fernandes and Sicre, 2000; Guo et al., 2004; Lein et al., 2012) and by the presence of molecular soil markers in the sediments (e.g. van Dongen et al., 2008; Cooke et al., 2009; Gustafsson et al., 2011; De Jonge et al., 2016). The brGDGT-based BIT_index (Sparkes et al., 2015; De Jonge et al., 2015a) revealed the presence of terrigenous bacterial OM in East Siberian Sea and Kara Sea surface sediments, respectively. Based on the distribution of brGDGTs in Kara Sea surface sediments several possible sources were described: i.e. riverine in-situ produced brGDGTs and an unknown contribution of soil-derived and coastal cliff-derived brGDGTs (De Jonge et al., 2015a). In modern Kara Sea sediments, in-situ production of riverine brGDGTs and their preferential degradation was postulated to influence the distributions delivered by the Yenisei River, resulting in large differences in brGDGT-based reconstructed MAT values and soil pH. Whether these mechanisms can have a significant impact on the sedimentary record was not known yet.

For this purpose, we have investigated the sedimentary GDGT record of the Kara Sea covering at least the last 13.3 kyr. During this period (Late Weichselian and the Holocene) the sea has experienced large shifts in sea level, resulting in a regression in the position of the Yenisei and Ob River mouths. A sediment core was collected from the St. Anna Trough, which was formed by a marine-based glacier during the Last Glacial Maximum (LGM; Polyak et al., 1997). The sedimentological history of the trough has been documented in a number of lithological studies (Polyak et al., 1997; Hald et al., 1999). These studies describe large changes in the sedimentation regimes in the trough, shifting from a glacial sedimentation regime dominated by deposition of glacial ice-rafted debris (IRD) and river-derived clastic material, to the modern setting. Here, the GDGT concentration, brGDGT distribution and BIT_index are used to track changes in the relative contribution of terrigenous OM and marine OM over time, and to identify processes that would have an impact on the brGDGT distribution in the sedimentary record.

2. Study site
The St. Anna trough is a North to South facing, open ended glacial trough located approximately between 77-82°N and 65-75°E at the outer Eurasian continental margin (Fig. 2A, B). It is bounded by the islands of Franz Joseph Land to the west, Novaya Zemlya to the south, the shallow bank area Central Kara Plateau in the east and the Arctic Ocean to the north. It is a major pathway for the export of water, sediment and ice between the Arctic Ocean and the Kara Sea (Stein et al., 2004). The core position is in the southern basin of the trough, 200 km to the northeast of Novaya Zemlya. The polar surface water in the study area (~1.75 to 0 °C, salinity 34-33.2‰; Hald et al., 1999) occupies the upper ca. 100 m of the water column and is formed partly in the Arctic Ocean and partly in the Kara Sea, where fresh water from the large Siberian rivers (Yenisei, Ob) and from sea ice cover is under the influence of low insolation. During summer, surface salinity is reduced to 32‰ and the temperature may increase by 2–3 °C. Because of its low salinity, the polar surface water forms a lid upon the warmer Atlantic water (Aagaard and Carmack, 1989). This intermediate, Atlantic-derived
water (33‰, 1.5°C) can move southwards into the trough at a depth from 100 to 400 m (Hanzlick and Aagaard, 1980; Hald et al., 1999). More saline (>34.60‰; e.g. Hald et al., 1999) polar water is formed below forming sea ice and forms the bottom water in the through (Midttun, 1985). During fall and winter, sea ice forms in the Kara Sea and the eastern and northern part of the Barents Sea (e.g. Aagaard and Carmack, 1989).

During the LGM, the temperature in Siberia was between 7 and 15 °C colder in winter (for both south and north Siberia; Frenzel et al., 1992a; Tarasov et al., 1999), and between 1 to 10 °C colder in summer (for south and north Siberia, respectively; Frenzel et al., 1992b; Tarasov et al., 1999; Osipov et al., 2010), than compared to modern-day temperatures. In the area of low-elevation Lake Baikal, LGM temperature values were reconstructed to have been 18 °C colder for winter months and 4 °C for summer months (Tarasov et al., 2009). In the period following the LGM, several large changes in the erosion of the Siberian continental soils were inferred, caused by the melting of large continental icesheets (i.e. Kleiber and Niessen, 2000).

3. Material and methods

3.1. Sediment collection

The gravity core (3.03 m) was collected at 78° 28' 9928 N, 72° 47' 8487 E, at a depth of 473 m below sea level, aboard the R/V Akademik Mstislav Keldysh. It was subsampled (n=32) on-board, after a detailed description of the lithology was made. For this purpose, the grain size classification as employed by Shepard et al. (1954) was used. The colour of the sediments was described using a standard Munsell colour chart (Munsell Color ©). Samples were taken from a 1 cm broad slot, where the top of the sediment slot is reported in Table 1 and the Supplementary Table 1. After subsampling, the sediments were immediately stored at -20 °C.

3.2. Bulk elemental analysis

The homogenized and freeze dried sediments were decalcified in an overnight reaction with 1.5 N HCL solution and rinsed 3x to 5x three to five times with bidistilled water to adjust the pH of to 4.5. After freeze drying and subsampling, the bulk geochemical parameters [total organic carbon (TOC), total nitrogen (TN), stable carbon isotopic composition of organic carbon (δ13Corg), stable nitrogen isotopic composition (δ15N)] were measured using a Flash 2000 Organic Elemental Analyzer.

3.3. Lipid extraction and GDGT analysis

Freeze dried, homogenized sediments (2.5 to 3 g) were extracted using accelerated solvent extraction (ASE; Dionex), with a 9:1 (v/v) mixture of CHCl3-dichloromethane and MeOH-methanol (100 °C, 3x). The extract was separated according to polarity over activated alumina and the polar fraction analyzed using high-performance liquid chromatography-atmospheric pressure chemical ionization-mass spectrometry (HPLC-APCI-MS), as described by De Jonge et al. (2014b).
was via selected ion monitoring (SIM; Schouten et al., 2007) using \textit{m}/\textit{z} 744 for the internal standard, \textit{m}/\textit{z} 1292 for crenarchaeol and \textit{m}/\textit{z} 1050, 1048, 1046, 1036, 1032, 1022, 1020 and 1018 for brGDGTs. Agilent Chemstation software was used to integrate peak areas in the mass chromatograms of the [M+H]\textsuperscript{+} ions. However, visual inspection revealed that the brGDGT with \textit{m}/\textit{z} 1020 often co-eluted with an unidentified compound to provide as a broad peak, so its concentration \textit{was} should be interpreted with caution.

