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Craig L. Moyer
Western Washington University, craig.moyer@wwu.edu

C. Geoffrey Wheat

Hans W. Jannasch

Josh N. Plant

Francis J. Sansone

See next page for additional authors

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Authors
Craig L. Moyer, C. Geoffrey Wheat, Hans W. Jannasch, Josh N. Plant, Francis J. Sansone, and Gary M. McMurtry

Continuous sampling of hydrothermal fluids from Loihi Seamount after the 1996 event

C. Geoffrey Wheat,[1, 2] Hans W. Jannasch,[3] Josh N. Plant,[3] Craig L. Moyer,[4] Francis J. Sansone,[5] and Gary M. McMurtry [5]

Abstract. For at least 9 years prior to July 1996, hydrothermal fluids flowed from Pele's Vents on Loihi Seamount, Hawaii. In July-August 1996 a tectonic-volcanic event occurred that destroyed Pele's Vents, creating a pit crater (Pele's Pit) and several sites with hydrothermal venting. In October 1996 we deployed two new continuous water samplers (OsmoSamplers) at two of these hydrothermal sites and collected fluids using traditional sampling techniques to monitor the evolution of crustal and hydrothermal conditions after the event. The samplers were recovered in September 1997, and additional discrete vent fluid samples were collected. The OsmoSampler located along the south rift at Naha Vents captured a change in composition from a low-chlorinity, high-K fluid (relative to bottom seawater) to a high-chlorinity, low-K fluid. These changes are consistent with the fluid cooling during ascent and being derived from several different sources, which include high- (>330°C) and low- (<150°C) temperature components and a source of magmatic volatiles. The other OsmoSampler, which was deployed on the rim of Pele's Pit at Lohiau Vents, captured warm hydrothermal discharge that originated from a high-temperature source (> 330°C) into which magmatic volatiles were added. During the deployment, thermal and fluid fluxes decreased. At Naha the transport of heat and chemicals was decoupled. The chemical and thermal evolution of hydrothermal fluids after the event on Loihi is consistent with previous models based on events that have occurred along mid-ocean ridges. The event at Loihi clearly had an effect on the local hydrography; however, the integrated effect of chemical fluxes to global budgets from similar events is uncertain. Chemical fluxes from similar events may have a global impact, if ratios of chemical (e.g., CO_2, Fe/Mn, Mg, sulfate, and K) to thermal anomalies greatly exceed, or are in the opposite direction to, fluxes from mid-ocean ridge hydrothermal systems.

1. Introduction

Changes in the chemical composition of hydrothermal discharge after tectonic-volcanic events have been documented along mid-ocean ridges [e.g., *Baker et al.*, 1987, 1998; *Butterfield and Massoth*, 1994; *Von Damm et al.*, 1995, 1997; *Massoth et al.*, 1995, 1998], and a conceptual model has been developed to explain the chemical evolution of venting fluids [*Butterfield et al.*, 1997; *Von Damm et al.*, 1997; *Delaney et al.*, 1998]. However, the timing of this evolution is uncertain. To date, observations of temporal variability in the chemical

composition of hydrothermal fluids have relied on repeated submersible operations and the collection of discrete samples. Thus, defining the timescale over which variability occurs is limited by the periods between expeditions. While this technique provides some temporal constraints, it does not provide a continuous record of chemical change. A continuous record provides a measure of the changing physical and biogeochemical conditions within the crust and thus is useful in elucidating the temporal scale of transformations in crustal conditions, especially those that influence the pattern of seawater circulation within the crust. A continuous record also allows one to monitor the path of evolution. For example, are changes in crustal conditions continuous or instantaneous? Do these changes result in changes in hydrothermal fluid chemistry that are monotonic or do chemical changes follow a circuitous pattern in response to changes in crustal plumbing?

We have developed a new water sampler (OsmoSampler (H. W. Jannasch et al., Long-term in situ osmotically pumped water samplers, submitted to *Deep Sea Research*, 2000, hereinafter referred to as Jannasch et al., submitted manuscript, 2000)) that allows for the continuous collection of fluid samples. Here we present vent fluid chemical and thermal data collected with two OsmoSamplers and compare these data to data obtained using traditional discrete sampling methods.

[1]Global Undersea Research Unit, University of Alaska, Fairbanks.
[2]Also at West Coast and Polar Regions Undersea Research Center, Moss Landing, California.
[3]Monterey Bay Aquarium Research Institute, Moss Landing, California.
[4]Biology Department, Western Washington University, Bellingham.
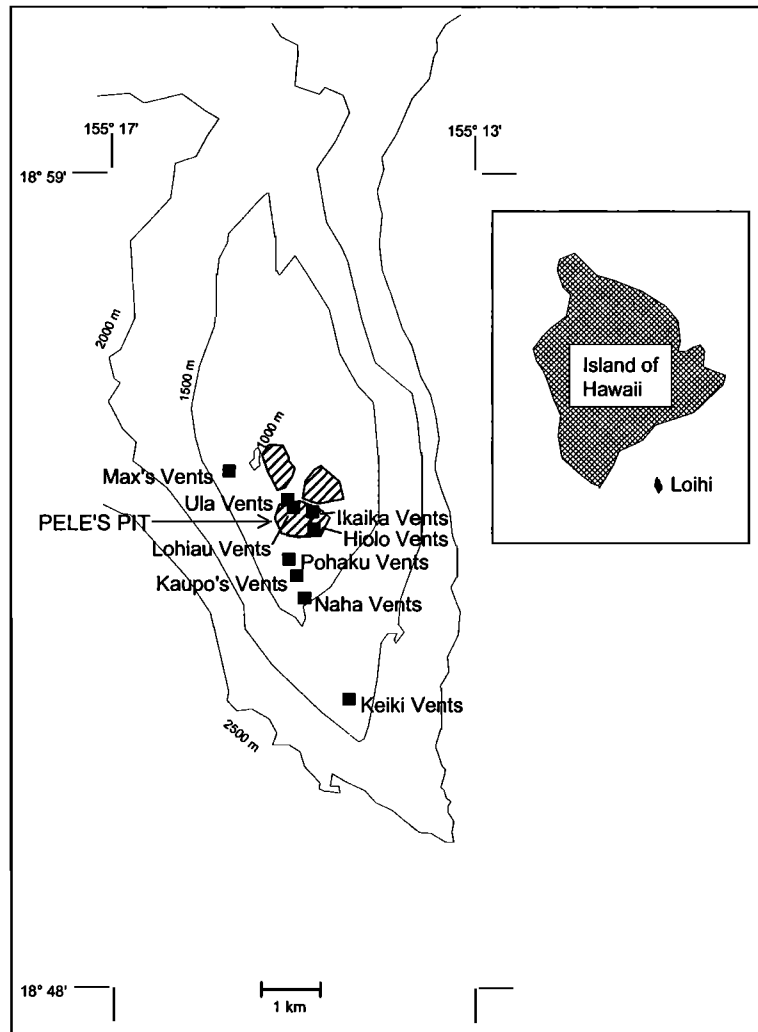[5]Department of Oceanography, University of Hawaii, Honolulu.

Figure 1. Location of the observed hydrothermal vent sites on Loihi Seamount, Hawaii. Depths are in meters. Shaded areas indicate the summit pit craters.

The samplers, which were deployed from October 1996 until September 1997, were positioned in hydrothermal outflow zones that formed after a tectonic-volcanic event on Loihi Seamount, which is a hydrothermally active, midplate, hot spot volcano located ~35 km southeast of the island of Hawaii. The event occurred from July 16 until August 9, 1996 and resulted in the formation of a 0.06 km³ pit (Pele's Pit) [*The 1996 Loihi Science Team*, 1997]. This transformation in crustal conditions altered the pattern of hydrothermal circulation through the seamount, changed the chemical composition of the effluent, reordered the structure of macrobiological and microbiological communities, and resulted in the formation of assemblages of sulfate and sulfide minerals that have previously not been found on the seamount [*The 1996 Loihi Science Team*, 1997; *Davis and Clague*, 1998]. Data from the OsmoSamplers and their comparison to data from fluid samples collected using traditional discrete sampling techniques allow us to document the temporal scale of chemical and thermal changes in the hydrothermal effluent. On the basis of these data we discuss changes in the conditions at depth after the perturbation and the potential global impacts of hydrothermal chemical fluxes resulting from such perturbations.

2. Background

2.1. Setting Prior to the 1996 Event

Loihi, the youngest volcano in the Hawaiian-Emperor Chain, rises ~4 km above the abyssal plain to a depth of ~970 m below sea level (mbsl) (Figure 1). Prior to the tectonic-volcanic event in 1996, the presence of hydrothermal discharge was deduced from chemical anomalies in the water column [*Gamo et al.*, 1987, *Sakai et al.*, 1987; *Karl et al.*, 1988; *Landsteiner et al.*, 1993] and from recovered Fe-rich oxides and smectites [*Malahoff et al.*, 1982; *DeCarlo et al.*, 1983]. These studies led to identifying and sampling sites of hydrothermal discharge [*Edmond et al.*, 1987; *Karl et al.*, 1988; *Sedwick et al.*, 1992, 1994; *Sansone et al.*, 1994, 1998]. Most of the known hydrothermal venting from Loihi Seamount prior to 1996 occurred at Pele's Vents at a depth of ~980 mbsl. This site was located just south and west of two pit craters and was destroyed during the formation of Pele's Pit (Figure 1). Pele's Vents were located in an area of ~20 m by 20 m, and fluids exited from a small portion (<0.1%) of this area. Other sites of hydrothermal venting were identified prior to 1996 (Max's Vents at a depth of 1249 m and Kaupo's Vents at

a depth of 1234 mbsl), but the low rate of fluid outflow or the rough terrain precluded the collection of vent fluid samples from these sites. An additional site of hydrothermal venting has been suggested at a depth of ~1800 mbsl based on chemical anomalies in the water column [*Gamo et al.*, 1987], but the source of this plume has not been identified.

