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Distributions of glycerol dialkyl glycerol tetraethers in surface soils of Qinghai–Tibetan Plateau: implications of GDGT-based proxies in cold and dry regions

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Abstract

The methylation index of branched tetraethers (MBT) and cyclization ratio of branched tetraethers (CBT) based on the distribution of bacteria-derived branched glycerol dialkyl glycerol tetraethers (bGDGTs) are useful proxies for the reconstruction of continental paleotemperature and soil pH. Several calibrations of the MBT-CBT index have been proposed based on global and regional soils and lake sediments. However, little is known about the distribution and applicability of GDGTs proxies in the Qinghai-Tibet Plateau (QTP), a critical region of the global climate system. Here, we investigated 33 surface soils covering a large area of the QTP. Redundancy analysis showed that soil pH was the most important factor affecting GDGT distributions, followed by mean 10 annual precipitation (MAP) and mean annual air temperature (MAT). The branchedisoprenoid tetraether (BIT) index, an indicator for estimation of soil organic matter in aquatic environments, varied from 0.48 to 1 and negatively correlated with soil pH $(r^2 = 0.38)$, suggesting that the BIT index should be used with caution in the QTP. A transfer function of the CBT index-soil pH was established to estimate paleo-soil pH in 15

- the QTP: pH = $8.33-1.43 \times \text{CBT}$ ($r^2 = 0.80$, RMSE = 0.27 pH unit). The local calibration of MBT-CBT index presented a weak, still significant correlation with MAT ($r^2 = 0.36$) mainly owing to the additional influence of MAP ($r^2 = 0.50$). Combining our data with previously reported GDGTs for Chinese soils resulted in a new calibration of MBT/CBT-
- ²⁰ MAT: MAT = $2.68 + 26.14 \times MBT 3.37 \times CBT$ ($r^2 = 0.73$; RMSE = 4.2 °C, n = 164). The correlation coefficient and residual error of this new transfer function is comparable with global calibrations, suggesting that MBT-CBT paleotemperature proxy is still valid in the QTP.



1 Introduction

The Qinghai–Tibetan Plateau (QTP), with an area of over 2.5 million km² and an average elevation of over 4000 m a.s.l., is the world highest and largest mountain plateau. The uplift of the QTP since early Cenozoic profoundly influences regional and global

- ⁵ climates such as the evolution of Asian monsoon which affects lives of over two billion people (An et al., 2001; Li, 1991; Lin et al., 2008; Wang et al., 2008). A number of studies have showed that the QTP is a highly sensitive area for global climate change (e.g., Kang et al., 2010; Liu and Chen, 2000; Qiu, 2008; Yao et al., 2007). The record of 97 meteorological stations located over 2000 m a.s.l. in China reveals that winter temper-
- ature rise is 0.32 °C per decade in the QTP since 1950s, approximately three times the global warming rate (Liu and Chen, 2000). However, the history of instrumental measurement is too short to fully record the evolution of the QTP climate. The reconstruction of the QTP temperature beyond instrumental measurement is challenging because few quantitative proxies are available. Microfossil assemblages based on pollen, diatom
- ¹⁵ or chironomid are commonly used paleothermometers, but they are also influenced by precipitation, salinity, nutrient or other environmental factors (Peterse et al., 2012). In addition, the δ^{18} O value of ice core in the QTP shows a good correlation with Northern Hemisphere temperature (Thompson et al., 1997; Yao et al., 2002). Unfortunately, ice core with a long term, continuous record is lacking in most QTP.

²⁰ Over the past decades, two molecular proxies have been developed for estimation of continental temperature. The first one, namely UK'37, is based on the distribution of haptophyte-produced long-chain alkenones. This proxy was originally proposed for paleoceanography (Brassell et al., 1986; Prahl et al., 1988), but was found applicable for reconstruction of lake surface temperature (e.g., Liu et al., 2006; Zink et al.,

25 2001). A major limitation of UK'37 is that long-chain alkenones are not present in all lakes, despite they have been detected in some QTP lakes (e.g., Chu et al., 2005; Liu et al., 2011, 2006). In addition, salinity also influences the distribution of long-chain alkenones in lakes (Liu et al., 2011). Besides UK'37, the methylation index of branched



tetraethers (MBT; Eq. 1) and cyclization ratio of branched tetraethers (CBT; Eq. 2) can be also used to infer past continental temperature, based on the distribution of branched glycerol dialkyl glycerol tetraethers (bGDGTs) (Weijers et al., 2007b):

$$MBT = \frac{I + Ib + Ic}{I + Ib + Ic + II + IIb + IIc + III + IIIb + IIIc}$$

$$CBT = -\log \frac{Ib + IIb}{I + II}$$

where roman numbers denote relative abundance of compounds in Fig. 1.

