

THE OFFICIAL MAGAZINE OF THE OCEANOGRAPHY SOCIETY

Oceanography

CITATION

Luther, G.W. III, A. Gartman, M. Yücel, A.S. Madison, T.S. Moore, H.A. Nees, D.B. Nuzzio, A. Sen, R.A. Lutz, T.M. Shank, and C.R. Fisher. 2012. Chemistry, temperature, and faunal distributions at diffuse-flow hydrothermal vents: Comparison of two geologically distinct ridge systems. *Oceanography* 25(1):234–245, <http://dx.doi.org/10.5670/oceanog.2012.22>.

DOI

<http://dx.doi.org/10.5670/oceanog.2012.22>

COPYRIGHT

This article has been published in *Oceanography*, Volume 25, Number 1, a quarterly journal of The Oceanography Society. Copyright 2012 by The Oceanography Society. All rights reserved.

USAGE

Permission is granted to copy this article for use in teaching and research. Republication, systematic reproduction, or collective redistribution of any portion of this article by photocopy machine, reposting, or other means is permitted only with the approval of The Oceanography Society. Send all correspondence to: info@tos.org or The Oceanography Society, PO Box 1931, Rockville, MD 20849-1931, USA.



Chemistry, Temperature, and Faunal Distributions at Diffuse-Flow Hydrothermal Vents

Comparison of Two Geologically Distinct Ridge Systems

BY GEORGE W. LUTHER III, AMY GARTMAN, MUSTAFA YÜCEL,
ANDREW S. MADISON, TOMMY S. MOORE, HEATHER A. NEES, DONALD B. NUZZIO,
ARUNIMA SEN, RICHARD A. LUTZ, TIMOTHY M. SHANK, AND CHARLES R. FISHER



Image taken at the East Pacific Rise Integrated Study Site mussel exclusion experiment at 9°50'N in 2004. Mussels communities were cleared to increase hydrothermal flux and colonization substrates arrayed with the In Situ Electro-Chemical Tool (INSECT) and temperature probes to capture the fluid chemistry in which microbial and faunal communities colonized available habitat.

ABSTRACT. Diffuse-flow, low-temperature areas near hydrothermal vents support life via chemosynthesis: hydrogen sulfide (and other reduced chemical compounds) emanating from the subsurface is oxidized with bottom-water oxygen through bacterial mediation to fix carbon dioxide and produce biomass. This article reviews the in situ diffuse-flow chemistry (mainly H₂S and O₂) and temperature data collected in 2006 and 2009 along the Eastern Lau Spreading Center (ELSC), and from 2004 to 2008 at 9°N along the East Pacific Rise (9 N EPR), predominantly around macrofauna that contain endosymbionts at these two hydrothermal vent regions. More than 48,000 and 20,000 distinct chemical and temperature data points were collected with a multi-analyte electrochemical analyzer in the diffuse-flow waters at 9 N EPR and the ELSC, respectively. Despite their different geological settings and different macrofauna (two different species of snails and mussels at the ELSC versus two different species of tubeworms and mussels at 9 N EPR), there are similarities in the temperature and chemistry data, as well as in the distributions of organisms. The pattern of water chemistry preferred by the provannid snails (*Alviniconcha* spp., *Ifremeria nautilei*) and *Bathymodiolus brevior* at the ELSC is similar to the water chemistry pattern found for the siboglinid tubeworms (*Tevnia jerichonana*, *Riftia pachyptila*) and the *Bathymodiolus thermophilus* mussels at 9 N EPR. The eruptions at 9 N EPR in 2005 and 2006 resulted in increased H₂S concentrations, increased H₂S/T ratios, and an initial change in the dominant tubeworm species from *Riftia pachyptila* to *Tevnia jerichonana* after the eruption created new vent habitats. In 2005, two sites at 9 N EPR showed major increases in the H₂S/T ratio from 2004, which suggested a probable eruption in this basalt-dominated system. At the ELSC, there was a decrease in the H₂S/T ratio from northern to southern sites, which reflects the change in geological setting from basalt to andesite and the shallower water depths at the southern sites.

INTRODUCTION

This paper compares and integrates temperature and diffuse-flow chemical data (primarily O₂ and H₂S) obtained at two Ridge 2000 Integrated Study Sites (ISSs): the Eastern Lau Spreading Center (ELSC) and 9°50'N on the East Pacific Rise (9 N EPR; Figure 1). Several papers have documented various aspects of the diffuse flow chemical data collected at the ELSC in 2005 (Waite et al., 2008; Podowski et al., 2009), 2006 (Mullaugh et al., 2008; Podowski et al., 2010), and 2009 (Gartman et al., 2011), and at 9 N EPR from 2004–2008 (Luther et al., 2008; Lutz et al., 2008; Nees et al., 2008, 2009; Crespo-Medina et al., 2009; Moore et al., 2009), including the change in chemistry after the 2005–2006 eruptions described by Tolstoy et al. (2006). In these studies, an in situ electrochemical analyzer (Luther et al., 2008) that can measure dissolved O₂, H₂S, and other sulfur species simultaneously with one applied voltage versus current scan at the solid state gold amalgam working

George W. Luther III (luther@udel.edu) is the Maxwell P. and Mildred H. Harrington Professor, School of Marine Science and Policy, College of Earth, Ocean and Environment, University of Delaware, Lewes, DE, USA. **Amy Gartman** is a graduate student in the School of Marine Science and Policy, College of Earth, Ocean and Environment, University of Delaware, Lewes, DE, USA. **Mustafa Yücel** completed his PhD at the University of Delaware, and is currently a postdoctoral researcher at the Université Pierre et Marie Curie, Laboratory of Benthic Ecogeochemistry, Observatoire Océanologique de Banyuls, Banyuls-sur-mer, France. **Andrew S. Madison** is a graduate student in the School of Marine Science and Policy, College of Earth, Ocean and Environment, University of Delaware, Lewes, DE, USA. **Tommy S. Moore** completed his PhD at the University of Delaware, and is currently at the Instituto Mediterráneo de Estudios Avanzados, Esporles, Islas Baleares, España. **Heather A. Nees** completed her master's degree at the University of Delaware, Lewes, DE, USA. **Donald B. Nuzzio** is President, Analytical Instrument Systems, Inc., Flemington, NJ, USA. **Arunima Sen** is a researcher in the Biology Department, Pennsylvania State University, University Park, PA, USA. **Richard A. Lutz** is Professor, Institute of Marine and Coastal Sciences, Rutgers University, New Brunswick, NJ, USA. **Timothy M. Shank** is Associate Scientist, Biology Department, Woods Hole Oceanographic Institution, Woods Hole, MA, USA. **Charles R. Fisher** is Professor, Biology Department, Pennsylvania State University, University Park, PA, USA.

electrode was used in conjunction with the deep-submergence vehicle (DSV) *Alvin* at 9 N EPR or the remotely operated vehicle (ROV) *Jason 2* at the ELSC. For 9 N EPR, over 3,000 individual chemistry data points unique in space and time were obtained, whereas over 20,000 were collected at the ELSC. Also, an autonomous electrochemical instrument (Luther et al., 2008; Moore et al., 2009) was deployed several times at different 9 N EPR locations, and over 45,000 individual chemistry data points around a total of 13 organisms were obtained. Regardless of the instrument used, we collected most of the data near macrofauna-hosting chemosynthetic endosymbiont bacteria to improve our ecological understanding

of these organisms, and to constrain the effects of temperature, chemistry, and biological interactions on faunal distributions in diffuse-flow vent waters. Because of the Ridge 2000 Program's emphasis on ISSs, the data sets described here offer a first-order comparison between two geologically different vent regimes and the different species that inhabit their diffuse-flow areas, which was not previously possible (Johnson et al., 1988; Luther et al., 2001; Le Bris et al., 2006a,b).

