Using microbial lipids in ancient sinters to elucidate past 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, the ecology of extremophiles, origin of life studies and astrobiology. 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. 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 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, 1-*O*-alkylglycerols and various hopanoids, whereas dominant archaeal lipids include archaeol and glycerol dialkyl glycerol tetraethers (GDGTs). The structure and distributions of these membrane lipids reflect the chemical and microbiological conditions present during the time of sinter formation. For example: the 1-*O*-alkylglycerols (monoethers) record the presence of *Aquificales* species; archaeal lipids, specifically GDGTs, are predominant at high temperatures and low pH; longer chain fatty acids are more abundant at higher temperatures; and hopanoids typically occur in aerobic bacteria.

We examined the lipids preserved in sinters from four different hot spring areas in the TVZ, with ages of up to thousands of years. In each, a wide range of functionalized lipids are preserved suggesting that silicification facilitates biochemical preservation. Most compounds 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 and in a 60-year old Rotokawa sinter, have been used to identify past changes in geothermal spring chemistry.