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Survey of glycerol dialkyl glycerol tetraethers (GDGTs) in Nevada and California hot springs and selected thermophiles

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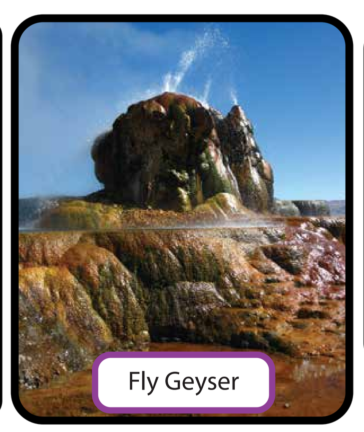
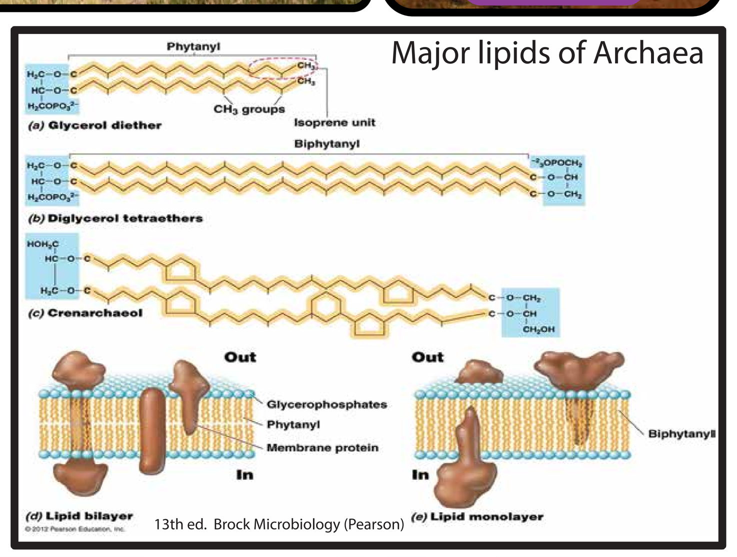
ABSTRACT

Glycerol dialkyl glycerol tetraethers (GDGTs) are core membrane lipids of many Archaea and some Bacteria found ubiquitously in soils and in many aqueous environments. Here, we examined the GDGT concentration in forty sediment samples from geothermal hot springs in the Great Basin (USA). Sediment samples were collected in tandem with extensive geochemical and site characterization. Hot spring temperatures ranged from 31 to 95°C and pH values from 6.8 to 10.7. Parametric Pearson's correlation coefficients and nonparametric Spearman's rho values were calculated to identify significant correlations between GDGT profiles and geochemical analytes. Isoprenoidal GDGTs (iGDGTs) negatively correlated with pH and positively correlated with temperature, Cr, and Cu, which is consistent with the importance of iGDGTs in the maintenance of membrane integrity at high temperature spring sources. In contrast, branched GDGTs (bGDGTs) displayed a negative relationship with temperature and a positive correlation with nitrate, nitrite and dissolved oxygen, demonstrating a niche for bGDGT-producing organisms in cooler, more oxidized springs away from the hottest geothermal sources. In addition, a collection of eleven thermophilic bacterial strains hypothesized to synthesize bGDGTs were tested; however, none synthesized GDGTs under the tested conditions. Our data provides insight into the environmental conditions under which archaeal and bacterial GDGTs are produced, which may improve the use of GDGTs as environmental proxies for understanding climates and conditions of the past and the future.

INTRODUCTION

- Glycerol dialkyl glycerol tetraethers (GDGTs) (Schouten et al. 2007, Weijers et al. 2006b)
  - Core membrane lipids of most Archaea and some Bacteria
  - Occur ubiquitously in many sediment types
  - Used as environmental proxies for paleoclimate (Zink et al. 2010)
- Isoprenoidal GDGTs are membrane-spanning lipids (Weijers et al. 2006b)
  - Two isoprenoid chains
  - Four ether bonds and two glycerol backbones
  - Found only in archaea
- Newly discovered group of membrane lipids, branched GDGTs (Weijers et al. 2009)
  - Ubiquitous in peat bogs and soils
  - Structures evolved within the Bacteria
  - Unknown source
- GDGTs occur in the environments as
  - Core lipids – represent "fossil" or old lipids
  - Polar lipids – represent live organisms
- Gaps in current understanding of GDGTs
  - Limited studies of iGDGT and bGDGT composition in hot springs
  - Unknown biological source of bGDGTs