Hydrothermal fluids at Pele's Vents emanated from cracks at the base of boulder-sized pillows and between pillows. These ~30°C fluids were sampled in 1987 [*Edmond et al.*, 1987; *Karl et al.*, 1988], in 1990 [*Sedwick et al.*, 1992], in 1991 [*Sedwick et al.*, 1994], and in 1993 [*Sansone et al.*, 1994]. From 1987 to 1993 the magnitude of chemical change was negligible for most chemical species, yet for some species (e.g., total CO_2, alkalinity, Ca, Mg), measurable changes did occur. These changes, however, were small (most <2% with the largest change <20%) when compared with changes observed after the event (>100%). In this paper we present chemical data from hydrothermal fluid samples collected in 1993 from Pele's Vents to represent the composition prior to the event. We report these data because they overlap earlier data sets and because we collected and analyzed these samples, thus minimizing any sampling and/or analytical biases.

2.2. Setting after the 1996 Event

The July-August 1996 event on Loihi lasted <1 month yet consisted of over 4000 earthquakes that were detected by the Hawaiian Volcano Observatory [*The 1996 Loihi Science Team*, 1997]. This activity represents the largest swarm of earthquakes ever observed at a Hawaiian volcano. About 1 month after the onset of the 1996 event, three dives were conducted with the submersible *Pisces V*. No hydrothermal vents were discovered because the particle load in seawater near the seafloor limited the visibility to <3 m. Subsequent dives in September 1996 located two sites of active venting, one in Pele's Pit (Ikaika Vents) and the other on the north rim of Pele's Pit (Lohiau Vents) (Figure 1). Unfortunately, no fluid samples were collected on the dive to Pele's Pit, and safety concerns prevented further dives to this site in 1996. In October 1996 we conducted seven dives with *Pisces V* during which we sampled three sites with hydrothermal venting (Lohiau, Naha, and Pohaku Vents). We also deployed a continuous water sampler (OsmoSampler) at each of two hydrothermal sites (Naha and Lohiau). In September 1997 we conducted five dives and returned to each of these sites. Additional hydrothermal sites (Ikaika, Hiolo, Kaupo's, and Keiki Vents; Figure 1) were discovered and sampled. The depth, maximum temperature, and number of discrete vent fluid samples collected at each of these sites are listed in Table 1.

Geologic settings in which hydrothermal vents were located after the event comprise three broad structural categories: diffuse fracture-controlled vents, diffuse talus-covered vents, and jets of hydrothermal fluids that penetrate a barite-rich base. Diffuse fracture-controlled vents were located along the flanks of the seamount (Naha, Pohaku, Kaupo's, and Keiki Vents). Here fluids flowed from large fractures (e.g., up to 1-3 m wide and tens of meters long at Naha) or between distinct pillows. Venting was patchy and each site covered an area of ~200 to 600 m^2. Similar to conditions at Pele's Vents before the event [*Malahoff et al.*, 1982; *DeCarlo et al.*, 1983], the seafloor at each of these hydrothermal sites, with the exception of Keiki, was covered with a reddish brown nontronite and iron-oxide film that was millimeters to centimeters thick. Many of the cracks from which fluids vented in 1996 lacked any sign of active venting in 1997. For example, the large fracture (1 to 3 m wide, several meters deep, and tens of meters long) at Naha had 19.2°C fluid venting from it in 1996 and was dormant on a return visit in 1997.

Diffuse hydrothermal venting through talus was located on a steep slope (~45°) that bounds the rim of Pele's Pit and a near vertical wall that defines the northern extent of the caldera (Lohiau and Ula Vents). This talus blanket was composed of pebble to cobble sized fragments of basalt and was stable. Stability is based on a marker that was placed on a talus slope in the middle of a chute. Even though this marker was in a seemingly perilous position, it did not move for a period of 1 year between repeat submersible operations. Venting also occurred along boundaries between talus and basaltic outcrops. Hydrothermal emissions from Lohiau Vents had maximum temperatures in the range of 53° to 77°C in 1996. The entire venting area was covered with a thin blanket (millimeters to centimeters in thickness) of nontronite and iron oxides in 1996 and a thick blanket (several centimeters) in

Table 1. Hydrothermal Vents Sampled During the October 1996 and September 1997 Dives on Loihi Seamount

			Max Temp, °C (Number of Discreet Samples)	
	Location	Depth, mbsl	Oct. 1996	Sept. 1997
Discovered October 1996				
Lohiau Vents	NW wall of Pele's Pit	1173	77 (13)	43 (2)
Ula Vents	NW wall of Pele's Pit	1099		
Naha Vents	South Rift	1325	23 (4)	11 (2)
Pohaku Vents	upper South Rift	1196	17 (4)	11 (1)
Maximilian Vents	west flank of summit	1249		
Ikaika "Forbidden" Vents	NE floor of Pele's Pit	1297-1310	200 (0)*	112-200 (14)
Discovered September 1997				
Hiolo Vents	SE floor of Pele's Pit	1288		59 (1)
Kaupo's Vents	upper South Rift	1234		15 (0)
Keiki Vents	lower South Rift	1714		25 (1)

* A. Malhoff (personal communication, 1996).

1997. Lohiau Vents included an area of ~100 m² from which hydrothermal outflow was focused through ~1% of the area in 1996. On the basis of visual observations, less than a few percent of the volumetric flow observed in 1996 was evident 1 year later.

Buoyant jets of hydrothermal fluids, with maximum temperatures of 200°C, have only been located in Pele's Pit (Ikaika and Hiolo Vents). These jets were located within several meters of the wall-floor contact. Much of this venting was associated with barite-rich mounds, which were up to a meter in diameter and several tens of centimeters high. No change in temperature was observed between repeat visits in 1996 and 1997.

2.3. Sample Methodologies

Samples of hydrothermal fluids were collected using discrete and continuous samplers. Discrete samples were collected using titanium 750-mL Walden-Weiss (Major) and 3-L Niskin samplers. Before discrete samples were collected, we monitored the temperature for 5 min at the point of venting or at the opening of a particular Niskin sampler; Niskin bottles were firmly attached to the basket on the submersible. Samples were then collected by either closing the Niskin sampler or by placing the snorkel of a Major sampler in the same location that was monitored for temperature before activating the sampler. Major samplers have a small void (~1% of the total volume) that must be filled with fluid to insure proper performance. We filled this void by priming each of the Major samplers with filtered background seawater collected at a depth of 1000 mbsl. Discrete samples from both samplers were filtered immediately upon recovery through 0.45-μm polycarbonate filters and stored in a variety of trace-metal clean, high-density polyethylene bottles with and without the addition of 6 N subboiled HCl. Unfiltered aliquots also were collected and analyzed for comparison.

Continuous samplers consist of an OsmoSampler and a miniature temperature probe (Figure 2). OsmoSamplers use the osmotic pressure that is created across a semipermeable membrane by solutions of differing salinity [*Theeuwes and Yum*, 1976]. This osmotic pressure drives water across the membrane at a rate that is dependent on the surface area of the membrane, type of membrane, salt gradient, and temperature. *Jannasch et al.* [1994] used osmotic pumps to deliver reagents into a sample stream for in situ chemical analysis. In contrast, the pumps in an OsmoSampler are used to continuously draw sample through small bore (0.8-mm I.D.) Teflon tubing that is initially filled with distilled water. We used a temperature probe with a resolution of 0.0014°C at 30°C that was programed to record a measurement every 10 min.

For deployment in a hydrothermal vent the intake for the sample tubing was positioned within a 40-cm-long T handle onto which a temperature probe was attached (Figure 2). A 2-m section of tubing separated the sample intake from the pump to allow the pump to be placed in an area without hydrothermal influence. Great care was given to insure that the pumps were not in contact with hydrothermal effluent because the rate of pumping is dependent only on temperature given an excess of salt on one side of the membrane and distilled water on the other side. Before either of the two samplers were deployed on Loihi, we monitored temperatures at the pumps. Temperatures at the pumps varied by <0.1°C for the two sites on Loihi. An increase of 1°C causes the pump rate to increase by <5%. Thus time stamps for individual samples were
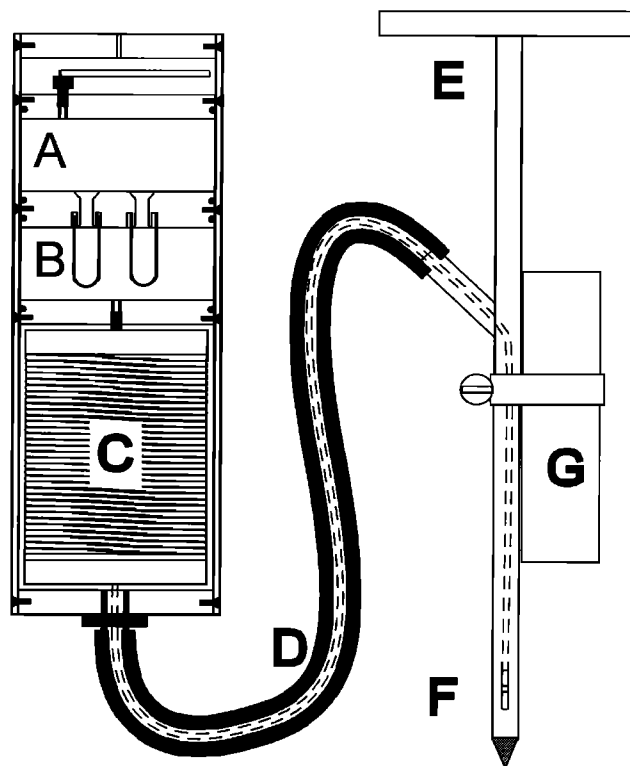