According to chemical structure, GDGTs can be divided into two groups, bGDGTs and isoprenoid GDGTs (iGDGTs). The bGDGTs are thought to be of a soil bacterial origin and usually dominate GDGTs in soils (Weijers et al., 2006a), whereas iGDGTs such as crenarchaeol (IV) are major constitutions of GDGTs in the marine environment (Schouten et al., 2013 and references therein). These facts led Hopmans et al. (2004) to develop a branched vs. isoprenoid tetraether (BIT) index to estimate relative abundance of soil organic matter in the marine environment, defined as:

 $\mathsf{BIT} = \frac{\mathsf{I} + \mathsf{II} + \mathsf{III}}{\mathsf{I} + \mathsf{II} + \mathsf{III} + \mathsf{IV}}$

- The value of the BIT index is generally close 1 in soils and 0 in marine environments without terrestrial organic matter inputs (Hopmans et al., 2004; Weijers et al., 2006b). So far, two species of Acidobacteria were identified to produce bGDGTs (Sinninghe Damsté et al., 2011), but the widespread distribution of bGDGTs in soils/peats, lakes and marginal seas suggest that the contribution of other bacteria is likely (Schouten et al., 2013) and references therein). By analyzing bGDGTs in 134 globally distributed
- et al., 2013 and references therein). By analyzing bGDGTs in 134 globally distributed soils, Weijers et al. (2007b) found that the MBT is controlled by mean annual air temperature (MAT) and to less extent by soil pH (Eq. 4), whereas CBT only relates to soil pH (Eq. 5). Such relationship was corroborated by the study of Peterse et al. (2012) who extended the dataset to 276 globally distributed surface soils (Eqs. 6 and 7).



(1)

(2)

(3)

pH = $8.76-2.63 \times \text{CBT}$ ($n = 114; r^2 = 0.70$) MAT = $-6.1-9.35 \times \text{CBT} + 50.0 \times \text{MAT}$ ($n = 114; r^2 = 0.77$) pH = $7.90-1.97 \times \text{CBT}$ ($n = 176; r^2 = 0.70$) MAT = $0.81-5.67 \times \text{CBT} + 31.0 \times \text{MBT}'$ ($n = 176; r^2 = 0.59$)

⁵ where MBT' is the modified form of MBT (Peterse et al., 2012), defined as:

$$\mathsf{MBT}' = \frac{\mathsf{I} + \mathsf{Ib} + \mathsf{Ic}}{\mathsf{I} + \mathsf{Ib} + \mathsf{Ic} + \mathsf{II} + \mathsf{Ib} + \mathsf{Ic} + \mathsf{III}}$$

Since the advent, the MBT(MBT')-CBT paleotemperature proxy has been successfully used for lakes (e.g., D'Anjou et al., 2013; Loomis et al., 2012; Sun et al., 2011), paleosol-loess sequences (e.g., Peterse et al., 2011; Zech et al., 2012), peat (Ballantyne et al., 2010) and marginal seas (e.g., Bendle et al., 2010; Weijers et al., 2007a; Zell et al., 2014). However, a relatively large scatter in global MBT-CBT calibrations (ca. 5 °C for root mean square error; RSME) suggests that other factors besides temperature may influence bGDGTs-based indices (Peterse et al., 2012; Weijers et al., 2007b). For example, in arid and semiarid areas such as western United States where

- ¹⁵ precipitation is the ecological limiting factor, mean annual precipitation (MAP) rather than MAT is the most important factor that affects bGDGT compositions (Dirghangi et al., 2013; Menges et al., 2014). The updated global calibration of MBT'-CBT indices (Peterse et al., 2012) also shows a weak correlation with MAT for those soils from arid regions (MAP < 500 mm). Some studies have demonstrated that a regional calibration</p>
- is needed to improve accuracy of the MBT-CBT paleotemperature proxy (e.g., Blyth and Schouten, 2013; Loomis et al., 2012; Pearson et al., 2011; Shanahan et al., 2013; Zink et al., 2010). More recently, Yang et al. (2014) investigated the GDGT distributions in 108 surface soils mainly from semiarid Chinese Loess Plateau, and established the local calibration of MBT-CBT with much smaller RSME (1.8 °C) than that of the global



(4)

(5)

(6)

(7)

(8)

calibrations (Peterse et al., 2012; Weijers et al., 2007b). However, the dataset of Yang et al. (2014) comprise only one sample from the QTP. Since the applicable range of the MBT-CBT index in Yang et al. (2014) is 5 to 20 °C, it is not clear whether their calibration is valid for the QTP where MAT is generally lower than 5 °C (Qiu, 2008 and 5 Supplement).

Although several researchers reported GDGTs in lakes, mountains, hot springs and paleo-soils from the QTP (e.g., Günther et al., 2014; He et al., 2012; Liu et al., 2013; Wang et al., 2012; Wu et al., 2013; Xie et al., 2012), few quantified the relationship between bGDGT distributions and environmental parameters. Wang et al. (2012) analyzed GDGTs in surface sediments of the Lake Qinghai and surrounding soils, showing that bGDGTs-inferred MAT and soil pH were consistent with measured values. In contrast, Wu et al. (2013) found that bGDGTs-derived MAT was higher than instrumentally

10

measured MAT in Kusai Lake sediments from the QTP. Based on the distributions of GDGTs in surface sediments of the QTP lakes, Günther et al. (2014) developed the lo-

- ¹⁵ cal calibration of MBT'-CBT ($r^2 = 0.59$; RSME = 1.2 °C). However, there are only 9 lake sediments included in Günther et al. (2014). For the application of MBT-CBT indices in lakes, bGDGTs in lake sediments must be exclusively derived from inputs of surrounding soils. However, in-situ production of bGDGTs occurs in various lakes (e.g., Blaga et al., 2009, 2010; Fietz et al., 2012; Pearson et al., 2011; Sinninghe Damsté
- et al., 2009; Tierney and Russell, 2009). Given these facts, direct investigation of soils is needed to understand environmental influences on the bGDGT distributions in the QTP.