3.4. Calculation of GDGT-based proxies

The BIT index was calculated according to Hopmans et al. (2004). The inclusion of 6-methyl brGDGTs (De Jonge et al., 2013) is mentioned explicitly:

\text{BIT index} = \frac{(I_a+II_a+III_a+II_a'+III_a')}{(I_a+II_a+III_a+II_a'+III_a'+IV)}. \tag{1}

The roman numerals refer to the fractional abundances of GDGTs in Fig. 1. Here, Ia, IIa and IIIa are 5-Me brGDGTs, IIa' and IIIa' are 6-methyl brGDGTs and IV is the isoprenoid GDGT (iGDGT) crenarchaeol, a GDGT specific for \textit{Thaumarchaeota} (Sinninghe Damsté et al., 2002).

The isomer ratio (IR) represents the fractional abundance of the penta- and hexamethylated 6-methyl brGDGTs vs. the total of penta- and hexamethylated brGDGTs (modified after De Jonge et al., 2014a):

\text{IR} = \frac{(II_{abc}'+III_{abc}')}{(II_{abc}+III_{abc}+II_{abc}'+III_{abc}')}. \tag{2}

\textit{Xabc} means that the index includes both the non-cyclopentane containing (Xa) and the cyclopentane containing (Xb,c) components (Fig. 1).

We calculated a reconstructed pH using the CBT' index following De Jonge et al. (2014b):

\text{CBT'} = \log_{10}\frac{(I_c+II_a'+II_b'+III_a'+III_b'+III_c')}{(I_a+II_a+III_a)}. \tag{3}

\text{pH} = 7.15 + 1.59 \times CBT' \tag{4}

The MAT\textsubscript{mr} was calculated as a multiple linear regression, based on the abundance of only the major brGDGTs Ia, IIa and IIIa (De Jonge et al., 2014b):

\text{MAT}_{mr}(°C) = 5.58 + 17.91 \times [Ia] – 18.77 \times [IIa] \tag{5}

The square brackets indicate that the fractional abundance of brGDGT Ia and IIa is calculated relative to the sum of the three major brGDGTs (Ia+IIa+IIIa). This calibration was chosen over the MAT\textsubscript{mr} calibration, which is based on the fractional abundance of the brGDGTs Ia, Ib, Ic and IIa, relative to all 15 brGDGTs, to exclude the brGDGT Ib, which co-eluted with an unknown compound, based on the peak shape.
3.5. Statistical analysis

Statistical analyses were performed with the software package R (3.2.1.). An unconstrained Q-mode principal component analysis (PCA), based on the correlation matrix, was performed on the standardized fractional abundances of the compounds, using the vegan package (Oksanen et al., 2015). The calculated brGDGT scores are proportional to the eigenvalues, and the site scores were calculated as the sum of the species scores. Squared Pearson correlation coefficients ($r^2$) reported have an associated $p$-value < 0.05.

4. Results

4.1. Lithology of core

The core (303 cm) consists of a number of clearly defined lithological units (Fig. 3A; Table 1, Supplementary, Table 1), based on a visual description. Underlying a fluffy top layer, a large lithological unit (Unit 1, 0-133 cm below sea floor; bsf) is present, composed of light olive grey (5Y5/2) silty clay; multiple ferrous and shell fragments are present. This unit overlies a second unit (133-210 cm bsf) composed of 4 thin subunits (Unit 2a-d) and a thicker Unit 2e. Unit 2a (133-139 cm bsf) is composed of silty clay laminae. No ferrous iron deposits were encountered in this section. Unit 2b (139-144 cm bsf) is characterized by a slightly different colouration, as it is composed of silty clay sediments with a colour between moderate olive brown (5Y4/4) and light olive brown (5Y5/6). The lower boundary of this section contains an oxidized lens, with an aberrant colour (OX I). Also, Unit 2c is only a few cm thick (144-148 cm bsf) and is composed of light olive grey (5Y5/2) silty clay. At the bottom of this section a second oxidized lens is present (OX II, 147.5 – 148 cm bsf), characterized by a moderate yellowish brown (10YR5/4) sandy clay and containing gravel particles and lenses of greyish-black sand. Unit 2d (148 – 155 cm bsf) is a light olive grey (5Y5/2) massive silty clay containing gravel particles. It overlies a much thicker Unit 2e (155-210 cm bsf) composed of a darker, greyish olive (10Y4/2) silty clay, with extensive banded ferrous precipitates. Particularly towards the lower boundary, rock material is present, containing pieces up to 4 cm long. The basal unit of the core, Unit 3 (210 – 303 cm bsf) is described as diamicton and is composed mainly of sandy clay, with gravel fragments of variable size.

4.2. Downcore variation in bulk OM properties

Total organic carbon (TOC) and total nitrogen (TN) contents, the ratio of TOC/TN (C/N) and the stable C and N isotopes ($\delta^{13}C_{org}$ and $\delta^{15}N$) were measured to trace potential downcore changes in the delivery of terrigenous and marine OM (Fig. 3B-F, Supplementary, Table 1). The TOC and TN content varied between 0.3 and 1.5% and 0.04 and 0.2% dry wt, respectively. The highest TOC content was in Unit 2b, the lower part of Unit 2e and the upper part of Unit 3. Furthermore, increased values were encountered in the most recent sediments (Fig. 3B). The TN profile did not mimic the
downcore pattern in TOC completely. Although increased values occurred in recent sediments, the highest TN content was in the upper layers of the diamictic Unit 3. Furthermore, increased values were present in Unit 2a and at the boundary between Unit 2d and 2e (Fig. 3C). Overall, the TOC and TN content downcore did not follow the change in lithology. Values of the C/N ratio (Fig. 3D), commonly used to differentiate between marine and terrigenous OM (e.g. Thornton and McManus, 1994), varied between 7 and 18. The highest values were in Unit 2b and in the deeper part of Unit 2e. They decreased from the bottom to the top of Unit 1, remaining relatively stable in the upper 60 cm bssf. Also δ13Corg and δ15N were measured to trace the source of the bulk sedimentary OM (e.g. Krishnamurthy et al., 2001). The δ13Corg had less negative values both in recent sediments and the upper part of diamictic Unit 3. The interval containing the oxidized layers (although the oxidized layers themselves were sampled) was characterized by more negative δ13Corg values (Fig. 3E). The δ15N values were lower in horizons with decreased TN content - the lower part of Unit 1, throughout Units 2b, 2c, 2d and in Unit 2e, excluding the boundary between Unit 2d and Unit 2e (Fig. 3F).