The primary or foundation species responsible for chemosynthetic primary productivity for 9 N EPR (Shank et al., 1998) are the sessile tubeworms *Riftia pachyptila* and *Tevnia jerichonana*, and the mobile mussel *Bathymodiolus*

thermophilus (Figure 2), whereas at the ELSC (Podowski et al., 2009, 2010), the dominant macrofaunal organisms are the mobile snails *Alviniconcha* spp. and *Ifremeria nautilei*, and the mobile mussel *Bathymodiolus brevior* (Figure 3). At 9 N EPR, the distance between sites investigated is 6 km, whereas at ELSC the distance between the northernmost and southernmost sites studied is about 150 km. At 9 N EPR, the dominant geological substrate is basalt, and at the ELSC there is a transition from basaltic lavas to more andesitic lavas going from north to south (Vallier et al., 1991), with the steepest transition between TowCam (TC) and ABE sites (Bézos et al., 2009; Escrig et al., 2009).

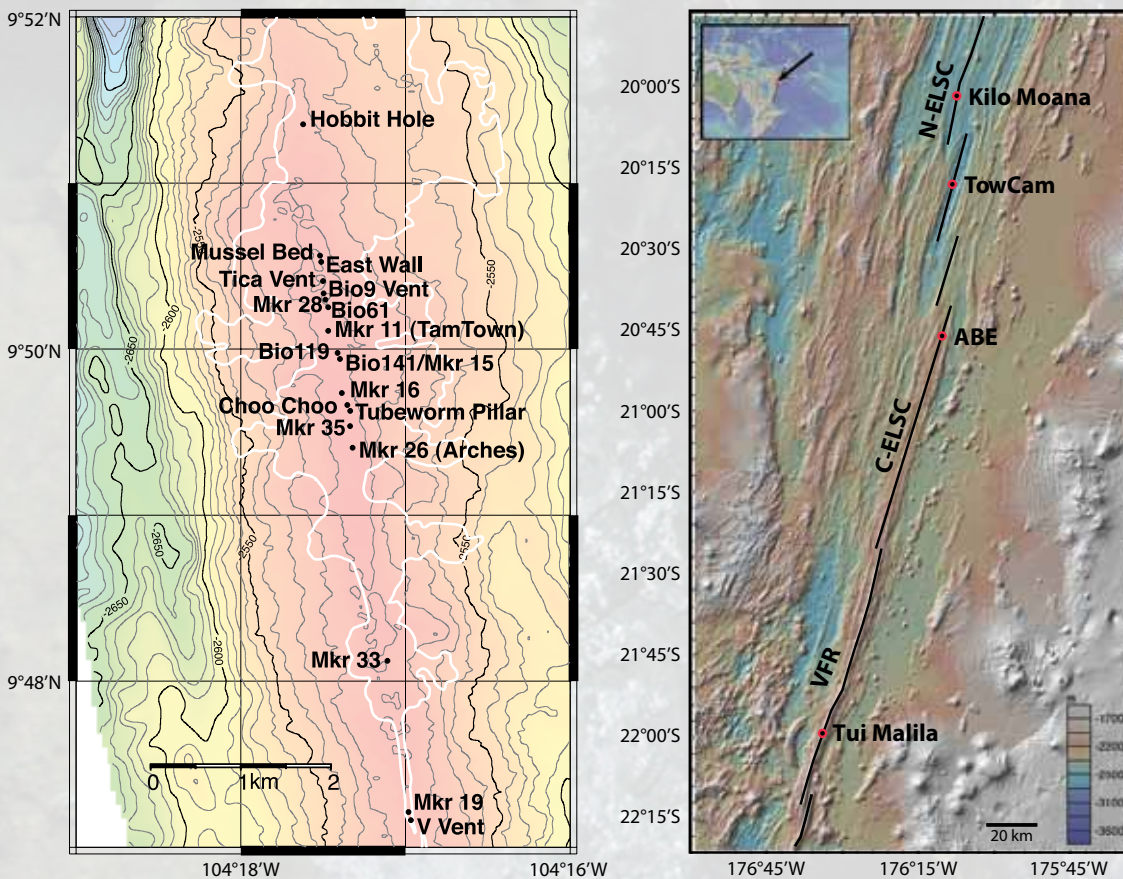


Figure 1. (left) East Pacific Rise study sites from 2004, 2005, 2006, 2007, and 2008; East Wall is north of Tica and L vent is north of 9°46'N. (right) Locations of the four major vent fields surveyed along the Eastern Lau Spreading Center in 2006 and 2009. Map courtesy of V. Ferrini (Ferrini et al., 2008; Ryan et al., 2009)

METHODS

The habitat areas chosen for study normally avoided areas where water temperatures were greater than 60°C in the diffuse-flow environments and where macrofauna were not found or abundant. Instead, the study areas and comparisons were in the high-density communities occupied by the main endosymbiont containing species.

The experimental details for data acquisition have been described by others (e.g., Luther et al., 2008; Moore et al., 2009; Podowski et al., 2010). The detection limit for H₂S (defined as the sum of H₂S and HS⁻) is 0.2 μM. As the pK_a of seawater is 13.19 (Millero, 2007), neutral pH in seawater is 6.595.

Because Le Bris et al. (2001) showed that around *Riftia* the average in situ pH is 7.0 with a range from 6.2 to 7.7, HS⁻ is the dominant sulfide species around *Riftia*. Less is known about pH around the other organisms. The detection limit for O₂ ranges from 5–15 μM pending the presence of high concentrations of H₂S, which can overwhelm the O₂ signal (see Podowski et al., 2009). Each data point is an applied voltage versus current scan that can measure one or more chemical species simultaneously (e.g., O₂ and H₂S). If there is no signal for the chemical species, its concentration is below the detection limit of the sensor.

Data and statistical analysis have been described in a series of publications

(e.g., Moore et al., 2009; Nees et al., 2009; Podowski et al., 2010; Gartman et al., 2011). Sulfide-to-temperature ratios are calculated from the slope of the regression of sulfide versus temperature plots. A variety of statistical methods (e.g., analysis of variance, analysis of covariance) were used to show there are significant differences between the chemistry and temperature surrounding organisms at different times and locations within 9 N EPR (Nees et al., 2008, 2009; Moore et al., 2009) or the ELSC (Podowski et al., 2009, 2010; Gartman et al., 2011).

In situ voltammetry measurements using the instrument deployed from DSV *Alvin* were collected

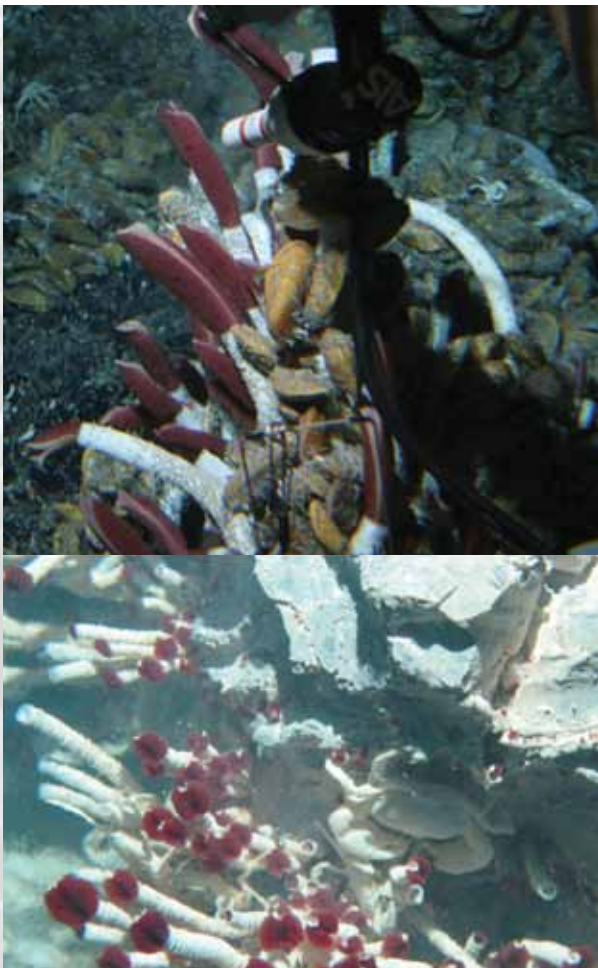


Figure 2. Photographs of the major macrofaunal organisms found at the East Pacific Rise. (top) The tubeworm *Riftia pachytila* with the mussel *Bathymodiolus thermophilus*. (bottom) The tubeworm *Tevnia jerichonana*.

