

THE OFFICIAL MAGAZINE OF THE OCEANOGRAPHY SOCIETY

# Oceanography

#### CITATION

Holden, J.F., J.A. Breier, K.L. Rogers, M.D. Schulte, and B.M. Toner. 2012. Biogeochemical processes at hydrothermal vents: Microbes and minerals, bioenergetics, and carbon fluxes. *Oceanography* 25(1):196–208, <http://dx.doi.org/10.5670/oceanog.2012.18>.

#### DOI

<http://dx.doi.org/10.5670/oceanog.2012.18>

#### 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](mailto:info@tos.org) or The Oceanography Society, PO Box 1931, Rockville, MD 20849-1931, USA.



# Biogeochemical Processes at Hydrothermal Vents

Microbes and Minerals,  
Bioenergetics,  
and Carbon Fluxes

BY JAMES F. HOLDEN, JOHN A. BREIER,  
KARYN L. ROGERS, MITCHELL D. SCHULTE,  
AND BRANDY M. TONER

An active black smoker chimney from the Boardwalk sulfide mound in the High Rise vent field at the Endeavour Segment of the Juan de Fuca Ridge emitting hydrothermal fluids up to 340°C. *Photo credit: Bruce Strickrott*

**ABSTRACT.** Hydrothermal vents are among the most biologically active regions of the deep ocean. However, our understanding of the limits of life in this extreme environment, the extent of biogeochemical transformation that occurs in the crust and overlying ocean, and the impact of vent life on regional and global ocean chemistry is in its infancy. Recently, scientific studies have expanded our view of how vent microbes gain metabolic energy at vents through their use of dissolved chemicals and minerals contained in ocean basalts, seafloor sulfide deposits, and hydrothermal plumes and, in turn, how they catalyze chemical and mineral transformations. The scale of vent environments and the difficulties inherent in the study of life above, on, and below the deep seafloor have led to the development of geochemical and bioenergetic models. These models predict habitability and biological activity based on the chemical composition of hydrothermal fluids, seawater, and the surrounding rock, balanced by the physiological energy demand of cells. This modeling, coupled with field sampling for ground truth and discovery, has led to a better understanding of how hydrothermal vents affect the ocean and global geochemical cycles, and how they influence our views of life on the early Earth and the search for life beyond our own planet.

## INTRODUCTION

Hydrothermal vents are unique among Earth's habitats as points of contact between the deep sea and the upper mantle. At these locations, seawater percolates through cracks and fissures in the oceanic crust until it reaches rock heated by shallow pockets of magma. The seawater is heated and chemically transformed through interactions with rocks and volcanic gases, and is converted into hydrothermal fluid. These hot, buoyant fluids then course their way rapidly back up to and through the seafloor, sometimes as black jets of superheated fluid billowing into the deep sea, and other times as diluted shimmering water rising from cracks in the seafloor. Perhaps most interestingly of all, this interface between hot hydrothermal fluid from the crust and cold seawater supports microbial life that is independent of organic material derived from photosynthesis and consequently is largely disconnected from the surface photosynthetic biosphere. This microbial life alters the chemistry of hydrothermal vent habitats and provides

nourishment for vent fauna.

Over the past 15 years, breakthroughs in hydrothermal vent microbiology and biogeochemistry include: (1) revelations of the "subsurface biosphere" (Holden et al., 1998; Butterfield et al., 2004; Von Damm and Lilley, 2004) and the "rare biosphere" (Huber et al., 2007); (2) expansion of the upper temperature limit of life to over 120°C (Kashefi and Lovley, 2003; Takai et al., 2008a); (3) isolation of organisms able to live at high temperatures under highly acidic vent conditions (thermoacidophiles) (Reysenbach et al., 2006); (4) discovery of new biochemical pathways for CO<sub>2</sub> fixation (Berg et al., 2010; Hügler and Sievert, 2011); (5) development of thermodynamic models of microbial growth and biogeochemical transformations (McCollom and Shock, 1997; Hoehler, 2004); (6) new insight into links between microbial population structure and geochemistry (Takai and Nakamura, 2010; Flores et al., 2011); (7) development of microbes for biofuel and bioenergy applications (see Girguis and Holden,

2012, in this issue); and (8) sequencing of dozens of bacterial, archaeal, and viral genomes and metagenomes. As a result, we are now poised to address the next generation of questions related to hydrothermal vent biogeochemical processes. What are the geochemical, mineralogical, and physical constraints on hydrothermal microbial life within, on, and above the seafloor? How does the production of new biomass in the vents compare with the rest of the ocean, and what is its impact on global biogeochemical processes? What record of life is left behind in vent environments, and how can we use this record to search for evidence of life on the early Earth and beyond our own planet?

## VENT HABITATS

It is important to understand the environmental context in which deep-sea hydrothermal vents are found in fast- and intermediate-spreading mid-ocean ridges. In these regions, the oceanic lithosphere is composed of the extrusive layer (0.5–1 km thick), the sheeted dike layer (1–2 km thick), and the gabbro layer (3–4 km thick) (Figure 1). The permeability of the extrusive layer ( $10^{-15}$  to  $10^{-11}$  m<sup>2</sup>) is much higher than those of the sheeted dike and gabbro layers ( $10^{-17}$  to  $10^{-15}$  m<sup>2</sup>) (Fisher et al., 2008), with higher permeabilities occurring in young oceanic crust (e.g.,  $10^{-13.4}$  to  $10^{-9.4}$  m<sup>2</sup> and  $\sim 10^{-13}$  to  $10^{-12}$  m<sup>2</sup> for the extrusive and sheeted dike layers, respectively, at the 9°50'N East Pacific Rise vent site; Stroup et al., 2009; Crone et al., 2011). At fast-spreading mid-ocean ridges, where new oceanic crust is formed along tectonic plate boundaries at the quickest pace in the ocean, the gabbro layer is partially molten and a thin lens of molten magma

forms at or near the sheeted dike layer boundary. Seawater percolates downward until it reaches hot fractured rock above the magma lens (Figure 1) where water-rock reactions cause the fluid to lose some chemical species ( $O_2$ ,  $Mg^{2+}$ ,  $SO_4^{2-}$ ) to the rock, gain others ( $H_2$ ,  $CO_2$ ,  $CH_4$ ,  $S^{2-}$ ,  $SiO_2$ , reduced metals), and increase in temperature. Some of this fluid exits the seafloor within the axial valley along the spreading center, while the remainder circulates laterally within the oceanic crust, primarily within the extrusive layer, in rock as old as 65 million years where the formation of alteration minerals eventually minimizes rock permeability (Stein and Stein, 1994). Ridge-crest hydrothermal flow contributes ~ 10% of all hydrothermal fluid mass but nearly half of the total hydrothermal heat flux (German and Von Damm, 2004). Hydrothermal circulation also forms at discrete points on the oceanic

crust in association with submarine volcanoes found over magmatic hot spots along mid-ocean spreading centers, plate boundary subduction zones, and in the center of tectonic plates (Figure 1).

