Dr. Penny Morrill's Project Report
Program: Lewis and Clark Fund for Exploration and Field Research in Astrobiology
Date of Award: Summer, 2006
Project Title: Identification of gaseous hydrocarbon formation from ultrabasic springs at a site of active serpentinization

Lewis and Clark Fund for Exploration and Field Research - Astrobiology: Summer of 2006 Project Report

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Amount of the Award: 3,400 USD
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Since the reports of gaseous hydrocarbons in ancient Earth rocks as old as 3.8 Ga, and on Mars, Titan and Europa, there has been renewed interest in the origins of these gases. When these gases are sampled, what measurements should be performed to determine their biological or non-biological origins? Distinguishing between biogenic (microbial and thermogenic) hydrocarbons and abiogenic hydrocarbons is directly related to the NASA Astrobiology Institution's Roadmap Goal 7, to 'determine how to recognize signatures of life on other worlds and on early Earth'.

While the geochemical indicators, mainly gaseous compositions, and stable carbon and hydrogen isotopes ($\delta^{13}C$ and $\delta^{2}H$ respectively), of biogenic hydrocarbons are well understood, less is known about unambiguously abiogenic hydrocarbons, because, they are rare and very little is known about the natural processes that produce them. One hypothesized pathway for abiogenic synthesis of hydrocarbons involves the reduction of CO_2, a Fischer-Tropsch type (FTT) reaction, accompanying hydrothermal alteration of minerals such as serpentinization. Funds were requested to go to the Cedars in Sonoma County CA (Figure 1) to collect hydrocarbon gases, with an unknown origin, from reducing springs flowing through areas of active serpentinization to determine the source of these gases using isotopic and compositional analyses.

Figure 1. The Cedars is located in Sonoma County, CA.

The Cedars is an extreme environment of unknown biological activity where serpentinization is creating ultrabasic reducing springs that bubble with gases mainly composed of methane, hydrogen, and nitrogen with lesser amounts of Ar and higher molecular weight hydrocarbons. The site is of astrobiological interest because the process of serpentinization is suspected to occur on early Earth, Mars and Titan, and is thought to produce abiogenic hydrocarbons, while also providing energy for chemolithotrophic life.

Forty samples from six ultrabasic reducing springs were collected during two field trips (July 1st – 3rd and

August 3rd to the 7th) to the Cedars. Waters were collected for dissolved inorganic carbon (DIC) and dissolved organic carbon measurements (DOC) to determine the sources and sinks of carbon is the system. The oxygen and hydrogen isotope values of the water will be measured to determine how recently the water has been in contact with the atmosphere, therefore constraining the source of the spring water. The gases dissolved in the ultrabasic spring waters and the gases bubbling from the same springs were sampled and analyzed for their compositional make-up (i.e. N2, H2, He, Ar, CO, CO2, O2, CH4, higher molecular weight alkanes), and the stable carbon and hydrogen isotope values of the carbon and hydrogen containing compounds. The isotope values will determine the source (biogenic or abiogenic) of the hydrocarbon gases. Separate gas samples were taken for He isotope measurements to determine the source (mantle or crustal) of the bubbling gases.

NS-1 (Figure 2) of the Mineral Springs Complex, was one of the most interesting springs because it was isolated from the surficial creek water. Because of this isolation, the spring water was not diluted by the creek water, and therefore it has the lowest oxidation reduction (redox) potential of all the springs sampled. The gases bubbling from all of the Mineral Springs Complex had the greatest amount of methane and the least amount of hydrogen, of all the springs at the Cedars (Figure 3). Suggesting that the hydrogen gas is consumed in the production of methane. However, This data can not distinguish between biogenic and abiogenic methane.