Figure 2. Schematic drawing of the OsmoSampler. A, salt reservoir; B, distilled water reservoir with osmotic membranes; C, 200 m of 0.8-mm I.D. Teflon tubing which is initially filled with degassed distilled water and is used for sample storage; D. 2-m-long flexible tubing within which the tubing from C is connected to F, the sample input, thus allowing the pump to remain at near-ambient bottom water temperature while the intake is positioned in a crack through which hydrothermal waters egress; E, T handle for submersible manipulation; and G, temperature probe. The thermistor in the temperature probe is attached to the housing near the sample intake and has a response time of 45 s and a resolution of 0.0014°C at 30°C. Laboratory tests in which sample input alternated between seawater and altered seawater confirm that dispersion resulting from diffusion and peak smearing is not significantly greater than that expected from molecular diffusion alone [*Jannasch et al.*, 2000, submitted]. Thus a step change in concentration is contained within a single 1-m section of 0.8-mm I.D. tubing after 3 months. Bacterial sheaths formed in F ~2 cm from the intake causing a failure in the OsmoSampler at Naha at the junction of B and C and a failure in the OsmoSampler at Lohiau in the sample tubing C.

determined by assuming a uniform temperature at the pump. This translates into a uniform rate of pumping for the duration of the deployment.

Chemical data were obtained by retrieving the sampler, cutting the Teflon tubing into 1- or 2-m sections, expelling the fluid from these sections into microcentrifuge tubes, storing the samples in a refrigerator, and analyzing the fluid for chemical species of interest. None of these samples were filtered, and alternating samples were acidified. No sampling or storage artifacts including evaporation of the sample were evident in laboratory tests, with the longest test lasting >3 months (Jannasch et al., submitted manuscript, 2000). Tests

included all of the major ions in seawater and some of the minor ions including Fe and Mn. Note that Fe was not problematic in laboratory studies.

2.4. Chemical Analyses

Standard potential and colorimetric titration techniques were used to measure concentrations of Cl, Mg, and Ca (1σ = 0.1%). Alkalinity was determined by potentiometric Gran titration on 20-mL aliquots of discrete samples (1σ = 0.5%) and on 0.5-mL aliquots of samples from the OsmoSampler (1σ = 2%). Few samples collected with the OsmoSamplers were analyzed for alkalinity because the analysis consumed the entire sample. Chlorinity, Ca, and alkalinity measurements were conducted at sea. In addition, some Mg analyses were completed at sea. Repeated and additional Mg analyses were completed ashore and confirmed the lack of evaporation, even with a small sample size of 0.5 to 1 mL. We also used standard inductively coupled plasma atomic emission spectrometry (ICP-AES) for determining concentrations of Mn, Fe, Sr, Si, Ba and B (1σ ~2%), ion chromotography for sulfate (1σ = 2%), and atomic absorption techniques for K (1σ = 2%). Only the ICP-AES analyses were conducted on acidified aliquots.

3. Results

In this section we present the deployment history of the two OsmoSamplers that were deployed in 1996, one at Naha Vents and the other at Lohiau Vents. We compare data from the OsmoSamplers with data collected using traditional discrete methods to show that OsmoSamplers provide an unbiased continuous record for many dissolved chemical species. We include data from Pohaku with data from Naha because (1) Pohaku is the only other site from which we acquired chemical data in 1996 and 1997, (2) both sites are located along the south rift, and (3) the chemical compositions of hydrothermal effluents from both sites are similar.

3.1. Deployment of OsmoSamplers (Naha and Lohiau)

We deployed an OsmoSampler at Naha ~3 m from the main fissure that lies parallel to the south rift. The sample intake was placed in a crack that split a basaltic pillow. Hydrothermal fluids that emanated from this crack in 1996 had a maximum temperature of 22.8°C using the probe attached to the submersible. This temperature is ~2°C warmer than the initial temperature measured by the temperature probe attached to the OsmoSampler. This difference is likely the result of the depth of penetration into the crack and the diffuse nature of flow from the crack that could have been altered when the probe was deployed. Given the similar temperature measurements, the OsmoSampler intake was well located.

An OsmoSampler and temperature probe were deployed for 351 days at Naha. The temperature probe recorded data throughout the deployment; however, the OsmoSampler failed after ~3 months. This failure was caused by precipitates that clogged the sample tubing within the first few centimeters of the sample intake in the T handle. When the precipitates became dense enough to generate sufficient resistance to flow, seawater was pulled into the distilled water reservoir at the junction between this reservoir and the sample tubing (Figure 2). Thus bottom seawater was collected and homogenized in the distilled water reservoir for the remainder of the year. Given the volume of this reservoir, the chlorinity of the fluid

in the reservoir (note that Cl cannot pass through the membrane and the chlorinity of this fluid was too low to have a significant effect on the rate of pumping), the amount of hydrothermal fluid in the sample coil, deployment and recovery dates, and a constant pump rate that is mandated by the lack of variation in temperature at the pump. This OsmoSampler collected fluids in the sample coil for 87 days before the failure occurred.

The failure was caused by the precipitation of iron oxide sheaths that are biological in origin. The microbial species responsible for these sheaths have been cultured and tentatively identified as iron-oxidizing bacteria, similar to those previously described by *Emerson and Moyer* [1997]. These iron-oxidizing bacteria are commonly found on Loihi Seamount and have had their relative abundance and phylogeny assessed [*Moyer et al.*, 1994, 1995]. In the sample tubing these bacteria were responsible for removing Fe from the vent fluids, resulting in measured concentrations <0.1 μmol Fe/kg. These precipitates would likely strip the hydrothermal fluid of P, V, Cr, U, and other elements that have an affinity for Fe-oxide surfaces, but analyses were not conducted for these elements. We show below that Mn and the other elements that were measured were not affected by this precipitation.

A second OsmoSampler with a temperature probe was deployed at Lohiau in a vent that exited through a talus pile on a 45° slope. This talus contained sulfates and sulfides [*Davis and Clague*, 1998] and was located less than a meter from an outcrop that extended ~2 m above the talus slope. The outcrop provided a secure site for the sampler yet allowed us to position the sample intake in a site where temperatures reached 53°C, based on measurements with the probe attached to the submersible. We excavated this site to secure the intake and covered the site with additional rocks to diminish the effects of dilution with bottom seawater. The temperature probe on the OsmoSampler measured an initial temperature of 27°C, indicating that there was significant dilution of the effluent at the intake of the OsmoSampler.

The sampler at Lohiau also became clogged with bacterial sheaths within centimeters of the sample intake. Resistance to flow from these sheaths caused a failure, allowing seawater to enter through a weak portion of the 200-m-long sample tubing. This break in the tubing occurred ~90 m from the junction between the distilled water reservoir and sample tubing. Using the arguments that were presented above, the failure occurred on the fifth day, resulting in a 1-m separation between temperature probe and the "new" fluid intake. Immediately after the failure the OsmoSampler collected mostly bottom seawater through the new intake. However, during the deployment an iron oxide-nontronite blanket formed over the pump and sample tubing. Hydrothermal fluids flowed below this blanket, thereby creating a reduced, anoxic environment around the sampler. This combination of the blanket and the break in the sample tubing provide us with a record of the composition of vent fluids under the blanket for the last 47 days of the 336-day deployment without complications from bacterial processes (e.g., formation of Fe-oxide sheaths). Samples from the preceding 276 days were lost because they were pumped through the sample tubing and into the distilled water reservoir where they were homogenized.

3.2. Data From Naha and Pohaku

The temperature record from Naha shows an increase from 20°C to 21°C within the first month of the deployment, after which the temperature slowly decreased with time (Figures 3
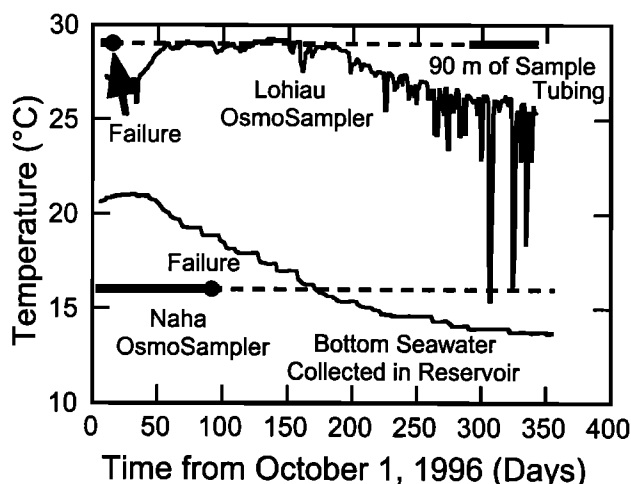
Figure 3. Temperature record for the probes deployed with the OsmoSamplers at Naha and Lohiau. Superimposed on this plot are time lines that illustrate when samples were collected in the sample tubing (heavy lines), when failures occurred (dots), and when fluids were collected but homogenized in the distilled water reservoir (dashed lines).

