DOEI Final Report:

Seafloor Observatory Science and Instrumentation: A Suspended Particle Rosette Sampler for Investigating Hydrothermal Plume Particulates

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J. Breier, B. Toner, and C. R. German received funding to build a multi-sampling system for collecting suspended particulates from deep-sea hydrothermal plumes during remotely operated vehicle and autonomous (e.g. moored) deployments. The main science objectives driving this technical development are 1) determining the extent to which abiotic and microbial processes interact within deep-sea hydrothermal plumes and 2) understanding how these processes modify the exchange of material between the lithosphere and the global ocean. One peer-reviewed publication based on this research has already been published (Breier et al., Deep Sea Research, 2009), a second is waiting coauthor comments and should be submitted shortly (Breier et al., Earth & Planet. Sci. Lett., prep.), and laboratory work to support at least two other papers resulting from this effort are currently underway. In addition, the scientific and engineering results of this research were presented at two national conferences (Breier et al., IEEE Oceans, 2007; Breier et al., Fall AGU, 2008) as well as the RIDGE 2000 meeting in Portland in 2008.

The goal of this project was to develop an optically-compatible, trace-metal clean, multi-sampling system that could be used on an ROV for precision sampling of deep-sea rising hydrothermal plumes and also forward deployed on a mooring to collect time-series samples in response to episodic events (Fig.1). In addition to simply collecting samples, this Suspended-Particle Rosette (SUPR) multi-sampler was also designed to host *in situ* optical analysis systems, particularly Raman and visible reflectance spectroscopy. It solves the problems of sample geometry and control for *in situ* analysis of suspended particles by concentrating and trapping them on two-dimensional filters. These filters can be presented to an optical analysis system for as long or as often as needed and in a repeatable manner that allows for a focused beam and a minimal amount of seawater in the optical path (Fig. 2).

The SUPR sampler was successfully field tested during moored deployments in the plumes above Tica vent at 9° 50’ N East Pacific Rise (EPR) in November 2007 (Fig. 3) and has been used subsequently on ROV *Jason II* to collect buoyant plume samples from 1) the Lucky Strike and Rainbow vent fields on the Mid-Atlantic Ridge (MAR) in 2008 (Fig. 4) and 2) a series of vent fields along the Eastern Lau Spreading Center in the south Pacific during the summer of 2009. We have been using this novel set of samples to take an unprecedented look at the fine scale (μm- and nm-range) mineralogical and biogeochemical composition of non-buoyant hydrothermal plume particles – using a combination of laser Raman spectroscopy, high energy synchrotron x-ray absorption spectroscopy, and bulk and trace elemental analysis. While analysis of the MAR and Lau samples is ongoing, the EPR samples show that a significant fraction of suspended plume particles are in fact micro-aggregates of inorganic and organic material, a composition that is not predicted by the current conceptual model of this process, and which is

likely to preserve reduced Fe phases in the presence of oxygenated seawater and significantly influence the transport and dispersal of this material within the ocean (Fig. 5, Breier et al., Fall AGU, 2008, Breier et al., Earth & Planet. Sci. Lett., in prep.). The data also suggests that biotic, possibly microbial, processes play a significant role in the formation of these structures. The following are responses to the DOEI questionnaire as well as a description of the SUPR sampler.

DOEI Questionnaire:

What were the primary questions you were trying to address with this research?

The motivation for this research is to understand the material transfer between the solid earth and the oceans. Hot-rock in newly-formed seafloor is reacting with seawater all along the mid-ocean ridge network that laces the planet. Resulting seafloor hot springs are highly enriched in metals, trace elements and volatile compounds. Processes within the mineral plumes emitted from these vents appear to crucially influence whether this material is dispersed in the oceans or buried again in the seafloor. We hypothesize that an interaction between the inorganic particle formation process and biology during the earliest stages of vent plume formation crucially determines the structure and fate of the material emitted from these systems.

Our knowledge concerning this material transfer has been very limited because samples from the youngest parts of these particle plumes, where the particle formation process starts, have been so hard to obtain. In this project we addressed that technical need by building a new sampling system capable of collecting these very hard to get samples.

What have you discovered or learned that you didn't know before you started this work?

As a result of this project we obtained samples that shows that hydrothermal plume material is an intimate mixture of organic and inorganic material even at the finest scales of particle structure. This organic/inorganic structure appears to be a controlling factor for how the inorganic material within these aggregates reacts with seawater, and also for the physical characteristics of size and density that determine how far these particles can travel in the water column.

What is the significance of your findings for others working in this field of inquiry and for the broader scientific community?

