# **Roy PRICE** Lewis & Clark Fund, Astrobiology

# Expanding Frontiers for Origin of Life Research: Serpentine-Hosted Shallow-Sea Hydrothermal Vents in New Caledonia

Dr. Roy Price, currently at SUNY Stony Brook, SoMAS, New York; formerly at University of Southern California, Los Angeles, California (at time of L&C grant).[note: This report is a summary of activity relating to the Lewis and Clark Fund Grant, received by Dr. Roy Price in order to investigate alkaline *shallow-sea* hydrothermal vents as analogs to early Earth environments important for origin of life. The following text is from a manuscript in prep. All methods, tables, figures and most interpretations have been left out of this summary report. It is anticipated that the manuscript, currently entitled, "Low temperature alteration of basalt and  $H_2 / CH_4$  production in a ridge-flank hydrothermal system: the shallow-sea, alkaline, Strytan Hydrothermal Field (SHF), Eyjafjördur, Iceland" will be submitted by the end of 2014. Please do not reproduce without the express written consent of Dr. Price.]

### **Background and Objectives**

On June 4<sup>th</sup>, 2012, Price received grant approval for his proposal "*Expanding frontiers for origin* of life research: Serpentinite-hosted shallow-sea hydrothermal vents". The goal of this research was to travel to New Caledonia (South Pacific) to collect samples from the Prony Hydrothermal Field (PHF), a shallow-sea vent site with a 38 m carbonate hydrothermal edifice and active alkaline venting, similar to the Lost City Hydrothermal Field (LCHF), off-axis mid-ocean ridge. Unfortunately, after receiving the funds, Price had difficulties in obtaining a sampling permit for collecting samples from the New Caledonia site. Unknown to him, a group of French scientists had started similar work to what was proposed. Due to overlap with their research objectives, the permit was denied. Price asked permission to switch the L&C funding to another, similar and perhaps more important, field site – the Strytan Hydrothermal Field (SHF), Eyjafjord, northern Iceland. Permission was granted, and the funds from the Lewis and Clark research grant were combined with funds already received from the National Science Foundation (CDEBI), and an expedition took place in July 2013. As noted in the attached "Financial Report", funding from the L&C grant were used entirely for supporting the SCUBA diving operations through the Strytan Diving Center. Additional logistical and scientific funds were obtained from the NSF Center for Deep Biosphere Interactions (CDEBI).

### Sampling

An expedition to the Strytan Hydrothermal Field took place July 2013. There are two main areas where cones and hydrothermal venting are present in Eyjafjord, and are referred to as "Arnarnesstrytan" and "Big Strytan" (Figure 1). Big Strytan was the first to be discovered, and is so called because of the presence of a very large cone, reaching up to 55 m height from the seafloor. There are series of other cones in the area of the Big Strytan, but our sampling only took place on the largest cone. Arnarnesstrytan is located north of Arnarnes, a small spit on the west side of the fjord. The system is comprised of several hydrothermal chimneys or clay-stacks forming a 500 m long line trending approximately north-south. Many individual and overlapping chimneys rise up to 10 m above the seafloor. Another site, off of the island of Hrisey, which consists of hydrothermal fluid venting through horizontal cracks in basalt rocks with no cone development, was also sampled (Figure 1). Abundant microbial mats were present where the hydrothermal fluids came into contact with overlying rocks.

During the second dive on July 9th at Arnarnesstrytan, Scuba divers noticed that, for unknown reasons, a small (~70 x 30 cm) cone was broken off, at approximately 20m water depth. Two days before, the cone was intact (Erlendur Bogason, pers. comm). We collected the cone for both microbiological and geochemical analyses, and this site was designated "A1". Subsequently, fluids were collected from the broken off area where the cone once existed. Site A2 was on a near-by large cone with significant fluid venting, and at a shallower depth (~12 m). Sites S1 and S2 were located on the biggest cone at Big

Strytan (Figure 1). S1 was located at ~24 m depth, on the rope side of the cone, to right of a blue rope used as a guide, and was a "big" vent, which has a focused vent opening of ~2" diameter. S2 was located above S1, at ~19 m depth. A single dive took place off the northeast point of the island Hrisey, and samples were taken for geochemistry using syringes. Seawater was sampled for background geochemistry directly out from the Strytan Dive Center.