Figure 3. Photograph of the major macrofaunal organisms found on a sulfide structure at the Eastern Lau Spreading Center. The snails *Alviniconcha* spp. are at the bottom in the center; *Ifremeria nautili* are above the crabs in the center with a few just on the outside edge of *Alviniconcha* spp.; the mussels *Bathymodiolus brevior* are at the top and on the edge of *Ifremeria nautili*.



on the EPR from 9°46'N to 9°52'N in 2004 (*Alvin* Dives 3996–4012), 2005 (*Alvin* Dives 4099–4113), 2006 (*Alvin* Dives 4201–4207), 2007 to 2008 (*Alvin* Dives 4297–4318), and 2008 (*Alvin* Dives 4400–4408). Study sites (see Figure 1, left, for locations)

pachyptila at two separate locations and *Bathymodiolus thermophilus* at a third), 2006 (*Riftia pachyptila* only at two locations at site Tam Town), and 2007 (*Riftia pachyptila* only at two locations at site Tica). A total of 13 individual mussel and tubeworm locations were

a maximum of six hours of bottom time per day before resurfacing. The autonomous instrument is able to stay in one location for even longer time periods than the ROV and can collect more data, depending on battery limitations.

“ DESPITE THEIR DIFFERENT GEOLOGICAL SETTINGS AND DIFFERENT MACROFAUNA... THERE ARE SIMILARITIES IN THE TEMPERATURE AND CHEMISTRY DATA, AS WELL AS IN THE DISTRIBUTIONS OF ORGANISMS. ”

where chemistry measurements on and near tubeworms were taken, included Alvinella Pillar (2005), Bio 9 (2005), East Wall (2004, 2005), Hobbit Hole (2007), L Vent (2007), Marker 15/141 (2007, 2008), Marker 19 (2007), Marker 26/Arches (2007), Marker 28 (2007), Marker 35 (2007, 2008), Marker 61 (2005), Tamtown (2006, 2007), and Tica (2004, 2005, 2007, 2008). Water depth at all of these sites is approximately 2,500 m, and they are basalt dominated.

In situ voltammetry measurements at 9 N EPR using the autonomous instrument were collected at a single location for each species in a given year (Moore et al., 2009): for 2003 (*Riftia pachyptila* only at site Tica), 2004 (*Bathymodiolus thermophilus* only at site BM119), 2005 (East Wall deployment 1: *Riftia pachyptila* at two separate locations and *Bathymodiolus thermophilus* at a third), 2005 (East Wall deployment 2: *Riftia*

studied. The electrodes were located as close to the plumes of the tubeworms as was possible with this instrument, which has been called the In Situ ElectroChemical Tool (INSECT).

In situ voltammetry measurements using the instrument deployed from ROV *Jason 2* were collected primarily at four vent fields with multiple sites at the ELSC near the Kingdom of Tonga in the South Pacific Ocean. From north to south, they are: Kilo Moana, TowCam, ABE, and Tu'i Malila (see Figure 1, right, for locations). The dive numbers in 2006 are J2:230 and J2:232–240, and those in 2009 are J2:421–428 and J2:430–433. The water depth for these sites decreases from north (~ 2,700 m) to south (~ 1,900 m).

Jason 2 is able to work for extended periods (two days was typical) without resurfacing. Thus, more data could be collected with the same instrumentation on the ROV than using *Alvin*, which had

EAST PACIFIC RISE:

Data from DSV *Alvin*

Figure 4 documents the temperature, dissolved oxygen, and sulfide data collected with DSV *Alvin* at 9 N EPR for all foundation organisms. The plots give the average, median, minimum, and maximum for all data. In Figure 4, the data at 9 N EPR are separated by year of data collection (2004, 2005, 2007, and 2008). Within each year, there are data for *Riftia pachyptila*, *Tevnia jerichonana*, and *Bathymodiolus thermophilus* (no data were collected near *Bathymodiolus thermophilus* in 2008 due to the limited number of dives and the organism's low abundance in the areas of the dives); the total number of data points is over 3,000 for the four years. Data for *Riftia pachyptila*, which can be as tall as 2 m, were collected at their bases and plumes. Nees et al. (2009) show that the plumes are in waters with higher sulfide concentrations than the bases. *Tevnia*, which grow to about 30 cm long, were not observed at our study sites in 2004 and 2005 prior to the eruptions of 2005–2006 (Tolstoy et al., 2006; see vertical dashed line in Figure 4), but were the dominant sessile species after the eruption. In 2007 and 2008, the presence of *Riftia pachyptila*, and in particular *Bathymodiolus thermophilus*, was sparse at our study sites. Based on the larger number of data points taken with DSV *Alvin* for 2004, 2005, and 2007, the best data comparisons are for those

years, and the number of data points is similar for the different organisms in those years. In 2007, some sites, such as East Wall, were almost totally destroyed and covered by lava, whereas Tica was partially destroyed. Although the exact same habitat locations (centimeter scale) could not be reoccupied, chemical comparisons in the vicinity can be made based on the effects of the eruption.

Figure 4 (top panel) shows that the observed temperature at 9 N EPR typically ranges from ambient bottom water (2°C) to about 30°C, except in 2005. The higher-temperature data for 2005 are related to the East Wall site, which was almost completely destroyed by the 2005–2006 volcanic eruptions (Nees et al., 2008, 2009; see below). The pattern for organisms in a given year shows that *Tevnia jerichonana* and *Riftia pachyptila* reside in waters with higher average (10–12°C) and median (6–11.5°C) temperatures than *Bathymodiolus thermophilus* (3.8–4.6°C average; 2.7–3.5°C median). *Tevnia jerichonana* are not observed to coexist with *Bathymodiolus thermophilus* at our study sites (Shank et al., 1998; Moore et al., 2009; Nees et al., 2009).

At 9 N EPR, ambient bottom water concentration for oxygen (Figure 4, middle panel) rarely exceeds 120 μM, and the temperature at which O₂ is no longer detected is about 10°C (Moore et al., 2009; calculated from the slope of O₂ versus T plots). Before the eruptions, the data show both *Riftia pachyptila* and *Bathymodiolus thermophilus* residing in waters with similar O₂ content (42.7–52.1 μM average). After the eruptions, there is a clear distinction in the organisms' chemical habitats. The pattern for organisms in a given year