The amount of microbial biomass below the seafloor could potentially be quite high. It was estimated that there is 0.7 Pg (Pg =  $10^{15}$  g) and 1.3 Pg of carbon in microbial biomass in the open ocean above and below 200 m depth, respectively (Figure 1; Whitman et al., 1998). In contrast, the estimated amount of bacterial and archaeal carbon in marine sediments is significantly higher (56–90 Pg; Parkes et al., 1994; Lipp et al., 2008). Sediment covers most of the seafloor, but its thickness in the open ocean ranges from virtually no sediment cover near mid-ocean spreading centers to up to 200 m over the abyssal plains and in excess of 1 km near continental margins where particle input and crustal

age increase. Therefore, most of this sedimentary biomass is confined to the continental margins due to the thicker and more organic-rich sediments. The extent of the microbial biosphere in oceanic crust and its biomass is poorly constrained, but it was estimated by calculating the volume of crust occupied by life using the 120°C isotherm as an upper temperature boundary (Heberling et al., 2010). Using this assumption, it was estimated that there is 200 Pg of bacterial and archaeal carbon in the oceanic lithosphere, and that 90% of this carbon is in the extrusive layer (Figure 1). This potentially large biomass of subseafloor microbes suggests that these organisms could significantly affect biogeochemical fluxes and carbon cycles in the deep ocean. The relatively large amount of geochemical energy available in hydrothermal fluids suggests that subseafloor and deep-sea biomass found in these fluids will be among the largest and most metabolically active. Yet, there has not been an estimate of microbial biomass associated directly with hydrothermal processes above or within the seafloor.

Deep-sea hydrothermal vents provide one of the best access points to the rocky subseafloor and hydrothermal plumes, and thus are an ideal starting point for understanding biogeochemical processes throughout the oceanic igneous crust and in the deep sea. Some hydrothermal fluids rise through the crust undiluted and exit the seafloor at temperatures up to 350–400°C (Figure 2). Upon contact with seawater, the dissolved metals and sulfides in the hydrothermal fluids precipitate, forming the billowing black jets and hydrothermal plumes typically associated with these environments. Cold seawater that is in direct contact with hot hydrothermal fluid is rapidly

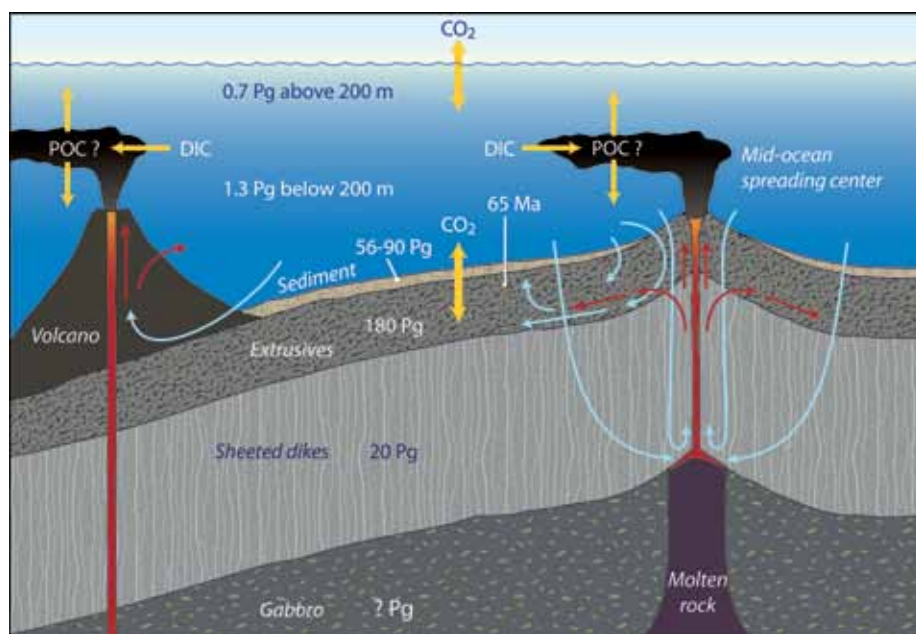


Figure 1. Cross section of the upper oceanic crust created at a fast-spreading mid-ocean ridge. Blue and red arrows show cold seawater and hot hydrothermal fluid circulation, respectively. The yellow double arrows indicate  $CO_2$  exchange among the atmosphere, the deep ocean, and the subsurface. The numbers indicate the estimated amount of bacterial and archaeal carbon in Pg ( $10^{15}$  g) in different regions of the ocean and the rock age where hydrothermal fluid circulation in the crust ceases (65 million years). DIC = dissolved inorganic carbon. POC = particulate organic carbon.

heated, causing seafloor precipitation of sulfate minerals that form a barrier between the exiting hydrothermal fluids and the surrounding seawater (Haymon, 1983). The resulting conduit serves as a scaffold for the accumulation of precipitated metal sulfides and the subsequent formation of what is known as a chimney (Figure 2). A temperature gradient forms across the wall of the chimney due to the mixture of seawater and hydrothermal fluid within the chimney wall. Often, hydrothermal fluids also mix with seawater in the crust and exit the seafloor at temperatures too low to cause sulfate precipitation (Figure 2). In these cases, diffuse vents form where 2°C to 150°C fluids flow directly out of cracks in the seafloor basalt without any associated metal-sulfide deposits. The chemical disequilibria between reduced volatiles and metals and oxidized compounds in seawater formed in the interior of black smoker chimneys, in hydrothermal vent plumes, and in diffuse vent fluids nourish the myriad microbes that inhabit these environments (Figure 2).

