Archaeal and Bacterial Tetraether Membrane Lipids in Soils of Varied Altitudes in Mt. Jianfengling in South China

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INTRODUCTION

Glycerol dialky glycerol tetraethers (GDGTs) are membrane lipids of archaea and some unknown bacteria. These GDGTs have been demonstrated to respond to temperature and pH variations based on global investigations on marine sediments and modern surface soils (Kim et al., 2008; Weijers et al., 2007). On this point, environmental proxies, TEX₈₆ and MBT/CBT (the methylation and cyclisation index of branched tetraethers), have been established and applied to reconstruct past sea surface and terrestrial temperatures (Zachos et al., 2006). However, TEX₈₆ and MBT/CBT should be investigated in diverse environments to test their applicability due to the lack of pure cultures of archaea and GDGTs-producing bacteria. Here we report the archaeal and bacterial GDGTs distributions in the surface soils across the different altitudes in Mt. Jianfengling in Hainan Province, South China, to explore the potential of indices used for environmental reconstruction.

MATERIALS AND METHODS

Fourteen surface soil samples along the altitude transect of a tropical rainforest in Mt. Jianfengling (18°43.0'N, 108°52.2'E) were collected at every 100 m interval from summit to piedmont on April 12, 2008. The soils were wrapped in aluminum foils and air dried in laboratory. After grinding into powder, ca. 15 g of soil samples were utrasonically extracted consecutively with 40 mL dichloromethane (DCM) : methanol (MeOH) (3 : 1, v/v), 10 mL DCM : MeOH (1:1, v/v) and 8 mL DCM : MeOH (1:3, v/v). The supernatants were collected by filtration and later condensed to 1-2 mL volume. The samples were then transferred to 5 mL vials and dried. Compound separation was achieved via column chromatography packed with silica gel. Alkanes and polar lipids were eluted respectively with hexane (ca. 5 mL) and methanol (ca. 5 mL). The polar fractions were completely dried and subjected to saponification with 0.6 N KOH/MeOH (ca. 1 mL water added) at 100 °C for 2 h. The resultant solution was extracted with hexane and dried. The dried samples were re-dissolved into ca. 500 mL hexane : isopropanol (99 : 1, v/v) and passed through 0.45 µm PTFE filters prior to instrumental analysis.

GDGTs were analyzed in duplicate on Agilent 1200 series liquid chromatography and tandem mass spectrometry (LC-MS/MS) equipped with autosampler and computer manager software. After 30 to 50 μ L of each sample was injected, GDGTs were sepa-

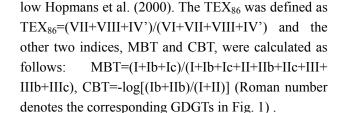
This study was supported by the National Natural Science Foundation of China (Nos. 40930210, 40921062), and the 111 Project (No. B08030).

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Manuscript received December 22, 2009. Manuscript accepted February 25, 2010.

rated on Agilent Zorbax NH_2 Column (150 mm×4.6 mm, 5 µm) and then ionized in the atmospheric pressure chemical ionization (APCI) chamber. Samples were scanned in single ion monitoring (SIM) mode to improve sensitivity and quantified by integrating the peak areas of each compound in extracted ion chromatograms. The conditions of mass spectrometry fol-



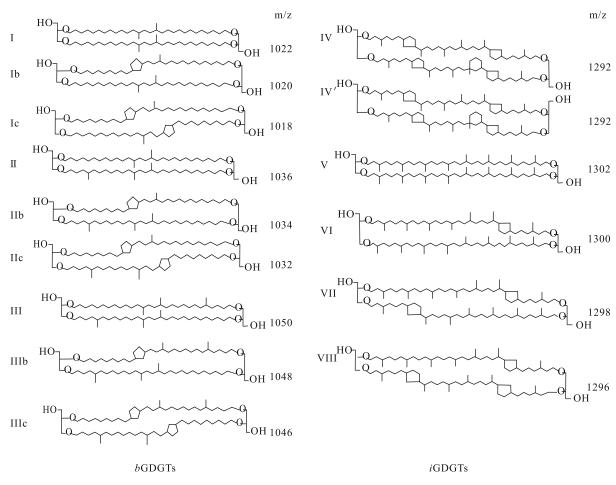


Figure 1. Structures of bacterial and archaeal GDGTs.

RESULTS AND DISCUSSION

The in-situ atmospheric and soil temperatures measured at different sampling heights correlate well with the altitudes of Mt. Jianfengling (Fig. 2). The atmospheric temperatures and the corresponding soil temperatures change very obviously, with an average lapse rate 0.58 °C/100 m. The atmosphere shows a relatively higher correlation (R^2 =0.93) with altitude than the soils (R^2 =0.89). Hence, the mean annual temperatures (MAT) at different sampling sites can be obtained based on above lapse rate and MAT (19.7 °C) from a meteorologic station at elevation of 820 m. The soils were extremely dry due to little precipitation

during the sampling season in the region. Meanwhile, the relatively low altitude of Mt. Jianfengling (86– 1 412 m) enables the evenly distribution of the rainfall amount throughout the transect. Therefore, soil moisture and precipitation may not fall into our consideration of environmental factors controlling the GDGTs distribution.