Here, we analyzed bGDGTs and iGDGTs in 33 surface soils from the QTP. Our main objectives are to (1) determine the abundance and compositions of bGDGTs and cre-

²⁵ narchaeol in the QTP soils, (2) evaluate the applicability of the BIT index as a proxy for soil organic matter in the QTP; and (3) calibrate the MBT-CBT paleotemperature proxy by compiling data from this study as well as the literatures (Günther et al., 2014; Peterse et al., 2011; Weijers et al., 2007b; Yang et al., 2014) and understand the influence of temperature, precipitation and soil pH on bGDGT distributions in the QTP.



2 Materials and methods

2.1 Sampling

A total of 33 surface soil samples (0–10 cm) were collected during two fieldworks in 2011 and 2012, which cover a large area of the QTP (84.64–101.20° E; 28.24–37.45° N) (Fig. 2). The local climate is dry and cold with MAT of 0.1 °C and MAP of 317 mm from 1951 to 2000 due to high elevation (3066 to 5418 m a.s.l). Sampling sites are typical alpine meadow, alpine steppe or alpine meadow steppe. The extremely dry winter results in the lack of persistent snow cover in most sampling sites.

The soil samples were air-dried and passed through a 2 mm mesh to remove large gravels. Fine roots (if present) were picked up by steel tweezers. Besides these samples, Chinese soils previously reported by Weijers et al. (2007b), Peterse et al. (2011), Yang et al. (2014) and Günther et al. (2014) were also included to estimate relationship between GDGTs and environmental parameters (n = 164). The detailed information on the sampling sites and environmental variables are listed in the Supplement.

15 2.2 Climate data

Direct observation data on temperature and precipitation are generally lacking due to very limited meteorological stations in the QTP. Consequently, we use the World-Clim dataset (Hijmans et al., 2005) to interpolate annual, seasonal and monthly mean precipitation and temperature. The integrated maps are derived from monthly temper-

ature and precipitation values gathered from thousands of weather stations around the world from 1950 to 2000 (47 554 locations for precipitation and 24 542 locations for temperature). The original point data was splines interpolated using latitude and longitude at a fine resolution, making it possible to obtain a reasonable estimation of climatic conditions at individual sites. The WorldClim GIS data used contain annual average of 10 climate variables at a 30 arc seconds resolution (~ 1 km resolution; http://www.worldclim.org). Besides MAT and MAP, additional eight climate variables



were also used to evaluate the relationship between climate and GDGT-based proxy, including Mean Temperature of Wettest Quarter (MWQT), Mean Temperature of Driest Quarter (MDQT), Mean Temperature of Warmest Quarter (MWQT'), Mean Temperature of Coldest Quarter (MCQT), Mean Precipitation of Wettest Quarter (MWQP), Mean Precipitation of Driest Quarter (MDQP), Mean Precipitation of Warmest Quarter (MWQP') and Mean Precipitation of Coldest Quarter (MCQP). A total of 164 sites from different climate regions of China such as semi-arid and arid Chinese Loess Plateau as well as semi-humid and humid areas in southern and eastern China (Supplement) were extracted by 10 climate variables using Arcgis 9.3. Among them, 124 data points show a strong correlation ($r^2 = 0.95$) with the reported data (Yang et al., 2014), suggesting that our approach is doable.

2.3 Soil pH and GDGT analyses

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For pH measurement, soils were mixed with deionized water in a ratio of 1/2.5 (gmL⁻¹). The soil pH values were determined by a pH meter with a precision of ± 0.01 pH. The pH was reported as an average of three duplicate measurements for each sample (± 0.05 pH unit for SD).

The detailed method for GDGTs analyses was described by Wu et al. (2014). About 6 g freeze-dried soils were mixed with 600 ng C_{46} GDGT (internal standard) and ultrasonically extracted with 20 mL dichloromethane (DCM) : methanol (3 : 1 v : v) for 15 min

²⁰ (3×). The combined extracts were concentrated to near dryness by a rotary evaporator and transferred to small vials. The concentrated extracts were completely dried under a mild stream of N₂ and re-dissolved in DCM. The total extracts were separated into two fractions by 5 mL hexane:DCM (9 : 1 v : v) and 5 mL DCM:methanol (1 : 1 v : v), respectively, on silica gel columns. The latter fraction containing GDGTs was dissolved in hexane : propanol (99 : 1 v : v) and filtered through a PTFE filter (0.45 µm pore size).