Most vent biogeochemistry studies are focused on one of three types of host rock: mafic rock, ultramafic rock, and dacitic/andesitic rock. Mafic and ultramafic rock hydrothermal environments are commonly found along mid-ocean spreading centers (Table 1). Both have high concentrations of MgO and FeO, but they differ in their silica content, with ultramafic rocks having silica concentrations less than 45% (by weight), while mafic rocks have concentrations above 45%. Serpentinization, the hydrous alteration of ultramafic rocks (containing primarily the mineral olivine) into serpentine, magnetite, and H<sub>2</sub>, often occurs where ultramafic rocks are exposed to circulating seawater

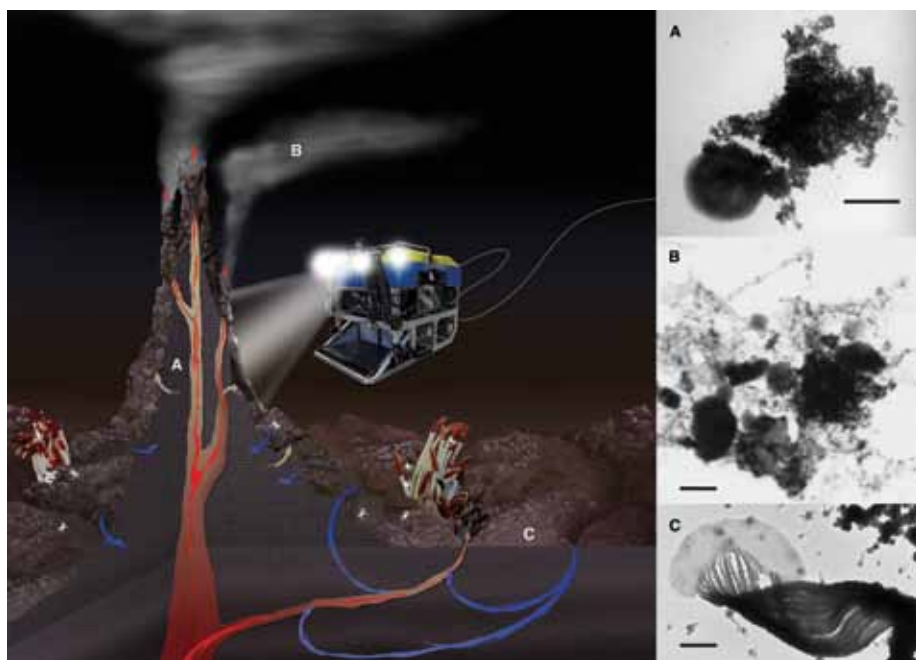


Figure 2. Cross section of (A) an active sulfide chimney, (B) hydrothermal plumes, and (C) diffuse fluid venting from basalt, with electron micrographs of microorganisms from each region. Red arrows show hot hydrothermal fluid circulation within flow channels; blue arrows, cold seawater through basalt and chimney pores; and tan arrows, a mixture of these two fluids flowing from the seafloor. The remotely operated vehicle *Jason 2* is shown approaching the vent site. The organisms in the electron micrographs are from (A) the hyperthermophilic iron reducer *Hyperthermus* sp. strain Ro04 from an active sulfide chimney (0.5  $\mu\text{m}$  scale bar; recent work of author Holden), (B) scanning transmission X-ray micrograph of a nonbuoyant plume aggregate from 9°N East Pacific Rise (2  $\mu\text{m}$  scale bar, recent work of author Breier and colleagues), and (C) the mesophilic iron oxidizer *Mariprofundus ferrooxydans* with its iron-oxide-coated stalk (0.5  $\mu\text{m}$  scale bar). Image C was reprinted by permission from Macmillan Publishers Ltd: *The ISME Journal*, Chan et al., copyright 2011.

(McCollom and Bach, 2009). The serpentinization reaction may also form CH<sub>4</sub> in the presence of CO<sub>2</sub>. As a result, ultramafic hydrothermal fluids typically have high concentrations of H<sub>2</sub> and CH<sub>4</sub> (Table 1). The reaction is inhibited by silica and is thus less common in mafic and felsic rocks (felsic rocks are > 65%

silica by weight). However, H<sub>2</sub>, CH<sub>4</sub>, and S<sup>2-</sup> concentrations in mafic hydrothermal fluids increase significantly following a volcanic eruption, as circulating fluids interact with a newly injected shallow dike (e.g., Main Endeavour Field, 9°N East Pacific Rise in Table 1; Lilley et al., 2003; Seewald et al., 2003; Von Damm

---

**James F. Holden** ([jholden@microbio.umass.edu](mailto:jholden@microbio.umass.edu)) is Associate Professor, Department of Microbiology, University of Massachusetts, Amherst, MA, USA. **John A. Breier** is Assistant Scientist, Applied Ocean Physics and Engineering Department, Woods Hole Oceanographic Institution, Woods Hole, MA, USA. **Karyn L. Rogers** is Research Scientist, Geophysical Laboratory, Carnegie Institution of Washington, Washington, DC, USA. **Mitchell D. Schulte** is Mars Exploration Program Scientist, Planetary Science Division, National Aeronautics and Space Administration Headquarters, Washington, DC, USA. **Brandy M. Toner** is Assistant Professor, Department of Soil, Water and Climate, University of Minnesota, St. Paul, MN, USA.

and Lilley, 2004).

In contrast, hydrothermal vents in dacitic-to-andesitic rock form along volcanic arcs at convergent plate boundaries. Hydrous minerals and silica accumulate in aging oceanic crust due to hydrothermal circulation and form more felsic rock, such as dacite and andesite. During subduction, minerals in the subducted slab melt and dehydrate forming more stable anhydrous forms. The hydrothermal fluids from these rocks tend to have lower pH, low H<sub>2</sub> and CH<sub>4</sub> concentrations, and higher dissolved metal concentrations (Table 1). The differences in the fluid chemistry in these three rock types ultimately influence the kinds of microbial activity and biogeochemical processes that occur.

### MICROBE-MINERAL INTERACTIONS

Many biological activities at the seafloor and in deep-sea hydrothermal environments involve interactions between organisms and minerals. Microbial interactions with minerals can be active, involving direct mineral utilization for energy generation or a trace metal requirement (e.g., Fe, Ni, Co, Zn, Mo, W), or passive where mineral interaction plays a secondary role, such as particle attachment. Even cells that are “passively” attached to a mineral may still be utilizing the mineral to satisfy their trace element requirements. Mineral utilization requires unique physiological mechanisms because the reactants are insoluble. These mechanisms

include direct protein contact with the minerals, secretion of chelators that solubilize and transfer mineral components (e.g., Fe) to the cell, and secretion of electron shuttles that transfer electrons between the cell and the insoluble metal (see review by Holden et al., 2011). These microbe-mineral interactions occur in the interiors and exteriors of active sulfide chimneys and diffuse vents, in cold extinct sulfide deposits and basalts, and in the plumes emitted from active hydrothermal systems. Understanding how vent microbes interact with minerals biochemically, the constraints on their mineral interactions, and the kinds of biologically mediated mineral transformations that occur are frontiers of future vent biogeochemical research.

