



Methylation and cyclisation of branched glycerol dialkyl glycerol tetraethers as temperature and pH proxies

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Branched glycerol dialkyl glycerol tetraethers (GDGTs) containing 0 to 2 cyclopentyl moieties were initially detected in peat deposits [1]. Through the analysis of a global set of soils samples Weijers et al. [2] showed that these GDGTs, probably of bacterial origin, are produced in situ in these soils. Rivers and direct run-off transport these compounds, together with other soil organic matter, to marine [3] and lake sediments [4, 5].

Recently, Weijers et al. [6] defined two indices that are based on branched GDGTs that are distinctively influenced by two environmental factors. The cyclisation ratio of the branched tetraethers (CBT) is related to soil pH and the methylation index of branched tetraethers (MBT) is related to temperature and soil pH. Lake sediments are often used for reconstructing past climatic changes. The presence of branched GDGTs in lake sediments potentially allows reconstruction of temperature and pH of the lake drainage area.

We performed organic geochemical analyses on a series of surface sediments from 82 lakes characterised by variable amounts of soil organic matter and from different geographical locations to establish the application of the MBT/CBT as a continental palaeothermometer.

Results show that in all of the 82 lakes substantial amounts of branched GDGTs are present (0.1-28% of total GDGTs). Besides the branched GDGTs crenarchaeol was also found in appreciable amounts (on average 23% of the total GDGTs). In the lakes from the northern hemisphere in fact the dominant GDGT is crenarchaeol (38% of total GDGTs) followed by the pentamethylated branched GDGT. In the southern hemisphere on the other hand we observe the hexamethylated branched GDGT as the dominant GDGT and crenarchaeol is here ten times less abundant than in the north (on average 3% of total GDGTs only).

The CBT, as defined by Weijers et al. [6], for the entire data set ranges from values close to 0 (0.14 for Lake Ohrid) to 1.7 (Lake Nyos). The MBT ratio, also as defined by Weijers et al. [6], for the sediments analyzed in this study varies between 0.09 (Lake Bourget) and 0.91 (Brazil52). A strong linear correlation was found between CBT and pH of the lakes in the northern hemisphere while in the southern hemisphere there was no correlation between CBT and pH or CBT and MAT. Mean annual air temperatures (MAT) and pH values were calculated using the CBT and MBT values and the soil calibration from Weijers et al. [6]. The temperatures calculated in this way were considerably lower than the measured values. Moreover the MBT to temperature correlation shows considerable scatter ($r^2 = 0.48$). Still, we observe that the lakes from high northern latitudes with lower temperatures have overall lower MBT values compared to the ones at southern lower latitudes, supporting previous studies [6,7]. Although the lacustrine environment offers a unique opportunity for calibrating MBT and CBT as it averages out small scale variability, it is not clear yet if only pH and temperature are the driving factors. Alternatively the balance between the allochthonous input and in-situ production of branched GDGTs might play an important role. Controlled growth experiments would ultimately be needed to unravel the individual effects of environmental parameters on the organisms producing branched GDGTs.

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