

ATL-15-32

Geochemistry Group Report

The area of operation for diffuse flow and focused flow work was from Biovent (x= 4389; y= 79186) in the north to Arches [x= 4864; y=76572; z= 2503] in the south. Biovent had some areas of diffuse flow around it with new *Tevnia*. Just east of Biovent where Scott Nooner placed benchmark 10 and Spahr Webb had a tripod without tide gauge [x= 4584; y= 78979], there was another new diffuse flow site without macrofauna.

Marker 15/141 [x= 4728; y= 77132; z= 2503] was less active than RESET 06 cruise and the *Tevnia* had rust coloration on their tubes. These worms were alive but not in particularly good health.

Marker 35 [x= 4804; y= 76906, 2504m] and marker 28 [x: 4671 y: 77738] were thriving with *Tevnia* and some *Riftia*.

TICA 4 [x = 4603; y= 78162] was thriving with *Tevnia* and some *Riftia* compared to January 2007. More mussels were present and the 3 large mussels collected on basalt had several juveniles around them.

Our perception is that *Tevnia* are still the dominant macrofaunal species in number at these locations.

Instruments

In situ Electrochemical Analyzer (ISEA)

We used the submersible mounted *in situ* electrochemical analyzer (ISEA) “wand” described by Luther et al. (2001; in press) and an autonomous (ISEA) “Insect” (Luther et al. in press) to measure H_2S/HS^- , FeS, Fe^{2+} , Mn^{2+} , O_2 , pH and temperature in various microhabitats in study areas. The analyzer has four gold-amalgam working electrodes that can be mounted individually in different areas for 3-dimensional mapping of the habitat. Precision placement of the electrodes will be facilitated using a seafloor-mounted cradle and micro-manipulator designed to minimize its effect on the flow field. The Insect was deployed at TICA via an “elevator”, collecting data from four electrodes every 15 seconds for up to five dives, in concert with discrete habitat characterization and biological colonization. The four working electrodes were coupled with VemcoTM temperature loggers.

Working details of the voltammetric analyzer, as well as standardization and conditioning of the electrodes are described by Brendel and Luther (1995) and Luther et al. (2001, 2002). Voltage is scanned while monitoring current; each electroactive substance gives a current that is proportional to concentration at a specific voltage. Detection limits (DL)

in μM are 0.2 for H_2S , 3 for O_2 , 5 for Mn(II) , and 10 for Fe(II) , and replicate scans agree within 2 to 5%. DL are based on a 100- μm diameter electrode but can be extended by changing electrode size and increasing scan rate (Bond 1980). Sulfide DL are at least an order of magnitude better than the commonly used Cline (1969) method on which most sulfide measurements are based.

AVS sulfide (acid volatile sulfide), pyrite and dissolved iron measurements will also be made on discrete fluid samples collected using *Alvin*'s titanium major sampling devices. These measurements will serve as an inter-comparison between *in situ* and discrete sampling methods, and to continue the sulfide time-series data collected to date from April 1991 to April 2005 (Shank et al. 1998; Shank, unpub data). These discrete samples will be analyzed onboard ship with a laboratory electrochemical analyzer and by the Cline (1969) method. Samples will also be preserved with zinc acetate to precipitate ZnS and then frozen for additional analysis in the laboratory at the University of Delaware. FeS_2 determination is accomplished by reduction with acidified Cr(II) after AVS determination by acidification with 3 M HCl (Rozan et al. 2002). AVS is the sum of the free sulfide ($\text{H}_2\text{S} + \text{HS}^-$), FeS and metal sulfides (ZnS , PbS , CdS) other than pyrite and copper sulfides. Solid phase samples will also be taken concomitantly with the faunal collections and the outer surface ($< 3\text{mm}$) will be analyzed to determine Fe(II) and Fe(III) (Kostka and Luther 1994; Rozan et al. 2002). About 0.10 g of sediment is leached in dark vessels with $\text{pH} = 2.5$ oxalic acid solution for 10 hr, then buffered to $\text{pH} = 4.5$ with acetate buffer. Ferrozine is added to an aliquot to detect Fe(II) ; ferrozine with the reductant, $\text{NH}_2\text{OH}\cdot\text{HCl}$, is added to another aliquot to determine total Fe [$\text{Fe(II)} + \text{Fe(III)}$].

Chemistry

An electrochemical sensor "wand" was used from *Alvin* on 7 of the 9 dives on this cruise [dives 4400 and 4404 did not have *in situ* chemistry]. An autonomous ISEA was deployed at Tica on dive 4401. Discrete samples were obtained from diffuse-flow and high-temperature vents to measure Fe(II) and pH . They also were treated with basic Zn(II) to precipitate sulfide for measurement of acid volatile sulfide (H_2S and FeS) and Cr(II) reducible sulfide (mainly pyrite) in the laboratory at the University of Delaware.

ISEA "wand" – *in situ* data collection from *Alvin*

Based on our previous published work, we planned to coordinate collection of our chemical with the biological data of Dr. Shank's student K Buckman to better understand why different organisms reside in different (or similar) ecological niches. Also, we planned to prospect for warm diffuse-flow waters, because the detection limit for H_2S is about 200 nanomolar for the gold-amalgam working electrodes used.