GDGTs were analyzed on an Agilent 1200 High Performance Liquid Chromatography-atmospheric pressure chemical ionization-Agilent 6460 mass spectrometer (HPLC-APCI-MS). The injection volume was 30 µL. The separation was



achieved on a normal-phase Alltech Prevail Cyano column (150 mm × 2.1 mm; 3 µm) at a constant flow of 0.3 mL min⁻¹. The solvent gradient was: 10 % B (hexane/isopropanol, 9 : 1, v/v; 5 min), then increasing the amount of B from 10 % at 5 min to 80 % in 45 min. The column was flushed with 100 % B for 10 min. The APCI and MS conditions were: vaporizer pressure of 4.2 × 10⁵ Pa, vaporizer temperature of 400 °C, drying gas flow of 6 Lmin⁻¹, temperature of 200 °C, capillary voltage of 3500 V, and corona current of 5 µA (3.2 kV). Peak integration was carried out using Agilent Chemstation. Samples were quantified based on comparisons of the respective protonated-ion peak areas of each GDGT to the internal standard in selected ion monitoring (SIM) mode. The protonated ions were m/z 1302, 1300, 1298, 1296, 1050, 1048, 1046, 1036, 1034, 1032, 1022, 1020, 1018 and 744 (C₄₆ GDGTs).

2.4 Statistical analyses

In order to assess the relationship of bGDGT distributions with environmental variables such as temperature, precipitation and soil pH, we performed redundancy anal ysis (RDA) (van den Wollenberg, 1977), a constrained form of the linear ordination method of principal components analysis (PCA). Species (the relative abundance of nine bGDGTs) were centered and standardized with zero average and unit variance before RDA analysis. The MAP was log-transformed to minimize the skewed distribution. The significance of the explanatory variances within a 1 % confidence interval was
 tested with 999 unrestricted Monte Carlo permutations. Subsequently, a series of partial RDAs (pRDA) were performed to constrain the unique and independent influence of individual environmental parameter alone, as well as compared to all other parameters. All statistical analyses were performed with the CANOCO version 4.5 software (Wageningen UR, USA).



3 Results and discussion

3.1 GDGTs abundance and distribution in QTP soils

Table 1 shows the concentration of bGDGTs and crenarchaeol expressed in ng g⁻¹ dry weight soil (ng g⁻¹ dws) in the QTP soils. Generally, all soils except for a desert soil (P790) contain detectable amounts of GDGTs, ranging from 16 to 3674 ng g⁻¹ dws (230 ng g⁻¹ dws on average). Such concentration is lower than that of soils from Chinese Loess Plateau which varied from 5.7 to 9230 ng g⁻¹ dws (946 ng g⁻¹ dws on average) (Yang et al., 2014), likely attributed to low productivity of soil bacteria and Thaumarchaeota under cold and dry climate.

- ¹⁰ The BIT value of surface QTP soils varied from 0.48 to 1.0 (0.84 on average), reflecting a predominance of bGDGTs over iGDGTs in most soils. This is not surprising since bGDGTs are primarily produced by soil bacteria, while iGDGTs are mainly of an aquatic archaea origin (Schouten et al., 2013 and references therein). However, the mean BIT value of the QTP soils is lower than that of global soils (> 0.9) (Hop-
- ¹⁵ mans et al., 2004; Weijers et al., 2006b). Günther et al. (2014) analyzed seven QTP soils, showing that the mean BIT value was 0.65 ± 0.18 . A similar BIT value (0.71 on average) was observed for surrounding soils of Qinghai Lake (Wang et al., 2012). All these results support the existence of in-situ production of iGDGTs in the QTP soils. Consequently, the BIT index should be used with caution for estimation of soil organic
- ²⁰ matter in the QTP lakes. In the QTP soils, the BIT index decreases with increasing soil pH owing to increased concentration of iGDGTs and decreased concentration of bGDGTs in alkaline soils (Fig. 3). Such change trend agrees with previous reports for different environments (Weijers et al., 2007b; Yang et al., 2014). Higher concentrations of iGDGTs in alkaline soils suggests that alkaline soils provide favorite environments
- for soil Thaumarchaeota, a major source organism for iGDGTs (Kim et al., 2012), while higher concentrations of bGDGTs in acidic soils suggests that bGDGTs-producing bacteria are more optimal at low pH ranges, as proposed by Weijers et al. (2007b).



Among nine bGDGT isomers, compounds II, I and III accounted for 91% of total bGDGTs, while bGDGTs with 1 or 2 cyclopentane moieties were minor constitutes (< 10%; Table 1). Unlike soil pH, both MAT and MAP show weak correlations with bGDGT amounts in the QTP soils ($r^2 = 0.02$; Fig. 3), further confirming that soil pH is a driving factor for the bGDGT amount in the QTP soils. This result contrasts with Menges et al. (2014) that bGDGT amounts in the Iberian Peninsula soils are mainly controlled by precipitation, suggesting that the species of bGDGT-producing bacteria vary space by space or have different responses under different environments.