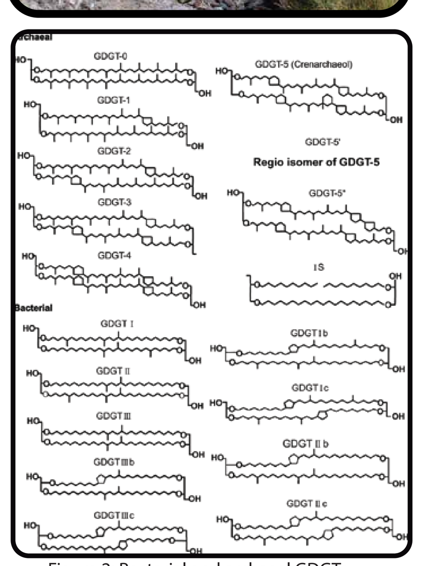
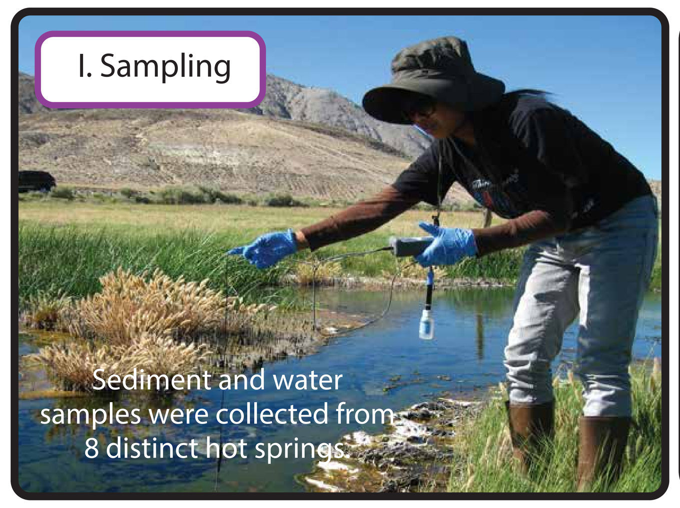


Figure 2: Bacterial and archaeal GDGTs. image from He et al. 2011.

METHODS



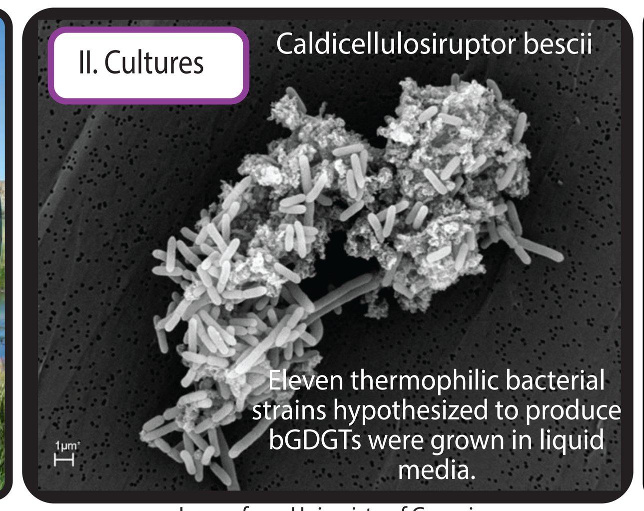
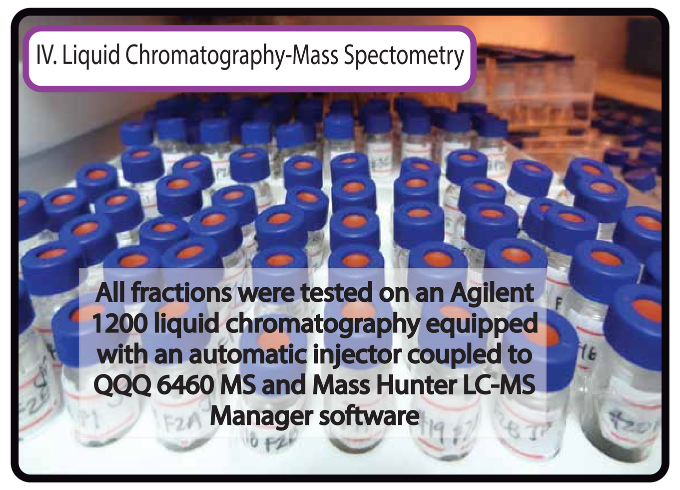