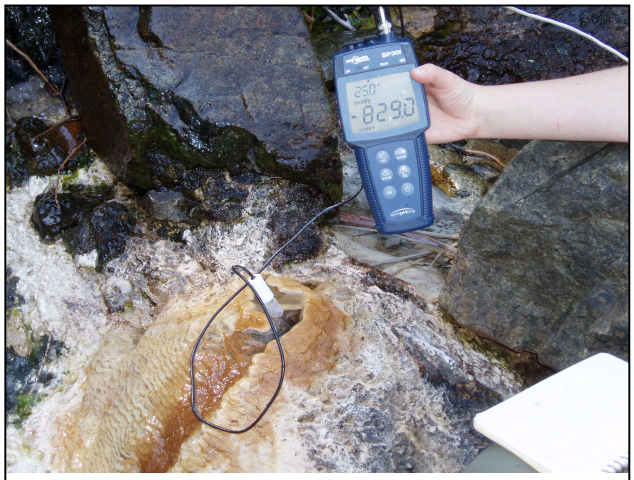

Figure 2. The NS-1 ultra basic reducing spring which is isolated from the water of Austin Creek, has a redox potential of –829 mS.

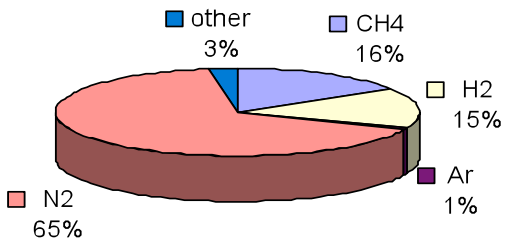

Figure 3. The percent by volume gaseous composition of the bubbling gas from NS-1. The 'other' category represents higher molecular weight hydrocarbons.

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The ratio of methane to the sum of ethane, propane, and butane (C1/C2+) has traditionally been used to differentiate gases created microbially from gases that are created by the thermal degradation of buried sedimentary organic matter (aka thermogenic gases). An abiogenic field has been added to this graph using my experimental data and that of Dr. Tom McCollom's. When the Cedars' gases are plotted on such a plot (Figure 4), the data indicates that the gases are primarily microbial in origin, but that there is a secondary unknown source of gas. The secondary source could be thermogenic or abiogenic. Further analyses of the samples, including stable hydrogen isotopes will constrain the origin of the secondary source(s) of gas.

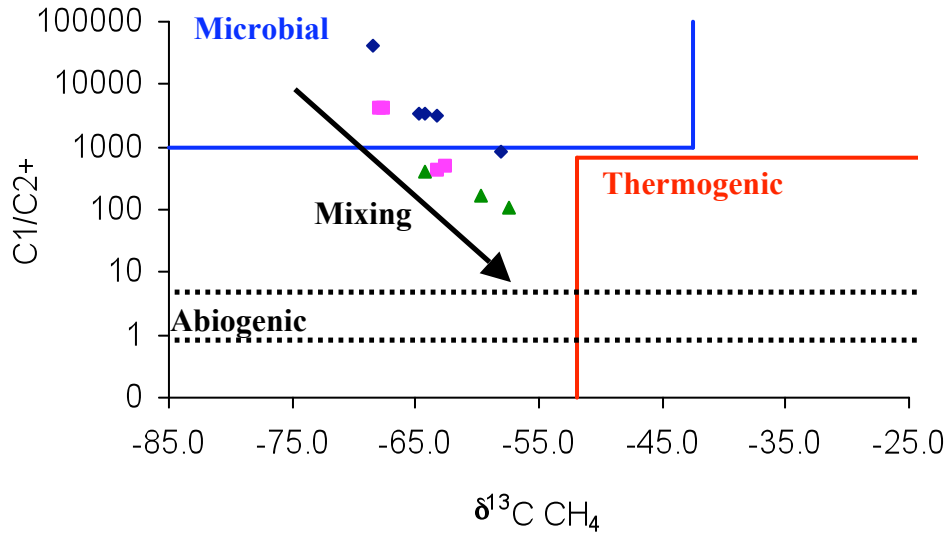

Figure 4. The Cedars gaseous data plotted on a natural gas classification scheme (*Bernard, B., et al. 1977. Offshore Technology Conference, Ninth, Houston, TX, pp. 435-438*). The Abiogenic field has been added using data from two abiogenic studies (*Morrill, P.L., et al. 2006. 2006 Join Assembly, Baltimore, Maryland*, and *McCollom, T.M., and Seewald, J.S., 2006. Earth and Planetary Science Letters 243, 74-84*). The blue diamonds and pink squares represent gas samples during the 2005 field season while the green triangles represents samples from the 2006 season.