### 4.3. GDGT abundance and distribution

Both brGDGTs and crenarchaeol were present in all the samples (Figs. 3G-H; Table 1). BrGDGTs had TOC-normalized abundance between 7 and 60 μg/gTOC, with the majority of the samples having a concentration < 30μg/gTOC. Crenarchaeol was present in comparable concentration, varying between 3 and 190 μg/g TOC, with substantially higher values in the upper part of the core. Values > 20 μg/g TOC were only encountered in Unit 1 (Fig. 3H). The contrasting downcore behaviour of brGDGTs and crenarchaeol was reflected in a distinct record of the BIT index (Fig. 3I; [Eq. 1]), with values varying between 0.01 and 0.87, with low (< 0.2) ones in Unit 1 and higher ones in all other units. Unit 2d was, however, characterized by lower BIT values than those of the sandwiching Units 2c and 2e.

To identify the end members of the brGDGT distributions, the variance in brGDGT distribution could be described in a principal component analysis (PCA), based on the standardized abundances of the 15 brGDGTs (Table 1). The first two PCs explained a large part of the variance, explaining 58 and 20% of the variance, respectively (Fig. 4A). The first PC (PC1) highlighted the good correlation between the fractional abundances of brGDGTs IIb, IIc, IIb’, IIc’, IIIa, IIIb’, IIIc’ (r² varies between 0.57 and 0.95). In general, these fractional abundances possess a negative correlation with that of brGDGT IIa (r² varies between 0.46 and 0.95). The second PC (PC2) indicated that, for a smaller part of the variance, the fractional abundance of brGDGTs Ia, Ic and IIC followed a different trend, anti-correlating with that of the brGDGT IIa’ (r² between 0.16 and 0.32) and, to a lesser extent, IIIa and IIIa’.

The downcore trends in brGDGTs, as captured by PC1 and PC2, are shown in Fig. 4B-C. The sediments of Unit 1 all plotted negatively on the first PC, indicating that the brGDGTs with a
negative score on PC1_{SAT} were relatively increased in the shallow sediments. The deeper sediments of Units 2 and 3 all scored positively on PC1_{SAT}. In the lower part of Unit 1 the score on PC1 gradually increased towards the values of PC1 in Unit 2 and 3. While the score on PC2_{SAT} was generally constant down-core (Fig. 4C), and close to 0 for the majority of the samples, the distribution at 150 and 153 cmbsf (Unit 2d), had highly negative values on this PC. The contrasting behaviour of the 5- and 6-methyl brGDGTs along PC1 was also reflected in the large variability in IR values (Eq. 2), that generally traced the down-core scores on PC1 (Fig. 4D). This illustrates the necessity of quantifying the 5- and 6-methyl compounds separately when studying down-core brGDGT variation.

Based on the PCA of the brGDGT distributions, we could identify three clear brGDGT end members (Unit 1; Unit 2d (especially 150 and 153 cmbsf) and the remaining sections of Units 2 and 3). These distributions are exemplified by those at 1, 153 and 200 cm bsf (Figs. 4E-G). The tetramethylated brGDGT Ia was the most abundant at all three depths. The distribution in Unit 1 (Fig. 4E; Table 1) was further characterized by a large fractional abundance of the 6-methyl brGDGTs, with IIb’ in larger fractional abundance than Ia’, which is an uncommon distribution. The distribution in Unit 2d (Fig. 4F) shows a high fractional abundance of Ia (49-56%), with a low abundance of the 6-methyl brGDGTs. The “deep” distribution (Fig. 4G) showed a contrasting one, dominated by non-cyclopentane-containing brGDGTs but with Ia less abundant (<38%) and with the 5-methyl brGDGTs in higher abundances than the 6-methyl brGDGTs, but not as extreme as in Unit 2d.

To evaluate the distributions down-core with those in suspended particulate matter (SPM) and surface sediments in the Yenisei River and its outflow to the Kara Sea, an extended dataset, composed of the standardized fractional abundances of the 15 brGDGTs in both the modern setting (De Jonge et al., 2015a) and in the down-core through sediments, was used to calculate PCA_{EXT}. The modern sediments (De Jonge et al., 2015) were collected in the Yenisei Outflow and Kara Sea, between 50 and 600 km from the Yenisei River mouth. The scores on the first two PCs (40 and 23% of the variance, respectively) of both brGDGTs and the various sites are indicated in Fig. 5. PC1_{EXT} (Fig. 5A) generally captured the same variance as PC1_{SAT} in the PCA of the down-core distributions (Fig. 4A), with cyclopentane-containing Ic, IIC, IIIb, IIb’, IIc’, IIIb’ and IIIc’ having low scores and 5-methyl brGDGTs Ia and IIIa high scores. In particular, the sediments from Unit 1 had a highly negative value on this PC, while the sediments from other units had scores close to 0. PC2_{EXT} captured the different trend in the fractional abundance of brGDGT Ia, and the contrasting behaviour of the 6-methyl brGDGTs Ia’ and IIIa’. On this second PC, the scores for the sediments of Units 1 to 2c were all close to 0, while Units 2e, 3 and 2d had increasingly positive values, reflecting a decrease in the fractional abundance of the Ia’ and IIa’, and a corresponding increase in the fractional abundance of Ia. The modern Yenisei River SPM had a highly negative loading on PC2_{EXT}, reflecting the high fractional abundance of Ia’ and IIa’ (De Jonge et al., 2014a; 2015a).

5. Discussion
5.1. Stratigraphy of core

Although no horizons were dated for the core, careful interpolation of the lithological strata with other dated St. Anna Trough cores (Polyak et al., 1997; Hald et al., 1999) allowed deriving an age for a few horizons (Fig. 3A). The deepest facies described by Hald et al. (1999) and Polyak et al. (1997) formed underneath a marine-based glacier, or in association with an ice sheet grounding line, locally disturbed by iceberg tracks. These sediments are present at 140 to > 400 cm b.s.f. in the trough, and at a depth between 150 and > 250 cm b.s.f. in cores from the vicinity of our coring site (Hald et al., 1999). The lithology of these sediments was described to be a massive diamicton with a high sand content (Polyak et al., 1997). The similar lithology and depth at the deepest unit in our core (Unit 3; 210 cm b.s.f.) indicate that this unit probably corresponds with the deepest horizons encountered in Polyak et al. (1997) and Hald et al. (1999).