Image from Univeristy of Georgia



V. Statistical Analysis

Parametric Pearson's correlation coefficients and nonparametric Spearman's rho values were calculated in SPSS at the 0.05 level of significance to identify correlative relationships between GDGT types and geochemical analytes.

RESULTS

- Forty sediment samples were collected from eight different hot springs.
  - Sampling sites had temperatures ranging from 31 to 95°C and pH values ranging from 6.8 to 10.7, including high temperature geothermal sources, cooler samples in outflow channels, and cooler spring sources.
  - Water samples were also collected at each site and analyzed for temperature, pH, Ca, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Sr, Zn, F , Cl, NO_2, NO_3, PO_4, SO_4 and NH_4 .

Table 1: Selected Pearson's parametric and Spearman's nonparametric correlations between lipid types and geochemical analytes.

CORE PARAMETRIC

Type	NO3 ppm	NO3 + NO2	Nitrate (by difference)
bGDGT Total	.668**	.735**	.738**
b + i Total	.360*	.400*	.450**

CORE NONPARAMETRIC

Type	F ppm	Cl ppm
iGDGT Total	-.495**	-.481**

KEY

$p < 0.05$, $r \geq 0.4$ Positive
$p < 0.05$, $r \geq -0.4$ Negative

POLAR PARAMETRIC

Type	Temp C	pH	NO3 ppm	NO3 + NO2	Nitrate (by difference)
bGDGT Total	-.365*	.126	.645**	.664**	.663**
iGDGT Total	.405**	-.478**	-.109	-.119	-.059
b + i Total	.340*	-.450**	-.004	-.011	.048

POLAR NONPARAMETRIC

TYPE	Temp C	pH	Oxygen (ppm)	Cr (ppm)	Cu (ppm)	F ppm	Cl ppm	NO3 ppm	NO3 + NO2	Nitrite	Nitrate (by difference)
bGDGT Total	-.583**	.388*	.421**	.156	.092	.034	-.124	.448**	.632**	.348*	.582**
iGDGT Total	.355*	-.415**	-.352*	.464**	.453**	-.502**	-.551**	-.271	-.036	-.007	-.066
b + i Total	.106	-.243	-.158	.400*	.379*	-.418**	-.502**	-.080	.112	.022	.131

CORE + POLAR PARAMETRIC

Type	Temp C	pH	NO3 ppm	NO3 + NO2	Nitrate (by difference)
bGDGT Total	-.340*	.107	.672**	.731**	.733**
iGDGT Total	.414**	-.408**	-.085	-.090	-.021

CORE + POLAR NONPARAMETRIC

TYPE	Temp C	Cr (ppm)	F ppm	Cl ppm	Nitrate (by difference)
bGDGT Total	-.411**	.166	-.150	-.085	.406*
iGDGT Total	.381*	.412**	-.553**	-.531**	-.086
b + i Total	.013	.318*	-.436**	-.347*	.185