Table 1. Biologically relevant chemistry of end-member hydrothermal fluids from various sites and host-rock environments

LOCATION	RANGE OF CONCENTRATIONS					REFERENCES
	pH	H <sub>2</sub> (mM)	CH <sub>4</sub> (mM)	H <sub>2</sub> S (mM)	Fe (mM)	
<b>MAFIC ROCK</b>						
Main Endeavour Field	4.2–4.5	0.16–1.5	1.8–4.5	2–29	0.53–1.36	Butterfield et al. (1994); Lilley et al. (2003); Seewald et al. (2003)
ASHES, Axial Volcano	3.5–4.4	0.07–0.27	0.07–0.28	7.1	0.01–1.07	Butterfield et al. (1990)
9°50'N East Pacific Rise	ND	0.33–8.91	0.05–0.75	6.2–23.2	0.2–6.64	Von Damm and Lilley (2004)
Kilo Moana, Lau Basin	2.9–4.0	ND	ND	5.4–6.3	2.5–3.8	Mottl et al. (2011)
Lucky Strike, Mid-Atlantic Ridge	3.5–4.9	0.02–0.73	0.30–0.85	1.4–4.6	0.03–0.86	Von Damm et al. (1998); Charlou et al. (2000)
<b>ULTRAMAFIC ROCK</b>						
Rainbow, Mid-Atlantic Ridge	2.8	16	2.5	1.2	24.1	Charlou et al. (2002)
Logatchev, Mid-Atlantic Ridge	3.3–3.9	12–19	2.1–3.5	0.8–2.5	2.4–2.5	Schmidt et al. (2007)
Kairei, Central Indian Ridge	3.4–3.5	7.9–8.2	0.08–0.20	3.9–4.1	3.5–6.0	Gamo et al. (2001); Gallant and Von Damm (2006)
<b>DACITIC/ANDESITIC ROCK</b>						
Mariner Field, Lau Basin	2.4–2.7	0.04–0.10	0.01	6.9–9.0	10.5–13.0	Takai et al. (2008b); Mottl et al. (2011)
DESMOS Caldera, Manus Basin	2.1–2.7	ND	ND	5.3–9.7	0.01–4.4	Gamo et al. (1997)
Brothers Volcano, Kermadec Arc	2.8–3.0	0.01–0.02	< 0.01	2.3–7.9	4.2–7.3	Takai et al. (2009)
<b>SEAWATER</b>						
Seawater	7.8	0.0004	0.00001	0	0.000061	Turekian (1968)

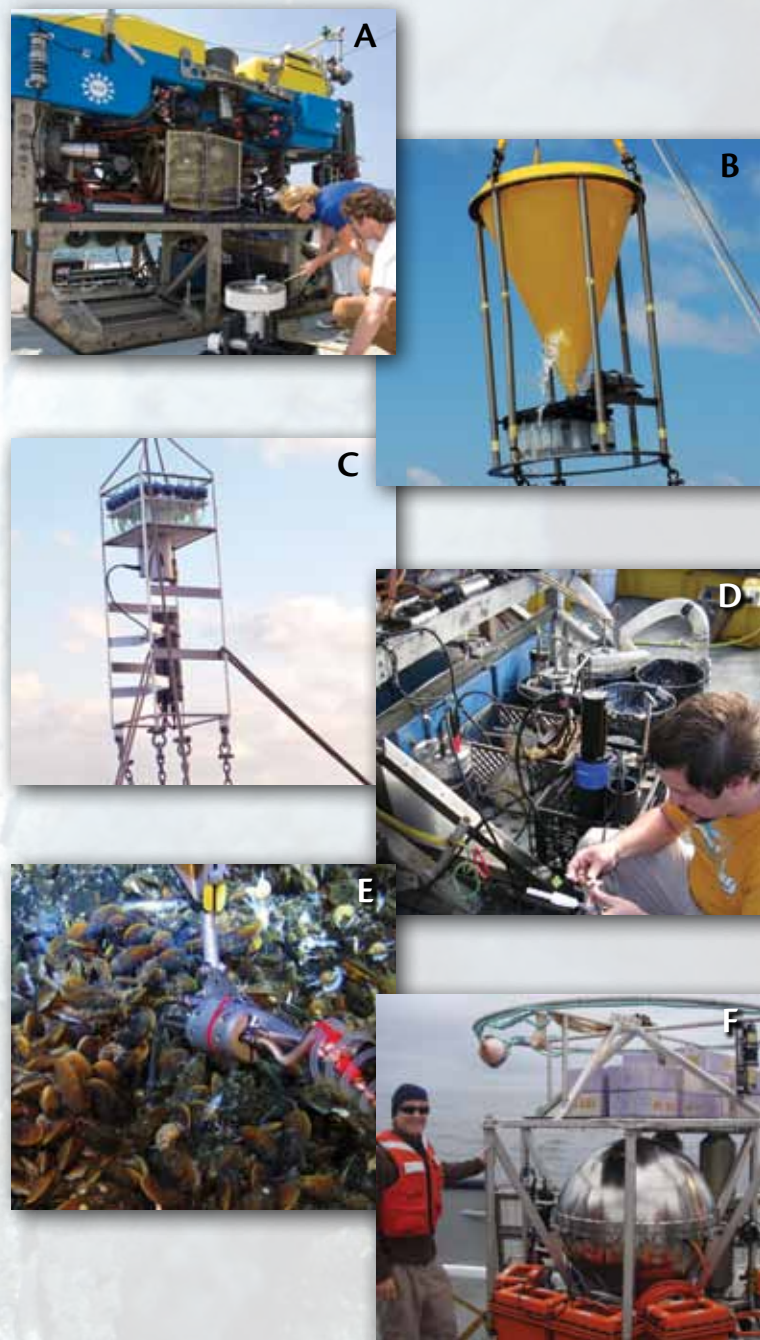
ND = not determined.

## BOX 1 | TOOLS OF VENT BIOGEOCHEMISTRY RESEARCH

Throughout most of the history of deep-sea hydrothermal vent research, combined sampling for microbiology and geochemistry has been difficult or impossible. Over the past decade, this limitation has changed with the advent of new biogeochemical sampling devices. Hydrothermal vents and plumes are accessed by using human-occupied vehicles, remotely operated vehicles (ROVs), autonomous underwater vehicles (AUVs), hybrid ROV/AUVs, conductivity, temperature, depth sensor/rosette hydrocasts, and moorings, all of which can be fitted with sampling devices and instruments for biogeochemistry research. Here, we provide a few example technologies (Box Figure 1).

The Hydrothermal Fluid and Particle Sampler (HFPS; Butterfield et al., 2004) and the Autonomous Microbial Sampler (AMS; Taylor et al., 2006) draw high- and low-temperature vent fluids as they exit the seafloor, measure fluid temperature, and collect up to 29 separate fluid and particle samples for chemical, mineral, and microbial analyses. Other specialized sampling systems include the Suspended Particle Rosette (SUPR; Box Figure 1A) multisampler that is used to collect geochemical and microbial samples from hydrothermal plumes on a mooring or during a hydrocast where larger water volumes are necessary. To accomplish this sampling, SUPR is equipped with a valve designed to allow higher filtering flow rates in order to rapidly filter 24 discrete large-volume samples (e.g., 30–100 L; Breier et al., 2009). The Bacterial Mat Sampler under development by author Breier and David Emerson of the Bigelow Laboratory for Ocean Sciences is an automated, 140 ml syringe-style multisampler designed for a variety of seafloor sampling tasks in conjunction with synoptic geochemical sensing. Ocean water column and hydrothermal fluxes are also measured as functions of time using sediment traps (Box Figure 1B,C) attached to seafloor moorings (see Toner et al., 2012, in this issue). Sediment traps allow for long-term sampling (months to years) and are currently the best option for integrated, vent-field-scale assessment of biogeochemical fluxes (Khripounoff et al., 2008; German et al., 2010).