These authors further postulated that the top of this unit was formed during the onset of the ice retreat, that had a minimum age of 13.3 ka in the trough. In the core here, this transition is probably the boundary between Unit 3 and Unit 2e. Overlying this basal unit, an intermediate section was described by Polyak et al. (1997) of < 1 m in thickness, comprising several lithological units, wherein alternating glacial deposits were described, whose characteristics indicated forwards and backwards shifts in the proximity of the trough and Novaya Zemlya glaciers (Hald et al., 1999).

The heterogeneity within the intermediate unit in our core (Unit 2), thus probably reflects the complex deglaciation sequence on Novaya Zemlya and in the trough. In these transitional horizons, Hald et al. (1999) reported the presence of laminations, indicating the periodic input of sediments, with little bioturbation. Similar laminations occur in Unit 2a. Another feature found throughout the trough (Polyak et al., 1997) is the presence of clear oxidized lenses within this section. Their formation suggests a relatively low deposition rate and oxic bottom waters, perhaps associated with a reduction in calving/melting of the glacier front, or with a permanent sea-ice cover (Hebbeln and Wefer, 1991; Polyak et al., 1997). In the Bering Strait, the presence of oxidized layers in the sediments was related to the presence of substantial amounts of seasonal sea ice, associated with decreased organic productivity during summer and intensive downwelling of O₂-rich brine during the winter months (Gardner et al., 1982). Two oxidized lenses are described in this core (OX I and OXII), based on the characteristic brown colour of the oxidized sediments. The colour shift can be attributed to the formation of Mn and Fe oxides, and the dissolution of biogenic carbonates in the subsurface sediment (e.g. Wilson et al., 1986), although downcore oxidized layers (6 ka) from the Bering Strait were described only as being enriched in Mn (Gardner et al., 1982). The widespread presence of two oxidized beds and two sandy beds resulted in their use as lithostratigraphic markers (Polyak et al., 1999). One oxidized layer was especially easily recognized, as it was described to directly overlie a dark grey sandy bed. It was dated as being deposited between 10 and 11 ka, by extrapolation of available radiocarbon ages in Polyak et al. (1997). Based on the similar lithology, we propose that the
layer OXII, overlying a distinct sandy bed (147.5-148 cm bsf; Unit 2c), was deposited at an estimated age of 10.5 ka in this core.

The upper unit in the trough has been described by both Polyak et al. (1997) and Hald et al. (1999) to be a homogenous, soft clayey mud, lacking glacial deposits and deposited under similar oceanic conditions as observed today. Overlying an initial phase with increased sedimentation speed related to a lower sea level, increased coastal erosion, and increased river discharge, an oxidized layer was described within the upper unit (Polyak et al., 1997) inferred to have an age of 8 ka. However, if this age is interpolated for the OXI layer in our core, Late Holocene sediments would have a linear sedimentation rate of 18 cm/kyr, while the Early Holocene sediments would have a linear sedimentation rate of only 1.6 cm/kyr. We thus postulate that the oxidized front in cores collected deeper in the trough (>600 m) is not observed here. Based on the homogenous nature of Unit 1, we postulate that the onset of the marine sedimentation regime, dated around 10 ka (e.g. Polyak et al., 1997), is coeval with the formation of the lower boundary of Unit 1. As the fluffy nature of the surface sediments indicates that the gravity core was successful in collecting the most recent sediment, the top of the core is assumed to be of a recent age (0 ka).

Based on the four dating points (Fig. 3A), the linear sedimentation rate is estimated to be 14 cm/kyr for the modern sedimentation regime (average for Unit 1), amounting up to 23 (average for Unit 2a, b, c) and 24 cm/kyr (average for Unit 2d, e) for deeper sediments. This agrees with the average Holocene sedimentation rate estimated to approach 12 cm/kyr for a core sampled close to the study site (0-11 ka; Stein et al., 2004). These authors further stated that the sedimentation rate during the Early Holocene (roughly corresponding with Unit 2), exceeded the sedimentation rate in the Late Holocene, corresponding roughly with Unit 1). Thus, although our dated horizons are based only on interpolated radiocarbon ages, the resulting linear sedimentation rates agree well with published values, and we are therefore confident that we are evaluating a minimum of 13.3 ka of sedimentation in the trough.

5.2. Terrigenous and marine sources of brGDGTs

Based on GDGT concentrations and the BIT index values (Hopmans et al., 2004: Table 1), three main phases could be identified in the trough sediments (Fig. 3G, H, I): (i) high brGDGT and low crenarchaeol concentrations and high (>0.7) BIT values throughout Unit 2e and Unit 3, (ii) low brGDGT concentration and increasing crenarchaeol concentration resulting in decreasing, generally low (<0.2) BIT values in Unit 1 and (iii) low crenarchaeol concentration and variable brGDGT concentration and BIT values in Units 2a-2d. The latter section reflects a transitional zone between Unit 3 and 2e and Unit 1.

