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# Distribution of glycerol dialkyl glycerol tetraethers in soils from two environmental transects in the USA

Sitindra S. Dirghangi [a,*], Mark Pagani [a], Michael T. Hren [b], Brett J. Tipple [c]

[a] Department of Geology and Geophysics, Yale University, New Haven, CT 06511, USA
[b] Center for Integrative Geosciences, University of Connecticut, Storrs, CT 06269, USA
[c] Department of Biology, University of Utah, Salt Lake City, UT 84105, USA

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ABSTRACT

Glycerol dialkyl glycerol tetraethers (GDGTs) of both archaeal and bacterial origin form the basis of new temperature proxies applicable to soil, and lake and marine sediments. In soil, branched GDGTs are prevalent and their abundance of methyl or cyclic groups has been calibrated to mean annual temperature (MAT) using MBT and CBT indices. However, soil pH is also known to be an important variable controlling the distribution of branched GDGTs. Precipitation amount helps control soil moisture, as well as pH, and soil moisture is a leading variable affecting microbial diversity and activity in soil. We have evaluated the distribution of GDGTs from two soil transects in the USA: a dry, western transect covering six western states and a wet, east coast transect from Maine to Georgia in order to assess the effect of precipitation on the distribution of soil GDGTs. Our results show distinctly different GDGT distributions across climatic regions, with dry western soils characterized predominantly by thaumarchaeotal isoprenoid (iso) GDGTs and as a consequence, low BIT index values (0.2–0.6) and moist-temperate, east coast transect soils expressing mostly branched (br) GDGTs and higher BIT values (0.9–1). The predominance of iso GDGTs in the western soils is related to the degree of aeration, which in turn is related to precipitation amount, and also to soil pH. We also observed a substantial increase in the offset between measured MAT and MBT/CBT-based MAT below an annual precipitation of 700–800 mm $yr^{-1}$, implying an impact of precipitation amount on MBT/CBT-based temperature reconstruction. The data suggest that, while soil tetraethers work well as a temperature proxy in moist-temperate regimes, they do not produce reliable measurements of temperature in sediments sourced from areas with < 700–800 mm $yr^{-1}$ precipitation. Moreover, erosion of soils with low BIT values into lacustrine or marginal marine environments will not be detected via the BIT index, which can potentially affect paleotemperature reconstruction from sediments, and so provide erroneous estimates of soil carbon delivery. BIT index values also show a correlation with precipitation amount. The abundance of iso GDGTs in western transect soils allowed calculation of $TEX_{86}$ values, but no correlation was found between $TEX_{86}$ calculated temperature and mean annual temperature.



## 1. Introduction

Reconstruction of ancient ocean and terrestrial temperature values is a fundamental aspect of paleoclimate research and several methodologies based on inorganic proxies (Epstein et al., 1953; Shackleton, 1967; Kennett and Shackleton, 1975; Wefer and Berger, 1991; Nürnberg et al., 1995; Rosenthal et al., 1997; Podlaha et al., 1998; Lear et al., 2000, 2002; Ghosh et al., 2006, 2007; Affek et al., 2008; Mutterlose et al., 2010) and organic proxies (Prahl and Wakeham, 1987; Prahl et al., 1988; Müller et al., 1998; Liu and Herbert, 2004; Conte et al., 2006; Herbert et al., 2010) have been established. In particular, proxies founded on the distribution of glycerol dialkyl glycerol tetraethers (GDGTs; Schouten et al., 2002; Wuchter et al., 2004, 2005; Weijers et al., 2006a) are being increasingly used for reconstructing ancient marine and terrestrial temperatures, given their ubiquitous occurrence in ocean and lake sediments and soils (Powers et al., 2004; Pagani et al., 2006; Sluijs et al., 2006; Weijers et al., 2007a,b; Schouten et al., 2008; Liu et al., 2009). Two types of GDGTs are found in natural environments: those of archaeal origin, consisting of isoprenoid (iso) chains, occur mainly in marine and lake environments (Schouten et al., 2000, 2007; Powers et al., 2004) and those of bacterial origin, consisting of branched (br) alkyl chains, occur predominantly in soils (Weijers et al., 2004, 2006a, 2007c).

