

## Tracking Proterozoic Biospheric Evolution and Marine Redox Structure using Lipid Biomarkers

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Molecular geochemical analyses of Proterozoic rocks and oils that have experienced a reasonably mild thermal history generally reveal a wide diversity of hydrocarbon compounds. Robust biomarker information can be recovered from many Proterozoic rocks given due attention to potential contamination and thermal preservation issues, and novel evolutionary insights include the earliest record of ecologically significant Cryogenian-age animal biomass from distinctive C<sub>30</sub> steranes from demosponges [1].

Despite speculation to the contrary [2], evidence for abundant anoxygenic photosynthetic bacterial primary production in mid-Proterozoic pelagic marine settings is not supported by fossil carotenoid biomarker evidence in most thermally immature sedimentary rocks and oils from China and Australia. Only in certain organic sedimentary facies of the 1.64 Ga Barney Creek Formation deposited in the northern depocenter of the Glyde Sub-basin [3], particularly for intervals influenced by dolomitic turbidite flows [4] bringing photosynthetic benthic mats from the shelf, are aromatic carotenoid markers for Chlorobiaceae and Chromatiaceae (green and purple S bacteria) detected in abundance. The biomarker assemblages associated with unusual organofacies reported from the Barney Creek Fm. in the Glyde Sub-basin has seemingly given a misleading picture of mid-Proterozoic ocean redox structure and the general mode of pelagic bacterial production, although poorly constrained groups of bacteria appear to be the dominant source organisms.

[1] Love et al. (2009) *Nature* **457**, 718-721. [2] Johnston et al. (2009) *PNAS* **106**, 16925-16929. [3] Brocks et al. (2005) *Nature* **3**, 653-659. [4] Davidson and Dashlooty (1993) *Australian Journal of Earth Sciences* **40**, 527-543.

## Nature Abhors a Vacuum: Geothermal gases at Yellowstone

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Though off limits to geothermal development, Yellowstone remains the world's most prominent single source of geothermal heat, with many high-temperature aquifers underlying thousands of square km of alpine terrain. Our studies of gas and water compositions provide many lessons for the assessment of geothermal resources and the source of heat, solutes, and gases in long-lived hydrothermal systems in the shallow continental crust. We highlight three below.

*Don't mix apples, oranges, and helium:* Components in geothermal fluids originate from separate sources. Based on stable isotopes of H<sub>2</sub>O, researchers recognized early on that >90% of the thermal water in Yellowstone comes from meteoric recharge. Yet most thermal waters have <sup>3</sup>He/<sup>4</sup>He ≥ 7R<sub>A</sub>, implying ~50% mantle He. Methane, a trace gas in meteoric waters and most magmatic gases is produced by thermogenesis of crustal sediments, and emerges in greatest abundance in the east side of the park. Additional CH<sub>4</sub> is generated through in situ equilibration of C-H-O gases. Each gas or isotope provides a different perspective on the source of heat, gas and water to a geothermal fluid.

*All good things come to those who wait:* An important insight from recent studies of gas composition and CO<sub>2</sub> flux at Yellowstone is that radiogenic He is emitted in quantities far too great to be accounted for by steady state ingrowth through radioactive decay. At the Heart Lake Geyser Basin, we measured thermal water discharge and the diffuse and fumarolic CO<sub>2</sub> flux. He isotopic ratios demand that 90-95% of the He is generated in the crust, yet discharge of 21 mmol L<sup>-1</sup> of dissolved CO<sub>2</sub>, and the CO<sub>2</sub>/He ratio of the gases requires that 4.6 x 10<sup>-4</sup> mol s<sup>-1</sup> of He are released from this small thermal area (~1% of the thermal water discharge at Yellowstone). A He flux of this magnitude would require steady-state ingrowth of U-rich crust (7 ppm U and Th/U = 3.5) equivalent to the entire area of Yellowstone National Park down to 8 km depth. This astonishing calculation implies: i) igneous heat liberates <sup>4</sup>He produced by millions (and in some cases billions) of years of radioactive decay and He storage, and ii) the fluid flow and crustal degassing is ultimately short-lived on a geologic timescale, generating remarkable bursts of crustal gas.

*A leopard cannot change its spots:* The CO<sub>2</sub>/<sup>3</sup>He ratio of Yellowstone gases is consistent throughout the park, with values between 10<sup>9</sup> and 10<sup>10</sup> and shows no correlation with either gas chemistry or isotopes. The constant ratio of these gases and the similarity to mantle values demonstrates that the crustal component of CO<sub>2</sub> is < 50% of total CO<sub>2</sub> and that crustal and mantle CO<sub>2</sub> are well-mixed at depth. Moreover, thermodynamic models for CO<sub>2</sub> fugacities in calcite-bearing geothermal systems predict 2-3 orders of magnitude variation in CO<sub>2</sub> pressure over the 100-300°C range of geothermal temperatures. Clearly, deep magmatic and metamorphic degassing flood the geothermal system with CO<sub>2</sub>. Low temperature solution-mineral equilibria provide little control on the CO<sub>2</sub>/<sup>3</sup>He ratio of emitted gases.