This work confirms what previous research suggested, that organic and inorganic material in this environment is aggregating on the finest scales and in the water column. Further it shows that the process is common, at least at the sites examined so far, and therefore a significant factor that has to be incorporated into our estimates of chemical exchange between seafloor crust and the oceans. This is of particularly relevance to researchers studying iron and trace element cycles and has implications for those studying chemosynthetic microbial communities.

What is the significance of this research for society?

The exchange of material between the solid earth and the oceans is a fundamental flowpath for material in the earth system, akin to rain, river discharge, and erosion, but poorly understood in

comparison. Increasing our knowledge of this deep-sea material exchange improves our understanding of how the earth operates and is specifically providing new insights into the relationship between geochemistry, microbiology and the factors controlling the environmental transport of these abiotic and biotic phases.

What were the most unusual or unexpected results and opportunities in this investigation?

We were very surprised by the intimate and structurally complex relationship between organic and inorganic material in our samples. Most exciting to us however are tantalizing suggestions that microbes are playing a role in the formation of these particles. We are now pursuing work to confirm this hypothesis.

What were the greatest challenges and difficulties?

Building and deploying something new, in this case a deep-sea sampling device, usually involves technical difficulties. We suffered our share of broken parts and software glitches but fortunately nothing that we were not able to overcome. The biggest challenge for us was working out the best way to use our new gear

In science sometimes the biggest challenge is getting the opportunity to implement your plan – we've been fortunate to have help from

When and where was this investigation conducted? (For instance, did you conduct new field research, or was this a new analysis of existing data?)

As part of this project we collected samples from deep-sea vent fields in both the Pacific and Atlantic oceans. The Pacific samples were collected at 9° 50' N East Pacific Rise south of Mexico and the Atlantic samples were collected from the Mid-Atlantic Ridge samples south of the Azores.

What were the key tools or instruments you used to conduct this research?

We deployed our new instrument, the Suspended Particulate Rosette Sampler, on two proven oceanographic tools, a deep-sea mooring and the remotely operated vehicle *Jason II*. *Jason II* is a high-tech vehicle that allows us to precisely position our sampler within rising hydrothermal plumes. In comparison moorings are low-tech but they allow us to leave the sampler in one place for much longer that *Jason II* can practically remain on the bottom.

Is this research part of a larger project or program?

This research is hopefully the start of a much larger program that will focus on the relationships between chemistry and microbiology through out the oceans. An immediate outgrowth of this work is a second sampler now being developed to collect precision samples from deep-sea microbial mat communities.

What are your next steps?

We are currently analyzing a newly collected set of samples from the south Pacific that we think will provide additional insight into our recent findings. We are also actively looking for opportunities to conduct more detailed studies at other vent fields.

Have you published findings or web pages related to this research? Please provide a citation, reprint, and web link (when available).

Breier, J.A., C. R. Rauch, K. McCartney, B. M. Toner, S. C. Fakra , S. N. White, and C. R. German, A suspended particle rosette multi-sampler for discrete, biogeochemical sampling in low particle density waters, Deep Sea Research I, 2009

I have an abstract of the work up on my webpage that I plan to add to soon
http://www.whoi.edu/hpb/viewPage.do?id=17018&cl=1

Please provide photographs, illustrations, tables/charts, and web links that can help illustrate your research.

This is the website for the EPR cruise where the SUPR sampler was first deployed
http://www.whoi.edu/science/B/atlantis-15-26/background.html

This is the website for the MAR cruise where the SUPR sampler was first used on *Jason II*
http://www.deepseavoyage.research.pdx.edu/

This is the website for the Lau cruise for which samples are currently being analyzed
http://laugeomicro.blogspot.com/

Photos and illustrations at end of document.

The Suspended Particulate Rosette (SUPR) Multi-Sampler

The suspended particulate rosette (SUPR) multi-sampling system is a new oceanographic tool that has been designed to rapidly, collect multiple spatially or temporally discrete suspended particulate samples from large volumes of seawater (Breier et al., 2007; Breier et al., Deep Sea Research, 2009). Existing large water volume (30-1,000s L) *in situ* filtration systems collect only a single integrated sample while collection of 10-30 liter water samples from Niskin bottles on a CTD-rosette is unsatisfactory on two counts: 1) sample sizes are often too small for detailed particulate analyses and 2) reactions occurring during the time required to filter on-deck results in a dissolved-particulate partitioning that is operationally less representative of the natural system being investigated. To overcome these limitations, the SUPR sampler has been designed to rapidly filter 24 large-volume water samples (10-100 liters per sample depending on particle concentration and filter material) for suspended particulates during a single deployment. Unconstrained by Niskin-bottle size, the SUPR system collects sufficient material to conduct a variety of measurements on each sample and to do so in a more quantitative manner by avoiding problems like particle adherence to internal Niskin-bottle surfaces. Further, only this *in situ* approach can accommodate the longer-term inclusion of *in situ* particle analysis using optical

methods such as laser Raman spectroscopy. The SUPR sampler is intended for CTD-water rosette, ROV, and moored deployments.

