P51F-1787 Lipid biomarker production and preservation in acidic ecosystems: Relevance to early Earth and Mars

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Acidic environments on the early Earth

Compared to relatively benign carbonate buffered marine environments, terrestrial Archean and Paleoproterozoic life was forced to cope with a broader range of pH values. In particular, acidic terrestrial ecosystems arose from the oxidation of reduced species in hydrothermal settings and crustal reservoirs of metal sulfides, creating acid sulfate conditions. While oxidation of reduced species is facilitated by reactions with molecular oxygen, acidic conditions also arose in Archean hydrothermal systems before the rise of oxygen (Van Kranendonk, 2006), expanding the range of time over which acidophiles could have existed on the early Earth. Acidic terrestrial habitats would have included acidic hydrothermal springs, acid sulfate soils, and possibly lakes and streams lacking substantial buffering capacity with sources of acidity in their catchments.

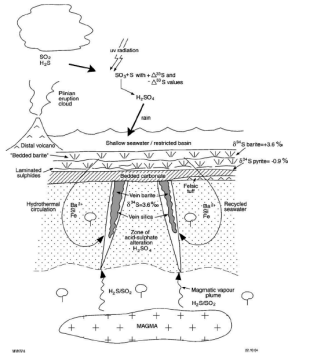
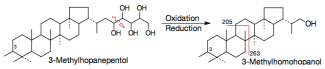


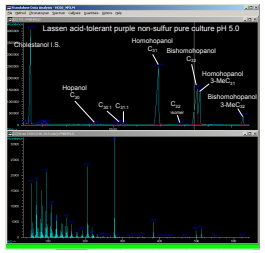
Fig. 29. Schematic model, in cross-section, of the components involved in development of the Dresser Formation hydrothermal system. Recycled seawater (and meteoric water) from a shallow water volcanic caldera is drawn down through the footwall metabasalts during the onset of hydrothermal circulation. H_2S/SO_2 contributed from the magmatic vapour plume reacts with this water, producing H_2SO_4 that forms a zone of intense acid-sulphate alteration. Hydrothermal fluid circulation leaches Si, Ba, and Fe from the footwalls and transports these elements towards the surface. Pulses of reduced (magmatic) fluid, rich in H_2S, react with excess Fe (and Zn and Pb) to form sulphides. Excess SO_4, liberated during acid-sulphate alteration, reacts with Ba to precipitate barite in lower temperature veins and at the surface. Plinian eruption was accompanied by voluminous H_2S/SO_2 degassing; these components disassociate to SO_4 and S^0 that undergo intense UV radiation in the low pO_2 Archaean atmosphere and develop $\Delta^{33}S$ values that fall off the Terrestrial fractionation line following the model of Farquhar et al. (2000).

Van Kranendonk, MJ (2006) Earth-Science Reviews 74, 197-240.

3-Methylhopanoids as biomarkers

Hopanoids methylated at the C-3 position are synthesized by aerobic methanotrophic bacteria and are often used as biomarkers for this process in natural environments, and in the rock record. Only one other bacterial group, the chemotrophic *Acetobacter,* have been known to produce 3-methylhopanoids (Rohmer et al., 1984). We have recently identified 3-methylhopanoids in several cultures of marine purple non-sulfur bacteria (PNS), and in a hypersaline gypsum crust mat (Jahnke et al., in press). Here we present data showing that an acid-tolerant PNS isolated from an acidic spring in Lassen Volcanic National Park also produces 3-methylhopanepolyol.

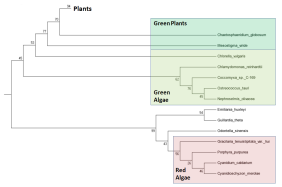




Hopanoid analysis of the acidic algal mat and sediment at Nymph Creek (center panel) also identified a 3-methylhopanoid, but not as a polyol. The Nymph Creek site contained 3-methyl bishomohopanol as a free alcohol.