New instruments are also being developed to obtain geochemical and genomic data in situ. These instruments include solid state voltammetric (micro)electrodes for  $O_2$ ,  $H_2S$ ,  $Fe^{2+}$ ,  $Mn^{2+}$ , and soluble molecular FeS, such as the In Situ Electrochemical Analyzer system (Box Figure 1D; Luther et al., 2008); mass spectrometers for  $H_2$ ,  $CH_4$ , and  $CO_2$  analyses (Box Figure 1E; Camilli and Duryea, 2009; Wankel et al., 2011); and laser Raman spectroscopy for suspended mineral phase speciation (Breier et al., 2010). In situ genomic sampling instruments include the Environmental Sample Processor, which is capable of in situ, real-time polymerase chain reaction (Preston et al., 2011), sample preservation (Ottesen et al., 2011), and sandwich hybridization assay and fluorescent in situ hybridization (Box Figure 1F; Scholin et al., 2009). All of these instruments are used as stand-alone units or in conjunction with the existing fluid and particle sampling devices described above.



Box Figure 1. Examples of sampling platforms, devices, and instruments used for hydrothermal vent biogeochemistry research. (A) Suspended Particle Rosette multisampler being prepared by Kaitlyn McCartney and Chip Breier for remotely operated vehicle deployment on *Jason 2*. Photo by Tom Kleindinst. (B) A sediment trap. (C) A time series sample collection system being recovered from mooring deployments. Photo courtesy McLane Research Laboratories, Inc. (D) The In Situ Electrochemical Analyzer system being prepared by Tommy Moore for deployment by *Jason 2*. Photo by Mustafa Yücel. (E) The in situ mass spectrometer developed by Peter Girguis being used to quantify the distribution of hydrogen around mussels at vents along the Mid-Atlantic Ridge. Photo by Nicole Dubilier. (F) The Environmental Sample Processor being prepared for deployment by Chris Scholin. Photo © MBARI 2011

## Hot, Hydrothermally Active Sulfide Chimneys and Diffuse Vents

In the interior of active sulfide chimneys, the pH of hydrothermal fluid that has been diluted with seawater to temperatures below 120°C (near the current upper temperature limit of life) is estimated to be < pH 3 to pH 7 depending on mixing styles and the chemical composition of the initial hydrothermal fluid (Tivey, 2004). Presumably, the pH range is similar in hot, basalt-hosted diffuse vent environments. Many of the thermophiles and hyperthermophiles (i.e., microbes that grow optimally above 50°C and 80°C) cultured from and detected in sulfide chimneys and diffuse vents are archaea and mild acidophiles to neutrophiles (i.e., optimal growth between pH 5 and 7; see Sievert and Vetrani, 2012, in this issue). However, isolation of the thermoacidophilic archaeon *Aciduliprofundum boonei* from a Mariner Field sulfide chimney with highly acidic hydrothermal fluids (Reysenbach et al., 2006) shows that other pH classes of microorganisms are also found.

Hydrogen concentrations in hydrothermal fluids also influence the types of autotrophs found in chimneys with hydrogenotrophic methanogens, most abundant at sites with higher H<sub>2</sub> concentrations (ultramafic and recent eruption sites). Other thermophilic H<sub>2</sub> oxidizers, such as iron reducers and microaerophiles, are more abundant than methanogens at sites with lower H<sub>2</sub> concentrations (mafic and dacitic/andesitic sites; Takai and Nakamura, 2010; Ver Eecke et al., 2009; Flores et al., 2011). Hyperthermophilic iron reducers from sulfide chimneys oxidize H<sub>2</sub> and transform ferrihydrite [Fe<sub>10</sub>O<sub>14</sub>(OH)<sub>2</sub>]

to magnetite [Fe<sub>3</sub>O<sub>4</sub>] and possibly other forms of magnetic iron (Ver Eecke et al., 2009) when in direct contact with the mineral through unknown energy-conserving mechanisms (Figure 2A). The high influx of seawater into sulfide chimneys at Endeavour Segment, coupled with mildly reducing conditions, leads to widespread oxidation of iron sulfide minerals and iron oxide formation within chimneys at this site (Kristall et al., 2006), where these organisms have been isolated (Kashefi and Lovley, 2003; Ver Eecke et al., 2009).

## Cold, Oxidizing Environments: Bacterial Mats, Inactive Sulfides, and Plumes

The cool outer surfaces of active sulfide chimneys and the interior of inactive chimneys each provide reduced compounds for (micro)aerobic chemolithoautotrophic metabolisms. However, the diversity of the microbial communities present in cold sulfides decreases with age, with few to no archaea detected as the reactivity of the sulfide component decreases and oxidized metal-bearing minerals accumulate (Rogers et al., 2003; Edwards et al., 2003). There is heavy accumulation of secondary Fe oxides as a result of mineral dissolution and the activity of neutrophilic iron oxidizing bacteria (Edwards et al., 2003). Iron-encrusted bacterial biofilms form preferentially on the sulfide mineral pyrrhotite [Fe<sub>1-x</sub>S; x = 0–0.2], and microbially produced Fe-complexing ligands may play critical roles in the delivery of Fe(II) to their cells as filamentous stalk structures accumulate iron oxyhydroxide minerals within the biofilm (Toner et al., 2009b). Biofilms occur above pits and inside pores of the sulfide mineral assemblages, and they are densely

populated with particles of twisted stalk morphologies of iron-oxidizing bacteria.

The obligately iron-oxidizing microaerophile *Mariprofundus ferrooxydans* (Figure 2C) was isolated from an iron-oxidizing mat from Loihi Seamount off Hawaii's Big Island and produced twisted filamentous stalk structures coated with iron oxyhydroxides like those reported above (Emerson et al., 2007). Time-lapse microscopy showed that *M. ferrooxydans* stalk formation begins with attachment to a solid surface followed by further stalk excretion as the cells grow and rotate away from the holdfast (Chan et al., 2011). Stalk filaments are initially lightly mineralized with poorly crystalline iron oxyhydroxide, but with age they are more heavily coated with crystals of lepidocrocite [ $\gamma$ -FeOOH]. A similar phenomenon occurs with the sulfide-oxidizing microaerophile *Arcobacter sulfidicus*. It excretes elemental sulfur from one end of the cell as thin filaments, which are colonized by other members of the population who deposit sulfur along the circumference of the protofilament, forming large flocs of native sulfur (Sievert et al., 2007). These sulfur flocs can be seen as "snowblower" diffuse vents immediately following a volcanic eruption (Haymon et al., 1993).