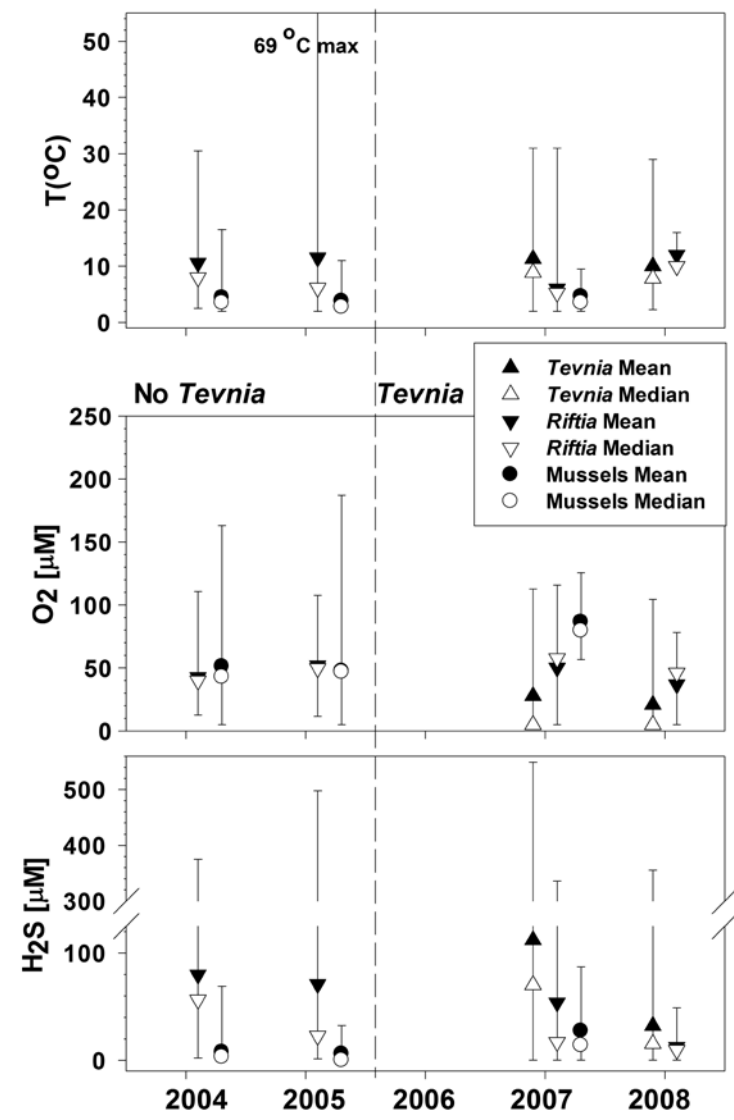


Figure 4. Mean, median, minimum, and maximum temperature, O₂, and H₂S data for 9°N on the East Pacific Rise (9 N EPR) from 2004–2008. The data represent over 3,000 electrochemical scans using DSV Alvin. Minimum and maximum data are the low and high points of the solid vertical lines. The dashed vertical line represents the start of the eruptions. The year corresponds to year of data collection and not the true date.

shows that *Tevnia jerichonana* lived in microaerophilic conditions during 2007 and 2008, as the median value is at the detection limit of 5–15 μM. In 2007, *Riftia pachyptila* were observed to reside in waters with an average and median O₂ concentration of 50 and 58 μM, respectively. In 2007, *Bathymodiolus thermophilus* resided in more oxygenated waters (87 μM) than *Riftia pachyptila*.

At 9 N EPR, the H₂S concentrations (Figure 4, bottom panel) range from the detection limit to 550 μM. H₂S versus temperature plots vary with

time, location, and organism (e.g., Nees et al., 2008, 2009; Moore et al., 2009; see below). For *Riftia pachyptila*, the average H₂S concentration is similar in 2004 (80 μM) and 2005 (71 μM), whereas the median (56 to 23 μM) drops by a factor of two. The higher range of H₂S concentrations for 2005 reflects the East Wall site, which was very active prior to the volcanic eruption. In 2007, after the eruption, *Tevnia jerichonana* became the dominant organism at all of our study sites, including Tica, and the maximum (549 μM), average (112 μM), and median

(70 μM) H_2S levels increased over 2004 and 2005 levels when *Riftia pachyptila* were dominant. In 2007, *Riftia pachyptila* and *Bathymodiolus thermophilus* were sparse. In 2007 and 2008, *Tevnia jerichonana* resided in waters containing more H_2S than did *Riftia pachyptila* by a factor of two to three. For 2008, the same sites that had been occupied in 2007 showed signs that the system was already changing, with average H_2S concentrations decreasing by a factor of three to four for *Tevnia jerichonana* and *Riftia pachyptila*, respectively. Observations in 2010 and 2011 (Stefan Sievert, Woods Hole Oceanographic Institution, pers. comm., 2011) indicate that the succession of *Tevnia jerichonana* to *Riftia pachyptila*, followed by *Bathymodiolus thermophilus* with low abundance of *Tevnia jerichonana*, originally determined

by Shank et al. (1998), has been completed. The data in Figure 4 build on the plots of H_2S versus temperature by organism (Moore et al., 2009; see next section) that show *Tevnia jerichonana* and *Riftia pachyptila* can collocate in the same chemical and temperature environment and that *Riftia pachyptila* and *Bathymodiolus thermophilus* can collocate, but that *Tevnia jerichonana* and *Bathymodiolus thermophilus* do not coexist in similar diffuse-flow waters.

EAST PACIFIC RISE: Data from Autonomous Instrument

Figure 5 (top panel) shows the temperature data for 9 N EPR foundation organisms, the 13 data sets collected with the autonomous instrument. Because these data are recorded at one location over

a period of time, the mean and median data have better coincidence, that is, have more similar values, when compared to those in Figure 4, which represent all sites at different times. In 2003, data collected around *Riftia pachyptila* show average temperature data of 2.07° and 2.01°C for two different locations; these data represent four consecutive days of data collection from December 4 to December 8. In 2005, there were two separate deployments at East Wall: six days at East Wall 1 (May 3 to May 9) and three days at East Wall 2 (May 7 to May 10). Here, the average temperatures recorded around *Riftia pachyptila* were 7.97°, 7.34°, 10.3°, and 10.3°C, whereas the average temperatures recorded around *Bathymodiolus thermophilus* were 3.31° and 4.64°C. In both 2006 and 2007, one temperature sensor failed,

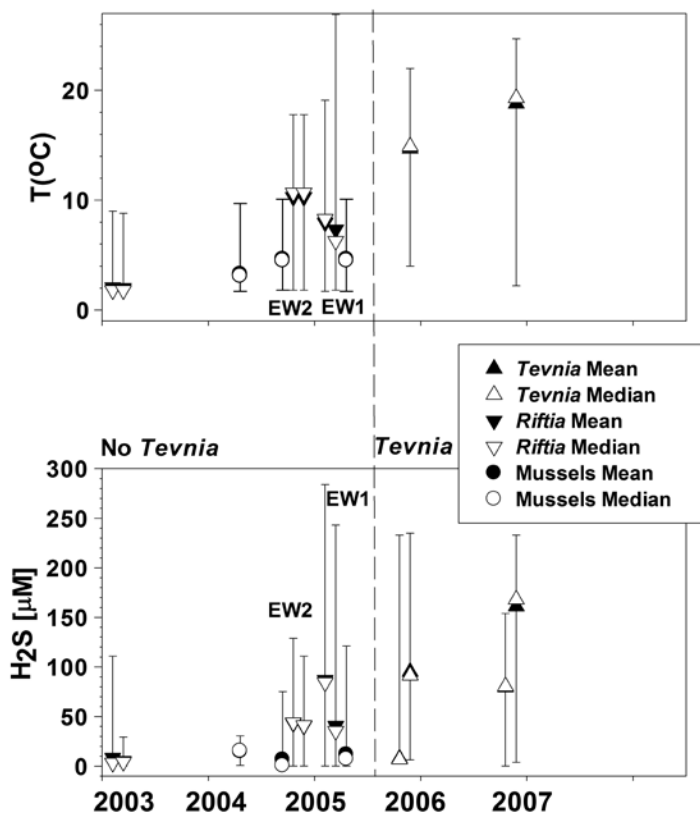


Figure 5. Autonomous instrument data for 2003 (3,947 scans at each *Riftia pachyptila*—Tica), 2004 (590 scans at *Bathymodiolus thermophilus* mussels—BM119), 2005 (4,121 scans each at *Riftia pachyptila* and *Bathymodiolus thermophilus* mussels—East Wall 1; 6,200 scans each at *Riftia pachyptila* and *Bathymodiolus thermophilus* mussels—East Wall 2), 2006 (1,621 scans each at *Tevnia jerichonana*—Tam Town) and 2007 (982 scans at each *Tevnia jerichonana*—Tica). Minimum and maximum data are the low and high points of the solid vertical lines. The dashed vertical line represents the start of the eruptions. The year corresponds to year of data collection and not the true date. EW1 and EW2 refer to two separate deployments near different organisms at the East Wall site. One temperature recorder failed in 2006 and in 2007.

but the temperatures were significantly higher than those observed prior to the eruption (Moore et al., 2009). The Tam Town data around *Tevnia jerichonana* for 2006 are for the period July 1–19, and the Tica data around *Tevnia jerichonana* for 2007 are for January 18–21.

