

## The estimation of paleotemperature of some terrestrial hydrothermal systems using tetraether geothermometer

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Several archaea, that belong to thermoacidophiles or marine group, have cyclopentane rings in their isoprenoidal chains of tetraether lipids. In the case of thermoacidophiles, the number of the ring increases with increasing growth temperature, and the average cyclization (Ac) has been used as an index (DeRosa et al., 1980). This relationship can be useful for estimation of paleotemperature of terrestrial hydrothermal systems (Kitajima et al., 2003). Schouten et al. (2002) reported that nonthermophilic marine crenarchaeota also would change the numbers of cyclopentane rings in their tetraether lipids with the Sea Surface Temperature (SST), and the TEX86 proxy can be useful for the estimation of SST (ranging from 0 to 30 degC) in the past. The relatives of marine group have been found also in terrestrial neutral or alkaline lacustrine systems (Pearson et al., 2004), and the TEX86 proxy has begun to be used more widely.

Sulfolobales, that belongs to thermoacidophilic archaea, contains Glycerol Dialkyl Calditol Tetraethers (GDCTs) together with Glycerol Dialkyl Glycerol Tetraethers (GDGTs). GDCTs have been found from only the archaea belonging to the order Sulfolobales, and GDCTs can be producer specific biomarkers, and this relationship can be useful as geothermometer ranging from 65 to 80 degC, in particular, for acidic hydrothermal systems where the relatives of marine group cannot be found. However, analysis of GDCTs requires HI/LiAlH<sub>4</sub> treatment, but intact GDGTs can be analyzed by HPLC-APCI-MS. The latter method is easy in the respect that it does not need conventional HI/LiAlH<sub>4</sub> treatment.

The Ac values of GDCTs are higher than those of total tetraether lipids, indicating that the Ac of GDCTs cannot be applied to the relationship between the Ac of total lipids and temperature. In this study, the relationship between the Ac of GDCTs and the growth temperature of Sulfolobales was examined, and paleotemperatures of three hot springs (Yahata-Jigoku, Yunono-Jigoku, and Gin'yu, located in the Kirishima area) were estimated using the obtained relationship. The estimated temperatures using GDCTs are in fair agreement (within 3 degC) with those using total lipids, in the case of Yahata- and Yunono-Jigoku.

The relationship between the number of cyclopentane rings of GDGTs derived from Sulfolobales and the growth temperature was also examined. In this study, evaporative light scattering detector (ELSD) was used instead of APCI-MS with intention of simplicity of use. Because the ether lipid composition of thermoacidophiles differs from that of marine group, the TEX86 proxy cannot be applied in this case. A new index, cyclization\*(C\*), was found to correlate with the growth temperature, and the relationship;  $T=17.6C^*+7.0$  was obtained.

A core sample was collected at the Gin'yu hot spring, and the analysis of GDGTs, total organic carbon (TOC), and population density of microorganisms were carried out. Crenarchaeol and its isomer were not found from the core by the HPLC-APCI-MS analysis, indicating the absence of the relatives of marine group archaea in this hot spring. Cultivation of thermoplasma, that has also cyclopentane rings in isoprenoidal chains, and is another typical thermoacidophile in lacustrine systems, was tried. However, growth was not observed, indicating the absence of this archaeon, and that the producer of GDGTs must be Sulfolobales. On the basis of the direct counting of population density, contribution of the GDGTs from the living cells is negligible. The estimated temperatures using C\* index are 77 degC, at the portion deeper than 15cm, suggesting geothermal activity in the past. The decrease of estimated temperature at 9-12cm is consistent with TOC and the lithology of the core sample.