3.2 Statistical evaluation of bGDGT distributions with environmental parameters in QTP

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A number of studies have demonstrated that temperature, precipitation and pH are the most important factors that affect the bGDGT distributions in soils (e.g., Dirghangi et al., 2013; Peterse et al., 2012; Weijers et al., 2006b, 2007b; Yang et al., 2014). In order to evaluate the contribution of these parameters to bGDGT distributions in ¹⁵ the QTP, RDA was performed (Fig. 4). The first component explains 47.4% of the variance, mainly reflecting the variation in soil pH and to less extent MAP. Soil pH presents strong relationships with relative abundance of bGDGTs I, II, Ib and IIb, which are dominant bGDGT compounds. Thus, pH is the most important factor for bGDGT variations in the QTP soil. The second component of the RDA plot explains 9.4% of

total variance, mainly reflecting the variation in MAT and MAP. The bGDGT-III shows a negative relationship with MAT (in the lower part of RDA), whereas bGDGT-I and Ib present weak positive relationship with MAT (in the upper part of RDA). These results support a presumed physiological mechanism that soil bacteria change the number of methyl branches of bGDGTs with temperature in order to maintain acceptable fluidity of their membranes (Weijers et al., 2007b).

Our RDA result shows that MAT, pH and MAP all have a significant independent effect on the bGDGT distribution in the QTP soils (Table 2). Soil pH explaining 39.7% is the largest contributor to the variance, followed by MAP (27.7%) and MAT (8.7%).



The predominant influence of soil pH on bGDGT distributions was also observed for global soils (Peterse et al., 2012) and Chinese soils (Yang et al., 2014). For the QTP soils, MAP has a stronger influence on the bGDGT distribution than MAT when all three variables are considered to the dataset. In order to estimate the independent, marginal effect of MAT, MAP and pH, pRDA was performed. The explained variance of pH still remains high (30.8%), indicating that bGDGT distributions are indeed linked to soil pH changes, whereas MAT and MAP contribute to a smaller, but about equal amount (ca. 19%) of the variance in the pRDA (Table 2). The comparison between RDA and pRDA suggests an increasing contribution of MAT (from 8.7 to 19.9%) and a decreasing (Table 2). Thus, there is a "synergistic effect" (an "antagonistic action") when MAP and pH (MAT and pH) are considered as covariables, resulting in a positive joint effect of 7.1% for total contribution of pH + MAT + MAP to bGDGT distributions in the QTP soils.

3.3 Calibration of MBT-CBT proxy in QTP

- The MBT and CBT indices have been increasingly used to reconstruct continental paleotemperature and soil pH (Peterse et al., 2009, 2011; Sinninghe Damsté et al., 2008; Weijers et al., 2007a, b). In some semiarid and arid regions, a strong correlation between MAP and MBT was observed (Dirghangi et al., 2013; Menges et al., 2014). Our RDA result (see Sect. 3.2) also supports that MAP (27.7%) has a greater contribution to bGDGT variation than MAT (8.7%). Considering the unique climate in the QTP,
- both global (Peterse et al., 2012; Weijers et al., 2007b) and regional (Yang et al., 2014) calibrations of the MBT-CBT index may not be applicable in the QTP.

3.3.1 Soil pH control on CBT proxy in QTP

The CBT values of the QTP soils ranged from 0.03 to 1.31, spanning about 60 and 50 % of the range for global soil dataset (0 to 2.17) (Weijers et al., 2007b) and Chinese soils (-0.09 to 2.69) (Yang et al., 2014), respectively. A strong linear correlation was



observed between CBT and instrumental measured soil pH (Fig. 5):

 $pH = -1.43 \times CBT + 8.33(r^2 = 0.80, RMSE = 0.27 pH unit, p < 0.001)$

The slope of our calibration (-1.43) is different from that of Chinese surface soils (-2.21) (Yang et al., 2014) as well as global surface soils (-1.97) (Peterse et al., 2012). ⁵ Meanwhile, our RMSE value (0.27 pH unit) is smaller than that of Yang et al. (2014) (0.93 pH unit) and Peterse et al. (2012) (0.80 pH unit). This is likely attributed to that soils in the QTP have smaller spatial heterogeneity and similar vegetation types (e.g., alpine meadow), resulting in a relatively narrow pH range (6.2–8.4). Compared to soil pH, temperature and precipitation have much weaker influence on CBT ($r^2 = 0.44$ and 0.03; Fig. 5). A weak correlation was also observed between MAP and soil pH in the QTP soils ($r^2 = 0.16$). These facts agree with earlier findings for regional and global

soils (Menges et al., 2014; Weijers et al., 2007b; Yang et al., 2014). Therefore, a tight relation of CBT index with soil pH is a common phenomenon in different environments.

3.3.2 Relationship of temperature and precipitation with MBT-CBT in QTP

- ¹⁵ In the QTP soils, four most abundant bGDGTs (bGDGT-I, II, IIb and III) presents different correlations with temperature. Among them, bGDGT-III has the best relation with MAT ($r^2 = 0.37$, p < 0.0001; data not shown), where the correlation of bGDGT-I, II and IIb with MAT is weak ($r^2 < 0.1$, p < 0.001; data not shown). A negative correlation between bGDGT-III and MAT is consistent with the results from global soils (Peterse et al.,
- 20 2012; Weijers et al., 2007b), supporting that the number of methyl group attached to the tetraether backbone of the bGDGTs decreases with increasing MAT. In order to examine if there is a seasonal bias on bGDGT distributions, we plot MBT vs. annual and seasonal temperature and precipitation (Figs. 6 and 7). Overall, MBT did not show much better correlations with seasonal temperature/precipitation, although MCQT and
- ²⁵ MDQT (MCQP and MDQP) have slightly stronger relationship than MAT (or MAP). Based on bGDGT distributions in 32 QTP soils, we developed a calibration to predict MAT and MAP following the approach of Weijers et al. (2007b):