Figure 5 (bottom panel) shows the H₂S data for 9 N EPR foundation organisms for six of the 13 data sets collected. Although there is a considerable range around the mean and median, the mean and median data have better coincidence (are more similar to each other) than data in Figure 4, which represent all sites at different times. These data demonstrate that diffuse-flow environments are highly variable on short time scales, as documented by others (Johnson et al., 1988; Le Bris et al., 2006a; Moore et al., 2009). In 2003, data collected around *Riftia pachyptila* showed average concentrations of 8.3 and 5.13 μM. At East Wall in 2005, the averages around *Riftia pachyptila* were 86.9, 40.5, 43.4, and 40.7 μM, and around *Bathymodiolus thermophilus* were 11.8 and 6.59 μM. The averages around *Tevnia jerichonana* were 7.62 and 95.1 μM in 2006, and 161 and 79.5 μM in 2007. These data from waters around individual organisms at a single location showed the same biological and chemical pattern as the data above for several organisms at different locations over a shorter period of time using the analyzer from DSV *Alvin*.

The temperature and H₂S data, as well as the H₂S/T ratios (see below) for the *Alvin* and autonomous instrumentation, show statistically significant increases after the 2005–2006 volcanic eruptions and for the 2005 data at Tica and East Wall prior to the eruption (see Moore et al., 2009; Nees et al., 2009).

EASTERN LAU SPREADING CENTER: Data from ROV *Jason 2*

The 2009 ELSC data in Figure 6 are from different vent fields from north to south—Kilo Moana, TowCam, ABE, and Tu'i Malila (see Figure 1, right, for locations). Within each site there are data for *Alviniconcha* spp., *Ifremeria nautilei*, and mussels (*Bathymodiolus brevior*); occasionally, the organisms live in patches or concentric rings with *Alviniconcha* spp. surrounded by *Ifremeria nautilei* that, in turn, are surrounded by *Bathymodiolus brevior* mussels (e.g., Podowski et al.,

2009, 2010). The total number of data points described is about 4,500. There was no eruption between the 2006 and 2009 cruises, and sites within a vent field could be revisited to assess temporal changes.

Figure 6 (top panel) shows the observed temperatures at the ELSC typically range from ambient bottom water to about 55°C, and thus are higher than those found at 9 N EPR. Higher temperatures are generally found at the southern sites. The average (17.8°C) and median (15.0°C) temperature around *Alviniconcha* spp. doubled at ABE when

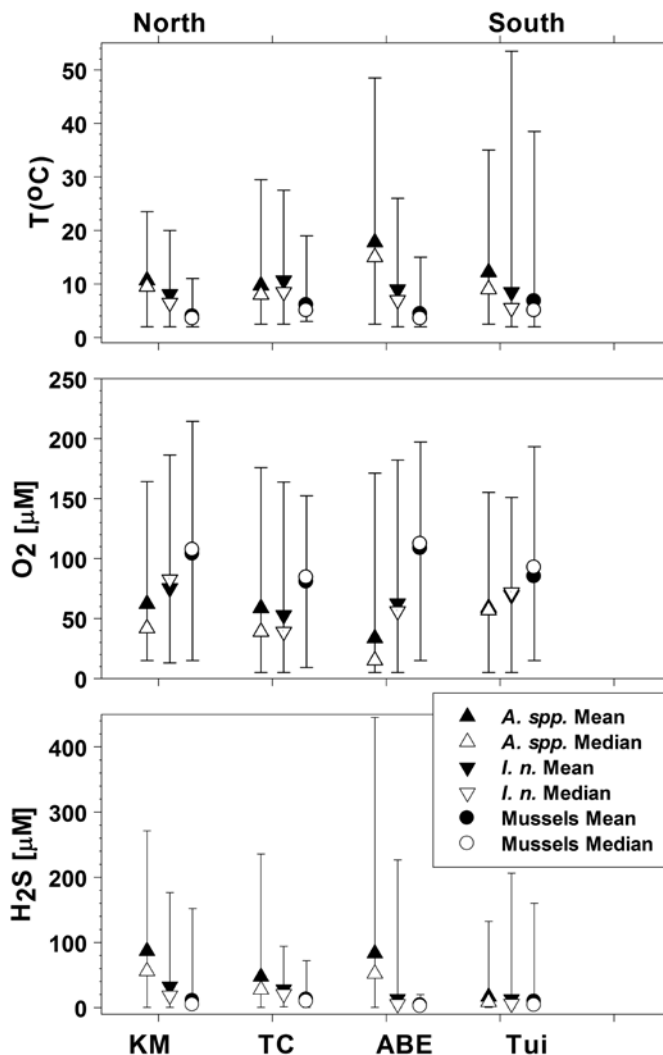


Figure 6. Mean, median, minimum, and maximum temperature, O₂, and H₂S data around macrofauna for the Eastern Lau Spreading Center in 2009. Minimum and maximum data are the low and high points of the solid vertical lines. The data represent over 4,500 electrochemical scans using the ROV *Jason 2*.

A. spp. = *Alviniconcha* spp.
I. n. = *Ifremeria nautilei*
KM = Kilo Moana
TC = TowCam
Tui = Tu'i Malila

compared to the other sites. The pattern for organisms within a given site shows that *Alviniconcha* spp. typically resides in warmer waters than *Ifremeria nautilei*, which resides in warmer waters than the *Bathymodiolus brevior* mussels, as found in 2005 (Podowski et al., 2009) and 2006 (Podowski et al., 2010).

At the ELSC, ambient bottom water concentration for oxygen (Figure 6, middle panel) rarely exceeds 170 μM . The temperature at which O_2 is no longer detected is calculated to be 18°C at KM, 19°C at TC, 24°C at ABE, and 23°C at Tui. Oxygen concentrations among animals at Lau appear to be generally higher than at 9 N EPR, which also has lower ambient bottom water concentrations.

Bathymodiolus brevior mussels live in the most oxygenated waters, with an average value range of 80.5 to 108 μM and a median value range of 84.1 to 112 μM , more highly oxygenated than the waters found around *Bathymodiolus thermophilus* at 9 N EPR, which range from 47.6 to 86.6 μM . *Alviniconcha* spp. generally reside in lower average concentrations of oxygen (ranging from 33.4 to 62.3 μM) than the *Ifremeria nautilei* (ranging from

52.9 to 75.3 μM), and the average oxygen concentrations around both snail species is lower than the average found around *Bathymodiolus brevior* mussels. Typically, *Alviniconcha* spp. and *Ifremeria nautilei* are observed to reside in waters with median O_2 concentrations ranging from 15 to 56.8 μM and 38.9 to 82.7 μM , respectively. These values overlap the median oxygen concentration for waters around *Riftia pachyptila* (40.1 to 57.7 μM). Although microaerophilic conditions were not as prevalent here as at 9 N EPR after the eruptions, *Alviniconcha* spp. can live in microaerophilic conditions as the median oxygen concentration value is near the detection limit of 5-15 μM for ABE.

At the ELSC, the H_2S concentrations (Figure 6, bottom panel) range from the detection limit of 0.2 μM to 450 μM . The average H_2S concentration is similar for *Bathymodiolus brevior* mussels at sites Kilo Moana (10.3 μM), TowCam, (12.3 μM), and Tu'i Malila (9.2 μM), and is only 3.4 μM at ABE. For *Ifremeria nautilei*, there is a decrease in the average H_2S concentration from northern to southern sites: Kilo Moana (32.4 μM) and TowCam (27.9 μM) to ABE (13.5 μM) and Tu'i Malila (12.9 μM).

