EXPLORING THE ENVIRONMENTAL CONTROLS ON THE BACTERIAL AND ARCHAEL GDGT DISTRIBUTION IN PEAT AND FIRST APPLICATION

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Introduction

Glycerol dialkyl glycerol tetraethers (GDGTs) are membrane-spanning lipids from Bacteria and Archaea that are ubiquitous in a range of natural archives and especially abundant in peat. Previous work demonstrated that the distribution of GDGTs mineral soils and marine sediments is correlated to environmental factors such temperature and pH (Schouten et al., 2002; Weijers et al., 2007). However, the influence of these parameters on GDGT distributions in peat is largely unknown. Here we investigate the influence of temperature and pH on the distribution of both archaeal isoprenoidal GDGTs (*iso*GDGTs) and bacterial branched GDGTs (*br*GDGTs) in 470 samples from 96 peatlands from around the world. Our database of modern peats has samples from virtually all modern peat forming environments with a broad range in mean annual air temperature (MAAT, ranging from −8 to 27 °C) and pH (ranging from 3 to 8). We developed peat-specific temperature and pH calibrations that were then applied to early Paleogene lignites to reconstruct terrestrial temperatures during this greenhouse period.

Results from modern peats

Our results demonstrate that the degree of cyclisation of *br*GDGTs in peat is positively correlated with pH, $pH = 2.49 \times CBT_{peat} + 8.07$ (n = 51, $R^2 = 0.58$, RMSE = 0.8) and the degree of methylation of *br*GDGTs is positively correlated with MAAT, $MAAT_{peat}$ (°C) = $52.18 \times MBT_{5me}' - 23.05$ (n = 96, $R^2 = 0.76$, RMSE = 4.7 °C, see figure 1). These peat-specific calibrations are distinct from the available mineral soil calibrations. In light of the error in the temperature calibration (~ 4.7 °C), we urge caution in any application to reconstruct late Holocene climate variability, where the climatic signals are relatively small, and the duration of excursions could be brief. Instead, these proxies are well-suited to reconstruct large amplitude, longer-term shifts in climate such as deglacial transitions and deep-time applications.

We found no significant correlation between the relative abundance of individual *iso*GDGTs with 0-4 cyclopentane rings (including crenarchaeol) in peat and pH or MAAT. Also the ring index (RI) and TEX_{86} have no clear correlation with MAAT or pH. The lack of correlation between the distribution of *iso*GDGTs and MAAT is likely because the *iso*GDGT pool is derived from a mixture of GDGT-producing archaeal communities that thrive in peats.

Surprisingly, for the first time we report *iso*GDGT-5 (as well as *iso*GDGT-6 and -7) in modern mesophilic settings. In the modern database their distribution appears to be controlled by both pH and MAAT. *iso*GDGT-5 is only present in significant amounts (>1% of total *iso*GDGTs) in tropical peats with a pH < 5.1 and MAAT > 19.5 °C. It is absent in all peatlands with a pH > 5.1 or MAAT < 12 °C and present only in trace proportions (<1%) in peatlands with MAAT between 12°C and 19.5 °C. The distribution of these compounds in modern peats provides strong evidence that proportions greater than 1% of the total *iso*GDGTs is evidence for tropical peatlands with combined high temperatures (>19.5 °C) and low pH (<5.1). We suggest that the proportional abundance of *iso*GDGT-5 (as well as isoGDGT-6) likely increases with temperature, although we have insufficient data to convert that into an empirical calibration.

We also compared the relative abundance of H-GDGTs, GDGTs with a covalent bond between the two alkyl chains, over regular GDGTs to peat pH and MAAT. Both the relative abundance of H-*iso*GDGTs and H-*br*GDGTs is correlated with temperature (R^2>0.5) with a higher amount of H-GDGTs in tropical low-latitude compared to high-latitude peats. These results suggest that both archaeal and bacterial H-GDGT-producing organisms respond similarly to changes in the environment or suggest that similar diagenetic processes control the formation of both types of H-GDGTs during burial.

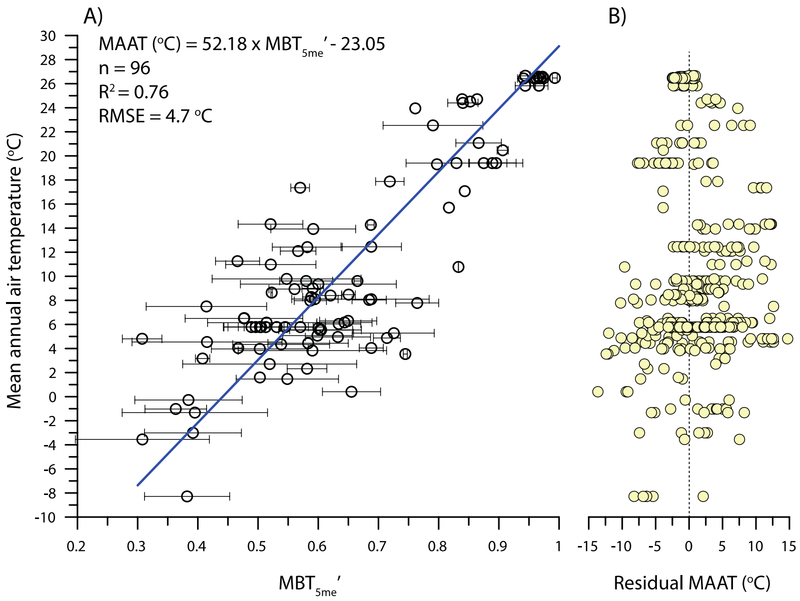

Figure 1 *Average MBT5me' for each peat versus MAAT (black circles). Horizontal error bars represent 1σ and are based on the analysis of multiple horizons from the same peat. Also shown is the residual MAAT of all analyzed peat samples (yellow circles).*

Application to ancient peat

We then determined the GDGT distribution in a range of early Paleogene lignites from Europe (46 and 48 °N paleolatitude), New Zealand (57 °S paleolatitude), and India (0 to 5 °N paleolatitude) using immature lignites formed during the early Paleogene. Using our newly developed peat-specific bacterial organic geochemical proxies we demonstrate that mean annual temperatures in peatlands at the mid/high latitudes were in excess of 22.5 °C. These temperatures are higher than most existing terrestrial temperature estimates (Huber and Caballero, 2011), but similar to estimates of sea surface temperatures (SSTs) of the early Paleogene (Inglis et al., 2015). The identification of *iso*GDGT-5 in all lignites further supports high terrestrial temperatures at the mid/high latitudes. Our results reinstate the debate about early Paleogene temperatures by demonstrating that terrestrial temperatures were not only much higher than present at mid/high latitudes but could have been analogous to the modern tropics, results that can be used to constrain the next generation of climate models.

References

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