Sterols as biomarkers

Steranes, the diagenetic product of sterols, are important biomarker molecules for eukaryotic organisms in the geological record. The distribution of sterol classes based on carbon number (C_{27}, C_{28}, C_{29}) has been shown to vary among the red and green algae (Kodner et al., 2008). Generally green algae are dominated by or trend toward C_{29} sterols, while red algae have a high proportion of C_{27} compounds. Many of the acidophilic algae represent basal lineages and their sterol compositions have higher proportions of C_{28} sterols. The Cyanidiales represent the red basal group and are well represented in acidic hot spring environments (40 to 56°C). The major sterol of *Cyanidium caldarium* and *Galdieria sulphuraria* are C_{28} with C_{28}>C_{29}. The basal green algal group tend to have much higher C_{29}>C_{28}. Among the green algae are a number of basal genera (*Chlorella, Chlamydomonas, Nannochloris*) that have simple unicellular morphology and are well represented in acidic environments at cooler temperatures. The sterol compositions of these genera are unknown. We have recently established several cultures from Yellowstone and Lassen which we will characterize.

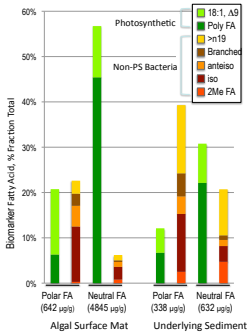


Consensus tree of the RuBisCO genes. From Computational Genomics of Photosynthetic Organisms. Note how deeply diverging red and green algae are.

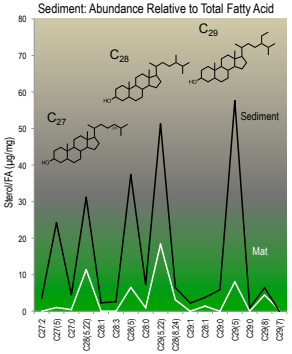
Acidic terrestrial hydrothermal systems

Nymph Creek, Yellowstone National Park

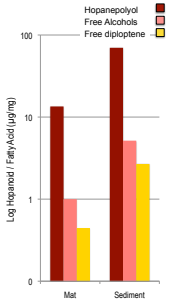
Nymph Creek: Distribution of Biomarker Fatty Acids in Algal Mat and Sediment



Sterol Survival in Nymph Creek Algal Mat &Underlying Sediment: Abundance Relative to Total Fatty Acid



Hopanoid Recovery from Nymph Creek Mat & Sediment

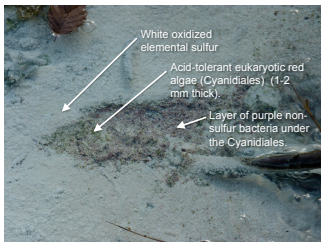


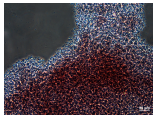
Initial results for a cooler region of Nymph Creek (37°C, pH 2.7) indicate that the surface mat is dominated by microalgae. Mat membrane **fatty acids** (FA) are primarily biomarkers for algae: both oleic acid (18:1 Δ9) and polyunsaturated FA are present as glycolipid. Fatty acids produced by non-photosynthetic bacteria (branched FA) are most abundant in the phospholipid fraction. These branched FA dominate the underlying sediment.

Mat **sterols** are essentially all C_{28} and C_{29} with C_{29}>C_{28}. Relative to FA, sterol abundance increased in the sediment. Di-unsaturated sterols were the most abundant in the surface mat, but saturated and monounsaturated sterols (primarily Δ5) dominated the sediment. Cholesterol and cholestanol also became major compounds in the sediment.

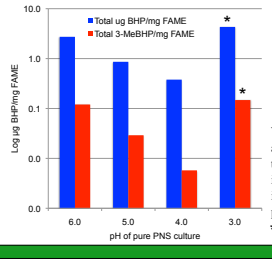
Hopanoids, primarily hopanepolyols, were abundant in the mat; however, relative to membrane lipid, higher amounts of hopanoid were recovered from the sediment. The relative proportion of individual compounds was similar in both mat and sediment. A novel 3-methylbishomohopanol was identified in the alcohol fraction.

Sulphur Works, Lassen Volcanic National Park





pH response of 3-methylhopanoid production



pH of pure culture	3-MeBHP/Total BHP Index
6.0	0.23
5.0	0.18
4.0	0.07
3.0*	0.18*

With increasing pH, both total bacteriohopanoid and 3-methylhomologs increased relative to total membrane fatty acid. Additionally, an increase in cyclopropane fatty acid (cy19) indicates a membrane response to increasing pH.

* sickly culture – cells lysing – low relative membrane fatty acid recovered

Acknowledgments

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