The highest brGDGT concentration in Unit 2e (up to 50 μg/g TOC), approaches the concentration in front of the Yenisei River Mouth in surface sediments (i.e. between 12 and 87 μg/g TOC; De Jonge et al., 2015a). The concentration of the marine end member, crenarchaeol, is low
throughout Units 2e to 3 (≤ 5 μg/g TOC), comparable with the concentration in surface sediments in front of the Yenisei River mouth (between 0.2 and 20 μg/g TOC; De Jonge et al., 2015a). Although the brGDGT concentration in the basal sediments (Unit 3) is lower than in Unit 2e, the resulting BIT values in both units vary between 0.7 and 0.85. These values are comparable with BIT values for modern Yenisei Gulf surface sediments, between 200 and 300 km from the river mouth (De Jonge et al., 2015a). Assuming a sea level drop of 50 m at 11 ka (Fairbanks et al., 1989; Bauch et al., 2001), the distance between the core location and the presumed mouth of the palaeo Yenisei and Ob Rivers (Stein et al., 2004; Dittmers et al., 2008) was ca. 350 km. The brGDGT concentration and crenarchaeol concentration in Units 2e and 3 thus reflect a setting where the core site was much closer to the Yenisei River mouth. We could therefore constrain the source of the brGDGTs in Unit 2e and Unit 3 by studying their distribution (Fig. 4). The sediments in Unit 2e and 3 have a similar brGDGT fingerprint, as reflected in their similar scores on both PC1SAT and PC2SAT. Compared with the brGDGT distribution in modern Yenisei and Kara Sea sediments and SPM, Units 2e and 3 have similar scores on PC1EXT and PC2EXT (and thus similar brGDGT distributions; Fig. 5B) as the Yenisei Gulf samples, although the distribution encountered in Unit 3 in particular shows an enrichment in the brGDGT5, with a high score on PC2EXT (increase in brGDGT Ia). Thus, the brGDGT concentration, as well as the high BIT index values and the comparable brGDGT distributions reflect the deposition of brGDGTs in a setting where the core site was significantly closer to the mouth of the palaeo-rivers Yenisei and Ob, comparable with the current situation in the Yenisei Gulf (ca. 250 km from the river mouth), where riverine transport delivered brGDGTs with a comparable distribution as in the modern Yenisei River Gulf sediments.

A contrasting GDGT content is present in the most recent sedimentary horizon—Unit 1. It contrasts with Units 2d and 3, as it is characterized by low (< 0.2) BIT values that are caused by a strongly decreased amount of brGDGTs and a crenarchaeol concentration that increases from the bottom to the top of this unit, reaching maximum levels at 100 cm bsf (Fig. 3H). The brGDGT concentrations (5-20 μg/g TOC) and BIT values (between 0.05 and 0.1) in this unit are similar to the modern values encountered in offshore sediments in the Kara Sea (i.e. 4 - 20 μg/g TOC and BIT values down to 0.09; De Jonge et al., 2015a), suggesting that conditions during this period resemble those of the current marine system throughout most of Unit 1. However, the crenarchaeol concentration (30-180 μg/g TOC) is significantly higher than in modern Kara Sea sediments, which are 30 μg/g TOC at the maximum (De Jonge et al., 2015a). They are more comparable with the crenarchaeol concentrations in the East Siberian Sea (varying between 38 ± 8 μg/g TOC in the river outflow to 358 ± 65 μg/g TOC at 300-400 km from the river mouths; Sparkes et al., 2015).

Regarding distributions, Unit 1 has highly negative values of PC1SAT (Fig. 4B), with increased amounts of the cyclopentane-containing Ib, Iib, Iic, IId, Ile, Ile', Illb, Illb', Illc, Illc', Illc', Illc, Illc and Illc' (Fig. 4A). The downcore decrease in the scores on PC1SAT reflects the increase in concentration of the marine iGDGT crenarchaeol (r² = 0.85), a specific biomarker for marine *Thaumarchaeota*, reflecting the
increased production of these cyclopentane-containing brGDGTs in a system with increasing marine
in situ production. Previous studies have used in situ production of brGDGTs in the marine coastal
and distal sediments to invoke changing brGDGT distributions compared with the brGDGTs delivered
from the continent (Svalbard Fjord, Peterse et al., 2009; Yangtze River, Zhu et al., 2011; Pearl River,
Zhang et al., 2012; Tagus River and Amazon River; Zell et al., 2014a,b) and in off-shore marine
sediments (Weijers et al., 2014). Overall, these authors describe an increase in the fractional
abundance of one or more cyclopentane-containing brGDGTs. As such, in situ production of marine
brGDGTs is in line with the observed increase of the cyclopentane-containing brGDGTs along PC1\textsubscript{SAT}
(Fig. 4A). Although minor cyclopentane containing brGDGTs were often below detection limit in the
modern Kara Sea sediments, in situ production was shown to increase the cyclopentane-containing Ib,
Ic, IIb, IIc, IIIb, IIIc and IIc', which generally agrees with the increase in these brGDGTs in Unit 1.
The gradually increasing marine signature of brGDGTs, as observed in the decreasing values of
PC1\textsubscript{SAT}, the increasing crenarchaeol concentration and the decreasing BIT index values indicate an
increasingly marine influence on the southern trough during deposition of Unit 1. Indeed, the rise in
sea level has been documented to continue until between 5 and 8 ka (Bauch et al., 2001 and Stein et al.,
2004, respectively) and can thus be traced in the lower part of the sediments in Unit 1.
The palaeoenvironmental changes from the Units 2a and 3, with a strong river-derived
terrigenous sedimentary signal to Unit 1, with a stronger marine signal, can clearly be recognized from
the GDGT concentration and distributions and is consistent with evidence based on sediment core and
seismic reflection data (e.g. Polyak et al., 2000; Stein et al., 2004). Units 2a-2d reflect the main phase
of transition from one phase to the other, although some changes are evident in the upper part of Unit
2c (i.e. start of the decrease in BIT index values; Fig. 3I) and the lowermost part of Unit 1 (i.e.
increase in crenarchaeol concentration; Fig. 3H). In Units 2a-2d, the crenarchaeol concentration is still
low, but the brGDGT concentration and resulting BIT index values show distinct trends. The
relatively high brGDGT concentration in Unit 2e decreases strongly in Unit 2d, but increases in Unit
2c again, before the onset of the gradual decrease in Unit 2b and 2a, that continues into the lowest part
of Unit 1. Since the concentration of the marine iGDGT, crenarchaeol, is low throughout these units,
and the scores on the PC1\textsubscript{SAT} remain high, there is no indication for a contribution of marine in-situ
produced brGDGTs in the sediments of Unit 2. In Units 2a-c the brGDGT distributions are similar to
the terrigenous, river-derived brGDGTs in Units 2e and 3, as they have similar scores on PC1\textsubscript{SAT} and
PC2\textsubscript{SAT}. This indicates that the contribution of river-derived terrigenous brGDGTs remains strong in
these sediments. However, the strong decrease in brGDGT concentration in Unit 2d corresponds with
a remarkable shift in the distribution, that is characterized by a shift along the PC2\textsubscript{SAT} (Fig. 4C), most
apparent from the substantial increase in the fractional abundance of brGDGT Ia. We postulate that
the strong shift in the brGDGT distribution in Unit 2d is related to a shift in the provenance of
terrigenous brGDGTs. The brGDGT signature in the modern Kara Sea sediments was described to be
a mixture of riverine in-situ produced, soil-derived and coastalcliff derived brGDGTs (De Jonge et al.,
2015a). These different sources, but also different sub-pools of brGDGTs within the Yenisei River watershed, are characterized by different distributions and BIT values (De Jonge et al., 2015a).