Hydrothermal vent fluids mix turbulently with seawater to produce a water-column plume in which a variety of abiotic and biotic pathways for oxidation-reduction and particle-forming reactions are favorable. Mineral particles form rapidly and abiotically, but there is a growing body of evidence that suggests that microorganisms are also actively forming mineral particles within these plumes and play roles that may have been overlooked previously. Microbial biomass, biomolecules



(transparent exopolymers and lipids), and mineral aggregates coated with an organic matrix are concentrated within hydrothermal plumes relative to the surrounding seawater, indicating that the plume is supporting their production (Cowen et al., 2001; Wakeham et al., 2001; Shackelford and Cowen, 2006; Bennett et al., 2008; Toner et al., 2009a). Concentrations of transparent exopolymer particles increased in the plume with plume age implying that the source is in situ production rather than the original hydrothermal effluent (Shackelford and Cowen, 2006). Organic carbon from biological activity can affect elemental cycles indirectly. For example, Fe(II) and Fe(III) complexes with dissolved and particulate organic carbon in plumes change the mobility of vent iron in the deep sea (Bennett et al., 2008; Toner et al., 2009a). Furthermore, direct activity of Mn-oxidizing microorganisms has been demonstrated for Guaymas Basin plumes (Dick and Tebo, 2010), and evidence for CH<sub>4</sub> and NH<sub>4</sub><sup>+</sup> oxidation in plumes also exists (De Angelis et al., 1993; Lam et al., 2008). Although work is underway to gain a better understanding of biogeochemical processes within plumes, it is evident that microbe-mineral interactions in the plumes make a significant contribution to metal cycling in the deep ocean.

#### BIOENERGETICS: GEOCHEMICAL SUPPLY AND ORGANISMAL DEMAND

The large scale and poor accessibility of deep-sea hydrothermal systems necessitates the use of models to predict vent biogeochemical processes. Bioenergetic models are currently the best tool available for these predictions. Chemical disequilibria are widespread at deep-sea

vents, and many of the abiotic processes that drive the system back toward equilibrium proceed slowly. Microbes accelerate these reactions and capture the energy released for their growth. Energy yields can be quantified using

chemical parameters, such as Gibbs energy ( $\Delta G_{r,T,p}$ ), which incorporates both the properties of the reaction constituents under hydrothermal conditions and the specific system composition. As described above, deep-sea hydrothermal fluid geochemistry can vary significantly (Table 1), and these variations lead to differences in energy availability and biological diversity. The goal of bioenergetic modeling is to evaluate the energy yields for potential metabolic reactions while accounting for variations in host rock composition, fluid chemistry, and flow regime. These models must be used in conjunction with estimates of microbial energy requirements and observed microbial diversity in order to understand how vent geochemistry supports diverse ecosystems.

Geochemical modeling has been used successfully to predict geochemical vent fluid characteristics that were later observed. Because many parts

of hydrothermal systems are difficult to reach through current sampling methods, geochemical models, field observations, and laboratory experiments are used and advanced in parallel to further our understanding of vent

“ UNDERSTANDING HOW VENT MICROBES INTERACT WITH MINERALS BIOCHEMICALLY, THE CONSTRAINTS ON THEIR MINERAL INTERACTIONS, AND THE KINDS OF BIOLOGICALLY MEDIATED MINERAL TRANSFORMATIONS THAT OCCUR ARE FRONTIERS OF FUTURE VENT BIOGEOCHEMICAL RESEARCH. ”

biogeochemistry (e.g., water-rock reactions, fluid mixing, conductive cooling, coupled reactive transport). For example, the metastability of organic compounds under hydrothermal conditions was predicted from geochemical modeling (Shock and Schulte, 1998), and subsequent fluid analyses confirmed the presence of organic compounds in hydrothermal systems (Seewald et al., 2003; Cruse and Seewald, 2006; Lang et al., 2010). Laboratory experiments where hydrothermal conditions are replicated are used to confirm and refine geochemical models (Foustoukos et al., 2011).

Although in situ fluid compositions are ideal for evaluating bioenergetics, they are difficult to obtain. Therefore, geochemical models are used to estimate fluid compositions at temperatures relevant to vent organisms and calculate the energy yields of potential metabolic reactions, the energetic costs of biomass

synthesis, and the variations in metabolic niches as a function of time and space (McCollom and Shock, 1997; McCollom, 2000; McCollom and Amend, 2005; Houghton and Seyfried, 2010; Amend et al., 2011). Early estimates suggested that aerobic respiration is favored at lower temperatures, while anaerobic respiration such as methanogenesis and sulfur/sulfate reduction are favored at higher temperatures (McCollom and Shock, 1997). Subsequent models and lab experiments suggest that an aerobic/anaerobic dichotomy does not exist when the sluggish kinetics of H<sub>2</sub> oxidation are considered (McCollom, 2000; Foustoukos et al., 2011). Additional work has shown that host-rock composition and H<sub>2</sub> concentrations in end-member fluids likely exert the greatest control on the extent of aerobic metabolisms in vent systems (Amend et al., 2011, and recent work of author Rogers). Furthermore, numerical models estimating the energetic costs of biomass synthesis suggest that formation of key cellular components is more favorable in more reducing (e.g., ultramafic) hydrothermal systems (McCollom and Amend, 2005; Amend et al., 2011).

Correlating metabolic reaction energetics with microbial diversity is complicated by a number of factors. First, co-sampling for both biological and geochemical analyses is difficult, and few corresponding data sets exist. Second, while metabolic plasticity exists in vents in response to thermal and chemical gradients, this trait makes it difficult to assign in situ metabolic function to observed microbial communities. Third, assessing energy requirements of microbes is challenging as energy consumption is a function of growth phase (Price and Sowers, 2004), species,

and physiological pathway. While some laboratory growth experiments indicate that biomass production is correlated to power consumption under optimal conditions (Smith and Shock, 2008), the minimum energy requirements for growth under adverse conditions are controversial (Schink, 1997; Jackson and McInerney, 2002). Finally, it has been suggested that while Gibbs energy availability might determine large-scale microbial diversity, it is *rate* of energy delivery (i.e., power), as determined by the rate of substrate delivery by fluid flow and diffusion, that might exert finer control on microbial metabolic diversity (Hoehler, 2004).