The SUPR system is novel because it collects many discrete filtered samples in a way that is easy to post process, offers multistage filtering, and is compatible with *in situ* optical measurements. Each inlet has: 1) a slitted viton membrane that acts as a simple check valve to positively retain the sample; 2) a location for a future optical window set at a fixed radius from the filter center. The inlet membranes and optical windows are set below the surface of the inlet plate to allow the introduction of an interface with optical instrumentation in future work. Clamped between the inlet plate and the filter membrane is a baffle and gasket combination that serves as a mask, creating the 24 discrete sample spots. The filtering head has been designed for trace metal-clean work with primarily polycarbonate components complemented with titanium for the few essential metal components required. Water is drawn through each sample-filter sequentially by actuating a stepper motor, which rotates the filter rosette to align the next sample port with the pump; control of the valve solenoid is handled by the pump controller.

Text from 2008 DOEI report article, "Deep-sea Smoke: New tools for a fresh perspective on the ocean's most violent chemical reaction"

"Black smoke" is the hallmark of mid-ocean ridge vent systems. It consists of metal-rich, microscopic particles that form when high-temperature vent fluid is quenched by cold, abyssal ocean water. Iron and sulfur minerals such as pyrite, or fool's gold, form first, followed by slower forming iron oxides. In addition, free floating organic debris from living organisms – and possibly abiotic, or non-living organic carbon formed directly from high temperature seawater/rock reactions – become incorporated into the metal-rich particles. These particles coalesce at high-temperature vent sites and are dispersed into the ocean. Some eventually sink to the seafloor; some dissolve back into the ocean. We now suspect that some provide the fuel to support a microbial habitat in the water column above deep-sea vent fields.

For decades oceanographers have chiefly used these particles as "smoke signals" to locate vent sites by mapping out particle concentrations in the horizontally dispersing plume that forms hundreds of meters above the seafloor. Many particle samples have been collected at vent mouths as well. These samples are the basis of our understanding of plume chemistry. Collectively, they suggest that processes active in hydrothermal plumes have a direct effect in regulating global seawater composition; but we don't fully understand the mechanisms behind how this happens or to what extent microbial processes play a role.

What we lack are samples from the vertically rising part of the plume, where most particles form. Only a handful of these samples have ever been taken. The main obstacle has been technical: collecting particle samples from a rising hydrothermal plume with traditional oceanographic equipment is like trying to thread a needle at arm's length. With our DOEI grant we overcame this hurdle and developed a compact, versatile, in situ optical-sensor-compatible particle-sampling system. The instrument, which we call a Suspended Particulate Rosette (SUPR) can systematically sample rising hydrothermal plumes from a remotely operated vehicle (ROV) like Jason.

We are using the novel samples we are collecting to take an unprecedented look at the structure and chemistry of hydrothermal "smoke" particles. In addition to traditional analytic techniques, Brandy Toner (now at the University of Minnesota) is using cutting-edge methods at the Berkeley Advanced Light Source to virtually deconstruct individual particles at a microscopic level, element by element. What we are seeing is a particle structure far more complex than previously imagined, with organic and inorganic constituents in intimate association. The samples we are collecting this summer, and in the future, will help explain how such complex structures are produced and how they affect particle/seawater reactions and microbial activity in the water column. – John "Chip" Breier

Publications

Breier, J.A., C. R. Rauch, K. McCartney, B. M. Toner, S. C. Fakra , S. N. White, and C. R. German, A suspended particle rosette multi-sampler for discrete, biogeochemical sampling in low particle density waters, Deep Sea Research I, 2009.

Breier, J.A., B. M. Toner, S. C. Fakra, M. Marcus, S. N. White, and C. R. German, Hydrothermal plume particle formation at 9N East Pacific Rise: evidence of biotic and abiotic interaction, Earth and Planetary Science Letters, In Prep.

Selected Abstracts

Breier, J.A., B. Toner, S.J. Manganini, and C.R. German, 2008, Hydrothermal plume particles deconstructed: evidence of biotic and abiotic interactions in particle formation at 9N East Pacific Rise, EOS Trans. AGU, 89(53), Fall Meet. Suppl., Abstract B21A-0339.