Enrichment of a brGDGT sub-pool can happen before or after deposition in the sediments. First, a change in the relative contribution of the sub-pools can happen during soil and coastal cliffferosion and riverine transport, prior to their delivery to the marine system. Second, the brGDGT distribution of terrigenous OM can be modified after its delivery to the marine system, if the various brGDGT sub-pools differ in degradability. The in-situ production of brGDGT Ia in marine sediments is unlikely, as it (i) does not follow the proposed trend of increasing marine conditions in this core and (ii) disagrees with the global pattern where cold and high pH environments favour the production of highly branched and cyclopentane containing brGDGTs compounds (De Jonge et al., 2014b).

Whether the changing brGDGT distribution in Unit 2d can be explained by a shift in brGDGT sources before burial in the sediments, may be constrained by comparing this distribution with the modern brGDGT signatures of the Kara Sea (Fig. 5B). However, the high score of Unit 2d on PC2 EXT, driven by the large fractional abundance of Ia, sets it apart from all the modern distributions. They contrast especially with the distribution produced in-situ in the Yenisei River SPM, where the fractional abundance of the 6-methyl brGDGTs IIa’ and IIIa’ is strongly increased, and the fractional abundance of Ia is decreased. Based on PCA SAT and PCA EXT, the shift in brGDGT distribution can thus possibly be caused by an increased contribution of a brGDGT sub-pool predominantly enriched in Ia, or a substantial decrease in the contribution of riverine in-situ produced brGDGTs, characterized by a relatively high abundance of 6-methyl brGDGTs. A temporary increase in the erosion of continental brGDGTs during the Early Holocene, possibly limited to only part of the Yenisei watershed, or a decrease in the production of in-situ produced brGDGTs may be related to the increased soil erosion during the deglaciation. Indeed, a ‘peak’ in meltwater runoff, dated between 10 and 13ka, was recognized in the Laptev Sea sedimentary record (Kleiber and Niessen, 2000). This observation was based on an increase in magnetic minerals sourced by the basaltic Putoran Massif, a plateau in the northern reaches of the Yenisei River watershed that was glaciated during the LGM. The brGDGT distribution in a peat overlying a buried glacier at a similar latitude as the Putoran Massif is similar to the distribution in Unit 2d (Fig. 4F), as it is also characterized by a high fractional abundance of Ia (63%; De Jonge et al., 2015a). However, as the geographical extent of brGDGT sub-pools enriched in Ia is unknown, we can-not constrain whether or not this meltwater pulse may have influenced the brGDGTs delivered to the Kara Sea during the formation of Unit 2d.

Post-depositional modification of brGDGTs is a second mechanism that can enrich a brGDGT sub-pool. The presence of oxidized lenses in Unit 2 of the Kara Sea sediments (Fig. 3A) reflects a marine system wherein post-depositional oxic degradation may have modified to a variable extent the OM delivered to the site. Unit 2d directly underlies OXII (which was not analysed), preventing direct analysis of the impact of the oxidation on brGDGT distribution, an oxidized lens present throughout the Kara Sea. The bulk OM parameters for the sediments underlying this
oxidized lenses indicate that O$_2$ possibly penetrated the surface sediments during the formation of the oxidized front, and possibly oxidized the brGDGT distribution in the subsurface. This is reflected in a slight decrease in TOC and TN, from 1 to 0.6% and from 0.08 to 0.06% respectively (Fig. 3B, C). A shift in the $\delta^{13}$C$_{org}$ and $\delta^{15}$N values at the depths of the oxidized lenses, from -24.5 to -26.0 ‰ and from 5.0 to 3.5 ‰ respectively (Fig. 3E, F), can also be attributed to degradation of the OM present in the sediments (e.g. Lehmann et al., 2002; Prahl et al., 2003; Robinson et al., 2012). The effect of degradation is also reflected in the C/N ratio (Fig. 3D), where increased values may reflect degradation of OM (e.g. Mariotti et al., 1984; Thornton and McManus, 1994). However, the extent of degradation, based on the bulk OM proxies, does not completely agree with the interval in the core where a different brGDGT provenance is observed. Furthermore, previous studies on the effect of oxic degradation on GDGTs, indicated a strong increase in the BIT index in oxidized sediments, following the preferential degradation of marine in-situ produced crenarchaeol (Huguet et al., 2008; Lengger et al., 2013). The decreasing BIT values in Unit 2d can only be caused by oxic degradation if crenarchaeol is dominantly derived from terrigenous sources, and differs between brGDGT sub-pools. Nonetheless, preferential degradation was inferred to explain the increase in brGDGT Ia in offshore Kara Sea sediments, and was thus already inferred to act on the brGDGT distribution during transport and incorporation into the sediments (De Jonge et al., 2015a). The increase in the fractional abundance of Ia, Ic and IICin Unit 2d indicates that a similar mechanism may further influence the distribution delivered to a marine sediment. Furthermore, if degradation acts on the distribution, it would be expected to act specifically on the brGDGTs produced in-situ in the Yenisei River, as this modern brGDGT pool would be degraded preferentially, as modern OM has less physical protection against degradation (Blair and Aller, 2012; Arndt et al., 2013). The contrasting score on PC2$_{EXT}$ of the Yenisei River SPM and Unit 2d distributions, respectively, indicates that brGDGTs Ila’ and IIIa’, that are strongly enriched in the Yenisei River SPM, have a decreased fractional abundance in Unit 2d. This observation can be explained by invoking the mechanism of preferential degradation. Although we do not know the mechanism causing the observed shift in the provenance of terrigenous brGDGTs, the score on PC2$_{EXT}$ may reflect this shift. Thus, the brGDGT distribution from Unit 2d represents the most intensely enriched/degraded distribution encountered in the modern and down core Kara Sea distributions.