## FUTURE OUTLOOK

### Life at Hydrothermal Vents and Biogeochemistry

Hydrothermal venting is distributed globally along the 67,000 km long mid-ocean ridge system and contributes large amounts of bioactive elements, such as iron, to the ocean from over 300 known sites (Elderfield and Schultz, 1996; Baker and German, 2004). Individual vents and vent fields are localized phenomena, and they create chemical gradients and biogeochemical zones having abundant chemical energy that can be used for primary production of biomass. We can use modeling to estimate the degree to which deep-sea hydrothermal venting and vent primary productivity affects the biogeochemistry of certain elements in the global ocean. However, the diversity of geologic settings, and therefore fluid compositions and potential microbial lifestyles that exist, makes extrapolation from a few studies to the global ocean precarious. An additional hazard is encountered when attempting to validate model results with the very few existing

measurements of microbial biomass or chemical fluxes in hydrothermal plumes (e.g., German et al., 2010).

To fill the void in our knowledge of vent microbial biomass, McCollom (2000) calculates the amount of microbial biomass produced per kilogram of vent fluid for a 21°N East Pacific Rise vent fluid. This calculation, for a single vent fluid (50 mg dry biomass per kg of vent fluid), suggests that global plume primary productivity is small compared to that of the marine photic zone, 10<sup>11</sup> g dry biomass/yr and 10<sup>17</sup> g dry biomass/yr, respectively (McCollom 2000). McCollom argues that hydrothermal plume primary productivity, while a small percentage of the global total, may represent an important source of organic carbon to the deep ocean and ocean sediment. Subsequent sediment-trap studies certainly support this idea. Fluxes to the seafloor in the 9°N East Pacific Rise area were up to 10% by weight particulate organic carbon (Toner et al., 2009a). We do not yet know how vent primary productivity affects ocean carbon biogeochemistry. However, there is evidence that localized carbon production at vents affects the biogeochemistry of other hydrothermally derived elements.

In hydrothermal plumes, evidence suggests that both dissolved and particulate organic carbon may stabilize vent-derived metals against precipitation as poorly soluble minerals (Sander et al., 2007; Bennett et al., 2008; Toner et al., 2009a; Sander and Koschinsky, 2011). Complexes with organic ligands have been observed to stabilize approximately 4% of iron as dissolved Fe(III) in nonbuoyant plumes near 5°S Mid-Atlantic Ridge (Bennett et al., 2008). Particulate organic carbon

enriched in Fe(II) was observed in sinking hydrothermal plume material at 9°50'N East Pacific Rise (Toner et al., 2009a). Particulate organic carbon was also enriched in rising and nonbuoyant plume suspended material at the same location (Bennett et al., 2011). The potential role for carbon as a transport vector for hydrothermal trace elements could require reconsideration of hydrothermal flux estimates. In the case of the Fe cycle, recent estimates indicate that hydrothermal plumes may supply up to 25% of all deep-ocean dissolved Fe (Bennett et al., 2008), and buffer the ocean Fe cycle over thousand-year timescales against shorter-term processes such as aerosol deposition (Tagliabue et al., 2010).

### Life on Early Earth and Astrobiology


In addition to recent advances in spacecraft exploration of extraterrestrial environments, studying hydrothermal vents on Earth offers a unique opportunity to explore how life might persist elsewhere in the solar system. Hydrothermal vents would have provided a reliable source of chemosynthetic energy and some refuge from the intense surface environment of the early Earth (Jakosky and Shock, 1998), and some suggest that the chemical energy in vents may have provided the fuel needed to initiate the onset of life (Baross and Hoffman, 1985). Isotopically light carbon (Schidlowski, 1993) and putative microfossils (Schopf, 1993; Wacey et al., 2011) suggest that life on Earth was well established by 3.4–3.8 billion years ago. Indeed, many extant chemolithoautotrophic thermophiles that inhabit vents are closely related phylogenetically to the last common ancestor of all life (Woese,

1987). Similar conditions may exist (or once have existed) on other extraterrestrial bodies, including Mars and the Jupiter moon Europa. There is evidence for liquid water (or brine) in modern and ancient Martian environments (Carr, 1996; McEwen et al., 2011), and volcanic activity could have supported hydrothermal systems similar to those on Earth. The geochemistry of Martian vents would be similar to hydrothermal environments on Earth and estimates of the bioenergetic potential of these environments suggest that chemolithoautotrophic life could have been viable on Mars (Jakosky and Shock, 1998; Varnes et al., 2003). Recent reports of CH<sub>4</sub> in the Mars atmosphere (Mumma et al., 2009) may reflect ongoing geochemical or biological processes in the subsurface. On Europa, it is thought that the ice shell at the surface is underlain by a ~ 100 km deep ocean that covers a silicate rock mantle (Chyba and Phillips, 2007). Tidal heating caused by the gravitational pull of Jupiter and two of its other moons, Io and Ganymede, could generate hydrothermal vents in the depths of Europa's oceans. Geochemical models suggest that sulfate reduction and methanogenesis are favorable metabolisms in these extraterrestrial environments (McCollom, 1999; Zolotov and Shock, 2003).

In conclusion, it is well documented that the rocks and gases underlying hydrothermal vents will determine the chemical and mineral composition of hydrothermal vent environments. This is important for setting the boundaries on the types of metabolisms present, which in turn dictates biogeochemistry and the types of microorganisms that are present. While significant advances have been made in understanding biogeochemical processes at vents, there remains much

more to learn, especially in the areas of microbial interactions with minerals and dissolved chemicals present in vent systems, and how their activity ultimately affects the chemistry and biology of the deep sea.

### ACKNOWLEDGEMENTS

Special thanks to our reviewers for their constructive comments. Research for this paper was supported by the National Science Foundation (NSF) Division of Ocean Sciences grants 0732611 for JFH, 0926805 and 1038055 for JAB, and 1038055 for BMT; and by the University of Missouri Research Board for KLR. This article resulted from the Biogeochemical Processes working group at the 2010 R2K Community Meeting supported by NSF Ocean Sciences grant 0838923. 

