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Data Analysis 2: Branched glycerol dialkyl glycerol tetraether paleothermometry

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Title: Branched Glycerol Dialkyl Glycerol Tetraether Paleothermometry

Throughout this series of videos, natural samples were extracted and purified in search of organic compounds, called biomarkers, that can relate information on climates and environments of the past. One of the samples analyzed was sediment. Sediments accumulate over geologic time in basins, depressions in the Earth into which sediment flows through the action of fluid (water or air), movement, and gravity. Two main types of basins exist, marine (oceans and seas) and lacustrine (lakes). As one might guess, very different types of life live in these settings, driven in large part by the difference in salinity between them. Over the last few decades, organic geochemists discovered a toolbox of biomarker proxies, or compounds that can be used to describe climate or environment, some of which work in marine environments and some of which work in lacustrine. We turn our attention here to the lacustrine realm and branched glycerol dialkyl glycerol tetraethers (**Figure 1**).

In this section we focus on analysis of terrestrial paleotemperature using branched glycerol dialkyl glycerol tetrathers (**Figure 1**; brGDGTs) and the MBT/CBT proxy. This proxy was initially described by Weijers *et al.* (2007) and is based on the distribution of ring and branch structures in brGDGTs. They found that the cyclization of branched tetraethers (CBT) was directly related to soil pH.

$$CBT = -\log((Ib + IIb) / (I + II))$$

And that the methylation of branched tetraethers (MBT) was determined by mean annual soil temperature (MAT) and, to a lesser extent, soil pH.

$$MBT = (I + Ib + Ic) / (I + Ib + Ic) + (II + IIb + IIc) + (III + IIIb + IIIc)$$

Thus, taken together and calibrated, MBT/CBT relates the distribution of brGDGTs to both soil temperature and pH.

$$MBT = 0.122 + (0.187 \times CBT) + (0.020 \times \mathbf{MAT})$$

Branched GDGTs are thought to be membrane spanning lipids and their production was initially attributed to anaerobic Acidobacteria bacteria living in soils and peat (Damste *et al*., 2011; Hopmans *et al*., 2004; Weijers *et al*., 2006a; Weijers *et al*., 2006b), but subsequent work suggested they could also be produced in oxic and anoxic lake and marine water columns and sediments (Chappe *et al*., 1982; Peterse *et al*., 2009; Tierney and Russell, 2009; Zhu *et al*., 2011). The hypothesis holds that Acidobacteria transform sites of methylation into cyclizations in response to lowering temperature in order to increase unsaturation (cyclization effectively removes two hydrogen atoms) and maintain

membrane fluidity (by analogy, saturated fat (butter) is a solid a room temperature while unsaturated fat (olive oil) is a liquid), but branched GDGTs have not yet been identified as the main membrane lipids in Acidobacteria cultures. Thus their exact provenance is unknown.

Calibration of branched GDGTs to environmental variables (temperature, pH, salinity, precipitation, etc.) is a topic of widespread research. Organic geochemistry laboratories all over the world are involved in the task of developing both global (PEARSON *et al*., 2011; WEIJERS *et al*., 2007) and regional (DAMSTE *et al.*, 2008; LOOMIS *et al*., 2012; TIERNEY *et al*., 2010) calibrations between branched GDGTs and (primarily) temperature. Thus, the equations given above are regularly being refined and perfected.
Branched GDGTs are usually extracted from lacustrine sediments, although coastal marine sediments have also been investigated. The extracts undergo a silica gel column to purify the GDGTs from other compounds which may not be LC amenable or that may co-elute with GDGTs chromatographically. The GDGTs come out in the polar fraction that elutes in methanol.

Once the total lipid extract is purified, the extracted and purified sample is run on a high performance liquid chromatograph coupled to a chemical ionization mass spectrometer. The relative concentration of the GDGTs is determined by obtaining the area under the curve for the selected mass ion (m/z; **Figure 1**) for each of the compounds on computer software designed for just this purpose (such as Agilent Chemstation). These areas are then put into the selected calibration equation in order to arrive at a paleotemperature determination.

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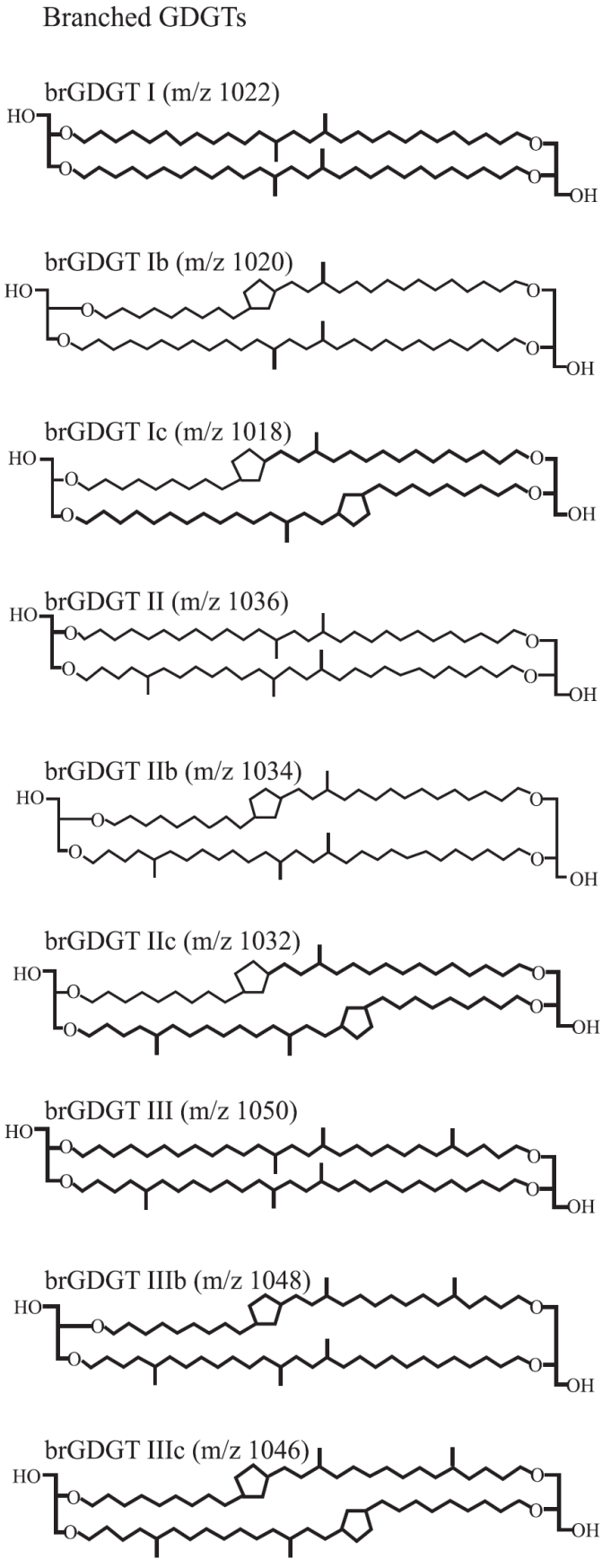

Figure 1. Structures of the branched GDGTs used for calculating temperature via MBT/CBT proxy (used with permission of Dr. Isla Castañeda, who produced the image)