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Geochimica et Cosmochimica Acta 125 (2014) 476–491

Geochimica et Cosmochimica Acta

www.elsevier.com/locate/gca

In situ produced branched glycerol dialkyl glycerol tetraethers in suspended particulate matter from the Yenisei River, Eastern Siberia ☆

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Received 10 May 2013; accepted in revised form 18 October 2013; available online 1 November 2013

Abstract

Soil-derived branched glycerol dialkyl glycerol tetraethers (brGDGTs) in marine river fan sediments have a potential use for determining changes in the mean annual temperature (MAT) and pH of the river watershed soils. Prior to their incorporation in marine sediments, the compounds are transported to the marine system by rivers. However, emerging evidence suggests that the brGDGTs in freshwater systems can be derived from both soil run-off and in situ production. The production of brGDGTs in the river system can complicate the interpretation of the brGDGT signal delivered to the marine system. Therefore, we studied the distribution of brGDGT lipids in suspended particulate matter (SPM) of the Yenisei River. Chromatographic improvements allowed quantification of the recently described hexamethylated brGDGT isomer, characterized by having two methyl groups at the 6/6′ instead of the 5/5′ positions, in an environmental dataset for the first time. This novel compound was the most abundant brGDGT in SPM from the Yenisei. Its fractional abundance correlated well with that of the 6-methyl isomer of the hexamethylated brGDGT that contains one cyclopentane moiety. The Yenisei River watershed is characterized by large differences in MAT (>11 °C) as it spans a large latitudinal range (46–73°N), which would be expected to be reflected in brGDGT distributions of its soils. However, the brGDGT distributions in its SPM show little variation. Furthermore, the reconstructed pH values are high compared to the watershed soil pH. We, therefore, hypothesize that the brGDGTs in the Yenisei River SPM are predominantly produced in situ and not primarily derived from erosion of soil. This accounts for the absence of a change in the temperature signal, as the river water temperature is more stable. Using a lake calibration, the reconstructed temperature values agree with the mean summer temperatures (MST) recorded. The brGDGTs delivered to the sea by the Yenisei River during this season are thus not soil-derived, possibly complicating the use of brGDGTs in marine sediments for palaeoclimate reconstructions.

1. INTRODUCTION

Branched glycerol dialkyl glycerol tetraethers (brGDGTs) are ubiquitous membrane lipids in peat and soils. They are derived from bacteria and possess 4–6 methyl substituents ('branches') on the linear C_{28} alkyl chains and up to two cyclopentyl moieties formed by internal cyclization (Fig. 1;

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http://dx.doi.org/10.1016/j.gca.2013.10.031

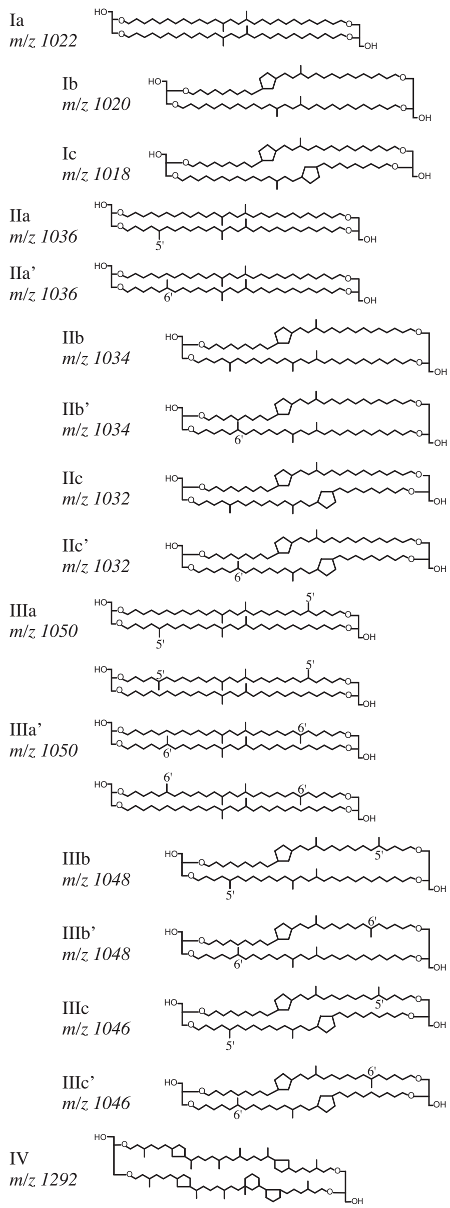

Fig. 1. Chemical structures of branched GDGTs (I–III) and crenarchaeol (IV). The chemical structures of the penta- and hexamethylated brGDGTs with cyclopentyl moiety(ies) IIb′, IIc′, IIIb′ and IIIc′ are tentatively assigned.