OsmoSampler, but samples collected in 1997 still had higher alkalinities than those collected before the event. In contrast, concentrations of Ca immediately following the event increased during the first 49 days of the deployment. The last 37 days of the continuous Ca record lie on the mixing line based on discrete samples that were collected during the September 1997 operations. More extreme changes in alkalinity and Ca for a given concentration of Si were observed at Pohaku. Within analytical uncertainty, concentrations of Sr did not change during the year at either site.

An inverse relationship was observed between concentrations of sulfate and Ba at Naha (Figure 6). Concentrations of sulfate in fluids from the OsmoSampler increased during the first 55 to 65 days of operation to concentrations above that in bottom seawater (27.8 mmol/kg). During this period concentrations of Ba decreased in these fluids. Molar ratios of sulfate/Si and Ba/Si in discrete samples from 1996 were lower at Pohaku than at Naha. In contrast to the data from Naha, molar ratios of sulfate/Si and Ba/Si increased slightly from 1996 to 1997 at Pohaku.

The chemical evolution of fluids from these two sites is different. For example, the 1996 K data from both sites and the 1997 K data from Pohaku lie along the same mixing line with respect to silica, a line with a positive slope pointing toward an end-member fluid with a concentration of K greater
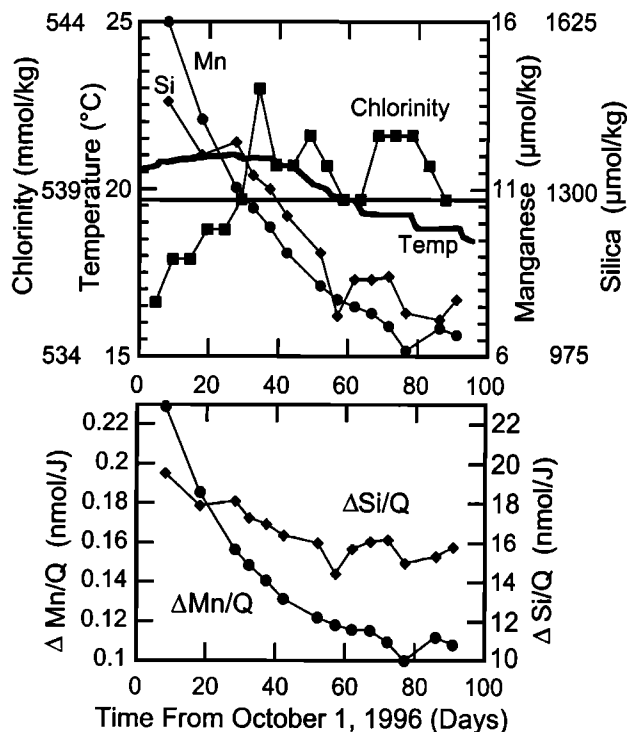
and 4). This decrease occurred as a series of step functions resulting in a stair-step appearance with time. The largest of these decreases in temperature was ~0.4 to 1.0°C, and the temperature at the time of recovery was 13.7°C, ~10°C above ambient. Temperature fluctuations were no greater than 0.2°C throughout the deployment.

An example of representative thermal and chemical changes that occurred during the first 87 days of the OsmoSampler deployment at Naha are shown in Figure 4. For example, in the first 30 days the chlorinity increased from a concentration that was 3 mmol/kg below that of bottom seawater (538.6 ± 0.5 mmol/kg) to one that was 2 mmol/kg above the concentration in bottom seawater (Figures 4 and 5). We also show concentrations of Mn and Si that decrease almost monotonically during the first 55 to 65 days, after which concentrations remained uniform (Figure 4). These decreases in concentration accompany a decrease in temperature with time. The ratio of the chemical to thermal anomaly also decreases with time (Figure 4).

To illustrate the good quality of these data and the lack of storage problems, we plot concentrations of both discrete and continuous data for various chemical species against a measure of the extent of dilution of a source fluid with bottom seawater. Here we use concentrations of dissolved silica as this measure. Mg is typically used in this context because it is depleted and nonreactive in the upwelling portion of typical hydrothermal systems on mid-ocean ridges. Mg was not used here because (1) concentrations of Mg generally remain within ±1% of the concentration in bottom seawater, in contrast to concentrations of Si which are elevated more than 16 times the concentration in bottom seawater and (2) concentrations of Mg at Naha in 1996 are even greater than that in bottom seawater, implying that there is a source of Mg to these fluids (Figure 5).

Hydrothermal fluids from Loihi Seamount before the 1996 event had anomalously high alkalinities [*Sedwick et al.*, 1992]. Alkalinities were even higher in vent fluids from Naha and Pohaku after the event (maximum of 10.1 mmol/kg, Figure 6). Alkalinities at Naha decreased during the deployment of the

Figure 4. Temporal changes in temperature and selected chemical (chlorinity, Si, Mn) data from the OsmoSampler at Naha. The chlorinity of bottom seawater (538.6 mmol/kg) is represented by a horizontal line. Chlorinity in fluids collected with the OsmoSampler increase during the first 30 days of the deployment. An almost monotonic decrease in the concentrations of Si and Mn was observed during the first 55 to 65 days of the deployment. These chemical trends in concert with a decrease in the ratios of Si/thermal and Mn/thermal anomalies with time are consistent with a change in the source fluid composition.
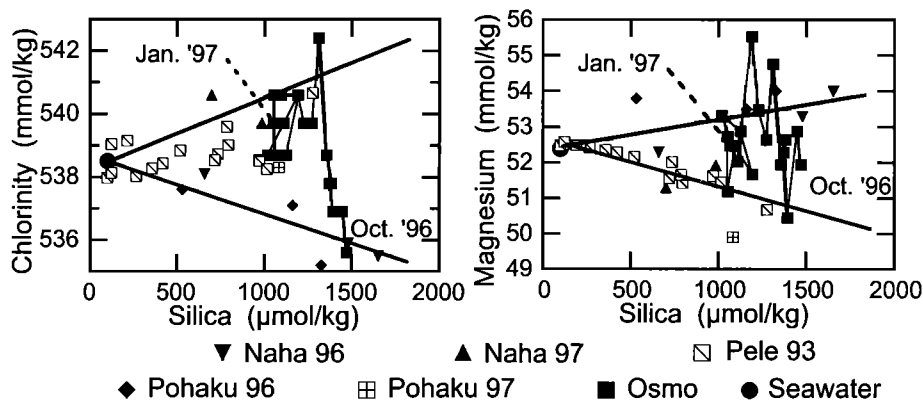
Figure 5. Plots of chlorinity and Mg versus Si for fluid samples collected with discrete and continuous samplers at Naha and with discrete samplers at Pohaku and Pele's Vents. Mixing (thick) lines are defined by concentrations of bottom seawater and hydrothermal effluent from discrete samples collected in 1996 and 1997 at Naha. Two mixing lines confirm a change in the fluid composition between submersible operations. Thin lines map the incremental changes in the concentration of samples collected with the OsmoSampler. Dates represent time stamps for the data from the OsmoSampler with the lowest concentrations of Si at the end of the record. Note that concentrations of Mg in many of these samples are greater than the measured concentration in bottom seawater (52.4 mmol/kg). Data from Pele's Vents before the 1996 event are included for comparison.

than that in bottom seawater (Figure 6). In contrast, concentrations of K at Naha decreased below this line and below the concentration in bottom seawater. This change occurred during the first 10 days after the deployment of the OsmoSampler and continued throughout the deployment. The last few samples from the 87-day record, however, lie along the mixing line defined by discrete samples collected in 1997.

Molar ratios of Mn/Si decreased with time at both sites (Figure 6). Data from the initial samples collected with the OsmoSampler match those from discrete samples, suggesting that no Mn was removed by inorganic or bacterial oxidation processes or by particle adsorption in the sample tubing. The lack of bacterial removal of Mn from these fluids is consistent with the lack of specific Mn-oxidizing bacteria. Several unsuccessful attempts have been made to enrich for and isolate Mn-oxidizing bacteria from Loihi Seamount (C. Moyer, unpublished data, 1999).

The good quality of the data from the OsmoSampler at Naha is evident from the fit of these data at the beginning of the deployment to mixing lines defined by bottom seawater and hydrothermal samples collected using discrete samplers in 1996.

3.3. Data From Lohiau

Temperature data from Lohiau show a general increase from 27.1 to 29.2°C in the first 6 weeks followed by a 15-week period of relatively uniform temperatures before decreasing gradually to 26.0°C at the end of the 336-day record (Figure 3). A few sporadic drops in temperature of ~2°C were observed during the first 7 months of the deployment. More frequent and larger drops in temperature (3-12°C) occurred during the last 18 weeks of the deployment. These temperature excursions lasted for as long as 1 to 2 days.

The 47-day record of chlorinity, temperature, Ca, and Fe from Lohiau obtained at the end of the deployment illustrates the "typical" trends observed in the other ions (Figure 7).

There is a change from a more hydrothermally altered fluid to a less altered fluid then back to a more altered fluid that is independent of perturbations in temperature recorded at the vent. This lack of dependence is not surprising given that the sample intake and temperature probe were separated by ~1 m throughout most of the operation.