Papers Presented at Meetings

Breier, J. A., C. G. Rauch, and C. R. German, 2007, A Suspended Particle Rosette Sampler for Investigating Hydrothermal Plumes, OCEANS 2007 IEEE Press, Vancouver, Canada.

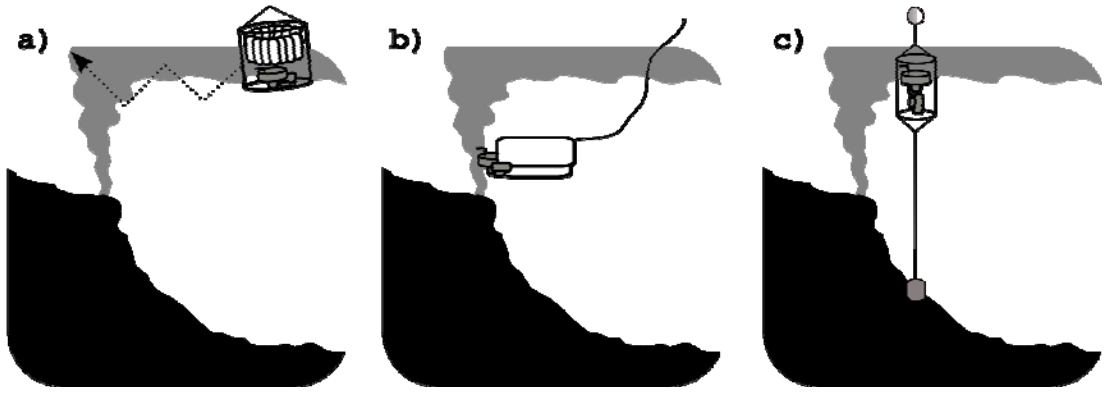

Figure 1. Hydrothermal plume suspended particulate will be collected by deploying the SUPR sampler in three ways: a) on the CTD rosette during tow-yos for spatial surveys of the nonbuoyant plume, b) on Jason for vertical profiling in the rising plume, and c) on moorings for time series sampling.

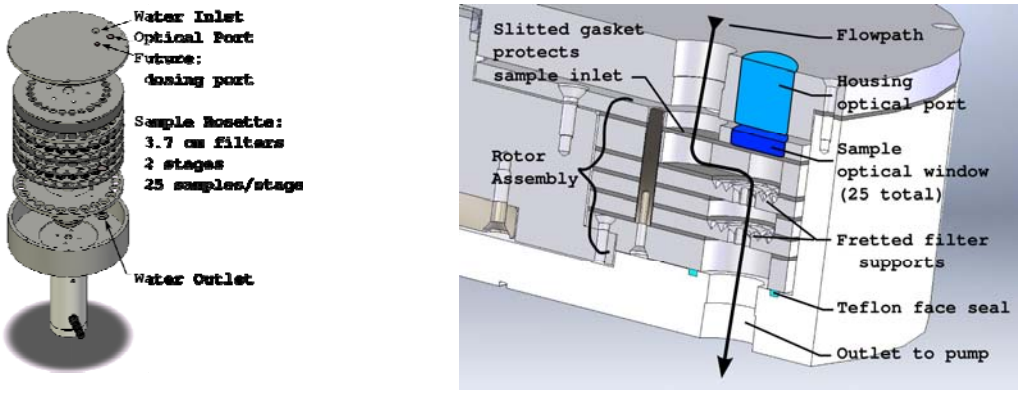

Figure 2. The optical sensor compatible suspended particulate rosette (SUPR) sampling head (left) consists of a rotating filter carousel made of a sequence of plates and gaskets, inside a stationary housing. A cross section of the SUPR sampler head (right) shows the offset flow path that provides optical access to the filtered samples (patent applied for). In the future, fused silica windows will be added to the current filter rosette to complete the optical design (Breier et al. 2009).

a) b) c)