5.3. Implications for brGDGT-based palaeoclimate reconstruction

In the modern Kara Sea SPM and sediments, the brGDGT distribution was shown to be influenced by in-situ production and by a contribution from several terrestrial sub-pools of brGDGTs (De Jonge et al., 2015a). In recent sediments, preferential degradation of a labile brGDGT pool, e.g. the in-situ produced riverine brGDGTs, and possibly also less refractory sub-pools of soil-derived brGDGTs was inferred to explain the changing provenance of brGDGTs in offshore sediments. This study indicates that these processes can also act on longer timescales. The in-situ production of
marine brGDGTs was shown to happen at the same depth as the increase in the marine iGDGT crenarchaeol, and both parameters trace the production of marine OM and the increasingly marine nature of the St. Anna Trough. Although in-situ production in sediments apparently did not influence the brGDGT distributions in Unit 2 and 3, these were in turn influenced by changes in the provenance of the terrigenous brGDGTs.

To evaluate the influence these various processes may have on the brGDGT-based palaeoclimate distributions, we can evaluate the reconstructed pH and MAT (Fig. 6). For pH reconstruction, we employed the CBT’ calibration, a calibration based on a log ratio (Eqs. 3 and 4) of the 6-methyl brGDGTs Ia’, IIb’, IIc’, IIIa’, IIIb’ and IIIc’ and brGDGT Ic, relative to Ia, IIa and IIIa.

The MAT temperature was reconstructed using MAT_mrs (Eq. 5), that is based only on the abundance of the three major non-cyclopentane containing brGDGTs Ia, IIa and IIIa, as brGDGT Ib was found to co-elute with an unknown compound in some samples (n=15). Both these-calibrations are based on a dataset of globally distributed soils (De Jonge et al., 2014b). Overall, the reconstructed pH is relatively stable throughout Units 3 and 2e (between 5.9 and 6.3), decreases sharply in Unit 2d to a pH of 5.8 and subsequently increases in the transitional Units 2c-a towards constant values of ca. 7.1 in Unit 1. Both in-situ production of marine brGDGTs and changes in the provenance of terrigenous brGDGTs would have an effect on the reconstructed pH. BrGDGTs produced predominantly in situ in the marine sediments (i.e. Unit 1) reflect the increased pH of the marine production site, although the reconstructed pH still underestimates the marine (pore)water pH, that is typically between 7.8 and 8.4 (e.g. Polukhin and Makkaveev, 2014). An extended dataset of brGDGTs in marine sediments, that were inferred to be in-situ produced in the sediments (Weijers et al., 2014), reported reconstructed pH values between 6.1 and 9.9. These authors postulated that the brGDGT distribution possibly reflected the more variable sedimentary porewater pH values, rather than the more stable pH of the water column. Furthermore, this apparent offset may be due to the fact that the soil pH calibration may not be applicable to marine in-situ produced brGDGTs. Alternatively, it may also indicate that the brGDGTs in Unit 1 represent a mixture of in-situ produced and terrestrial brGDGTs. The sediments in Unit 2d and 3 resemble the current brGDGT distribution in the Yenisei Gulf, and thus reflect a mixture of riverine in-situ produced and coastal-cliff derived brGDGTs. The brGDGT distribution in Unit 2d probably represents a strongly enriched brGDGT sub-pool. The reconstructed pH in this unit approaches the average pH encountered in the watershed soils (5; De Jonge et al., 2014a).

Based on a soil calibration, the reconstructed temperatures in the deepest part of the core (Units 2d and 3; between 6 and 9°C) are slightly below those calculated for Unit 1 (between 8 and 11°C). The distinct brGDGT distribution in Unit 2d results in a strongly increased reconstructed MAT at these depths (13-16°C). As the increase in cyclopentane-containing and 6-methyl brGDGTs, typical for marine in-situ production, does not influence the MAT_mrs-based temperatures, it may possibly be an appropriate palaeothermometer for the reconstruction of temperatures in marine sediments where in-situ production is probable. The muted change in temperature since the LGM (±2°C) when compared
with previous reconstructions (6-12 °C; e.g. Frenzel et al., 1992a, 1992b) is possibly due to the problematic reconstruction of the MAT from frozen soils (De Jonge et al., 2015a). However, the effect of a changing provenance of terrigenous brGDGTs, as exemplified in Unit 2d, has a large effect (> 4 °C) on the reconstructed temperature in the Kara Sea system. As in-situ production of riverine brGDGTs has been documented in rivers globally (e.g. Kim et al., 2012; Zell et al., 2014a, 2014b) and the watershed of large rivers drains several different soil types, the brGDGT distribution delivered to the marine system globally can be assumed to consist of several sub-pools with different brGDGT distribution. In the case these sub-pools are exported to a different extent on a geological timescale, or if they differ in degradability, this mechanism has to be taken into account when reconstructing palaeotemperature values in shelf seas around the globe.

6. Conclusions

The brGDGT distribution in the St. Anna Trough reveals large changes in terrigenous material delivered since the last regression of marine glaciers from the trough (minimum age 13.3 ka). The brGDGT and crenarchaeol concentration and the BIT index reflect the transition from a sedimentation regime during a sealevel lowstand, where the proximity of the palaeo Yenisei River mouth and Ob River mouth to the core site results in a strong signal from terrigenous river-derived brGDGTs. The rising sea level caused the increase in the fractional abundance of marine in-situ produced brGDGTs (Ib, IIb, IIC, IIIC, Iib, Iic, IIb’, Iic’, IIA, IIb’ and IIc’) and absolute concentration of crenarchaeol. This increase in marine production is reflected in an increase in the marine in-situ produced brGDGTs. A clear shift in the provenance of terrigenous brGDGTs can be observed at a depth of 150-153 cm bsf, characterized by an increase in the fractional abundance of predominantly brGDGT Ia. The mechanism causing this shift is unknown as both increased continental erosion and increased degradation in the marine sediments can result in this enrichment.

Both in-situ production of brGDGTs and shifts in the provenance of terrigenous brGDGTs have to be taken into account when reconstructing continental palaeoenvironments. Separating these processes from palaeoclimate-induced changes is a challenge for palaeoclimate reconstruction that can only be solved using a multi-proxy approach involving several (lipid-based) biomarkers and sedimentary characteristics.

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Associate Editor – B.E. van Dongen

References


(Siberia): Implications for the use of brGDGT-based proxies in coastal marine sediments.