(9)

 $MAT = -4.6 + 34.8 \times MBT - 3.8 \times CBT \quad (r^2 = 0.36, RMSE = 2.4 °C, p < 0.001)$ (10) $MAP = 380.5 + 464.2 \times MBT - 214.7 \times CBT$ (r² = 0.50, RMSE = 64 mm, p < 0.001) (11)

Compared to previous calibrations of MBT(MBT')-CBT paleotemperature proxy for
global soils (r² = 0.59) (Peterse et al., 2012) and Chinese soils (r² = 0.86) (Yang et al., 2014), our calibration has a lower correlation coefficient (r² = 0.36), which is likely attributed to two reasons. Firstly, other environmental parameters besides temperature influence bGDGT distributions. This explanation is supported by recent findings for soils from arid and semiarid areas where hydrological conditions play an important role in bGDGT compositions (Dirghangi et al., 2013; Menges et al., 2014). Since our samplings sites all have MAP of < 500 mm (Supplement), the influence of precipitation on bGDGT distributions is likely. Secondly, due to harsh environmental conditions in the QTP, the meteorological stations are sparse. Consequently, climate data used in our study are derived from interpolation, which surely have larger uncertainty than
instrumental measurement. Nevertheless, the RMSE of our calibration (2.4 °C) is substantially smaller than that of global calibrations (ca. 5 °C) (Peterse et al., 2012; Weijers et al., 2007b) and similar to that of Chinese soils (1.8 °C) (Yang et al., 2014), suggesting

that MBT-CBT indices are still useful paleotemperature proxies in the QTP.

In our calibration, MAP shows a better correlation with MBT-CBT proxy ($r^2 = 0.50$)

- than MAT, suggesting that precipitation is a more important driving factor for the bGDGT distributions. This result contrasts with the result of Yang et al. (2014) for soils from other Chinese regions that MAP has almost 0% contribution to variance in bGDGTs. Most previous studies attributed the strong correlation of MAP and the MBT-CBT index to the covariation of MAP and MAT (Weijers et al., 2007b; Yang et al., 2014). For exam-
- ple, in the dataset of global soils, MAP and MAT are significantly correlated with each other ($r^2 = 0.31$, p < 0.0001) (Peterse et al., 2012). However, in the QTP, a weak correlation was observed between MAP and MAT ($r^2 = 0.06$), indicating that precipitation

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is indeed linked to bGDGT distributions in the QTP soils. Such conclusion agrees well with the results of Menges et al. (2014) for Iberian Peninsula, Dirghangi et al. (2013) for western United States and Wang et al. (2013) for surrounding area of Qinghai Lake. All these results suggest that in the arid and semiarid regions (like QTP), bGDGT-producing bacteria are less productive due to water stress, reflected by lower bGDGT abundance (Table 1), and therefore have to adapt their membranes to water availability at the stress that a productive due to water stress to water availability and therefore have to adapt their membranes to water availability and the stress that a productive due to water stress to water availability and the stress the stress to water availability and the st

ity rather than temperature, resulting in a higher correlation coefficient with MAP than MAT.

3.4 Recalibration of MBT-CBT for Chinese soils

¹⁰ Among previous calibrations of the MBT-CBT paleotemperature proxy, very limited samples are from the QTP (Yang et al., 2014 and references therein). Here, we combine data from our study (33 QTP soils) and literatures including 7 QTP soils (Günther et al., 2014), 104 soils mainly from arid and semiarid Chinese Loess Plateau (Yang et al., 2014), 18 soils from southern China (Weijers et al., 2007b) and 2 soils from ¹⁵ Chinese Loess Plateau (Peterse et al., 2011) to test if the MBT-CBT index is suitable for estimation of paleotemperature in the QTP. Applying a 3-D plane correlation model for 164 Chinese soils, we recalibrated the MBT/CBT-based MAT equation as following

(Fig. 8a):

MAT = $2.68 + 26.14 \times MBT - 3.37 \times CBT$ ($r^2 = 0.73$; RMSE = $4.2 \degree C$, P < 0.001) (12)

The correlation coefficient of MBT-CBT paleotemperature proxy in new calibration (r² = 0.73) is slightly lower than that of Yang et al. (2014) (r² = 0.86), but higher than that of the updated global calibration (r² = 0.59) (Peterse et al., 2012). The RMSE of our calibration (4.2 °C) is close to that of the global calibration (5.0 °C) (Peterse et al., 2012), but larger than that of Chinese Less Plateau (1.8 °C) (Yang et al., 2014). Relatively large scatter of our calibration suggests the bGDGTs-producing bacteria in the QTP may have a different response to soil temperature from other Chinese regions.



Nevertheless, our new calibration has successfully extended the minimum applicable threshold from 5 to -5 °C.