The median H_2S concentration shows similar patterns around *Bathymodiolus brevior* mussels and *Ifremeria nautilei*. Around *Alviniconcha* spp., the average H_2S concentration (~ 85 μM) is similar to that found at Kilo Moana and ABE, but is a factor of two smaller than at TowCam and a factor of five smaller than at Tu'i Malila. The median H_2S concentration follows a similar pattern as the average, but is smaller than the average concentration by ~ 50%. Within a site, *Alviniconcha* spp. typically reside in more sulfidic waters than *Ifremeria nautilei* or *Bathymodiolus brevior* mussels (Podowski et al., 2009, 2010).

TEMPORAL CHANGES AT BOTH SITES

Figure 7 shows the calculated H_2S versus temperature slopes from linear regression of all data collected in 2006 (~ 10,000 scans) and 2009 (~ 10,000 scans) at the four ELSC sites. The average $\text{H}_2\text{S}/T$ ratios are slightly higher at Kilo Moana, TowCam, and ABE and slightly lower in Tu'i Malila in 2009 compared to 2006. As Gartman et al. (2011) show, there was a statistical increase in both H_2S concentrations and temperatures measured among animals from 2006 to 2009. Whether these increases are due to a difference in the locations of the measurements taken or due to other factors, including a geophysical change at the Lau sites, is unknown. In both years, the $\text{H}_2\text{S}/T$ ratio decreases from north to south, and this behavior was observed for focused-flow high-temperature hydrothermal vents at the ELSC in 2005 (Mottl et al., 2011).

Figure 8 shows the calculated H_2S versus temperature ($\text{H}_2\text{S}/T$) slope from linear regression of all data collected in

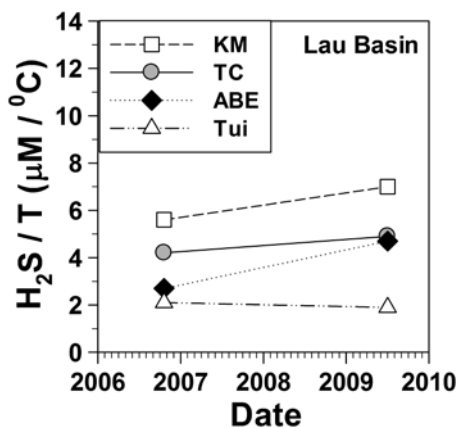


Figure 7. Sulfide versus temperature ratios for all ELSC data collected in 2006 and 2009. Total data are > 10,000 electrochemical scans in each year using the ROV Jason 2. The errors in the slopes are less than the size of the symbols.

2004 (~ 570 scans), 2005 (~ 750 scans), and 2007 (~ 1,500 scans) for *Tevnia jerichonana*, *Riftia pachyptila*, and *Bathymodiolus thermophilus* habitats at 9 N EPR. Each of these slope values is statistically different from the others (Nees et al., 2009). The solid vertical lines indicate the period of the 2005–2006 eruptions (Tolstoy et al., 2006). The average H_2S/T ratio increased fourfold from 2004 (1.9 $\mu M/^\circ C$) to 2005 (8.5 $\mu M/^\circ C$) for *Riftia pachyptila* at East Wall (most *Riftia pachyptila* data were collected at these sites) and over twofold at Tica (4.1 to 10.6 $\mu M/^\circ C$). The increases in the ratio indicate that the system was increasing its output of H_2S prior to the eruption and may be another indicator for a possible eruption to occur, as the East Wall and Tica sites were heavily impacted by the eruptions. Thus, diffuse-flow chemistry serves as an additional indicator of eruptions. The *Bathymodiolus thermophilus* mussel sites, many of which were devoid of *Riftia pachyptila*, had a decreasing output of H_2S prior to the eruption. In 2007, the overall H_2S/T ratio (10.9–12.7 $\mu M/^\circ C$) was similar at all sites studied, and many of these sites were new diffuse-flow vent sources, which had been colonized mainly by *Tevnia jerichonana* residing in waters with a H_2S/T ratio of 12.7 $\mu M/^\circ C$. Interestingly, Tica had only a few pre-eruption *Riftia pachyptila* remaining in 2007, and they were found in waters with a lower H_2S/T ratio (5.8 $\mu M/^\circ C$), as Tica was colonized primarily by *Tevnia jerichonana*. The few *Bathymodiolus thermophilus* mussels found were in waters with a higher H_2S/T ratio (10.9 $\mu M/^\circ C$) than in 2004 and 2005. These significant changes in H_2S/T ratios (Nees et al., 2009) also show that

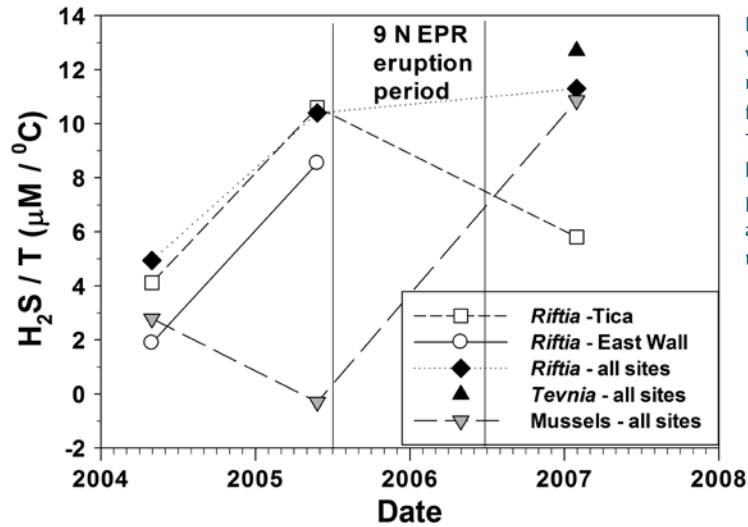


Figure 8. Sulfide versus temperature ratios for 9 N EPR from 2004–2008. The two vertical lines represent the period during which a volcanic eruption took place.

an average ratio calculated from all sites is not an appropriate indicator of H_2S concentration (Le Bris et al., 2006b).

SULFUR SPECIATION

The sensor can also detect the sulfur species thiosulfate, $S_2O_3^{2-}$, and polysulfides, S_x^{2-} , at 30 and 0.2 μM detection limits, respectively (Luther et al., 2008). Polysulfides are among the first byproducts formed during H_2S oxidation, whereas thiosulfate is farther along the oxidation pathway, with polysulfides as one of the intermediates that can produce thiosulfate. Polysulfides have rarely been detected at both the ELSC and 9 N EPR (Luther et al., 2001, 2008; Gartman et al., 2011). Thiosulfate has only been detected at the ELSC (Mullaugh et al., 2008; Waite et al., 2008; Gartman et al., 2011) and in less than 4% of the scans. Thiosulfate is formed near brownish sediments containing iron(III) (oxy)hydroxides and manganese(III,IV) oxides and (oxy) hydroxides, which are known to oxidize H_2S rapidly (Pyzik and Sommer, 1981; Yao and Millero, 1996; Herszage and Afonso, 2003). Gartman et al. (2011)

and Luther (2010) reviewed the slow abiotic oxidation kinetics of H_2S with O_2 , and showed that polysulfides and thiosulfate should not be detectable within the time frame of H_2S leaving the geological or biological substrate. It is possible that sulfur species can be formed and released during the chemosynthetic oxidation of sulfide by microorganisms (Gartman et al., 2011; Luther et al., 2011).