Soils are characterized by a dominance of br GDGTs (Weijers et al., 2004, 2006a, 2007c), which were first observed in peat bogs (Weijers et al., 2006b), and consist of a group of nine compounds (VIIa,b,c, VIIIa,b,c and IXa,b,c; Fig. 1) with varying numbers of alkyl

* Corresponding author. Tel.: +1 203 606 1268.
*E-mail address:* sitindra.dirghangi@yale.edu (S.S. Dirghangi).

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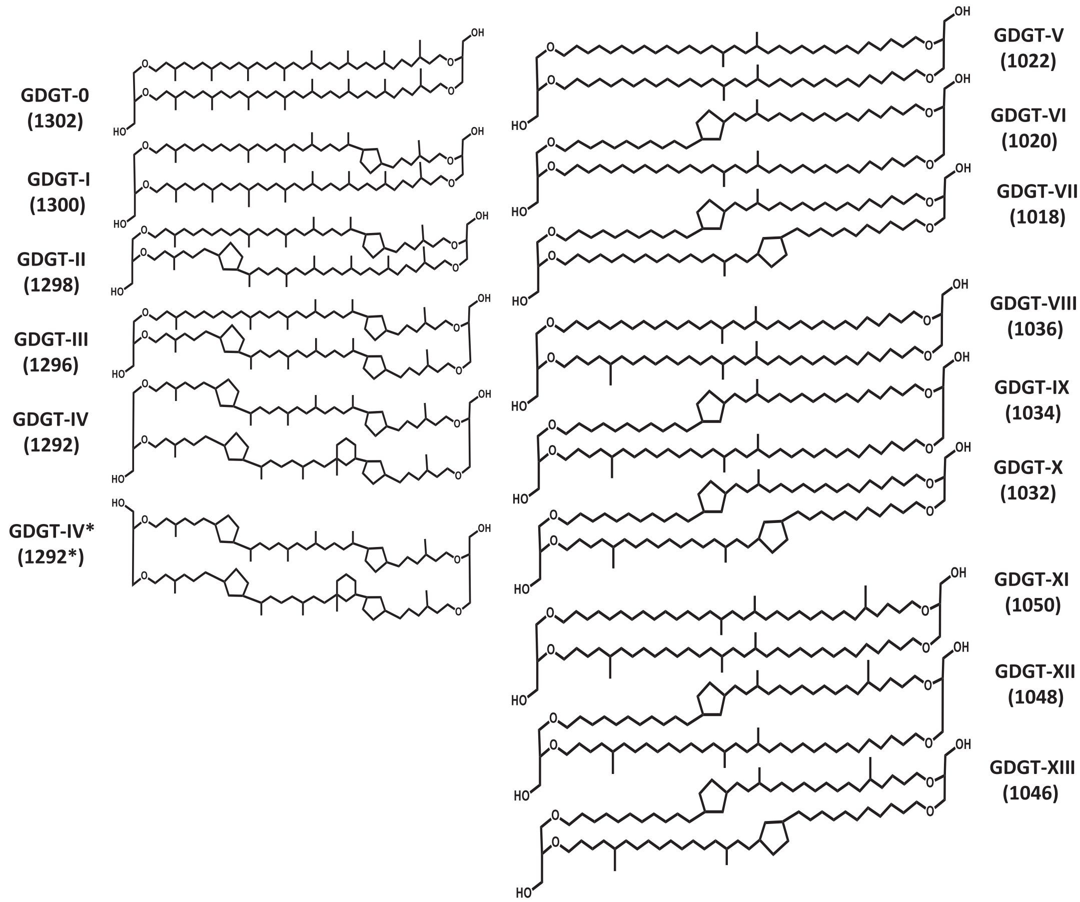


**Fig. 1.** Structures of GDGTs in soils and sediments; GDGT-0 to GDGT-IV and GDGT-IV* (crenarchaeol regioisomer) are the isoprenoid GDGTs of thaumarchaeal origin, and GDGT-V to GDGT-XIII are the branched GDGTs of bacterial origin.

