Organic Geochemistry 83-84 (2015) 158–169

Contents lists available at ScienceDirect

Organic Geochemistry

journal homepage: www.elsevier.com/locate/orggeochem

Archaeal and bacterial tetraether lipids in tropical ponds with contrasting salinity (Guadeloupe, French West Indies): Implications for tetraether-based environmental proxies

Arnaud Huguet [a,b,*], Vincent Grossi [c], Imène Belmahdi [a,b], Céline Fosse [d], Sylvie Derenne [a,b]

[a] Sorbonne Universités, UPMC Univ Paris 06, UMR 7619, METIS, F-75005 Paris, France
[b] CNRS, UMR 7619, METIS, F-75005 Paris, France
[c] Laboratoire de Géologie de Lyon, Université Claude Bernard Lyon 1, Université de Lyon, CNRS, LGLTPE UMR 5276, Villeurbanne F-69622, France
[d] PSL Research University, Chimie ParisTech – CNRS, Institut de Recherche de Chimie Paris, F-75005 Paris, France

ARTICLE INFO

Article history:
Received 17 July 2014
Received in revised form 19 February 2015
Accepted 25 February 2015
Available online 7 March 2015

Keywords:
GDGTs
Archaeol
Salinity
Environmental proxies
Coastal ponds
Guadeloupe

ABSTRACT

The occurrence and distribution of archaeal and bacterial glycerol dialkyl glycerol tetraether lipids (GDGTs) in continental saline environments have been rarely investigated. Here, the abundance and distribution of archaeal isoprenoid GDGTs (iGDGTs) and archaeol, and of bacterial branched GDGTs (brGDGTs) in four tropical water ponds of contrasting salinity in two islands from the French West Indies, Grande-Terre and La Désirade, have been determined. The sedimentary distribution of the GDGTs strongly differed between the two islands. Caldarchaeol was largely predominant among iGDGTs in the (hyper)saline ponds from Grande-Terre, suggesting a substantial contribution of iGDGTs derived from methanogenic Archaea. In contrast, both caldarchaeol and crenarchaeol were present in high relative abundance in the low salinity ponds from La Désirade, suggesting that iGDGTs were derived from mixed archaeal communities. In addition, the relative proportion of the most methylated brGDGTs was much higher in Grande-Terre ponds than in La Désirade ponds. The applicability of different proxies based on GDGTs and archaeol was tested for these specific environments. The relative abundance of archaeol vs. caldarchaeol (ACE index) was comparable for the four ponds, independent of salinity, showing that the ACE index might not necessarily track salinity change. Moreover, the relative proportion of caldarchaeol vs. total iGDGTs was unexpectedly observed to increase with salinity, suggesting production of this compound by halophilic Archaea. The supposed high abundance of methanogenic Archaea in Grande-Terre ponds prevented the application of TEX_{86} as a temperature proxy, whereas TEX_{86} could be successfully used for local temperature reconstruction in La Désirade ponds. BrGDGTs seem to be produced predominantly in situ (water column and/or sediment) in hypersaline ponds from Grande-Terre, but in La Désirade ponds likely result from a mixture of soil and aquatic sources. In Grande-Terre ponds, brGDGT-derived temperature estimates generated using either soil or lacustrine calibrations were much lower than expected. The mismatch between expected and estimated temperature might be explained by the presence of halophilic microbial communities producing specific brGDGT distributions in the saline ponds from Grande-Terre. The study shows that the sources of brGDGTs, iGDGTs and archaeol (i) may strongly differ in aquatic environments of varying salinity, even at a regional scale, and (ii) have to be constrained before tetraether-derived proxies in such settings can be confidently applied.