CONCLUSIONS

The diffuse-flow chemistry data at both the ELSC (> 20,000 data scans) and 9 N EPR (> 3,000 data scans from DSV *Alvin* and > 45,000 data scans from the autonomous instrument) have similar characteristics. Measurements among animals at the ELSC had higher average and median temperature than among animals at 9 N EPR before the eruption, but average and median values were similar for the ELSC and 9 N EPR after the 2005–2006 eruptions along the EPR. Higher average and median H_2S concentrations among animals were more prevalent at 9 N EPR, especially after the eruptions. At the ELSC

for a given time and site, the organisms generally live in an increasing temperature and H₂S regime with the order *Bathymodiolus brevior* mussels, *Ifremeria nautili*, then *Alviniconcha* spp. At 9 N EPR, the order of organisms residing in increasing temperature and

before the eruption. The 2005 EPR data at East Wall and Tica show increased H₂S/T ratios and sulfide concentrations over previous measurements. Because these sites were highly affected by the 2005–2006 eruptions, the H₂S/T ratios likely signaled the impending eruption.

same chemical and temperature niche as mussels. The chemical habitat of *Ifremeria nautili* overlaps that of *Alviniconcha* spp., and the chemical habitat of *Riftia pachyptila* overlaps that of *Tevnia jerichonana*.

“ BECAUSE OF THE RIDGE 2000 PROGRAM'S EMPHASIS ON [INTEGRATED STUDY SITES], THE DATA SETS DESCRIBED HERE OFFER A FIRST-ORDER COMPARISON BETWEEN TWO GEOLOGICALLY DIFFERENT VENT REGIMES AND THE DIFFERENT SPECIES THAT INHABIT THEIR DIFFUSE-FLOW AREAS, WHICH WAS NOT PREVIOUSLY POSSIBLE. ”

H₂S is *Bathymodiolus thermophilus* mussels, *Riftia pachyptila*, then *Tevnia jerichonana*. The average and median O₂ data for both sets of organisms follow an inverse order from the temperature and H₂S. *Tevnia jerichonana* and perhaps to a lesser extent *Alviniconcha* spp. have the ability to reside in waters that exhibit microaerophilic conditions about half the time based on median O₂ data and the detection limit of the sensor.

The highest H₂S/T ratios were observed at 9 N EPR after the eruptions. In 2009, *Alviniconcha* spp. at Kilo Moana resided in waters with a H₂S/T ratio of 11.5 (Gartman et al., 2011), which is similar to post eruption data at 9 N EPR. All other data for organisms at ELSC show a H₂S/T ratio < 6 (Gartman et al., 2011), which is a similar value to that at 9 N EPR

H₂S/T ratios decreased from north to south at the ELSC sites, which may be due to a combination of the geological substrate and the larger geological mass or volume (due to shallower water column depths in the south) for H₂S in the source fluids to penetrate and react with solid substrate and reduce source H₂S concentrations before reaching the bottom waters.

The pattern and type of water chemistry that *Alviniconcha* spp., *Ifremeria nautili*, and *Bathymodiolus brevior* mussels reside in at the ELSC is similar to that found for *Tevnia jerichonana*, *Riftia pachyptila*, and *Bathymodiolus thermophilus* mussels at 9 N EPR. *Alviniconcha* spp. and *Tevnia jerichonana* do not reside in waters with similar chemistry as mussels. *Ifremeria nautili* and *Riftia pachyptila* can inhabit the

ACKNOWLEDGEMENTS

This work was supported by NSF grants OCE-0240896, OCE-073243 (ELSC), OCE-0308398 (OTIC), OCE-0326434, and OCE-0937324 (EPR) to GWL; ESI-0087679, OCE-9529819, and OCE-0327353 to RAL; OCE-0327261, OCE-0328117, OCE-0451983 to TMS; and OCE 0240985 and OCE 0732333 to CRF. We thank the *Jason* and *Alvin* groups for their support and patience, which includes pre- and post-cruise planning as well as performing the detailed manipulations to collect the data. We also thank C. Vetriani, T. Waite, J. Tsang, R. Holyoke, E. Podowski, E. Becker, S. Ma, K. Mullaugh, C. Janzen, and E. Metzger for help with this work. ☒

REFERENCES

- Bézos, A., S. Escrig, C.H. Langmuir, P.J. Michael, and P.D. Asimow. 2009. Origins of chemical diversity of back-arc basin basalts: A segment-scale study of the Eastern Lau Spreading Center. *Journal of Geophysical Research* 114, B06212, <http://dx.doi.org/10.1029/2008JB005924>.
- Crespo-Medina, M., A.D. Chatziefthimiou, N.S. Bloom, G.W. Luther III, D.D. Wright, J.R. Reinfelder, C. Vetriani, and T. Barkay. 2009. Adaptation of chemosynthetic microorganisms to elevated mercury concentrations in deep-sea hydrothermal vents. *Limnology and Oceanography* 54:41–49, <http://dx.doi.org/10.4319/lo.2009.54.1.0041>.
- Escrig, S., A. Bézos, S.L. Goldstein, C.H. Langmuir, and P.J. Michael. 2009. Mantle source variations beneath the Eastern Lau Spreading Center and the nature of subduction components in the Lau Basin–Tonga arc system. *Geochemistry Geophysics Geosystems* 10, Q04014, <http://dx.doi.org/10.1029/2008GC002281>.

