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USING MICROBIAL MEMBRANE LIPIDS IN MODERN AND MATURE SINTERS TO ELUCIDATE GEOTHERMAL CHEMISTRY AND MICROBIOLOGY

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The study of geothermal settings, in particular their chemistry and microbiology, is of broad scientific interest with respect to the formation of mineral deposits (Jones *et al.*,1997; Konhauser *et al.*, 2001), the ecology of extremophiles, origin of life studies and astrobiology (Stetter, 1996; Nisbet and Sleep, 2001). Lipid biomarkers, in comparison to DNA and RNA, are relatively well preserved in geothermal sinters and it is likely that such compounds, once encased in the silica matrix, could persist for extended periods of time (Pancost *et al.*, 2005). Consequently they can be used to gain insight into former spring activity and assess past changes in environmental conditions.

Here we examine the preservation of biomarker signals in modern and mature siliceous sinters from the Taupo Volcanic Zone (TVZ), New Zealand. This area is the most frequently active and productive silicic volcanic system on Earth. Bacterial biomarkers in TVZ sinters include free fatty acids, 1,2-di-*O*-alkylglycerols (diethers), 1-*O*-alkylglycerols (monoethers) and various hopanoids, whereas dominant archaeal lipids include archaeol and glycerol dialkyl glycerol tetraethers (GDGTs) (Fig.1a). The structure and distributions of these membrane lipids reflect the chemical and microbiological conditions present during the time of sinter formation. For example: monoethers record the presence of *Aquificales* species; archaeal lipids, specifically GDGTs, are predominant at high temperatures and low pH; and longer chain fatty acids are more abundant at higher temperatures.

We examined the lipids preserved in modern and mature sinters (with ages of up to ca. 800 years) from four different hot spring areas in the TVZ. In each, a wide range of the aforementioned functionalized lipids are preserved suggesting that silicification facilitates biochemical preservation. At Champagne Pool, dominant compounds include bacterial non-isoprenoidal diethers and archaeol (Fig.1a), however concentrations vary with sample age. In the younger sinters bacterial diethers are numerous, occur in high abundance and are typically coupled to a high abundance of archaeol. In contrast, the more mature sinters exhibit much lower abundances of the bacterial diethers relative to archaeol (Fig.1b), suggesting a possible

change in microbial assemblage as a result of changing environmental conditions. Non-isoprenoidal diethers are predominant membrane lipids in several thermophilic bacterial species, including *Thermodesulfobacterium commune*, which is consistent with molecular analyses.

Most compounds at each study site have been diagenetically or thermally altered; for example, free fatty acids, derived from phospholipid hydrolysis, predominate, and bacteriohopanoids have been converted into less functionalised products with a range of isomers present. Nonetheless, the altered structures can still be related to specific biological precursors, which, in combination with molecular methods, can be used to reconstruct spring chemistry and microbiology.

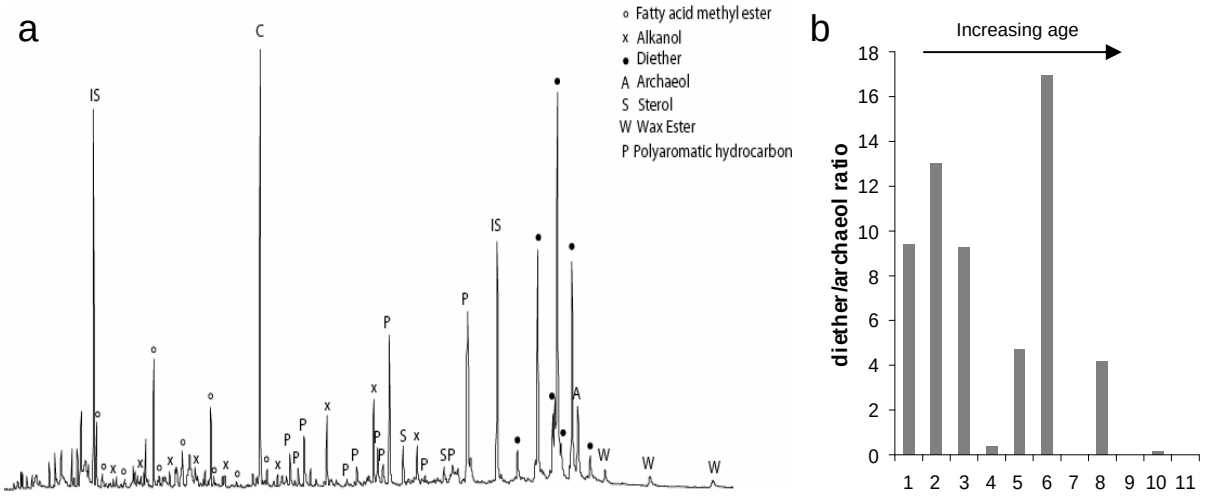

Figure 1(a) Partial gas chromatogram showing the polar fraction of a sample from Champagne Pool, TVZ. Internal standards are denoted by IS, and C denotes contamination by phthalate; (b) Profile of diether/archaeol ratios in Champagne Pool. Samples 7, 9 and 11 lack bacterial diethers, though archaeol is present in high abundance.

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