## Chemical and Isotope Characterization of Aqueous Carbon Compounds in Hydrothermal Fluids from Back-Arc Spreading Centers

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15-month, Final Report

I began my DOEI Postdoctoral Fellowship on March 28<sup>th</sup>, 2005 and left for a cruise to the Lau Basin the following morning. As is typical for WHOI postdocs, it is this access, access to cruises, resources and knowledge, that has typified the past year of my fellowship. Jeff Seewald, my postdoctoral supervisor, has provided invaluable advice in the three realms of oceanographic work: at sea, in the laboratory, and in front of the computer. This report provides a slight update to the 1-year report issued in May 2006, mostly detailing the additional work completed regarding carbon-14 measurements at NOSAMS, as well as the progress towards manuscript preparation.

Over my 15-month DOEI fellowship I participated in two cruises, a 5-week expedition to the Lau Basin that visited the Eastern Lau Spreading Center and the ValuFa ridge with R/V Melville and the ROV Jason II, and a 3-week expedition to the Lost City Hydrothermal Field on the Mid-Atlantic Ridge with R/V Ron Brown and the ROV Hercules. On the Lau Basin cruise I worked with, and under the supervision of, Jeff Seewald to sustain the day-to-day water sampling activities. This included the rubbing, cleaning and maintenance of the Isothermal Gas-Tight samplers, making decisions of where to sample, overseeing the sampling processes in the control van, and, of course, processing the samples. During the course of this expedition we collected over 70 water samples that were preserved for gas analysis, an impressively large dataset.

One of the primary objectives of the Lost City cruise was to test the feasibility of using a satellite link to keep the PI's in a land-based control center, making the decisions, and have a skeleton crew at sea overseeing laboratory and ROV operations. During this expedition I was picked to be the lead-at-sea scientist. Often, however, my duties boiled down to those of the chiefscientist. While the satellite and "tele-presence" technology was definitely proved during the course of this cruise, the land-based science community was left with a sense of detachment from the process. I, on the other hand, got a taste of what it is like to be a chief scientist, that is to say to, got the feeling that I was involved in everyone's activities, problems, and emotions. It is one thing to deliver a command from 5000 miles away, and another to execute that command when its implementation requires multiple crews from multiple arenas (ship/ROV/science/TV-production). However, at the end of the cruise I felt as though I had gained valuable insight and experience on how to run a cruise, how to motivate a crew, and how to get science done on an ever-evolving plan. My personal science objectives were met, as I collected six water and gas samples that are extremely valuable to the augmentation of my thesis work.

In the laboratory over the 15 months of my DOEI fellowship, I had the opportunity to hone my skills in method development and implementation using gas chromatographic and mass spectrometric techniques. I have measured the concentrations and carbon and hydrogen isotopic compositions of CO<sub>2</sub>, CH<sub>4</sub>, and the C<sub>2</sub>-C<sub>4</sub> alkanes from the Lau Basin and Lost City. Several of these measurements were on quantities of less than 10 nL of gas, pushing the known analytical limits of isotopic gas measurements on alkanes. In order to perform these measurements on the limited quantities of gas a method, based on previous work by Terri Rust and Frank Sansone, was developed that cryogenically focused a pulse of the sample on a section of packed capillary tubing, then ballistically heated and inlet into the mass spec. The apparatus that alternately cools and heats the trapped sample was nicknamed the "trolley" system, based on the striking similarity to a steam locomotive, and was built entirely in-house. Sean Sylva played a vital role in the day-to-day oversight of the mass spectrometer, as well as during method development, and is always a valuable source of information and advice regarding analytical isotopic techniques. In addition to stable isotope measurements, the inlet techniques developed were transferred to the "Dirt Burner" vacuum line at NOSAMS in order to isolate and measure low concentrations of CH<sub>4</sub> from Lost City and CO<sub>2</sub> from Lau Basin for carbon-14. The measurements from 2005 Lost City samples were carried out to confirm previous results of radiocarbon dead CH<sub>4</sub>. The  $^{14}$ C measurements from low-Mg, low-CO<sub>2</sub> samples in the Abe vent field (Lau Basin) provided a unique opportunity to investigate the removal of seawater bicarbonate during hydrothermal circulation.

While in front of my computer during my fellowship, I authored one NSF proposal on which I am the principle investigator (January 2006), resubmitted this proposal after rejection (August 2006), and contributed to another NSF proposal on which I was a co-PI (January 2006). While this was my first foray into NSF proposal writing as a PI, I was well supported by advice and encouragement from Jeff Seewald as well as the informal WHOI Proposal Writing Seminar run by Jim Price. After an overhaul, the focus of the proposal was shifted to the hydrogen isotope composition of  $C_1$ - $C_4$  alkanes, and included important data produced from this DOEI fellowship. This proposal, "Sources of Organic Compounds in Submarine Hot-Springs: An Experimental Investigation", was resubmitted in August 2006, and was funded in January 2007, for \$199,693 with a start date in May 2007.

Additionally, I submitted three papers from my graduate and postdoctoral work, with one published in Chemical Geology, one in review (includes Lost City alkane measurements made during my fellowship), and one in revision review. The data evolved from this DOEI fellowship was the source of three abstracts and presentations, the Lost City data was presented at the 2005 AGU Fall Meeting, and the Lau data was presented at the Ridge Theoretical Institute in Mammoth, CA June 2006, and an update will be presented at the 2007 AGU Fall Meeting. Currently, a manuscript is in preparation that relates the changes in volatile chemistry to the changes in ridge morphology in the Lau Basin. It is conceivable that another manuscript, describing specific vent alkane compositions, will result. During the period of my DOEI sponsored postdoc I gave two talks, one a WHOI MC&G Tuesday talk, and another at Harvard OEB. I attended the ORION planning meeting in March 2006 in Salt Lake City, and found it to be fairly interesting scientifically, but more helpful as a networking venue.

I regard my DOEI fellowship as a success, as it yielded two abstracts, data in one paper, one manuscript in preparation, and critical data that was parlayed into a funded NSF grant. I am grateful for the funding from DOEI and am honored to continue on at WHOI as a Postdoctoral Investigator, experimentally producing alkanes in simulated hydrothermal environments in Jeff Seewald's lab.