IDENTIFICATION OF NOVEL 7-METHYL AND CYCLOPENTANYL BRANCHED GLYCEROL DIALKYL GLYCEROL TETRAETHERS IN LAKE SEDIMENTS

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Intruction

Branched glycerol dialkyl glycerol tetraethers (brGDGTs) are bacterial membrane lipids that are widely used as valuable paleoenvironmental proxies. The recently discovered 6-methyl brGDGTs improved the accuracy of the proxies for temperature "methylation branched tetraethers (MBT)" and soil pH "cyclization branched tetraethers (CBT)". However, the calibration uncertainties are still substantial for brGDGT-derived proxies (e.g., 5 °C for MBT'$_{5ME}$).

Results

Here we report a series of novel 7-methyl brGDGT isomers that co-eluted with the known 5- and 6-methyl brGDGTs in commonly applied normal phase high performance liquid chromatography (HPLC). Using an optimized HPLC gradient the mean relative abundance of 7-methyl brGDGTs could be determined to be in the range of 6 % of the total brGDGTs in Chinese and Cameroon lake sediments. In addition to the 7-methyl brGDGTs, we identified a novel pentamethylated brGDGT based on the mass spectra of ether cleaved hydrocarbon products. IIa$_7$ shows the best correlation with sediment pH (R^2 = 0.44, root-mean-square error = 0.26 pH unit), a result that motivates the re-analysis of brGDGTs in soils and sediments in order to determine the source of 7-methyl brGDGTs and to further reassess brGDGTs-based proxies.

Conclusions

We identified a novel class of brGDGTs with methylation at C-7 that contribute 6.2% of the total brGDGTs in Chinese lake sediments (IIIa$_7$ 1.4%, IIIb$_7$ 0.3% and IIa$_7$ 4.5% of total brGDGTs) and 4.3% in *Lake* of *Baleng in Cameroon* (IIIa$_7$ 1.4% and IIa$_7$ 2.9% of total brGDGTs).
IIa$_7$ shows the best correlation with sediment pH in Chinese lake sediments, this finding has important implications for the improvement of existing pH proxies such as CBT and IBT based on brGDGTs. Follow-up studies should acknowledge the presence of these novel compounds and test whether 7-methyl brGDGTs could be attributed to specific environmental conditions or microorganism.

In addition we found that the known brGDGTs (*m/z* 1034) with one cyclopentane moiety, IIb_5 and IIb_6, are actually composed of two structural isomers that can further complicate previously defined brGDGT-based proxies. The mechanism upon which bacteria produce different brGDGT membrane lipid isomers is still needed to be further studied based on improved HPLC methods that allow individual quantification of tetraether compounds.

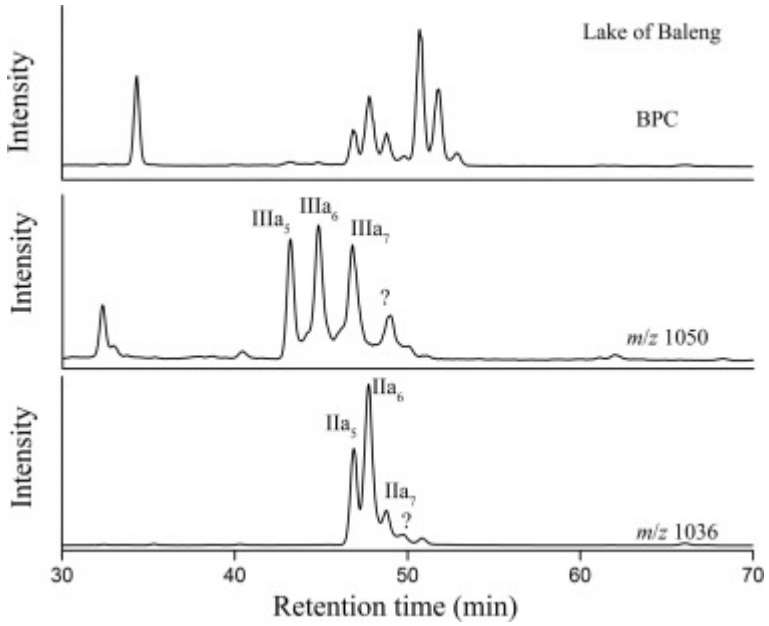

Fig. 1 HPLC–APCI-MS chromatograms of brGDGTs from the sediment of Lake of Baleng in Cameroon, including BPC, m/z 1050 and 1036 extracted ion chromatograms.