1. Introduction

Glycerol dialkyl glycerol tetraethers (GDGTs) are complex lipids of high molecular weight (>1000 Da), present in membranes of Archaea and some Bacteria. Archaeal membranes are formed predominantly of isoprenoid GDGTs (iGDGTs) with acyclic or ring-containing biphytanyl chains (Fig. 1). The iGDGTs occur ubiquitously in marine (Kim et al., 2008; Lipp and Hinrichs, 2009; Schouten et al., 2012) and lacustrine water columns and sediments (Sinninghe Damsté et al., 2009; Powers et al., 2010), as well as in peat and soil (Weijers et al., 2006a,b; Huguet et al., 2010a,b). One particular GDGT, crenarchaeol (VI; Fig. 1), contains one cyclohexane moiety and four cyclopentane moieties. It is biosynthesized by *Thaumarchaeota*, recently proposed as a new phylum within

---

* Corresponding author at: Sorbonne Universités, UPMC Univ Paris 06, UMR 7619, METIS, F-75005 Paris, France. Tel.: + 33 144 275 172; fax: +33 144 275 150.
E-mail address: arnaud.huguet@upmc.fr (A. Huguet).

http://dx.doi.org/10.1016/j.orggeochem.2015.02.010
0146-6380/© 2015 Elsevier Ltd. All rights reserved.

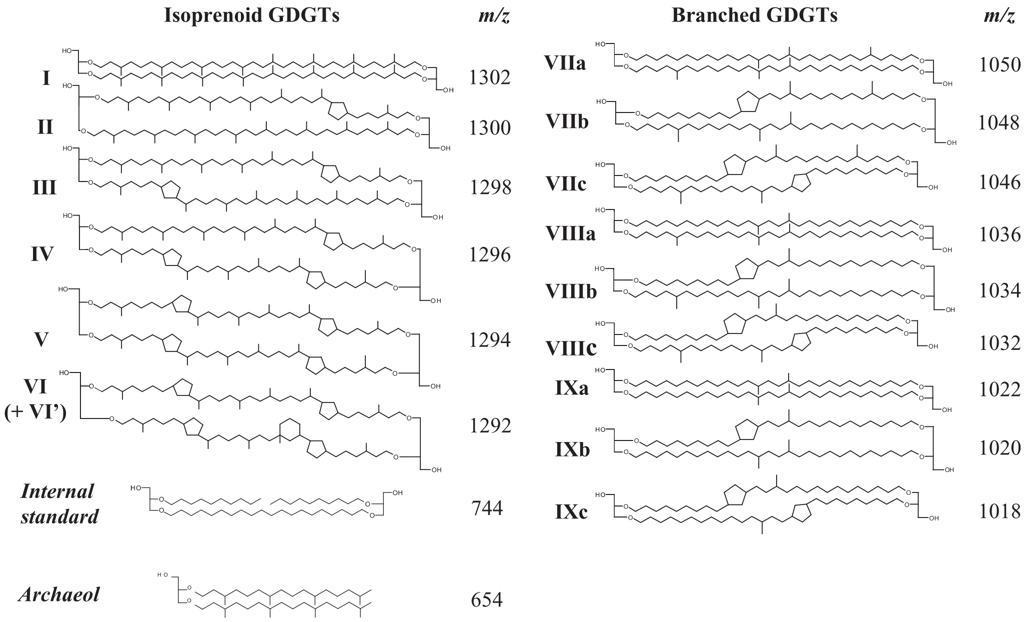

Fig. 1. Isoprenoid and branched glycerol dialkyl glycerol tetraether (GDGT) core lipids, archaeol and internal standard (IS).

the domain Archaea (formerly known as Group I Crenarchaeota; Brochiet-Armanet et al., 2008), even though it has been recently suggested that it could also be produced by Marine Group II *Euryarchaeota* (Lincoln et al., 2014). *Thaumarchaeota* are among the most abundant oceanic microorganisms (Karner et al., 2001; Agogué et al., 2008). Schouten et al. (2002) showed that the relative distribution of iGDGTs in *Thaumarchaeota* depends on environmental conditions, the number of cyclopentyl moieties increasing with sea surface temperature (SST). The correlation between the temperature at the surface of the oceans and the membrane lipid composition of *Thaumarchaeota* was expressed in the TEX_{86} index. Subsequent analysis of iGDGTs in a wide range of marine (e.g. Kim et al., 2008) and lacustrine (e.g. Powers et al., 2010; Pearson et al., 2011) sediments revealed that TEX_{86} correlated linearly with marine and lacustrine surface water temperatures. Consequently, it has been increasingly used for the reconstruction of past oceanic (e.g. Schouten et al., 2003; Castañeda et al., 2010) or lacustrine (e.g. Powers et al., 2005; Berke et al., 2012) temperatures. Nevertheless, its applicability to lakes was shown to be limited and sometimes biased by (i) a high input of iGDGTs produced in surrounding soils (Blaga et al., 2009) and (ii) the production of iGDGTs by types of microorganisms other than *Thaumarchaeota* (e.g. methanogenic Archaea) thriving in the water column and/or lacustrine sediments (Blaga et al., 2009; Powers et al., 2010).