Since MCQT shows a stronger correlation with bGDGTs than MAT (Fig. 6), we test whether the MBT-CBT proxy more relates to the seasonal temperature than MAT. Application of 164 soil dataset results in the following equation (Fig. 8b):

MCQT = -11.05 + 30.82 × MBT - 2.10 × CBT

 $(r^2 = 0.84, \text{RSME} = 3.7^{\circ}\text{C}, P < 0.0001)$

Compared to MAT, MCQT only presents slightly stronger correlation and slightly smaller RSME with the MBT-CBT, suggesting that the MBT-CBT is slightly biased towards win-

ter season. This is unusual since the QTP is under strong influence of Asian Monsoon which is characterized by warm/humid summer (June to August) and dry/cold winter (December to February) (An et al., 2001; Qiu, 2008). So the bGDGTs-producing bacteria are more productive in summer than winter. The reason for the slight bias of MBT-CBT towards winter season is that although more amounts of bGDGTs are produced in summer, more variation in bGDGT compositions occurs in winter. Recent study also found significant non-growing-season soil respiration in the QTP where extremely dry winter causes no persistent snow cover (Wang et al., 2014).

4 Conclusions

By investigating GDGTs in surface soils from the Qinghai–Tibet Plateau (QTP), a unique and critical region of the Earth climate system, we have reached four conclusions on the applicability of GDGTs-based proxies. Firstly, BIT, a proxy for estimation of soil organic matter in aquatic environments, presents large variability from 0.48 to 1.0 (0.84 on average), confirming the presence of in-situ production of iGDGTs in the QTP soils (particularly those alkaline soils). Consequently, the BIT index should



(13)

be used with caution in the QTP. Secondly, pH is the most important contributor to the variance in bGDGTs, followed by MAP and then MAT. With increasing soil pH from 6.2 to 8.4, the bGDGT abundance decreases whereas the iGDGT abundance increases, reflecting different responses of bGDGTs-producing bacteria and iGDGTs-producing ⁵ archaea to the change in soil pH. Thirdly, the CBT index strongly correlates with soil pH ($r^2 = 0.80$), resulting in a local calibration with sufficient accuracy to reconstruct paleo-soil pH in the QTP (RSME = 0.27 pH unit). Compared to previous global and regional calibrations of the MBT-CBT index, our local calibration has a weak, but still significant correlation with MAT ($r^2 = 0.36$). This difference is partially attributed to significant influence of MAP on the MBT-CBT index in the QTP ($r^2 = 0.50$). Therefore, our 10 finding supports that in the arid/semiarid area, hydrological conditions must be considered when interpretation of MBT/CBT climatic records. Finally, the compilation of present and previously reported data resulted in the calibration of MBT/CBT paleotemperature proxy for Chinese soils (MAT = $2.68 + 26.14 \times MBT - 3.37 \times CBT$; n = 164). This new transfer function has a comparable correlation coefficient ($r^2 = 0.73$) and residual 15 error (RMSE = 4.2 °C) as the global calibration, suggesting that the MBT/CBT index is still a useful paleotemperature proxy in the QTP particularly for large climate changes

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such as Quaternary glacial/interglacial cycles.

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Table 1. Concentrations $(ngg^{-1} dws)$ of bGDGTs, iGDGTs and crenarchaeol in surface soils from the QTP. Roman numbers refer to the compounds in Fig. 1.