To illustrate changes in the composition at this site, we plot dissolved ions versus Mg. Mg is used here as the measure for the dilution of a source fluid with bottom seawater even though there is evidence for the addition of Mg to the hydrothermal fluid as this fluid ascends within the crust. Mg was chosen because the Mg anomaly is sufficiently large relative to the analytical precision, and concentrations of dissolved silica were likely affected by precipitation reactions underneath the Fe-oxide-nontronite blanket before these fluids were collected in the sample tubing. Precipitation is surmised because all of the silica data from the OsmoSampler are centered ~2 mmol/kg (Figure 8). This concentration is well below the concentration expected based on discrete samples and is about the expected value for equilibrium with amorphous silica at 25°C [*Walther and Helgeson*, 1977]. The alternative hypothesis is that Si precipitated in the sample tubing. This hypothesis is unlikely, given that the most recent samples from Lohiau were only days old when the sampler was recovered and concentrations of Si during a 5-day deployment of an OsmoSampler on Axial Seamount maintained the in situ concentration of 16.5 mmol Si/kg (data are not shown).

Only three discrete samples were collect from Lohiau in 1997. Each of these samples was collected from the location where the T handle was deployed. These three samples commonly plot along the same mixing line that was determined by samples from 1996, most of which were from this same location (e.g., chlorinity; Figure 8). A comparison between the discrete data and data from the OsmoSampler illustrate that the OsmoSampler collected fluids from a different source. For example, the chlorinity data from the last
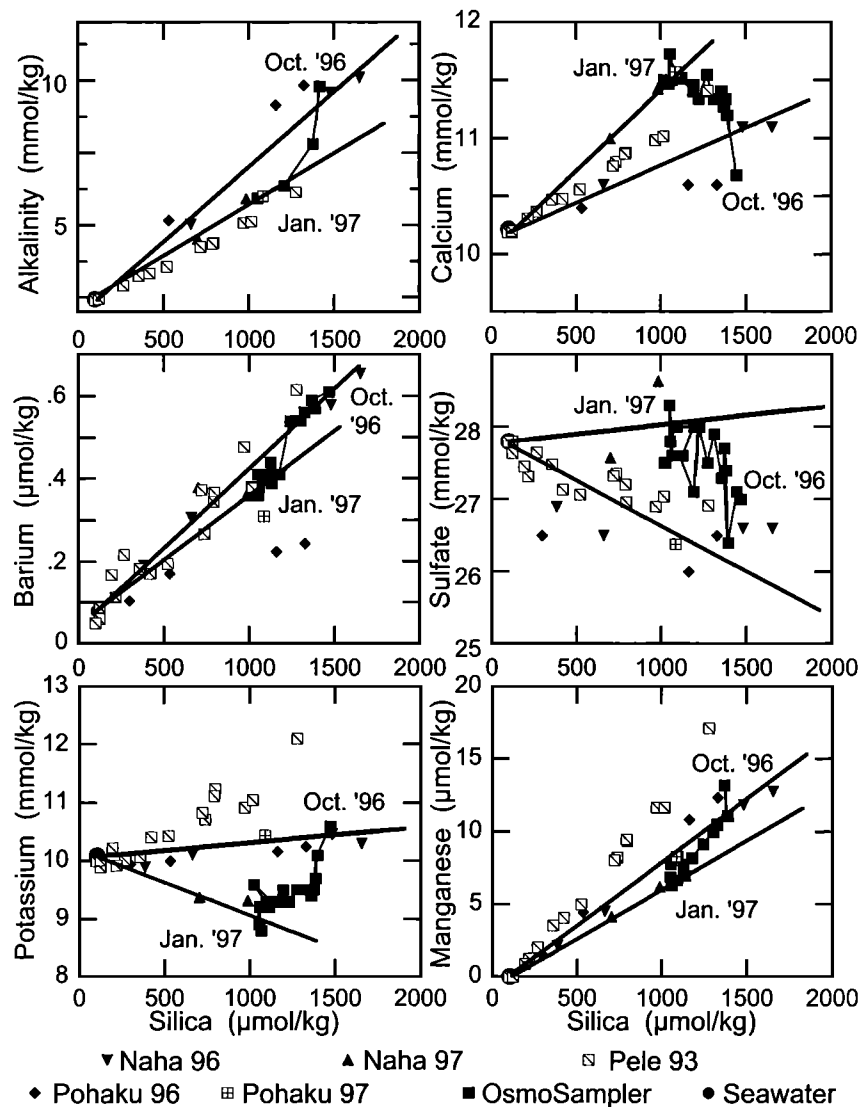
▼ Naha 96   ▲ Naha 97   ◨ Pele 93
◆ Pohaku 96   ⊞ Pohaku 97   ■ OsmoSampler   ● Seawater

Figure 6. Plots of concentrations of dissolved chemical species (alkalinity, Ca, Ba, sulfate, K, and Mn) versus Si for samples from Naha and Pohaku. As in Figure 4, we included mixing lines (thick lines) for discrete samples from Naha, the incremental change (thin line) in concentration recorded by the OsmoSampler at Naha, dates that correspond to samples collected by the OsmoSampler, and data from Pele's Vents before the 1996 event. Two mixing lines confirm a change in the fluid composition between submersible operations. Most of the data from the OsmoSampler are bounded by theses two mixing lines. Data from the beginning of the OsmoSampler record match data from discrete samples collected in 1996 and data from the end of the OsmoSampler record match data from discrete samples collected in 1997.

47 days of the deployment are higher for a given concentration of Mg than any of the discrete vent fluids that were collected and the few samples from the first 5 days of the deployment. This distinction between samples from the OsmoSamplers and discrete samplers is not as evident in the other chemical data, with the possible exception of the sulfate and Ba data (Figure 9). This result is not surprising, given that the break in the sample tubing resulted in a 1-m separation between the new sample intake and the T handle and the porous talus cover likely allows for various degrees of subsurface mixing with bottom seawater and hydrothermal fluids.

Data for other chemical species also are consistent with the presence of a variety of chemically different fluids that vent from this hydrothermal site. For example, three discrete hydrothermal samples from an orifice that was located ~5 m

from the location where the OsmoSampler was deployed have a lower alkalinity for a given change in Mg relative to samples from the orifice where OsmoSampler was deployed (Figure 9). Similarly, a plot of Fe versus Mn reveal that these three discrete samples are distinct from the other discrete samples collected at this site (Figure 10). Data from the OsmoSampler reside between the mixing lines defined by the data from these two orifices (Figures 9 and 11). In contrast to the alkalinity and Fe data, two distinct mixing trends are not observed in Ca, Ba, sulfate, K, and Mn data from discrete samples collected in 1996 (Figure 9). Trends of Sr versus Mg are similar to the Ca versus Mg trends and are not shown.

The inverse relationship between sulfate and Ba that was observed at Naha also was observed at Lohiau. Relative to discrete samples, higher concentrations of sulfate in samples
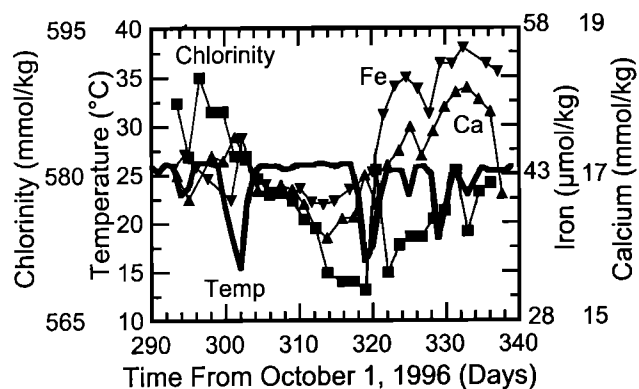
Figure 7. Temporal changes in temperature and selected chemical (chlorinity, Fe, Ca) data from the OsmoSampler at Lohiau. Chemical data map one another, illustrating that OsmoSamplers can be used to monitor redox-sensitive dissolved metals. Chlorinity and temperature scales are different from those in Figure 4.

from the OsmoSampler coincide with lower concentrations of Ba (Figure 9). Sulfate and Ba data from the first 5 days of operations at Lohiau imply that we altered the system when we excavated to deploy the sample intake. In contrast, K and Mn data from the OsmoSampler both before and after the failure generally fall along the trend defined by the discrete samples. The good quality of the data, including the Fe data (Figure 11), from the OsmoSampler at Lohiau is evident from the fit of these data from near the end of the deployment to a mixing line defined by samples collected using discrete samplers in 1997.

4. Discussion

The data presented above illustrate that OsmoSamplers are useful for monitoring temporal changes in the composition of hydrothermal vent fluids. In this section we discuss the water-rock and thermal conditions at depth that impart a signature

upon hydrothermal discharge. We then present evidence that the hydrothermal system on Loihi is cooling and compare our results with a model for the evolution of hydrothermal systems after an event. Finally, we present concerns for estimating oceanic geochemical fluxes from hydrothermal systems altered by magmatic-tectonic events.

4.1. Implications of Observed Chemical Changes

The sampler at Naha captured a fundamental change in the chemical composition of the venting fluid from a fluid with a lower chlorinity than bottom seawater to one with a higher chlorinity. This change occurred during the first 30 days of the deployment. The low chlorinities could reflect (1) the addition of magmatic water, from either a slightly evolved chamber gas generated by a parental magma (type 1 [*Gerlach and Greaber*, 1985]) or from the complete crystallization of a dike [*Shanks et al.*, 1995]; (2) phase separation followed by phase segregation [*Massoth et al.*, 1989; *Butterfield et al.*, 1990; *Von Damm et al.*, 1995]; and/or (3) the precipitation of Cl-bearing minerals [*Seyfried et al.*, 1986]. A temperature above ~330°C, which is the boiling temperature at the depth of Naha [*Bischoff and Rosenbauer*, 1988], is required for any of these processes to occur. Higher temperatures in excess of 375°C are required if phase separation occurred at a depth of 1 km below the vents. A slightly higher temperature is required to generate Cl-rich phases [*Seyfried et al.*, 1986], and an even higher temperature is associated with the release of magmatic water near the source of this water.

