

Letters of Intent: Endeavour
Target Date: February 15, 2003

Formate Enrichment in Hydrothermal Event Plumes and Phase-Separated Flows Following Eruptive Events

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Description of planned research for a proposal to be submitted to the RIDGE 2000 Program (Endeavor Integrated Study Site) for the February 15, 2003 NSF target date:

Several recently published observations lead us to predict that hydrothermal flows in both sedimented and sediment-starved ridge systems undergo a period of highly elevated formate flux following recent volcanic activity. Experiments to investigate abiogenic methane production from CO₂ at ridge system pressures and temperatures have revealed facile production of formate in the presence of iron-nickel catalysts (Horita and Berndt, 1999). The formate may represent an intermediate in the formation of methane in their experiments. McCollom and Seewald (2001), however, in experiments simulating the serpentinization of olivine under hydrothermal conditions, demonstrated production of formate from CO₂ that far exceeded methane production and may have reached metastable equilibrium with hydrogen rather than behaving as an intermediate. Zeng and Liu (2000) reported analyses of formate, acetate, and propionate in fluid inclusions from hydrothermal minerals. These inclusions, thought to represent hydrothermal fluid at the time the minerals were formed, had organic acid concentrations (dominated by formate) that in some cases exceeded chloride and fluoride.

We hypothesize that abiologically produced formate represents a major carrier of reducing power from the reaction zone, where recently exposed hot rock interacts with seawater, to shallower depths where it is a readily accessible energy currency for biological communities within and above the seafloor. Decreases in hydrogen and organic acid fluxes with time may come about abiotically, through loss of reducing capacity in a system that is still sterile due to high temperature, or through growth of microbial communities that utilize these substrates within the plumbing after further dilution/cooling. From the abiotic production standpoint, we expect formate concentrations to parallel hydrogen concentrations except in systems where CO₂ may be depleted (e.g. Sansone et al., 1998). Therefore, in a basaltic system like the Endeavor ISS, we expect formate enrichment in vent flows and event plumes following eruptive events, to spike sharply and tail off on a timescale of weeks to months as has been seen with hydrogen (Kelley et al. 1998, McLaughlin-West et al., 1999). This enrichment may more-or-less coincide with the period of venting of lower salinity, phase-separated fluids. Based on limited data, it appears in ultramafic hydrothermal systems, like the Rainbow field on the Mid-Atlantic Ridge, high hydrogen fluxes continue into the brine-venting phase (Charlou et al. 2002) and we would expect formate to exhibit the same behavior.

Because of the event-detection capabilities with the SOSUS array near the Endeavor ISS, we propose to participate in rapid-response cruises to sample vents and event plumes formed by new eruptions to follow the evolution of their chemistry through time. In particular, our role will be to measure concentrations and turnover times of low molecular weight organic acids as well as their $\delta^{13}\text{C}$ signatures. The $\delta^{13}\text{C}$ measurements may help sort out biological versus non-biological processes that affect their concentrations. We have been in contact with Jim Cowen about this project and understand the logistical constraints on these time-dependent studies that require rapid-response and follow-up sampling. This suite of measurements adds a new and (we believe) critical component to the already extensive set of measurements being made. In the broader context of the time-dependent studies group, these data will be related to time since eruption, heat flux, chlorinity, fluxes of other reduced compounds and particle dynamics. Of these, hydrogen is most critical to our data interpretation because it is convertible to formate biologically or abiologically (at high temperature). Hydrogen is also probably the only biological substrate more labile than formate in the event plumes.