DISCUSSION

- This study is the most detailed biogeochemical survey investigating the distribution of GDGTs and the first to examine the relationship of bGDGTs to geochemical analytes within hot spring environments.
  - iGDGTs in hot spring sediments
    - Relationship between iGDGTs and pH
      - Confirms negative relationship between lipid GDGT-4 and pH
      - Negative relationship between crenarchaeol and pH contrasts with previous studies (Pearson et al. 2008)
    - Relationship between iGDGTs and temperature
      - Positive relationship between total amount of core and polar iGDGTs and temperature
    - Relationship between iGDGTs and other analytes
      - Newly recognized positive correlations between iGDGTs and Cr and Cu; negative relationships between iGDGTs and F and Cl
      - Relationships of iGDGTs to geochemical analytes may be tied to pH or source of groundwater feeding the springs
  - bGDGTs in hot spring sediments
    - Relationship between bGDGTs and pH
      - Weak positive relationship between total bGDGTs and pH
      - Previous studies showed a negative correlation between pH and the number of cyclopentane rings (Weijers et al. 2007)
    - Relationships between bGDGTs and temperature
      - New negative relationship identified between bGDGTs and temperature
      - May indicate an upper temperature limit to organisms or production of bGDGTs
    - Relationships between bGDGTs and other analytes
      - First to show a positive relationship between bGDGTs with NO_3^- and NO_2^-
      - NO_3^- and NO_2^- co-vary with temperature along outflow systems; this demonstrates a niche for bGDGT-producing organisms in cooler, more oxidized springs away from the hottest geothermal sources.
- None of the pure cultures of organisms produced bGDGTs
  - GDGTs might be produced by other organisms within same phyla
  - Difficult to replicate natural environment
  - Use different extraction methods in the future

CONCLUSIONS

- Relationships
  - Negative correlations between iGDGTs and pH, F and Cl
  - Positive correlations between iGDGTs and Cr, Cu, and temperature.
  - Positive correlations between bGDGTs and pH, NO_3^- and NO_2^-
  - Negative correlations between bGDGTs and temperature
- Application
  - Environmental proxies for past
  - Future climate change
- Future work
  - Calculate cyclization and methylation of branched tetraethers indices (CBT, MBT) and the branched and isoprenoid tetraether index (BIT)
  - Compare GDGT composition of soils with hot spring sediments
  - Pyrotag sequencing

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REFERENCES

He, L., Zhang, C.L., Dong, H., Fang, B., and Wang, G. 2011. Distribution of glycerol dialkyl glycerol tetraethers in Tibetan hot springs. Geoscience Frontiers. 3:289-300.

Pearson, A., Huang, Z., Ingalls, E., Romanek, C.S., Weijers, J.W.H., Freeman, K.H., Smittenberg, R.H. and Zhang, C.L. 2004. Nonmarine crenarchaeol in Nevada hot springs. Applied and Environmental Microbiology. 70:5229-5237.

Pearson, A. Pi, Y., Zhao, W., Li, W., Li, Y., Inskeep, W., Perevalova, A, Romanek, C., Li, S. and Zhang, C.L. 2008. Factors controlling the distribution of archaeal tetraethers in terrestrial hot springs. Applied and Environmental Microbiology. 74:3523-3532.

Pitcher, A., Schouten, S. and Sinninghe Damsté, J.S. 2009. In situ production of crenarchaeol in two California hot springs. Applied and Environmental Microbiology. 75:4443-4451.

Schouten, S., van der Meer, M. T. J., Hopmans, E. C., Rijpstra, I.C., Reysenbach, A.L., Ward., D.M. and Sinninghe Damsté, J.S. 2007. Archaeal and bacterial glycerol dialkyl glycerol tetraether lipids in hot springs of Yellowstone National Park. Applied and Environmental Microbiology. 73:6181-6191.

Weijers, J. W. H., Panoto, E., van Bleijswijk, J., Schouten, S., Rijpstra, W.I.C., Balk, M., Stams, A.J.M. and Sinninghe Damsté, J.S. 2009. Constraints on the biological source(s) of the orphan branched tetraether membrane lipids. Geomicrobiology Journal. 26:402-414.

Weijers, J. W. H., Schouten, S., van der Donker, J. C., Hopmans, E.C. and Sinninghe Damsté, J.S. 2006b. Environmental controls on bacterial tetraether membrane lipid distribution in soils. Geochimica et Cosmochimica Acta. 71:703-713.

Zhang, C. L., Pearson, A., Li, Y.L., Mills, G. and Wiegel, J. 2006. Thermophilic temperature optimum for crenarchaeol synthesis and its implication for archaeal evolution. Applied and Environmental Microbiology. 72:4419-4492.

Zink. K. G., Vandergoes, M. L., Mangelsdorf, K., Dieffenbacher-Krall, A.C. and Schwark, L. 2010. Application of bacterial glycerol dialkyl glycerol tetraethers (GDGTs) to develop modern and past temperature estimates from New Zealand lakes. Organic Geochemistry. 41:1060-1066.