Site		IIIb	IIIc	II	llb	llc	I	lb	lc	IV	bGDGT	iGDGT*	Total
P751	6.5	1.9	0.0	35.6	10.7	0.5	5.2	1.8	0.7	28.4	62.8	41.2	104.0
P756	4.8	0.6	0.0	14.9	2.8	0.3	2.8	1.4	1.3	11.5	29.0	26.8	55.8
P760	16.7	3.4	0.0	48.2	19.9	0.2	10.7	6.5	0.7	9.6	106.2	24.2	130.4
P765	11.6	3.2	0.0	51.8	13.5	0.9	15.4	7.9	2.4	14.3	106.6	24.6	131.1
P772	23.1	3.8	0.0	67.0	23.5	1.3	14.4	7.8	2.6	22.1	143.5	67.5	211.0
P773	16.1	4.0	0.0	63.3	23.6	0.9	15.0	8.1	2.6	12.8	133.6	27.6	161.3
P775	13.2	3.1	0.0	56.3	21.4	0.9	13.5	7.7	2.0	15.1	118.1	41.9	160.0
P782	8.5	1.2	0.0	25.6	9.6	0.3	3.5	2.0	0.7	16.6	51.4	24.1	75.5
P787	7.1	0.0	0.0	20.0	5.0	0.3	4.2	1.9	0.9	16.1	39.4	55.6	95.0
P796	14.7	3.3	0.0	40.2	20.2	0.7	6.9	3.6	0.3	16.2	90.0	36.4	126.4
P801	3.0	0.5	0.0	8.4	2.7	0.0	1.5	0.7	0.2	8.1	17.0	13.9	30.8
P802	3.4	0.6	0.0	8.9	3.5	0.2	1.5	0.8	0.2	14.7	19.1	24.0	43.1
P804	2.4	0.3	0.0	7.2	1.7	0.0	1.2	0.5	0.4	4.2	13.7	10.1	23.8
P816	1.7	0.2	0.0	10.6	2.5	0.2	3.6	1.5	0.3	2.5	20.5	4.8	25.3
P817	24.8	0.4	0.0	152.9	6.6	0.7	84.9	5.9	0.5	5.3	276.7	11.1	287.7
P818	20.1	0.0	0.0	99.4	4.4	0.4	53.4	4.1	1.8	3.3	183.5	6.6	190.2
P819	24.8	0.8	0.0	143.3	12.6	0.9	79.6	10.7	2.2	4.6	274.9	10.8	285.7
P820	17.2	0.7	0.0	76.0	8.3	0.4	36.3	6.5	0.9	6.1	146.3	12.9	159.3
P821	15.4	0.0	0.0	68.3	7.2	0.0	32.4	6.2	0.6	5.2	130.1	9.1	139.3
P831	4.5	0.5	0.0	13.7	5.4	0.5	2.4	1.5	0.7	8.6	29.3	13.9	43.2
P833	4.2	1.7	0.0	21.0	17.4	1.1	6.7	8.4	0.8	0.3	61.2	1.5	62.7
P839	22.2	0.4	0.0	53.0	2.6	0.0	17.2	1.0	1.0	6.9	97.4	14.1	111.5
P840	5.3	0.0	0.0	13.5	1.3	0.0	2.8	0.5	0.0	5.5	23.4	11.3	34.7
P848	3.0	0.4	0.0	8.6	4.2	0.2	2.2	0.9	0.1	2.8	19.7	8.8	28.5
P851	3.2	0.2	0.0	11.6	0.7	0.1	2.4	0.6	0.2	4.0	19.0	6.7	25.7
P855	1.1	0.2	0.0	5.7	1.1	0.0	1.3	0.4	0.2	2.6	10.0	6.5	16.6
P858	34.3	0.8	0.0	113.4	11.1	1.3	34.8	4.8	4.7	12.0	205.2	23.4	228.6
P859	34.0	0.0	0.0	131.5	5.8	1.0	55.0	3.7	3.3	5.4	234.4	16.4	250.7
P860	34.1	0.5	0.0	157.9	6.3	0.7	76.7	5.3	0.7	3.8	282.1	8.9	291.0
P861	15.7	0.0	0.0	59.7	2.7	0.1	28.1	1.5	1.9	3.3	109.8	7.0	116.8
P862	408.2	3.4	0.2	2035.7	103.7	3.2	1042.8	71.3	6.0	8.2	3674.6	144.2	3818.8
P863	5.1	0.0	0.0	19.2	1.1	0.0	8.7	1.6	0.1	2.2	35.9	3.6	39.5

 * iGDGT denotes the concentration of total isoprenoid GDGTs with m/z from 1292 to 1302 (Schouten et al., 2013).



Table 2. Results of RDA and partial RDA (pRDA) showing the total and unique contributions of soil pH, MAT and MAP to the variance in bGDGT distributions in the QTP soils. All components of variance are significant (p < 0.01).

Variables	Total co	ntribution (%)	Unique contribution (%)			
	p Value	Eigenvalues	<i>p</i> Value	Eigenvalues		
рН	0.002	39.7	0.001	30.8		
MAT	0.045	8.7	0.001	19.9		
MAP	0.001	27.7	0.001	18.3		
All variables	0.001	76.1				
Joint effects				7.1		
MAT + pH	0.001	43.1				
MAT + MAP	0.002	31.8				
MAP + pH	0.001	55.0				





Figure 1. Molecular structures of branched GDGTs (bGDGTs) and one isoprenoid GDGT (crenarchaeol) used in this study.







Figure 2. Locations of soil sampling sites (n = 164) in China. Pink solid circles, green solid circles, black solid circles and gray solid circles denote soil samples from this study, Günther et al. (2014), Yang et al. (2014) and Weijers et al. (2007b)/Peterse et al. (2011), respectively.



Figure 3. Plots of **(a)** soil pH vs. BIT, **(b)** soil pH vs. bGDGT concentration, **(c)** soil pH vs. iGDGT concentrations, **(d)** bGDGT concentration vs. MAT, and **(e)** bGDGT concentration vs. MAP. Data are from surface soils from the QTP. The P862 (a wetland soil) was not included due to unusually high GDGT concentration.







Figure 4. RDA triplot showing the relationship between bGDGTs%, MAT, MAP and soils from the QTP. Numbers in the plot correspond to the soils in Supplement.









Figure 6. Plots of MBT in surface soils vs. annual and seasonal air temperature in the QTP: (a) MAT, (b) MWQT, (c) MDQT, (d) MWQT', (e) MCQT.





Figure 7. Plots of MBT in surface soils vs. annual and seasonal precipitation in the QTP: (a) MAP, (b) MWQP, (c) MDQP, (d) MWQP', (e) MCQP.





Figure 8. 3-D regression plot for the MBT-CBT calibration on MAT (Eq. 12) and MCQT (Eq. 13) for Chinese soils. The circle and triangle denote data from this study and previous reports, respectively (see Supplement).