Table 1

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Table notes:
- Fractional abundances and concentration of brGDGTs down-core in St. Anna Trough sediments and resulting proxy values.
\[ \begin{array}{cccccccccccc}
284 & 36 & 6 & 2 & 24 & 2 & 0 & 14 & 0 & 0 & 7 & 2 & 0 & 5 & 1 & 0 & 0.6 & -0.2 & 20 & 5 & 0.78 & 0.73 & 6.1 & 8 \\
292 & 35 & 6 & 2 & 24 & 3 & 0 & 14 & 0 & 0 & 8 & 2 & 0 & 6 & 0 & 0 & 0.5 & 0 & 23 & 6 & 0.77 & 0.72 & 6.2 & 8 \\
\end{array} \]

*Score on first 2 PCs of PCA_{SAT}.*
### Supplementary Table 1

Bulk OM characteristics of samples.

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Figures

**Fig. 1.** Structures of brGDGTs (I-III) and crenarchaeol (IV). The structures of the hexa- and pentamethylated brGDGTs with cyclopentyl moiety(ies) IIb', IIc', IIIb' and IIIc' are tentatively assigned.

**Fig. 2.** (A) Bathymetric map of the Arctic Ocean, showing the location of the Kara Sea, modified after Jakobsson et al. (2012). (B) Map showing bathymetry of central part of the Kara Sea, with approximate boundaries of the St. Anna Trough indicated. The location of the core site is indicated by “N9”. (C) Map showing current distribution of land masses (dark grey), with extent of the coastline during a sea level drop of 50 m, reflecting the conditions at 11 ka (Fairbanks, 1989; Bauch et al., 2001), indicated in light grey. The map is simplified, as it is based on the current 50 m isobath, and assumes that isostatic rebound was negligible. The course of the palaeo Yenisei and Ob rivers is indicated with an arrow, after Stein et al. (2004).

**Fig. 3.** (A) Lithological description and sampled intervals. The sediments were sampled over an interval of 1 cm, and the top of each interval is indicated with a cross symbol. The arrows indicate characteristic horizons that allowed interpolation with dated horizons as reported by Polyak et al. (1997) or Hald et al. (1999) based on radiocarbon determinations reported in these studies. The colour and pattern per lithological unit, based on the Munsel colour scale and grain size classification, refers to the legend. Downcore distribution of (B) TOC content (%), (C) TN content (%), (D) bulk C/N), (E) $\delta^{13}$Corg, (F) $\delta^{15}$N, (G) TOC-normalized concentration of summed brGDGTs (μg/g TOC), (H) TOC-normalized concentration of crenarchaeol (GDGT IV; μg/g TOC), (I) BIT index values (Eq. 1). The boundaries of the lithological units
and depths (cm below sea floor) are indicated on the scale on the left, yellow lines indicating the presence of oxidized lenses, based on lithological description.

**Fig. 4.** PCA based on standardized fractional abundances of the 15 brGDGTs in the St. Anna Trough core, plotting (A) the scores of the brGDGTs on the first two principal PCs. The scores of the downcore distributions are plotted vs. depth (cm bsf) in panel B and C. The IR values are plotted vs. depth in panel D. For B-D the depth (cm bsf) and boundaries of the lithological units are indicated on the scale on the left, and yellow lines indicate the presence of oxidized lenses, based on lithological description. Panels E-G show brGDGT distribution at three depths (1, 153 and 200 cm bsf) that are characteristic for the three end members of the brGDGT distributions in the core. The colour of the bars refers to the brGDGT structures, as reflected by the legend.

**Fig. 5.** PCA based on standardized fractional abundances of 15 brGDGTs in the trough core and the modern Yenisei and Kara Sea SPM, sediments, coastal cliff and soil samples, described by De Jonge et al. (2015a). Panel A shows the scores of the 15 brGDGTs on the first 2 PCs. Panel B shows the scores of the sites and depths. The downcore distributions are indicated with a number (1-3) that corresponds with the lithological unit, as defined in Fig. 3.

**Fig. 6.** (A) Downcore reconstructed soil pH (based on CBT′, Eqs. 3 and 4) and (B) reconstructed MAT (based on the MATₘ₉₈, Eq. 5). Scale on the left indicates depth (cm bsf) and the lithological units as described in Fig. 3, and yellow lines indicate the presence of oxidized lenses, based on lithological description.
Figure 1
Figure 3

Lithology and stratigraphy:

- Unit 1
- Unit 2a
- Unit 2b
- Unit 2c
- Unit 2d
- Unit 2e
- Unit 3

Depth (cm bsf):

- 0.0
- 0.5
- 1.0
- 1.5
- 2.0

OX I: 10.5 ka

OX II: 0 ka

Lithology and stratigraphy:

- Light olive grey (5Y5/2) - silty clay
- Moderate olive brown (5Y4/4) - silty clay
- Grayish olive (10Y4/2) - silty clay
- Grayish olive (10Y4/2) - sandy clay

TOC (wt.%):

- 0.4
- 0.8
- 1.2

TN (wt.%):

- 0.04
- 0.08
- 0.12
- 0.16

C/N:

- 6
- 10
- 14
- 18

$\delta^{13}C_r$ (‰):

- 2.5
- 3.5
- 4.5
- 5.5

$\delta^{15}N$ (‰):

- 10
- 20

brGDGTs (µg/g TOC):

- 0
- 50
- 100
- 150

Crenarchaeol (µg/g TOC):

- 0.2
- 0.4
- 0.6
- 0.8

BIT:

- 0.0
- 0.2
- 0.4
- 0.6
- 0.8
- 1.0
Figure 4

Explains 20% of the variance

Explains 58% of the variance

Tetramethylated brGDGTs
5-methyl brGDGTs
6-methyl brGDGTs

Depth (cm bsf)

Fractional abundance

Unit 1
Unit 2a
Unit 2b
Unit 2c
Unit 2d
Unit 2e
Unit 3

Fractional abundance

E 1 cm bsf

F 153 cm bsf

G 200 cm bsf
Figure 5

Explains 23% of the variance

Explains 40% of the variance

PC1
PC2

SPM
Sediment
Coastal cliff
Watershed soil

Yenisei River
Mountain Rivers
Yenisei R. mouth
Yenisei Gulf
Yenisei Outflow
Kara Sea
Khalmyer Bay
Khalmyer Gulf
Ob outflow

PC1
PC2
Explanations of the variance

Explains 23% of the variance

Explains 40% of the variance