The low chlorinity of Naha and Pohaku fluids from 1996 thus requires a high-temperature component, but there is evidence suggesting that these fluids also have a low-temperature component. Concentrations of K in Naha fluids were 0.5 mmol/kg above that of bottom seawater (10.1 mmol/kg) during submersible operations in 1996 and in the first sample collected with the OsmoSampler. Ten days after the OsmoSampler was deployed, however, the concentration of K decreased below the concentration in bottom seawater and continued to decrease during the first 2 months of the deployment, even though chemical weathering in acidic CO_2-rich environments should enhance the extraction of K from the

▼ Lohiau 96   ▲ Lohiau 97   ◙ Pele 93
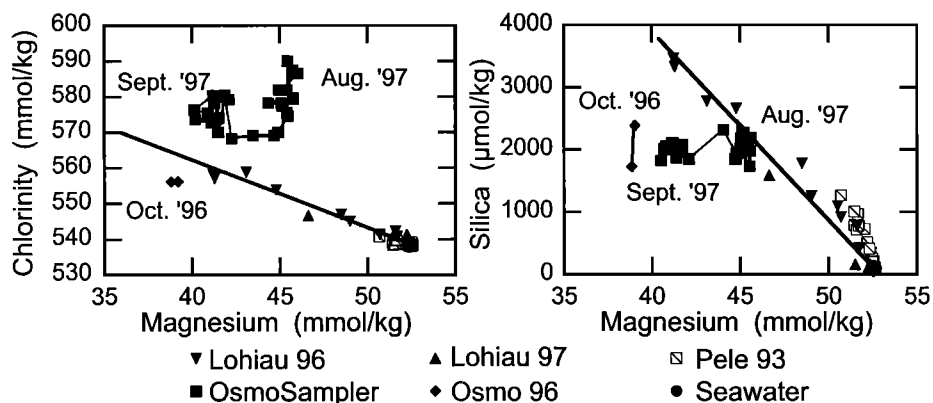■ OsmoSampler   ◆ Osmo 96   ● Seawater

Figure 8. Plots of chlorinity and Si versus Mg for samples collected with discrete and continuous samplers at Lohiau and with discrete samplers at Pele's Vents. A single mixing (thick) line is defined by concentrations of bottom seawater and hydrothermal effluent from discrete samples, suggesting that the chemical composition of the source fluid during submersible operations is the same even though samples were collected ~1 year apart. Thin lines map the incremental changes in the concentration of samples collected with the OsmoSampler. Dates represent time stamps for the data from the OsmoSampler. Osmo '96 refers to the few samples that were collect during the first few days of the deployment before the failure. Data from Pele's Vents before the 1996 event are included for comparison.
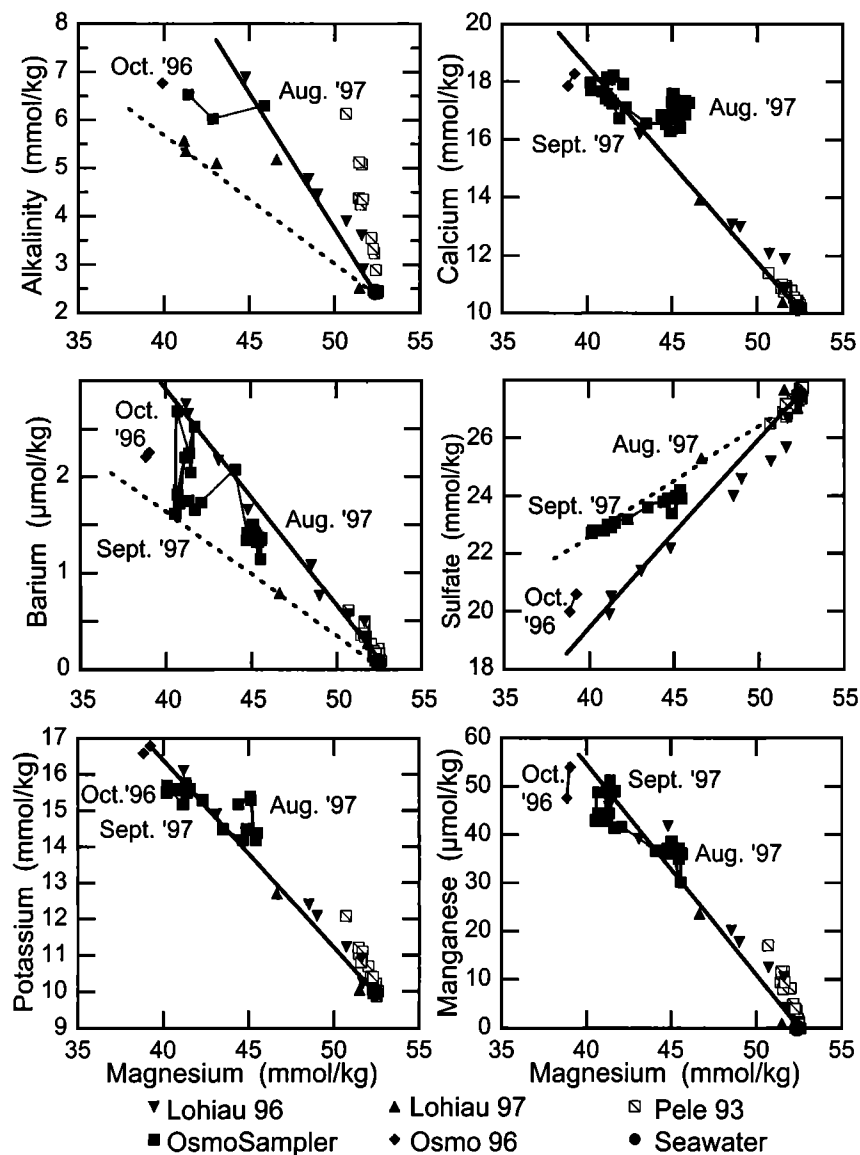
Figure 9. Concentrations of dissolved chemical species (Alkalinity, Ca, Ba, sulfate, K, and Mn) versus Mg. As in Figure 8, mixing lines (thick lines) and the incremental change (thin lines) in concentration recorded by the OsmoSampler at Lohiau are shown. A second mixing line (dashed line) for the alkalinity plot is defined by three discrete samples collected from an orifice that was ~5 m from where the OsmoSampler was deployed. Additional mixing lines (dashed lines) for Ba and sulfate are based on one sample collected during 1997. Dates correspond to samples collected by the OsmoSampler and allow for estimating time-dependent trends. Different symbols (diamonds, Osmo '96) are used for the samples collected during the first few days of the deployment before the failure. Data from Pele's Vents before the 1996 event are included for comparison.

crust [*Mackenzie and Garrels*, 1966]. One possibility for the observed change in composition is a decreasing contribution from a vapor component. There is a near-constant K/Cl molar ratio (~0.043) of vapor-dominated hydrothermal fluids from Axial Volcano [*Butterfield et al.*, 1990], which is a hot spot volcano with hydrothermal fluids that are rich in CO_2 and vent at depths similar to those found on Loihi. The K/Cl molar ratio in Naha fluids, however, is not constant and thus is inconsistent with a simple temporal decrease in the flux of a vapor component. An alternative and more likely hypothesis is that the low concentrations of K result from the influence of a low-temperature component. Hydrothermal fluids that react with basalt are enriched with K given reaction temperatures in

excess of 150°C [*Seyfried and Bishoff*, 1979]. At lower temperatures, K is removed from circulating seawater in basaltic basement [e.g., *Seyfried and Mottl*, 1982; *Alt et al.*, 1996; *Elderfield et al.*, 1999; *Wheat and Mottl*, 2000]. In conclusion, given the two K-Si mixing lines and changes in the Mn/thermal and Si/thermal anomalies, fluids from Naha have two or more distinct sources, one generated by reaction of seawater with basalt at low temperatures and at least one that includes volatile gases that are magmatic in origin [*Sedwick et al.*, 1994; *Sansone et al.*, 1994, 1998].

The OsmoSampler at Lohiau recovered fluids with an Fe/Mn molar ratio of ~6, the value determined from discrete samples collected both during deployment and recovery
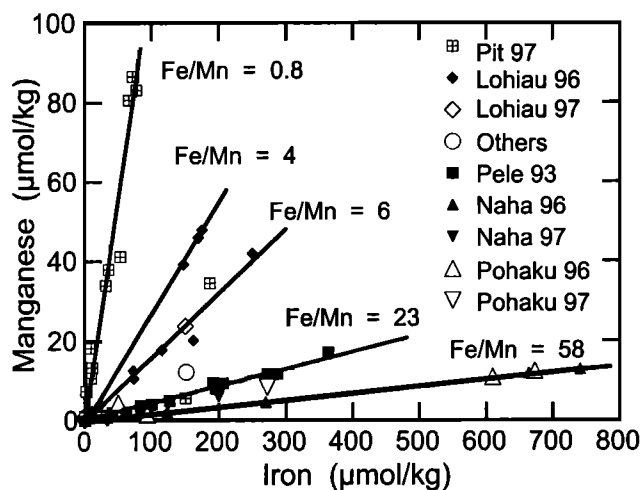
Figure 10. Mn versus Fe for all of the discrete vent samples collected in 1993 through 1997. The range in the Fe/Mn molar ratio is the largest measured to date. Fluid samples with higher molar ratios have higher alkalinities, implying that the weathering of basaltic crust at depth is enhanced by inputs of magmatic volatiles. Note that there are two Fe/Mn molar ratios for fluids from Lohiau in 1996. Fluids with Fe/Mn equal to 6 are from the orifice where the OsmoSampler was deployed. The three samples from Lohiau with Fe/Mn equal to 4 were collected from an orifice ~5 m from where the OsmoSampler was deployed. These fluids also have lower alkalinities for a given Mg anomaly (dashed line in the alkalinity versus Mg plot in Figure 9).