To accomplish these goals, an *in situ* electrochemical analyzer "wand" (ISEA by Analytical Instrument Systems, AIS) was placed on *Alvin* and was mated with four gold-amalgam working electrodes, a counter electrode and reference electrode. A temperature probe was also mounted in the wand, but the temperature probe was damaged on dive 4401 and it was not possible to resurrect it. The holster, which houses the wand, had an

open bottom so that water flowing upwards could be monitored for sulfide and the discovery of diffuse flow and/or vent areas.

On *Alvin* dive 4408, an electrical connection caused a malfunction that resulted in no data collection. The ISEA wand successfully collected chemical data around *Tevnia*, *Riftia*, mussels, amphipods, fish, etc. Preliminary data analysis indicates that *Tevnia* reside in higher temperature, higher sulfide and lower oxygen waters. *Riftia* reside in more moderate temperature, sulfide and oxygen environments. Mussels and amphipods reside in near ambient oxygen and low sulfide water.

For all other dives, we obtained good chemistry. This also included chemistry of amphipods for several minutes during dive 4401.

ISEA “Insect”- autonomous *in situ* data collection

We deployed an autonomous ISEA, named the “insect”, on dive 4401 and recovered it n dive 4405. The system used four gold-amalgam electrodes to measure O₂, H₂S, iron and sulfur species. Each electrode was coupled with a VemcoTM temperature probe. The ISEA also contained a radio communication device which was successfully used on three separate dives (4401,4405, 4407) by three different operators. The communication is described in detail in a separate report by Don Nuzzio.

Date	Dive	Electrode	Color	Vemco	Housing
6/05/08	4401	B7	Red	1118	219
6/05/08	4401	B4	White	2879	215
6/05/08	4401	B1	blue	2875	208
6/05/08	4401	B13	Yellow	2884	256

Table 1 . Deployment schedule of ISEA with electrode identification numbers, color of exterior electrical tape, VemcoTM and housing identification numbers.

Hydrothermal Vent Fluid and Black Smoker Chimney Sampling

A total of 5 titanium major pairs are used for sampling high temperature vent fluids and 1 major pair is used for sampling diffuse flow. Two chimneys are sampled, from P vent and Bio9 vent. These samples are going to be analyzed for their metal content and metal isotopic composition later on shore.

On board Analyses of Hydrothermal Vent Fluids

We performed chemical analysis of samples from major pairs on board the ship. Fe(II) was analyzed by the ferrozine method, without the addition of any reductant such as hydroxylamine hydrochloride. pH measurements were also made. Samples were treated with basic Zn(II) to precipitate sulfide for measurement of acid volatile sulfide (H₂S and FeS) and Cr(II) reducible sulfide (mainly pyrite) in the laboratory at UDel. Portions of the vent samples were set aside for mercury and radionuclide analysis which are going to be performed by collaborator groups.

A predetermined volume of sample was filtered through 0.22 μm polycarbonate disc filters, and the filtrate was then ultrafiltered through a 10 kDa membrane in an effort to separate further the discrete molecular sized species present. After the filtration scheme, dissolved Fe(II) was determined in each filtered fraction. A set of filtered, unfiltered, and ultrafiltered samples were then frozen immediately while another set was acidified with nitric acid. ICP-MS analysis will be conducted at Georgia Tech to determine the elemental composition of the dissolved, <10kDa, and particulate phases present in hydrothermal vent fluids.

The anions Cl⁻ and SO₄⁻² were determined in the vent fluids using ion chromatography (IC) and will provide information regarding any vapor/brine phase separation occurring at high temperature zones in the spreading center and also the extent of seawater mixing during sampling. These species may also provide a basis for chemical speciation modeling of metal binding upon ICP-MS analysis of the vent fluids. Additionally, an high pressure liquid chromatographic technique (HPLC) provided quantification of polythionates (mainly S₂O₃⁻² and S₄O₆⁻²), which were determined to be a significant chemical component in the fluids upon measurement on the ship.

Ex-situ voltammetric analysis was also conducted on the vent samples after dilution with 0.54 M NaCl, chosen as the dilution media in to minimize changes in pH and ionic strength of the vent fluids. This analysis was able to estimate free ΣH₂S, S₂O₃⁻², FeS_(aq), and Mn⁺² in the vent fluids as well and provide insights as to their behavior at the Au/Hg amalgam electrode.

Niskin Samples

Niskin bottle samples were collected at the entire series of benchmarks placed during the geophysical portion of the cruise. These benchmarks were strategically located both along and across axis. After collection and on board the ship, a predetermined volume of sample was filtered through 0.22 μm polycarbonate disc filters. A set of filtered and unfiltered samples were frozen immediately while another set was acidified with nitric acid. The filters were also frozen. ICP-MS analysis of the samples will be conducted at Georgia Tech to determine the elemental composition of the dissolved and particulate phases as a function of distance from hydrothermal vents.