TEMPERATURES AND ALTITUDES AT SAMPLING SITES

LC-MS analysis shows that bacterial branched GDGTs dominate over the archaeal isoprenoid GDGTs in all samples, with GDGT-I being the most

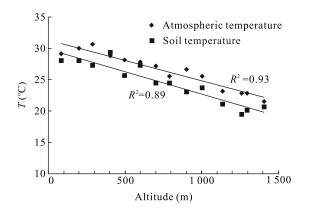


Figure 2. Linear correlation between atmospheric (diamond)/soil (solid square) temperatures and altitudes at sampling sites

abundant compound, which is in agreement with GDGTs distribution pattern in temperate soils reported by Weijers et al. (2007). The crenarchaeol and caldarchaeol account for the principal archaeal GDGTs fractions, while some archaeal GDGTs, i.e. GDGT-VI, VII and VIII in some samples, were below the detection limit.

All the available four TEX₈₆ values have a quite well linear correlation with MAT at different altitudes $(R^2=0.999)$, indicating that TEX₈₆ may respond to the soil temperature variations (Fig. 3). The correlation equation for TEX₈₆ and MAT in our soil samples differs from global marine calibration reported by Kim et al. (2008). This difference between the two equations can be explained by distinctive chemical properties in soils, i.e. the pH values of our soils ranging from 4.03 to 6.2 were quite lower than those for the alkaline marine water, which may result in a different membrane adaptation to ambient temperature variations. Due to the only four TEX₈₆ values available here, further confirmation with more data should be performed to test the applicability of TEX₈₆ in soil environments.

The MBT values correlate with CBT and MAT significantly, yielding to a local calibration for MBT/CBT index, MBT=0.538+0.086CBT+0.012MAT ($R^2=0.62$, n=13) (Fig. 4). This equation is to some extent similar to the global calibration given by Weijers et al. (2007). However, the temperature calculated from the global soil calibration was found to be much higher than the MAT measured at the sampling sites of different elevations, revealing that

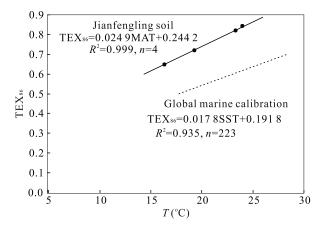


Figure 3. The linear correlation (solid line) between TEX₈₆ values and MAT at different elevations of our study, along with global marine calibration (the dashed line) reported by Kim et al. (2008).

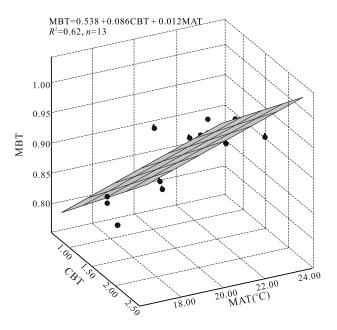


Figure 4. A 3-D calibration plot of MBT vs. CBT and MAT at different altitudes.

the global calibration needs to be revised before the accurate local temperature reconstruction could be achieved as the investigation carried out by Weijers et al. (2007) involves the soils with a large pH range (from acid to alkaline). Therefore, local calibration for MBT/CBT proxy should be conducted before any temperature reconstruction is made.

CONCLUSIONS

Bacterial *b*GDGTs show a dominance over archaeal *i*GDGTs in the surface soils across an altitude transect of Mt. Jianfengling in South China. Archaeal GDGTs-based TEX₈₆ for soils correlates well with the altitudes and the in-situ temperature, suggesting that archaeal GDGTs in soils may also be applicable in paleotemperature reconstruction. Besides, a local soil calibration is needed for the accurate temperature reconstruction on the basis of MBT/CBT index.

REFERENCES CITED

Hopmans, E. C., Schouten, S., Pancost, R. D., et al., 2000. Analysis of Intact Tetraether Lipids in Archaeal Cell Material and Sediments by High Performanceliquidchromatography/Atmospheric Pressure Chemical Ionization Mass Spectrometry. *Rapid Communications in Mass Spectrome-* try, 14: 585-589

- Kim, J. H., Schouten, S., Hopmans, E. C., et al., 2008. Global Sediment Core—Top Calibration of the TEX₈₆ Paleothermometer in the Ocean. *Geochimica et Cosmochimica Acta*, 72(4): 1154–1173
- Weijers, J. W. H., Schouten, S., van den Donker, J. C., et al., 2007. Environmental Controls on Bacterial Tetraether Membrane Lipid Distribution in Soils. *Geochimica et Cosmochimica Acta*, 71: 703–713
- Zachos, J. C., Schouten, S., Bohaty, S., et al., 2006. Extreme Warming of Mid-Latitude Coastal Ocean during the Paleocene–Eocene Thermal Maximum: Inferences from TEX₈₆ and Isotope Data. *Geology*, 34: 737–740