- Ferrini, V.L., M.K. Tivey, S.M. Carbotte, F. Martinez, and C. Roman. 2008. Variable morphologic expression of volcanic, tectonic, and hydrothermal processes at six hydrothermal vent fields in the Lau back-arc basin. *Geochemistry Geophysics Geosystems* 9, Q07022, <http://dx.doi.org/10.1029/2008GC002047>.
- Gartman, A., M. Yücel, A.S. Madison, D.W. Chu, S. Ma, C.P. Janzen, E.L. Becker, R.A. Beinart, P.R. Girguis, and G.W. Luther III. 2011. Sulfide oxidation across diffuse flow zones of hydrothermal vents. *Aquatic Geochemistry* 17:583–601, <http://dx.doi.org/10.1007/s10498-011-9136-1>.
- Herszage, J., and M. dos Santos Afonso. 2003. Mechanism of hydrogen sulfide oxidation by manganese(IV) oxide in aqueous solutions. *Langmuir* 19:9,684–9,692, <http://dx.doi.org/10.1021/la034016p>.
- Johnson, K.S., J.J. Childress, and C.L. Beehler. 1988. Short-term temperature variability in the rose garden hydrothermal vent field: An unstable deep-sea environment. *Deep-Sea Research* 35:1,711–1,721, [http://dx.doi.org/10.1016/0198-0149\(88\)90045-3](http://dx.doi.org/10.1016/0198-0149(88)90045-3).
- Le Bris, N., P.M. Sarradinand, and S. Pennec. 2001. A new deep-sea probe for in situ pH measurement in the environment of hydrothermal vent biological communities. *Deep-Sea Research Part I* 48:1,941–1,951, [http://dx.doi.org/10.1016/S0967-0637\(00\)00112-6](http://dx.doi.org/10.1016/S0967-0637(00)00112-6).
- Le Bris, N., B. Govenar, C. Le Gall, and C.R. Fisher. 2006a. Variability of physico-chemical conditions in 9°50'N EPR diffuse flow vent habitats. *Marine Chemistry* 98:167–182, <http://dx.doi.org/10.1016/j.marchem.2005.08.008>.
- Le Bris, N., P. Rodier, P.M. Sarradin, and C. Le Gall. 2006b. Is temperature a good proxy for sulfide in hydrothermal vent habitats? *Cahiers de Biologie Marine* 47:465–470. Available online at: <http://archimer.ifremer.fr/doc/2006/publication-3609.pdf> (accessed December 9, 2011).
- Luther, G.W. III, 2010. The role of one and two electron transfer reactions in forming thermodynamically unstable intermediates as barriers in multi-electron redox reactions. *Aquatic Geochemistry* 16:395–420, <http://dx.doi.org/10.1007/s10498-009-9082-3>.
- Luther, G.W. III, A.J. Findlay, D.J. MacDonald, S.M. Owings, T.E. Hanson, R.A. Beinart, and P.R. Girguis. 2011. Thermodynamics and kinetics of sulfide oxidation by oxygen: A look at inorganically controlled reactions and biologically mediated processes in the environment. *Frontiers in Microbiology* 2:1–9, <http://dx.doi.org/10.3389/fmicb.2011.00062>.
- Luther, G.W. III, B.T. Glazer, S. Ma, R.E. Trouwborst, T.S. Moore, E. Metzger, C. Kraiya, T.J. Waite, G. Druschel, B. Sundby, and others. 2008. Use of voltammetric solid-state (micro)electrodes for studying biogeochemical processes: Laboratory measurements to real time measurements with an *in situ* electrochemical analyzer (ISEA). *Marine Chemistry* 108:221–235, <http://dx.doi.org/10.1016/j.marchem.2007.03.002>.
- Luther, G.W. III, T.F. Rozan, M. Taillefert, D.B. Nuzzio, C. Di Meo, T.M. Shank, R.A. Lutz, and S.C. Cary. 2001. Chemical speciation drives hydrothermal vent ecology. *Nature* 410:813–816, <http://dx.doi.org/10.1038/35071069>.
- Lutz, R.A., T.M. Shank, G.W. Luther III, C. Vetriani, M. Tolstoy, D.B. Nuzzio, T.S. Moore, F. Waldhauser, M. Crespo-Medina, A. Chatziefthimou, and others. 2008. Interrelationships between vent fluid chemistry, temperature, seismic activity and biological community structure at a mussel-dominated, deep-sea hydrothermal vent along the East Pacific Rise. *Journal of Shellfish Research* 27:177–190, [http://dx.doi.org/10.2983/0730-8000\(2008\)27\[177:IBVFCT\]2.0.CO;2](http://dx.doi.org/10.2983/0730-8000(2008)27[177:IBVFCT]2.0.CO;2).
- Millero, F.J. 2007. The marine inorganic carbon cycle. *Chemical Reviews* 107:308–341, <http://dx.doi.org/10.1021/cr0503557>.
- Moore, T.S., T.M. Shank, D.B. Nuzzio, and G.W. Luther III. 2009. Time-series chemical and temperature habitat characterization of diffuse flow hydrothermal sites at 9°50'N East Pacific Rise. *Deep Sea Research Part II* 56:1,616–1,621, <http://dx.doi.org/10.1016/j.dsr2.2009.05.008>.
- Mottl, M.J., J.S. Seewald, C.G. Wheat, M.K. Tivey, P.J. Michael, G. Proskurowski, T.M. McCollom, E. Reeves, J. Sharkey, C.-F. You, and others. 2011. Chemistry of hot springs along the Eastern Lau Spreading Center. *Geochimica et Cosmochimica Acta* 75:1,013–1,038, <http://dx.doi.org/10.1016/j.gca.2010.12.008>.
- Mullaugh, K.M., G.W. Luther III, S. Ma, T.S. Moore, M. Yücel, E. Becker, E. Powdowski, C.R. Fisher, R.E. Trouwborst, and B.K. Pierson. 2008. Voltammetric (micro)electrodes for the *in situ* study of Fe²⁺ oxidation kinetics in hot springs and S₂O₃²⁻ production at hydrothermal vents. *Electroanalysis* 20:280–290, <http://dx.doi.org/10.1002/elan.200704056>.
- Nees, H.A., R.A. Lutz, T.M. Shank, and G.W. Luther III. 2009. Pre- and post-eruption diffuse flow variability among tubeworm habitats at 9°50' north on the East Pacific Rise. *Deep Sea Research Part II* 56:1,607–1,615, <http://dx.doi.org/10.1016/j.dsr2.2009.05.007>.
- Nees, H.A., T.S. Moore, K.M. Mullaugh, R.R. Holyoke, C.P. Janzen, S. Ma, E. Metzger, T.J. Waite, M. Yücel, R.A. Lutz, and others. 2008. Hydrothermal vent mussel habitat chemistry pre- and post-eruption at 9°50' on the East Pacific Rise. *Journal of Shellfish Research* 27:169–175, [http://dx.doi.org/10.2983/0730-8000\(2008\)27\[169:HVMHCP\]2.0.CO;2](http://dx.doi.org/10.2983/0730-8000(2008)27[169:HVMHCP]2.0.CO;2).
- Podowski, E.L., S. Ma, G.W. Luther III, D. Wardrop, and C.R. Fisher. 2010. Biotic and abiotic factors affecting realized distributions of mega-fauna in diffuse flow on andesite and basalt along the Eastern Lau Spreading Center, Tonga. *Marine Ecology Progress Series* 418:25–45, <http://dx.doi.org/10.3354/meps08797>.
- Podowski, E.L., T.S. Moore, K.A. Zelnio, G.W. Luther III, and C.R. Fisher. 2009. Distribution of diffuse flow megafauna in two sites on the Eastern Lau Spreading Center, Tonga. *Deep Sea Research Part I* 56:2,041–2,056, <http://dx.doi.org/10.1016/j.dsr2.2009.07.002>.
- Pyzik, A.J., and S.E. Sommer. 1981. Sedimentary iron monosulfides: Kinetics and mechanism of formation. *Geochimica et Cosmochimica Acta* 45:687–698, [http://dx.doi.org/10.1016/0016-7037\(81\)90042-9](http://dx.doi.org/10.1016/0016-7037(81)90042-9).
- Ryan, W.B.F., S.M. Carbotte, J.O. Coplan, S. O'Hara, A. Melkonian, R. Arko, R.A. Weisel, V. Ferrini, A. Goodwillie, F. Nitsche, and others. 2009. Global multi-resolution topography synthesis. *Geochemistry Geophysics Geosystems* 10, Q03014, <http://dx.doi.org/10.1029/2008GC002332>.
- Shank, T.M., D.J. Fornari, K.L. Von Damm, M.D. Lilley, R.M. Haymon, and R.A. Lutz. 1998. Temporal and spatial patterns of biological community development at nascent deep-sea hydrothermal vents (9°50'N, East Pacific Rise). *Deep-Sea Research Part II* 45:465–515.
- Tolstoy, M., J.P. Cowen, E.T. Baker, D.J. Fornari, K.H. Rubin, T.M. Shank, F. Waldhauser, D.R. Bohnenstiehl, D.W. Forsyth, D.W. Holmes, and others. 2006. A sea-floor spreading event captured by seismometers. *Science* 314:1,920–1,922, <http://dx.doi.org/10.1126/science.1133950>.
- Vallier, T.L., G.A. Jenner, F.A. Frey, J.B. Gill, A.S. Davis, A.M. Volpe, J.W. Hawkins, J.D. Morris, P.A. Cawood, J.L. Morton, and others. 1991. Subalkaline andesite from Valu Fa Ridge, a back-arc spreading center in southern Lau Basin: Petrogenesis, comparative chemistry, and tectonic implications. *Chemical Geology* 91:227–256, [http://dx.doi.org/10.1016/0009-2541\(91\)90002-9](http://dx.doi.org/10.1016/0009-2541(91)90002-9).
- Waite, T.J., T.S. Moore, J.J. Childress, H. Hsu-Kim, K.M. Mullaugh, D.B. Nuzzio, A.N. Paschal, J. Tsang, C.R. Fisher, and G.W. Luther III. 2008. Variation in sulfur speciation with shellfish presence at a Lau Basin diffuse flow vent site. *Journal of Shellfish Research* 27:163–168, [http://dx.doi.org/10.2983/0730-8000\(2008\)27\[163:VISSWS\]2.0.CO;2](http://dx.doi.org/10.2983/0730-8000(2008)27[163:VISSWS]2.0.CO;2).
- Yao, W., and F.J. Millero. 1996. Oxidation of hydrogen sulfide by hydrous Fe(III) oxides in seawater. *Marine Chemistry* 52:1–16, [http://dx.doi.org/10.1016/0304-4203\(95\)00072-0](http://dx.doi.org/10.1016/0304-4203(95)00072-0).