branches and cyclopentanyl rings and synthesized by facultative anaerobic heterotrophic bacteria, probably belonging to the phylum acidobacteria (Hopmans et al., 2004; Weijers et al., 2004, 2006b, 2010). Stereochemical studies and carbon isotope measurements indicate a bacterial and heterotrophic origin, respectively (Weijers et al., 2006b, 2010; Oppermann et al., 2010). The $\delta^{13}C$ values of alkyl moieties released from GDGTs V–XIII by ether cleavage were very similar to (generally depleted by < 1‰) $\delta^{13}C$ values of total organic carbon (TOC; Pancost and Sinninghe Damsté, 2003; Weijers et al., 2010). This observation is consistent with the br GDGT-producing acidobacteria utilizing, as substrate, components of TOC, namely carbohydrates and proteins that are more $^{13}C$ enriched (Weijers et al., 2010). Further, two strains of acidobacteria have been observed to produce a br GDGT in culture experiments (Sinninghe Damsté et al., 2011). Two indices based on the distribution of br GDGTs have been established (Weijers et al., 2007c): MBT (methylation index of br tetraethers) and CBT (cyclisation ratio of br tetraethers). Methylation of br GDGTs appears to be dominantly controlled by mean annual air temperature (MAT) and soil pH, and the cyclisation of br GDGTs is controlled mainly by pH (Weijers et al., 2007c). MAT can thus be estimated using both MBT and CBT (Weijers et al., 2007c) and both have been utilized to infer variations in temperature and environmental conditions during various time periods in the past (Weijers et al., 2007a,b; Donders et al., 2009; Rueda et al., 2009; Hren et al., 2010). Br GDGTs are introduced from soils to shallow marine and lacustrine environments via erosion, although recent evidence indicates an additional in situ aquatic, rather than soil, provenance in lacustrine environments (Tierney and Russell, 2009). However, apart from br GDGTs, some iso GDGTs of thaumarchaeotal origin are also observed in soils, generally in small amount, as evident from BIT or br isoprenoid tetraether index values in soils that are generally < 0.99 with an average value of 0.90 (Schouten et al., 2013 and references therein, e.g. Weijers et al., 2006a; Sinninghe Damsté et al., 2008, 2009; Peterse et al., 2009; Huguet et al., 2010; Kim et al., 2010b; Loomis et al., 2011). This is due to the ubiquitous occurrence of thaumarchaeota in soils (Leininger et al., 2006).

Iso GDGTs are the dominant ones in marine environments (Schouten et al., 2002, 2007; Wuchter et al., 2004, 2005) and are abundant in lacustrine environments (Powers et al., 2004). They derive from archaea and comprise a group of six tetraethers with 86 carbons (Fig. 1). Given the available information, GDGT-0 or caldarchaeol (I) is produced predominantly by methanogenic euryarchaea; GDGT-1, -2, and -3 (II–IV) are synthesized by both thermophilic and mesophilic crenarchaea, which have recently been proposed to belong to the phylum Thaumarchaeota (Spang et al., 2010; Pester et al., 2011) and methanotrophic euryarchaea (Schouten et al., 2000; Zhang et al., 2011); Crenarchaeol (V) and the its regioisomer (VI) are produced only by thaumarchaea (de la Torre et al., 2008; Sinninghe Damsté et al., 2012). The relative abundance of specific iso GDGTs forms the basis of the $TEX_{86}$ index (tetraether index of tetraethers consisting of 86 carbons; Schouten et al., 2002; Wuchter et al., 2004), which has been shown to correlate with sea surface temperature (SST; Schouten et al., 2002; Kim et al., 2008, 2010a) and lake surface temperature (Powers et al., 2004; Tierney et al., 2010), consistent with mesocosm culture experiments (Wuchter et al., 2004; Schouten et al., 2007). Because of the ubiquitous distribution of iso GDGTs, $TEX_{86}$ values have been applied to infer