In addition to iGDGTs, Archaea also synthesize diphytanyl glycerol diethers, including archaeol (Fig. 1). Turich and Freeman (2011) compared the abundance of archaeol and caldarchaeol (GDGT I; Fig. 1) in a wide range of environments with varying salinity. They observed an increase in the ratio of archaeol to caldarchaeol with increasing salinity and thus proposed the development of a paleosalinity index, the ACE (archaeol and caldarchaeol ecometric). The ACE was subsequently shown to successfully track changes in salinity in Tibetan lakes (Wang et al., 2013), but does not seem to be of use for all saline environments (Günther et al., 2014).

Another group of GDGTs, containing branched instead of isoprenoid alkyl chains (VII–IX; Fig. 1), was recently discovered in peat deposits (Sinninghe Damsté et al., 2000). Based on the structures and stereochemistry, these branched GDGTs (brGDGTs) were suggested to be produced by unknown soil bacteria (Weijers et al., 2006a), which might belong to the phylum *Acidobacteria* (Weijers et al., 2009; Sinninghe Damsté et al., 2011, 2014). They occur ubiquitously in soil (Weijers et al., 2007a; Huguet et al., 2010a) and peat (Huguet et al., 2010b, 2013; Weijers et al., 2011), as well as in lakes (Tierney et al., 2010; Pearson et al., 2011) and coastal marine sediments (Hopmans et al., 2004; Kim et al., 2007). The analysis of brGDGTs in ca. 130 surface soils distributed worldwide showed that the distributions depend primarily on air temperature and soil pH (Weijers et al., 2007a). The degree of cyclization of brGDGTs, expressed in the cyclization ratio of branched tetraethers (CBT), correlates rather well with soil pH. The degree of methylation of the same compounds, expressed in the methylation index of branched tetraethers (MBT), depends on mean annual air temperature (MAAT) and to a lesser extent on soil pH. The initial MBT/CBT calibration (Weijers et al., 2007a) was extended to a larger number of soils (Peterse et al., 2012). This new soil calibration is based on the CBT and a simplified form of the MBT defined as MBT'. The MBT/CBT proxy is increasingly being used to reconstruct past air temperatures, for example in deltaic and coastal regions (Weijers et al., 2007b; Donders et al., 2009), Chinese loess (Peterse et al., 2011) and lakes (Fawcett et al., 2011; Sinninghe Damsté et al., 2012a). Nevertheless, several recent studies have suggested that brGDGTs present in lakes can also originate from an in situ production in the water column or underlying sediment (e.g. Tierney and Russell, 2009; Wang et al., 2012), thereby complicating the use of the MBT/CBT proxy for lakes. This explains why several brGDGT based on lake sediments have been developed in recent years (e.g. Tierney et al., 2010; Pearson et al., 2011; Loomis et al., 2012). Based on the assumption that brGDGTs were synthesized mainly in soil, Hopmans et al. (2004) proposed another index, the BIT (branched isoprenoid tetraether) index, to track terrigenous organic matter (OM) input to aquatic settings. However, the in situ production of brGDGTs in aquatic environments and a terrestrial input of crenarchaeol questions the interpretation of BIT values (Schouten et al., 2013 and references therein).

To date, the distribution of bacterial and archaeal ether lipids in continental saline environments has been rarely investigated (Günther et al., 2014). Here, we have examined the concentration and distribution of iGDGTs, brGDGTs and archaeol in surficial sediment cores from four ponds of contrasting salinity, located in two islands from Guadeloupe (French West Indies). The two pools of GDGTs, present as either core lipids (CLs) or derived from intact