(Figure 10). This ratio is significantly lower than the ratio of ~23, which was the measured ratio before the event. Fe/Mn ratios in vent fluids from Loihi range from 58 in fluids from Naha and Pohaku to 0.8 in fluids from Pele's Pit (Figure 10). Low Fe/Mn ratios measured in fluids from Pele's Pit likely result from high temperature rock-dominated, water-rock reactions similar to those reproduced in laboratory experiments [Seyfried and Mottl, 1982] and measured during chronic

high-temperature venting on mid-ocean ridges (0.05 to 3.8 [Massoth et al., 1989, 1995, 1998; Butterfield et al., 1990; Butterfield and Massoth, 1994]). These low values may in part result from the subsurface removal of Fe by precipitation with sulfide. Subsurface precipitation at Loihi is consistent with the low concentrations of hydrogen sulfide (<11 μmol/kg) in all of the vent fluids collected to date. In contrast to samples from Pele's Pit, samples from Naha and Pohaku have a Fe/Mn ratio of 58, which is about that measured in whole rock samples from Loihi (~54 [Frey and Clague, 1983]).

The Fe/Mn molar ratio increases with alkalinity. For example, fluids from Naha and Pohaku have alkalinities that are >10 mmol/kg, almost twice the highest value measured before the event. Even high-temperature (200°C) fluids from Pele's Pit have higher alkalinities than that in bottom seawater but are much lower than concentrations in fluids before the event. In contrast, typical high-temperature hydrothermal systems have alkalinities that are less than the value in bottom seawater and often negative. An additional correlation between the Fe/Mn ratio and alkalinity is the observed decrease in the Fe/Mn ratio of vent fluids from Naha and Pohaku (Figure 10) that coincides with a decrease in alkalinity for a given concentration of Si (Figure 6). Given that the pH of fluids from discrete samples is ~5.2 in 1996 and 1997, the measured decrease in alkalinity likely corresponds to a decrease in the extent of magmatic inputs of CO_2. Similarly, samples from Lohiau with a low Fe/Mn ratio (Figure 10) also have a lower alkalinity for a given concentration of Mg (Figure 9). On the basis of this correlation of the Fe/Mn ratio and alkalinity, we suggest that the CO_2 content and the subsequent weathering of basalt that produces acidity controls the Fe/Mn ratio in hydrothermal fluids at Loihi and not the water-rock ratio or complexation with chloride [Ding and Seyfried, 1992; Seyfried and Mottl, 1992]. The role of residence time is unclear; however, a longer residence time affords more complete weathering reactions and possibly a higher Fe/Mn ratio. The role of temperature may also be important, because experimental evidence indicates that the reactivity of CO_2 with rhyolite is at its maximum between 150° and 200°C and relatively unreactive at temperatures >270°C [Bischoff and
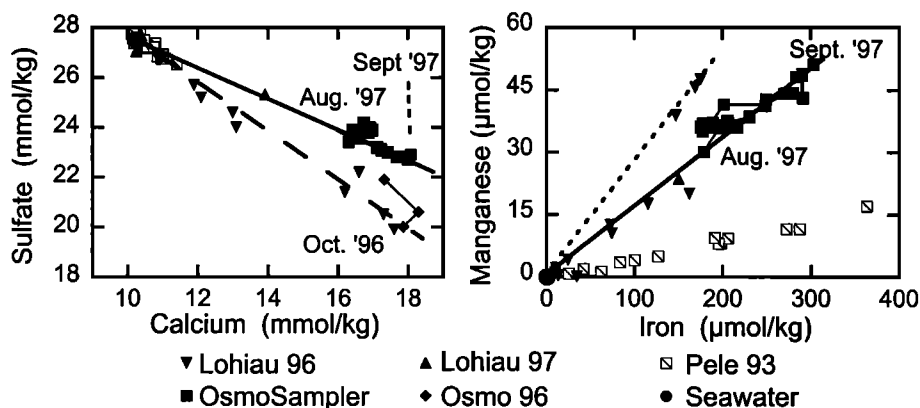

Figure 11. Plots of concentrations of dissolved chemical species (sulfate versus Ca and Mn versus Fe) at Lohiau. Mixing (thick) lines are defined by concentrations of bottom seawater and hydrothermal effluent from the last month of the deployment of the OsmoSampler. Dates correspond to samples collected by the OsmoSampler. Samples that fit this mixing line reflect various degrees of mixing of a common source with bottom seawater. Additional mixing lines (Dashed) are included. The two mixing lines in the sulfate versus Ca plot are consistent with a change in plumbing between submersible operations. The two mixing lines in the Mn versus Fe plot illustrate that fluids with different compositions vent near one another. Data from Pele's Vents before the 1996 event are include for comparison.

Rosenbauer, 1996]. In conclusion one might expect a correlation between the Fe/Mn ratio and the flux of magmatic CO_2 into a hydrothermal system. If we expand upon this suggestion and consider that hydrothermal plumes generated from events have a Fe/Mn ratio of 7 ± 3 based on data from eight plumes that have been sampled to date [*Massoth et al.*, 1998], higher Fe/Mn ratios in event plumes may in part result from the enhanced weathering of basaltic crust due to the production of acid from inputs of CO_2 or from other acid-producing weathering reactions [*Resing and Sansone*, 1999].

4.2. Implications of Observed Thermal Changes

Temperature data from Naha show an overall decrease throughout the year (Figure 3). This decrease could be caused by (1) slower flow and conductive cooling, which results in an increase in the chemical to thermal anomaly; (2) greater mixing with bottom seawater, which retains the initial chemical to thermal anomaly; or (3) changes in the source fluid. During the initial 87-day period at Naha, ratios of chemical to thermal anomalies decreased and chemical molar ratios changed consistent with changes in the composition of the source fluid (Figure 4 and 6). At the end of this 87-day period the composition of hydrothermal fluid from the last sample collected by the OsmoSampler (January 1997) matched the composition of the most Si-rich discrete sample collected in September 1997 (Figure 6). During this period the hydrothermal temperature decreased from 18.5°C to 13.5°C (background temperature of ~4°C). The constant composition and decrease in temperature during this period result in an increase in the chemical to thermal anomaly consistent with the loss of heat from conduction during ascent. This result illustrates that the thermal and chemical transport mechanisms are decoupled. Visual observations confirmed at least an order of magnitude decrease in the fluid flux between submersible operations. This decrease in fluid flux may have produced the stair-step-like features in the temperature data (Figure 3).

The effluent temperature and fluid flux from Pohaku also decreased between submersible operations in 1996 and 1997. Given the similar geologic setting and composition of vent fluids between this site and Naha, we conclude that the two sites were initially hydrologically similar. Even though the fluid compositions at both sites remain similar in 1997, they have distinctly different concentrations of K. This difference is consistent with a change in the hydrologic regime shortly after the deployment of the OsmoSampler.

The temperature record at Lohiau and visual observations from the submersible are consistent with a decrease in the fluid flux at this site as well. Much of this decrease probably occurred after the seventh month of the deployment when more frequent, larger magnitude, and shorter duration decreases in temperature were recorded (Figure 3). Similar thermal spikes have been documented at other hydrothermal sites [*Tivey et al.*, 1990; *Chevaldonne et al.*, 1991; *Schultz et al.*, 1992; *Fornari et al.*, 1998]. Because the temperature probe at Lohiau was buried beneath talus, it was more susceptible to cooling by and mixing with bottom seawater than the sampler at Naha. In contrast, the temperature probe at Naha recorded relatively smooth and monotonic variations, which are consistent with the lack of influence from mixing caused by variations in bottom currents (Figure 3). The thermal spikes at Lohiau could in part result from changes in the fluid flux, consistent with a single mixing trend for discrete samples (Figure 9). The hydrologic setting, however, is more complex. For example, the Fe and Mn data from the OsmoSampler fall

on the mixing line defined by discrete samples at the beginning and end of the chemical record, but for 17 days the OsmoSampler collected fluids with a lower Fe/Mn ratio, consistent with the presence of more than one hydrothermal fluid (Figure 11). Similar changes were observed in the Ca and sulfate data (Figure 11).

4.3. Evolution of the Hydrothermal System

During and immediately following the event, heat, volatile gases, and hydrothermal fluids issued from Loihi seamount, principally from Pele's Pit. These reduced fluids rapidly oxidized and precipitated, clouding the summit area. Hydrocasts recovered some fluids that contained several micromoles per kilogram of hydrogen sulfide and a conductivity-temperature-pressure (CTD) package detected low-salinity lenses within the pit. These lenses must have resulted from inputs of a vapor phase and/or magmatic degassing/dewatering. The emission of a vapor phase caused by phase separation and segregation during the event would require temperatures >330°C. These high temperatures are likely, given the presence of pyrrhotite, wurtzite, and rare chalcopyrite in the talus at Lohiau [*Davis and Clague*, 1998]. Venting of this effluent was short lived and ceased before our dive operations, which occurred <3 months after the onset of the event. We expect that much of the magmatic CO_2 degassed near the summit during this period.