Sinninghe Damsté et al., 2000; Weijers et al., 2006a). The distribution of the different brGDGTs depends on the prevailing mean annual temperature (MAT) and soil pH (Weijers et al., 2007). With decreasing temperature, the number of methyl groups in the alkyl chains increase and with a higher soil pH the prevalence of the cyclopentyl moieties will increase. A global soil calibration is thus based on the methylation of branched tetraethers (MBT) and cyclisation of branched tetraethers (CBT) ratios (Weijers et al., 2007). This calibration was recently extended by Peterse et al. (2012), proposing a modified MBT ratio, the MBT′.

Branched GDGTs have also been found in coastal marine sediments, where they are likely deposited by rivers, after erosion and transport of soil particles (Hopmans et al., 2004). The amounts of soil-derived bacterial brGDGTs and the marine Thaumarchaeotal isoprenoid GDGT (iGDGT) crenarchaeol (Sinninghe Damsté et al., 2002) can be expressed in the branched isoprenoid tetraether (BIT) index, which has been used to estimate the amount of soil-derived material in aquatic environments (Hopmans et al., 2004). Furthermore, the distribution of soil-derived brGDGTs in river fan sediments can be used to reconstruct the continental MAT and soil pH of the watershed of the river and this principle has been successfully used for palaeoclimate reconstructions (Weijers et al., 2007). However, complications can arise if the watershed is affected by changes in the supply of organic matter and the source area of the sediments (Bendle et al., 2010). Furthermore, overestimations of MAT have been reported (Schouten et al., 2008; Donders et al., 2009). Recently, structural isomers that partially co-elute with the brGDGTs that are used for these proxy calculations have been described (De Jonge et al., 2013; IIa, IIa′, IIIa, IIIa′; Fig. 1). The abundance and variability of these isomers in the environment is currently unknown, as is their impact on MAT and pH reconstructions based on CBT/MBT indices.

BrGDGTs also occur ubiquitously in lake sediments (e.g. Blaga et al., 2009, 2010) and, since they were thought to be derived from erosion of surrounding soils, the sedimentary record of the BIT index has been applied as an indicator of past variations in the intensity of rainfall in an equatorial lake (Verschuren et al., 2009). The CBT/MBT indices of sedimentary brGDGTs have subsequently also been applied to a variety of lakes, to reconstruct local MAT and pH changes in their watershed (e.g. Tierney et al., 2010, 2012; Niemann et al., 2012; Wang et al., 2012). However, in these studies the CBT/MBT-inferred temperatures using soil-based calibrations often considerably underestimated MAT. The discrepancy between soil and lake brGDGT distributions points to potential in situ production of brGDGTs in lakes (Tierney and Russell, 2009; Sinninghe Damsté et al., 2009; Loomis et al., 2011). Since the prevailing lake temperature still controls the distributions of the brGDGTs in the surface sediments of the lakes this has led to alternative (aquatic) calibrations being created (Tierney et al., 2010; Pearson et al., 2011; Sun et al., 2011; Loomis et al., 2012).

Although rivers are the main pathway for the transport of brGDGTs to ocean sediments, there is a remarkable lack of studies that assess the potential effect of in situ production in rivers. The occurrence of branched GDGTs and crenarchaeol has been reported in suspended particulate material (SPM) from the European Rivers Rhine, Meuse, Niers, and Berkel (Herfort et al., 2006) as well as in the Têt and Rhone Rivers in France (Kim et al., 2007). BrGDGTs have also been shown to occur in three East-Siberian Rivers, the Lena, Indigirka and Kolyma Rivers (van Dongen et al., 2008). A small set of sediments from a tropical river system (Tierney and Russell, 2009), showed an offset between the prevailing soil and river CBT/MBT values. Kim et al. (2012) compared the brGDGT distributions in the Amazon River SPM and sediments and soils from the Amazon watershed and concluded that aquatic