### **Geochemistry Results**

In total 5 sites were sampled for hydrothermal fluids during the expedition. Two from the Big Strytan area (S1 and S2), two from the Arnarnesstrytan area (A1 and A2), and one from Hrisey Island (H1). Temperatures ranged from 66.6 to 78.1°C, with the highest temperature measured at the A2 site. Hrisey temperatures measured 67.4°C, while the A1 and A2 sites were 66.6 and 78.1°C, and the S1 and S2 sites were 72.1 and 73.4 °C, respectively. Various other temperature measurements where fluid samples were not taken fall within this range. The pH of the fluids at Hrisey ranged from 9.16 to 9.37, while the range for A1 (9.6 to 9.86), A2 (9.83 to 10.08), S1 (10.14 to 9.79), and S2 (9.91 to 10.22), all fall within a narrow range of values. The ambient seawater temperature was approximately 7 °C, and the pH was 8.12, and variability in both temperature and pH should be affected by seawater mixing). Thus, these values should be taken as minimum, relative to the deeper hydrothermal reservoir fluids.

Oxidation-reduction potential (ORP), which is the activity of all oxidizers and reducers in the solution relative to a platinum electrode (Myron-L meter), were always negative for samples from Arnarnesstrytan and Big Strytan (-76 (A2) to -160 (S1)), and positive for Hrisey (+103 to +156). A negative ORP indicates the ability to donate electrons; the higher the negative charge, the greater the ability to provide electrons and the more reducing the fluids. Thus, hydrothermal fluids from the SHS in general are highly reducing. Seawater ORP measured +217, and thus it is possible that the Hrisey site has mixed with oxidized seawater, either during or prior to sampling, or that the shallow-circulating source fluids are more oxygen-rich compared to the cone systems. Hrisey Island is very small, and it is thus likely that the fluids circulating through the system have not had adequate time to become reducing, and are still oxygen-rich. Using TDS as an estimate of salinity, it is clear that the hydrothermal fluids from all sites, including the Hrisey site, were very dilute compared to seawater. For example, seawater TDS was 36450 ppm, while the range for the hydrothermal fluids were as follows, also in ppm: A1 (527 to 5758), A2 (305 to 3367), S1 (464 to 3781), S2 (300 to 2430), and Hrisey (1990 to 5106). Previously, Marteinsson et al. (2001) indicated that the Big Strytan fluids were primarily derived from meteoric water with low concentrations of major seawater salts and  $\delta^{18}$ O and  $\delta^{2}$ H ratios nearly identical to local precipitation. Our data agree with this evaluation, and it is likely that not only the Big Strytan site, but also the Arnarnesstrytan and Hrisey sites are derived from local meteoric water which penetrates through the ground, is heated up, and discharges into the fjord.

Sulfide measurements indicate low but significant concentrations, which at pH 9-10 is probably in the form HS<sup>-</sup> and/or the completely deprotonated form S<sup>2-</sup>. Hrisey concentrations were lowest, ranging from 0.1 to 0.5  $\mu$ M, while A1 and A2 (6.5 to 7.6 and 7.2 to 9.8  $\mu$ M, respectively) and S1 and S2 (11.9 to 12.5 and 11.9 to 12.4, respectively) were much higher. Note that concentrations at Arnarnesstrytan versus Big Strytan were consistently lower.

Typically, all major seawater elements correlate along a mixing line between seawater and the hypothetical hydrothermal end-member, close to a zero-salt meteoric water. Calcium is the only element among this suite that seems to be slightly different for the Hrisey samples. Even though the TDS measurement of our seawater values were near what is expected for typical seawater (e.g., ~35000 ppm), our major element concentrations are consistently approximately 40% lower than the IAPSO seawater standard. This could be due to 1) analytical error, and/or 2) groundwater discharge at the site of collection. Given the wet conditions in the area, the latter is certainly possible. Thus, seawater major chemistry from our sample should be taken with caution. Of the elements analyzed in this study, Na, Mg, K, Ca, Cl, Br, B, and Sr all more or less correlate with one another, falling on a mixing line with seawater concentrations of these elements. Another trend, however, is observed in most of the trace elements (e.g.,

Si, Al, As, V, Mo, W, and although less clear, Cr, Cu, and Zn). These relationships are almost certainly controlled by the solubility of minerals contained within the Icelandic basalts. For example, predicted (quartz) silica solubility at ~75 °C is around 1.5 mM. Our samples are slightly higher than this value, suggesting a higher reservoir temperature. These data are currently undergoing a more in-depth synthesis.

