PRODUCTION OF BRANCHED TETRAETHER LIPIDS IN THE MARINE REALM: SVALBARD FJORDS REVISITED

F. Peterse[1] and J.S. Sinninghe Damsté[1,2]

[1] Utrecht University, Utrecht, The Netherlands
[2] NIOZ Royal Netherlands Institute for Sea Research, and Utrecht University, Texel, The Netherlands

Branched glycerol dialkyl glycerol tetraethers (brGDGTs) are membrane lipids of bacteria. Their ubiquitous occurrence in surface soils worldwide has lead to the assumption that they are primarily produced in soils, which is supported by the decreasing trend in brGDGT concentrations with increasing distance from land that is generally found in marine sediments. Due to the relation of the distribution of brGDGTs with mean air temperature, these compounds can be used as a proxy for continental temperature reconstruction. Indeed, the initial application of the brGDGT-paleothermometer on a sediment core from the Congo River fan resulted in a seemingly reliable temperature record of deglacial tropical Africa (Weijers et al., 2007). However, a study comparing brGDGT distributions in fjord sediments and nearby soils on Svalbard indicated that marine brGDGT production had to take place in order to explain observed distributional offsets (Peterse et al., 2009). As a consequence, brGDGTs in coastal marine sediments represent a mixed signal from soil and aquatic in situ production, so that the temperature transfer function based on brGDGTs global surface soils can actually not be directly applied.

Here, we revisit Svalbard data to further identify and characterize brGDGT production in the marine realm. We use the chromatography method that enables the separation 5- and 6-methyl brGDGT isomers to re-analyse the Svalbard soils and fjord sediments collected in 2007, and add a second set of sediments collected at the same locations in 2008. For the latter we separated core lipids (CL) from intact polar lipid (IPL)-derived fractions to identify the signature of in situ produced brGDGTs. We find that brGDGTs in both soil and fjord sediments have a large contribution of 6-methyl brGDGTs. Although the isomer ratio (IR) of pentamethylated brGDGTs is lower, and the IR_{hexa} higher in the fjord sediments than in the soils, all values are still within the range of the global soil dataset, and can thus not be used to identify in situ production in coastal marine settings (cf. Sinninghe Damsté, 2016). On the other hand, the fjord sediments are immediately separated from the soils when plotting their brGDGT fractional abundances in a triplot (Fig. 1a), as does plotting the degree of cyclisation (#rings) of tetra- and penta-methylated brGDGTs (Fig. 1b). BrGDGTs in the fjord sediments are characterized by relative amounts of hexamethylated brGDGTs and #rings that are higher than in any other environment studied so far, suggesting that the soil contribution to these sediments is negligible. Unexpectedly, IPL-derived brGDGTs in some samples have a substantially lower $\#rings_{tetra}$ (up to 0.52) than the CLs. Smallest offsets (~0.15) in $\#rings_{tetra}$ between CL and IPL-derived brGDGTs are found at the head of the fjord, where the input glaciers reduces the salinity of the water. The offset peaks towards the open ocean, with increasing salinity and at a water depth of about 200-300 m.

Although this study confirms that a high $\#rings_{tetra}$ of CL brGDGTs can be used to identify in situ production in coastal marine sediments, the generally lower $\#rings_{tetra}$ and large variation for IPL-derived brGDGTs in the Svalbard fjord sediments suggests that brGDGTs must be produced in different configurations during the year in order to match the pool of CLs in the

sediment. Alternatively, assuming that the microbial community in the fjord has remained constant, this may suggest that the producers of brGDGTs incorporate additional cyclopentane moieties in the tetramethylated brGDGTs during their lifespan.

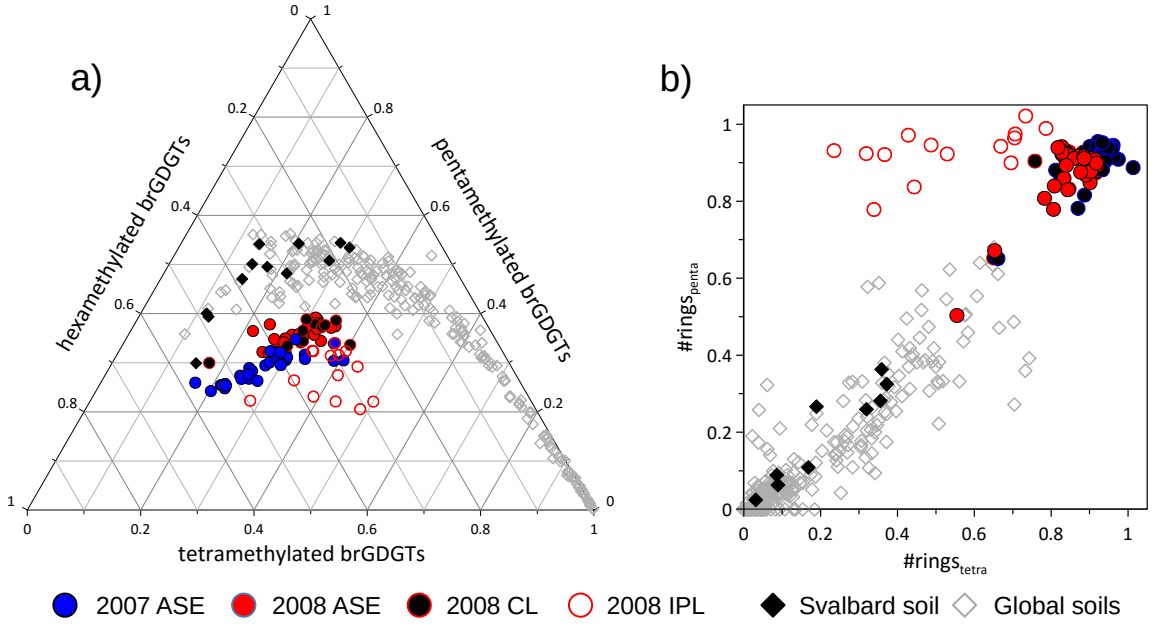

Figure 1 *a) Triplot showing brGDGT distributions, and b) the degree of cyclisation (#rings) of tetramethylated versus pentamethylated brGDGTs in Svalbard fjord sediments and soils collected in 2007 and 2008. Soils and sediments were either extracted using accelerated solvent extractor (ASE), or using Bligh & Dyer and subsequent separation into core lipid (CL) and intact polar lipid (IPL)-derived fractions. BrGDGTs in soils from the global soil calibration set (De Jonge et al., 2014) are plotted for comparison.*

References

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