THE ISOTOPIC CHARACTERISATION OF TETRAETHER LIPIDS BY HIGH TEMPERATURE GC-IRMS

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Introduction

Large polar compounds such as glycerol dialkyl glycerol tetraether lipids (GDGT) are widely used as biomarkers for organisms or biogeochemical processes (Schouten et al., 2013), and their stable carbon and hydrogen isotopic composition bear the potential to provide large amounts of information about source organism, provenance, hydrology and biogeochemistry. Due to their high molecular weight, analysis is usually carried out by liquid chromatography-mass spectrometry rather than gas chromatography (GC). In order to render GDGTs amenable to compound specific isotope ratio mass spectrometry (GC-IRMS), chemical degradation procedures must be applied (Schouten et al., 1998). One of their disadvantages is the inherent loss of structural complexity and, consequently, biomarker specificity. Further, the harsh chemical treatment could potentially affect the stable carbon and hydrogen isotopic composition. However, high temperature GC-methods (HTGC, up to 430°C) are applicable to the analysis of GDGTs (Nichols et al., 1993). More recently, HTGC coupled to time-of-flight mass spectrometry has been employed to produce spectra of GDGTs from an archaeal culture and in environmental samples as their trimethylsilyl ether-derivatives (Lengger et al., in prep.; Sutton and Rowland, 2012). Here, we modified these methods for HTGC-IRMS, to determine the stable hydrogen isotopic composition of GDGTs.

Results

A sample from a Black Sea methane seep microbial mat, and polar fractions obtained from a mixture of marine sediments, and an ombrotrophic peat bog, were analysed. GC-IRMS with a short column of high temperature stability and a slightly modified interface was used and allowed the use of an *n*-alkane standard mixture for normalisation onto the V-SMOW-SLAP line (Mix B, A. Schimmelmann, University of Indiana), but also the accurate determination of the δ^2H values of a C_{40}, C_{50} and C_{60} *n*-alkane and of triacylglycerides with 45 to 69 carbon atoms (10 ‰ precision, comparison to bulk IRMS), and the analysis of GDGTs. The GDGTs from the methane seep (Fig. 1) showed, as expected, δ^2H values very close to those of archaeol and hydroxyarchaeol (-220 ‰ for the GDGTs and -240/-250 ‰ for archaeol and hydroxyarchaeol, respectively). GDGT-0 in the marine sediment sample and Crenarchaeol were slightly more depleted (both -340 ‰). These values compare favourably to the natural ^2H abundances determined from chemically degraded GDGTs in a marine sediment, which revealed δ^2H values of -295 to -349 ‰ (Wegener et al., 2012). brGDGTs and GDGT-0 from the ombrotrophic peat bog revealed δ^2H values of -205 and -226 ‰, respectively, indicating that these values are related to source water δ^2H values, and microbial metabolism.

Conclusions

HTGC-based methods were used to isotopically characterise the stable isotopic composition of GDGTs in environmental samples. HTGC-IRMS revealed the stable hydrogen isotopic composition of GDGTs to be comparable to other biomarkers and values determined *via* degradation. HTGC-based analysis (δ^2H and $\delta^{13}C$) enables the isotopic characterisation of

intact GDGTs in environmental samples. Better knowledge of their isotopic distributions will prove useful for provenance and source determinations, and hydrological and biogeochemical characterisations.

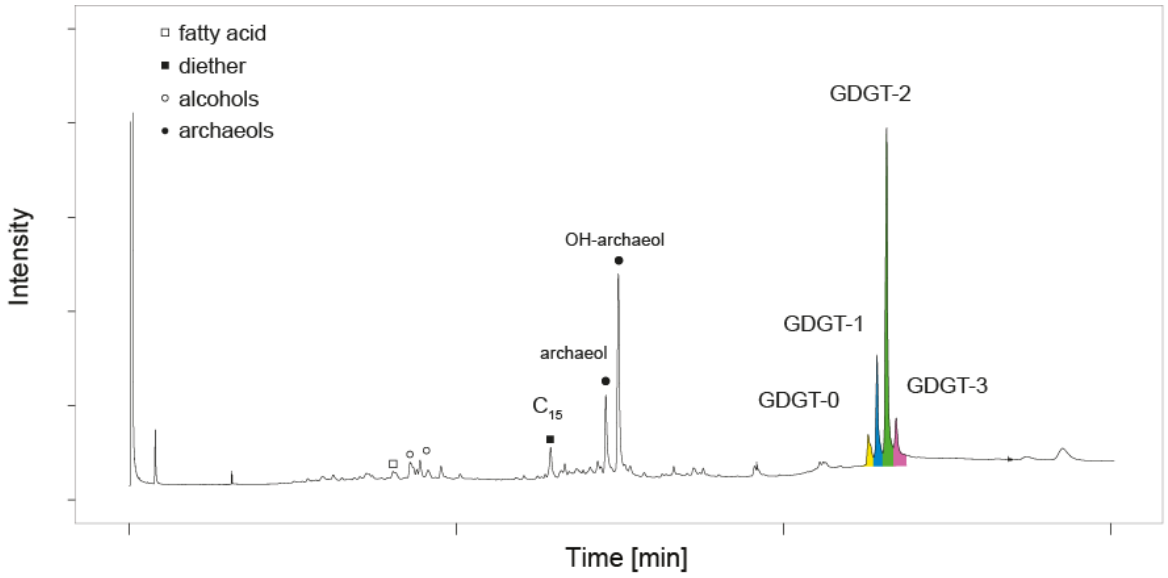

Figure 1 *GC chromatogram of a sample from a methane seep in the Black Sea, showing di- and tetraether lipids.*

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