Summary of *In situ* electrochemical analyzer (ISEA by AIS) data and discrete sample data

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We have three areas where chemical contributions were made. The first two are real time or *in situ* data collection experiments. First, an ISEA was used from *Alvin*. Second, a second ISEA was deployed at a diffuse flow site (marker #8). Third, discrete samples were obtained 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 our laboratory back in Delaware.

Alvin – *in situ data collection*

Goals/Objectives

Based on our previous published work, we planned to coordinate collection of our chemical with the biological data of Drs. Lutz, Shank, Vetriani, Siefert and Taylor 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.

Experimental design

To accomplish these goals, an *in situ* electrochemical analyzer (ISEA by AIS) was placed on *Alvin* and was mated with two gold-amalgam working electrodes, a counter electrode and reference electrode. Two gold-amalgam electrodes were mounted in a titanium wand on the port front side of the basket. Temperature and pH probes were also mounted in the wand. The pH probe is a new experimental design and was tested on all dives. 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.

Accomplishments

On dive 4201, electrochemistry data showed that *Alvin* caused contamination of the water column as mud from the Gulf of Mexico cruise was still in the aluminum tubes that are the frame of the *Alvin* basket. During the cruise, sulfide was released from the muds and easily detected in the waters at the front of the basket as the submersible descended through the water column. Because a switch in *Alvin* malfunctioned, the dive was aborted. After this dive, George Luther and Anton Zafereo, from the *Alvin* group, cleaned the mud from the insides of the aluminum tubes.

On dive 4202, an electrical connection caused a malfunction that resulted in no data collection. This was corrected and data was collected on all subsequent dives.

On dive 4203, electrochemistry data were collected to maximize biological sampling and video analysis in diffuse flow areas. At the end of the dive, a diffuse flow area near old marker 82 was found with a temperature of 30 ^{o}C. *In situ* sulfide measurements indicated the site had near 1 mM sulfide concentration. Markers (8 and 11) were deployed and this site was eventually selected for INSECT and McLane pump deployments.

On dives 4204 and 4205, electrochemistry data were obtained; however, the electrode wand was not removed from its holster to collect data that would correlate with diffuse flow areas and biological features. The dive plan was not adhered to by the observers. Still, warm diffuse flow waters were observed because the wand was in a holster with an open bottom.

On dive 4206, electrochemistry data was collected to maximize biological sampling and video analysis in diffuse flow areas. In particular, data were collected (1) at coordinates X=4511; Y=77875 before the sediment trap was released and (2) at diffuse flow about 5m from Marker #10 where 3 sandwiches were deployed. Data were also obtained at the colonization area where markers #8 and 11 reside.

On dive 4207, electrochemistry data were collected to maximize biological sampling and video analysis in diffuse flow areas. Specifically, data were collected at the site prior to releasing the Siefert McLane pump near marker #11 (near old marker #82). Then data were collected to properly place TAMS and Rounds. Data were then collected at several areas along the diffuse flow fissure to ascertain optimal placement of the INSECT electrodes.

Unattended electrochemical analyzer for short and/or long term deployments (we use the term INSECT that was coined by one of the *Alvin* pilots) – *in situ data collection*

Goals/Objectives

We planned to deploy an unattended ISEA which would be recovered during our January, 2007 cruise. The system would use four gold-amalgam electrodes to measure O_2, H_2S, iron and sulfur species. Long term monitoring would document the chemical changes at the diffuse flow habitat so that a better understanding of colonization of microbes and macrofauna could be achieved.

Accomplishments

After dive 4206, the unattended ISEA from AIS (INSECT) powered by 4-24 V DC batteries was sent down on an elevator to marker #11 for a six month deployment. Four electrodes and temperature sensors were then placed in different diffuse flow areas at marker #11 on dive 4207. We plan to recover the system and download data in January 2007.

Lab based analyses for Fe(II), pH, sulfide and Cr(II) reducible sulfide

Goals/Objectives

We planned to help with chemical analysis of samples from major pairs. Fe(II) was analyzed by the ferrozine method without the addition of any reductant such as hydroxylamine hydrochloride.

Accomplishments

Thirty samples from major pairs (15 samples with some collected in duplicate) were analyzed for Fe(II) and a selection of these were analyzed for pH. Twenty-six of these samples were from vents and 4 were from diffuse flow. Several of these samples were treated with basic Zn(II) to precipitate sulfide and then frozen for subsequent analysis back home.

One basalt sample from dive 4202 had orange coloration. A few mg of orange material were scraped and placed into a plastic test tube. Ferrozine and hydroxylamine were added. A purple color developed overnight indicating that Fe(III) was present.