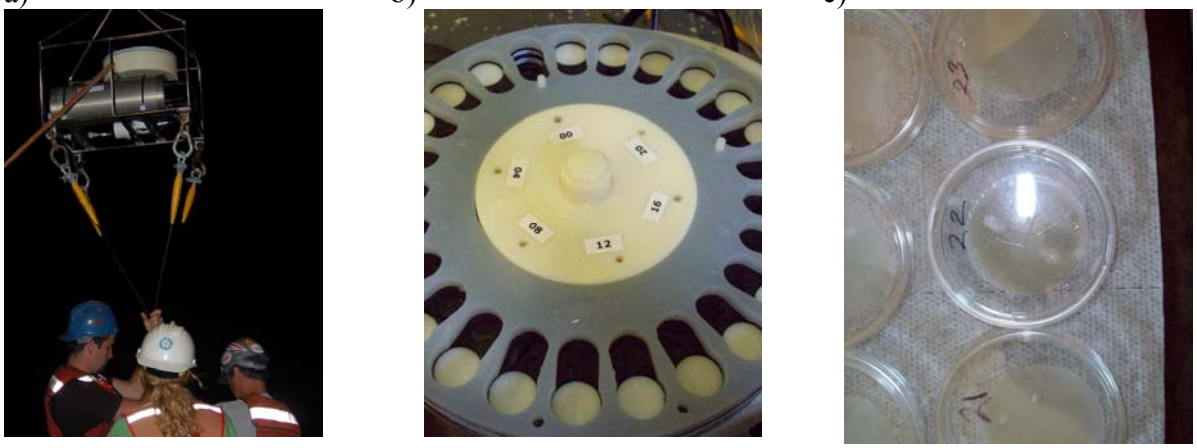

Figure 3. The a) SUPR sampler was successfully field tested during a 3-day moored deployment in the hydrothermal plumes of the East Pacific Rise 9° 50' N in November 2007. The sampler collected b) 24 hydrothermal plume samples during the time series; filtering as much as 120 liters of water for each sample and c) achieving higher than expected particle loadings on the 37mm diameter,1 micron polycarbonate filters. The center image is of the filter rosette with the external and internal covers removed; in use the samples are isolated from one another by membrane closures covering each of their inlets.

Figure 4. The WHOI SUPR sampler: a discrete particulate sample collection system for ROVs. The particulate samples were collected by *in situ* filtration from rising plume hydrothermal plums at Rainbow vent field, Mid-Atlantic Ridge. *Jason II* illustration by Oberlander and on deck photo by Kleindinst (Breier et al. 2009).

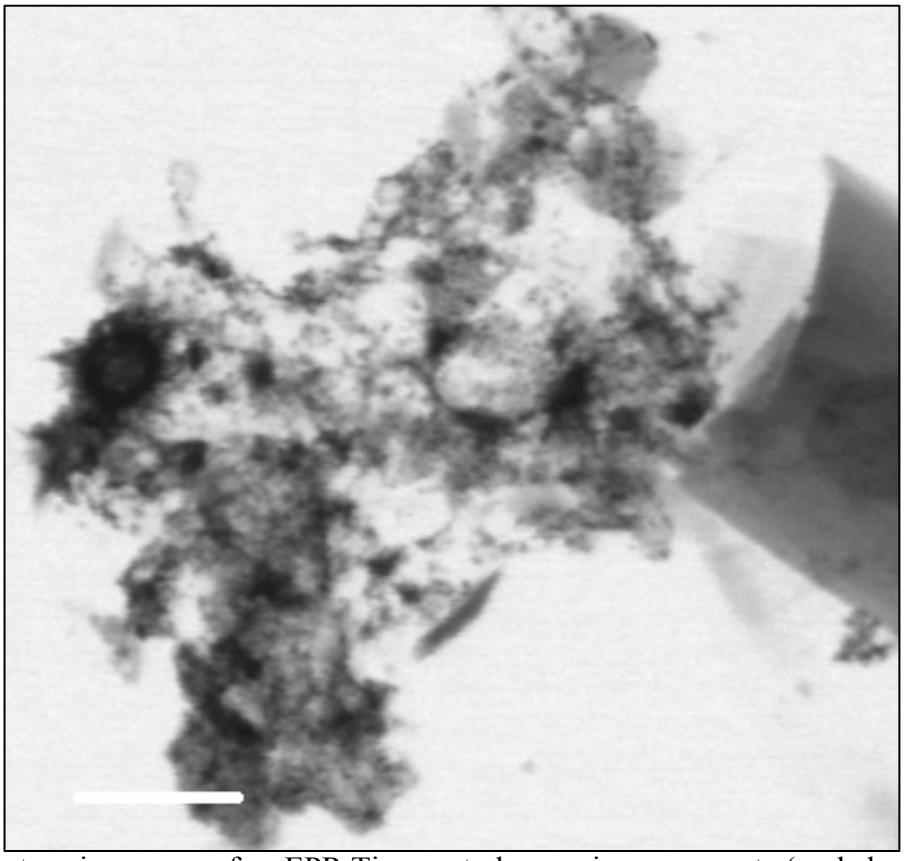

Figure 5. Spectromicroscopy of an EPR Tica vent plume micro-aggregate (scale bar is 2 thousandths of a millimeter) (Breier et al. 2009). The dark materials are iron particles, which are embedded in organic matter that appears light gray.