Organic acid analyses included lactate, acetate, formate, propionate, butyrate, and valerate. Of all these, propionate was the only one consistently elevated in concentration in hydrothermal fluids. All measurements of these organic acids in seawater were below detection. No patterns were observed versus site and/or other geochemical parameters, although the highest concentrations of propionate were in the lowest TDS samples, suggested a deeper, hydrothermal source. DIC concentrations ranged from 0.2 to 0.8 mM, while seawater values were greater than 1.4 mM. This suggests that DIC is quite low in the hydrothermal fluids. Dissolved gases  $CH_4$ ,  $H_2$ , and CO were measured in hydrothermal fluids. While low, generally the concentrations of  $CH_4$  and  $H_2$  were elevated compared to normal seawater values. The carbon isotopic signature of the  $CH_4$  as a function of  $CH_4$  (and  $H_2$ ) in this basalt-hosted system is intriguing, as it broadens the range of potential origin of life environments significantly.

### Microbiology Results

There are two sets of microbiological data: 1) 16s rRNA clone library classifications, and 2) intact polar lipid analysis results. Lipids indicated both Archaea and Bacteria were present, although Bacteria dominated all samples (excluding H1) with the exception of S1. Up to 50% of the lipids at S1 site were archaeal. This site was the most focused vent, and therefore could be bringing up deeper subsurface Archaea. Abundant lipids included "PC" and tetraethers (GDGTs). The lipid 'PC' is found in many alpha- and gamma-proteobacteria, as well as in some gram positive and Bacteroides-Flavobacteria. Tetraethers (GDGTs) are abundantly present in different archaeal kingdoms.

Due to the patterns represented by the lipids (e.g., S1 dominated by Archaea), clone library synthesis has to date focused on sites S1 and A2 due to their similar temperature regimes. No clear differences in clone libraries could be made, however, between sites. Bacterial sequences were dominated by betaproteobacteria, particularly the genus *Dechloromonas sp.* This organism is a soil microbe known to conduct dissimilatory perchlorate reduction as well as denitrification ((i.e. the reduction of nitrate to N2) combined with the oxidization of aromatic compounds (NCBI Blast results). Deltaproteobacteria were the second most dominant group, particularly the genus *Desulfovibrio sp.* a sulfate reducer commonly found in aquatic environments with high levels of organic material, and which are major community members of extreme oligotrophic habitats such as deep granitic fractured rock aquifers. Archaeal results indicate a dominance of Crenarchaeota. Particularly, Thermoproteales, which are typical acidophiles found in Icelandic sulfataras that form H<sub>2</sub>S and CO<sub>2</sub> from elemental sulfur and organic substrates. The second most dominant archaeal group was Desulfurococcales, which are Ignicocci with optimum growth temperatures of 90°C. This group can reduce elemental sulfur to hydrogen sulfide using molecular hydrogen as the electron donor (Huber et al., 2002). A unique symbiosis with (or parasitism by) nanoarchaea has also been reported (Huber et al., 2002).

#### **Future Objectives**

The future objectives for this L&C funded work include completion of the geochemistry manuscript, and further data gathering for the microbiological characterization of the system. The microbiological data are currently being collected and synthesized by colleagues Jan Amend and Brandi Kiel Reese at the University of Southern California. It is anticipated that data collection will be completed by the end of the year, with submission of a microbiology manuscript early in 2015. It is absolutely clear that this Lewis and Clark grant will provide significant publishable results, along with seed data for submission of a larger proposal.

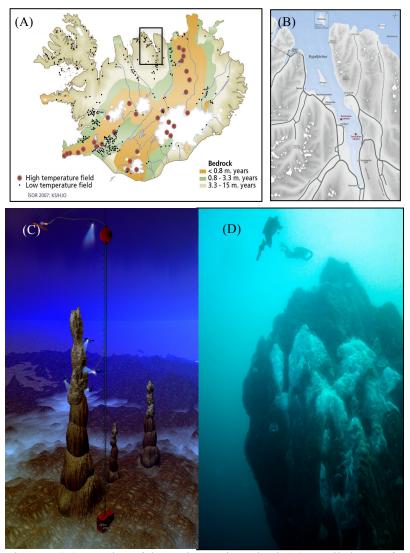


Figure 1. (A) Location of the study area in Iceland. (B) Detailed area of the Eyjafjord area, including the location of the Strýtan hydrothermal cones. (C) Schematic of the Strýtan cones (D) Underwater photograph of an actively venting portion of the cones. White areas are sites where hot hydrothermal fluids react with seawater to form mineral precipitates.