In October 1996, degassing from magmatic inputs was still evident at each of the hydrothermal sites that were sampled [*Hilton et al.*, 1998]. Along the south rift at Naha and Pohaku, hydrothermal effluent included a freshened component. Here the flux of freshened fluids decreased continuously during the first month that the OsmoSampler was deployed at Naha. Continuous changes in the chemical composition and ratios of chemical to thermal anomalies also were evident during the first 2 months of the deployment (e.g., Mn and Si, Figure 4). During this period the concentration of K in vented fluids became less than that in bottom seawater, consistent with there being a low-temperature component to this fluid. The composition of these fluids from Naha and their evolution are clearly distinct from those that issue from Lohiau (Table 2), implying that the two hydrothermal systems are hydrologically distinct. The likely source for fluids from Lohiau is a high-temperature (>350°C) end-member similar to ones that have been sampled along mid-ocean ridges where typical fluids are depleted in Mg and sulfate, have high concentrations of K relative to seawater, and have slightly elevated chlorinities [i.e., *Von Damm*, 1995]. However, fluids from Lohiau have higher concentrations of dissolved magmatic gases than typical mid-ocean ridge hydrothermal fluids. These gases in part aid weathering reactions that result in anomalously high concentrations of sulfate, Mg, and alkalinity in the vented fluids [*Sedwick et al.*, 1992].

Our observations of hydrothermal systems on Loihi after the 1996 event are similar to those described by a model of hydrothermal evolution based on the 1993 event on the CoAxial Segment of the Juan de Fuca Ridge [*Butterfield et al.*, 1997]. The model predicts a decrease in thermal, fluid, and hydrogen sulfide fluxes with time, a short-lived vapor phase, and a gradual decrease in the flux of a brine component. Although the timing of these observations is different, a decrease in thermal and fluid fluxes with time was observed at both Naha and Lohiau. In general, fluxes of hydrogen sulfide have diminished with time. For instance, hydrogen sulfide in samples from the water column was only observed during the

Table 2. Composition of the Most Altered Hydrothermal Fluid From Representative Vents on Loihi Seamount and Seawater at 1000 mbsl

	Seawater	Naha 96	Naha 97	Lohiau
Alkalinity	2.44	10.1	5.9	6.9
Calcium	10.2	11.1	11.4	17.3
Magnesium	52.4	54.0	51.4	41.2
Sulfate	27.8	26.5	28.6	19.9
Silica	0.10	1.6	1.0	3.5
Potassium	10.0	10.3	9.3	16.1
Chlorinity	538.5	535.5	540.5	558.8
Fe/Mn	—	58	30	6

Units are mmol/kg except for Fe/Mn, which is a molar ratio.

expedition that occurred ~1 month after the onset of the 1996 event. A short-lived vapor phase also is evident from the lack of low-salinity lenses in Pele's Pit after the initial response cruise and the observed changes at Naha and Pohaku. The gradual decay in the output of a brine phase is highlighted by measured chlorinities greater than that of bottom seawater and the order of magnitude decrease in fluid fluxes between yearly visits to each site. The flux of magmatic CO_2 remains high well after the termination of vapor formation, suggesting that the two processes are decoupled at Loihi.

4.4. Concerns for Geochemical Fluxes

Given a global convective heat loss associated with hydro-thermal processes, ratios of elemental to thermal anomalies have been used to calculate global geochemical fluxes [e.g., Edmond et al., 1979, Elderfield and Schultz, 1996]. Of great concern are those fluxes associated with low-temperature venting on ridge axes that account for significant portions of the thermal and fluid fluxes along mid-ocean ridges [Schultz and Elderfield, 1997]. While some of these low-temperature hydrothermal sites vent simple mixtures of bottom seawater and a high-temperature end-member, data from Loihi illustrate that the composition of low-temperature hydrothermal fluids can be drastically different than those of high-temperature fluids. For example, fluids from Naha have concentrations of Mg and sulfate that are greater than that of bottom seawater. This results in a net flux of these elements out of the crust, in contrast to fluxes from typical mid-ocean ridge hydrothermal systems. Similarly, fluxes of the alkali metals, such as K at Naha, may be into the crust.

The net effect of chemical fluxes from Loihi after the tectonic-volcanic event is poorly constrained because the temporal record of fluid fluxes is unknown. The one constraint that we do have is the thermal flux associated with volcanic events. This flux is limited to the heat available in the uppermost third of newly formed oceanic crust. On the basis of thermal fluxes from events on the CoAxial Segment of the Juan de Fuca Ridge, Baker et al. [1998] estimate that the thermal flux from events is only 5% of the flux from chronic venting. Thus, for these events to have an impact on global geochemical fluxes, the ratio of chemical to thermal anomalies of these venting fluids must be at least an order of magnitude greater than that measured in high-temperature black smokers (e.g., as is the case for CO_2 and Fe/Mn), or water-rock reactions must result in chemical fluxes that are

opposite to those from typical high temperature venting (e.g., Mg, sulfate, and K at Naha).

Finally, the chemical composition of hydrothermal fluids from mid-ocean ridges appears to be distinct from those fluids generated by off-axis volcanism, which accounts for ~20% of the yearly influx of new oceanic crust [Schilling, 1973] of which half results from intraplate volcanism [Kennett, 1982]. For example, volatile gasses play a major role in controlling the chemical composition of the fluids from Loihi, Kasuga, Macdonald, and Teahitia Seamounts [McMurtry et al., 1993; Cheminee et al., 1991; Michard et al., 1993]. At each of these sites, measured alkalinities are greater than that in bottom seawater, with the highest measured alkalinity of 31.8 mmol/kg, which is more than 3 times greater than the highest measured value in hydrothermal fluids from Loihi. In contrast, alkalinities in hydrothermal fluids from mid-ocean ridges are typically negative [Von Damm, 1995]. The high alkalinities found in non-mid-ocean ridge settings likely result from the exhalation of magmatic CO_2 that enhances chemical weathering. This enhanced chemical weathering can apparently result in chemical fluxes that are not unidirectional in these systems. For example, chemical compositions of hydrothermal fluids from Naha result in fluxes of K, Mg, and sulfate that are either into or out of the crust.

5. Conclusions

Chemical data from discrete and continuous fluid samplers are presented. Each sampler has its own strengths and weaknesses. Discrete samplers provide large volume (750-mL) samples from which one can measure concentrations for most of the elements in the periodic table and a variety of isotopes but are restricted, even today, to those times when good weather conditions allow the use of ships and submersibles to collect samples and are limited by the amount of dive time at a given site. In contrast, OsmoSamplers provide the means to collect samples continuously and thus provide a mechanism to elucidate processes at a range of temporal scales (hours to years) and in a variety of geologic settings. Yet sample volume is limited and thus the extent of an analytical program is limited.

We have illustrated that OsmoSamplers are tools that can be used to observe chemical changes associated with tectonic-volcanic events. For example, relative to the composition of bottom seawater, the OsmoSampler at Naha Vents captured a gradual change from a hydrothermal fluid with a lower chlorinity and higher concentration of K to a fluid with higher chlorinity and lower concentration of K. These changes occurred during the first 2 months of the deployment and are consistent with two or more distinct sources, one of which has a low-temperature component. The OsmoSampler at Lohiau Vents captured changes that were caused by variations in mixtures of hydrothermal sources and bottom seawater. Fluids collected by both samplers have been greatly influenced by magmatic gases and have anomalously high alkalinities. Fluids with the highest alkalinity also had the highest Fe/Mn molar ratio, which range from 58 to 0.8.

Unfortunately, these OsmoSamplers worked for only a portion of the time on the seafloor. In contrast to the laboratory experiments, biological activity within centimeters of the sample intakes precipitated Fe-oxide sheaths that eventually restricted sample collection. Newly designed OsmoSamplers include in-line acidification to hinder biologically mediated Fe oxide formation. Additional samplers are being designed to

obtain more frequent aliquots, to maintain in situ concentrations of dissolved gases and trace metals, and to preserve microbial community structure.

Results from Loihi illustrate that thermal and mass fluxes resulting from the 1996 event impacted the regional hydrography, but the integrated impact of these fluxes on oceanic geochemical cycles from similar events is less certain. Data from Loihi also accent our concern for including fluxes from low temperature, nonridge axis, and event sources in estimates of geochemical fluxes from hydrothermal systems. For example, fluid fluxes from event or low-temperature sources can result in chemical fluxes that are opposite to those from chronic venting on mid-ocean ridges. The composition of hydrothermal discharge from Loihi is not unique and is in many ways similar to the composition of hydrothermal discharge from other non-mid-ocean-ridge axis hydrothermal systems (e.g., rich in Fe and CO_2). Additional sampling of other non-mid-ocean ridge, event, and low-temperature hydrothermal systems are required before reliable estimates of chemical fluxes associated with mid-ocean hydrothermal circulation can be adequately quantified.

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H. W. Jannasch and J. N. Plant, Monterey Bay Aquarium Research Institute, 7700 Sandholdt Road, P. O. Box 628, Moss Landing, CA 95039. (jaha@mbari.org) (jplant@mbari.org)

G. M. McMurtry and F. J. Sansone, Department of Oceanography, SOEST, 1000 Pope Road, University of Hawaii, Honolulu, HI 96822. (garym@soest.hawaii.edu) (sansone@soest.hawaii.edu)

C. L. Moyer, Biology Department, Western Washington University, Bellingham, WA 98225. (cmoyer@fire.biol.wwu.edu)

C. G. Wheat, West Coast NURC, P.O. Box 475, Moss Landing, CA 95039. (wheat@mbari.org)