### REFERENCES

- Amend, J.P., T.M. McCollom, M. Hentscher, and W. Bach. 2011. Catabolic and anabolic energy for chemolithoautotrophs in deep-sea hydrothermal systems hosted in different rock types. *Geochimica et Cosmochimica Acta* 75:5,736–5,748, <http://dx.doi.org/10.1016/j.gca.2011.07.041>.
- Baker, E.T., and C.R. German. 2004. On the global distribution of hydrothermal vent fields. Pp. 245–266 in *Mid-Ocean Ridges: Hydrothermal Interactions between the Lithosphere and Oceans*. C.R. German, J. Lin, and L.M. Parson, eds, Geophysical Monograph Series, vol. 148, American Geophysical Union, Washington, DC.
- Baross, J.A., and S.E. Hoffman. 1985. Submarine hydrothermal vents and associated gradient environments as sites for the origin and evolution of life. *Origins of Life and Evolution of the Biosphere* 15:327–345, <http://dx.doi.org/10.1007/BF01808177>.
- Bennett, S.A., E.P. Achterberg, D.P. Connelly, P.J. Statharn, G.R. Fones, and C.R. German. 2008. The distribution and stabilisation of dissolved Fe in deep-sea hydrothermal plumes. *Earth and Planetary Science Letters* 270:157–167, <http://dx.doi.org/10.1016/j.epsl.2008.01.048>.
- Bennett, S.A., P.J. Statham, D.R.H. Green, N. le Bris, J. McDermott, F. Prado, O.J. Rouxel, K.L. Von Damm, and C.R. German. 2011. Dissolved and particulate organic carbon in

- hydrothermal plumes from the East Pacific Rise, 9°50'N. *Deep-Sea Research Part I* 58:922–931, <http://dx.doi.org/10.1016/j.dsr.2011.06.010>.
- Berg, J.A., D. Kockelkorn, W.H. Ramos-Vera, R.F. Say, J. Zarzycki, M. Hügler, B.E. Alber, and G. Fuchs. 2010. Autotrophic carbon fixation in archaea. *Nature Reviews Microbiology* 8:447–460, <http://dx.doi.org/10.1038/nrmicro2365>.
- Breier, J.A., C.G. Rauch, K. McCartney, B.M. Toner, S.C. Fakra, S.N. White, and C.R. German. 2009. A suspended-particle rosette multi-sampler for discrete biogeochemical sampling in low-particle-density waters. *Deep-Sea Research Part I* 56:1,579–1,589, <http://dx.doi.org/10.1016/j.dsr.2009.04.005>.
- Breier, J.A., S.N. White, and C.R. German. 2010. Mineral-microbe interactions in deep-sea hydrothermal systems: A challenge for Raman spectroscopy. *Philosophical Transactions of the Royal Society A* 368:3,067–3,086, <http://dx.doi.org/10.1098/rsta.2010.0024>.
- Butterfield, D.A., G.J. Massoth, R.E. McDuff, J.E. Lupton, and M.D. Lilley. 1990. Geochemistry of hydrothermal fluids from Axial Seamount Hydrothermal Emissions Study vent field, Juan de Fuca Ridge: Subseafloor boiling and subsequent fluid-rock interaction. *Journal of Geophysical Research* 95:12,895–12,921.
- Butterfield, D.A., R.E. McDuff, M.J. Mottl, M.D. Lilley, J.E. Lupton, and G.J. Massoth. 1994. Gradients in the composition of hydrothermal fluids from the Endeavour Segment vent field: Phase separation and brine loss. *Journal of Geophysical Research* 99:9,561–9,583, <http://dx.doi.org/10.1029/93JB03132>.
- Butterfield, D.A., K.K. Roe, M.D. Lilley, J.A. Huber, J.A. Baross, R.W. Embley, and G.J. Massoth. 2004. Mixing, reaction and microbial activity in the sub-seafloor revealed by temporal and spatial variation in diffuse flow vents at Axial Volcano. Pp. 269–289 in *The Subseafloor Biosphere at Mid-Ocean Ridges*. W.S.D. Wilcock, E.F. DeLong, D.S. Kelley, J.A. Baross, and S.C. Cary, eds, Geophysical Monograph Series, vol. 144, American Geophysical Union, Washington, DC.
- Camilli, R., and A.N. Duryea. 2009. Characterizing spatial and temporal variability of dissolved gases in aquatic environments with in situ mass spectrometry. *Environmental Science Technology* 43:5,014–5,021, <http://dx.doi.org/10.1021/es803717d>.
- Carr, M.H. 1996. Water erosion on Mars and its biological implications. *Endeavour* 20:56–60.
- Chan, C.S., S.C. Fakra, D. Emerson, E.J. Fleming, and K.J. Edwards. 2011. Lithotrophic iron-oxidizing bacteria produce organic stalks to control mineral growth: Implications for biosignature formation. *The ISME Journal* 5:717–727, <http://dx.doi.org/10.1038/ismej.2010.173>.
- Charlou, J.L., J.P. Donval, E. Douville, P. Jean-Baptiste, J. Radford-Knoery, Y. Fouquet, A. Dapigny, and M. Stievenard. 2000. Compared geochemical signatures and the evolution of Menez Gwen (37°50'N) and Lucky Strike (37°17'N) hydrothermal fluids, south of the Azores Triple Junction on the Mid-Atlantic Ridge. *Chemical Geology* 171:49–75, [http://dx.doi.org/10.1016/S0009-2541\(00\)00244-8](http://dx.doi.org/10.1016/S0009-2541(00)00244-8).
- Charlou, J.L., J.P. Donval, Y. Fouquet, P. Jean-Baptiste, and N. Holm. 2002. Geochemistry of high H<sub>2</sub> and CH<sub>4</sub> vent fluids issuing from ultramafic rocks at the Rainbow hydrothermal field (36°14'N, MAR). *Chemical Geology* 191:345–359, [http://dx.doi.org/10.1016/S0009-2541\(02\)00134-1](http://dx.doi.org/10.1016/S0009-2541(02)00134-1).
- Chyba, C.F., and C.B. Phillips. 2007. Europa. Pp. 388–423 in *Planets and Life: The Emerging Science of Astrobiology*. W.T. Sullivan III and J.A. Baross, eds, Cambridge University Press, Cambridge, UK.
- Cowen, J.P., M.A. Bertram, S.G. Wakeham, R.E. Thomson, J.W. Lavelle, E.T. Baker, and R.A. Feely. 2001. Ascending and descending particle flux from hydrothermal plumes at Endeavour Segment, Juan de Fuca Ridge. *Deep-Sea Research Part I* 48:1,093–1,120, [http://dx.doi.org/10.1016/S0967-0637\(00\)00070-4](http://dx.doi.org/10.1016/S0967-0637(00)00070-4).
- Crone, T.J., M. Tolstoy, and D.F. Stroup. 2011. Permeability structure of young ocean crust from poroelastically triggered earthquakes. *Geophysical Research Letters* 38, L05305, <http://dx.doi.org/10.1029/2011GL046820>.
- Cruse, A.M., and J.S. Seewald. 2006. Geochemistry of low-molecular weight hydrocarbons in hydrothermal fluids from Middle Valley, northern Juan de Fuca Ridge. *Geochimica et Cosmochimica Acta* 70:2,073–2,092, <http://dx.doi.org/10.1016/j.gca.2006.01.015>.
- De Angelis, M.A., M.D. Lilley, E.J. Olson, and J.A. Baross. 1993. Methane oxidation in deep-sea hydrothermal plumes of the Endeavour Segment of the Juan de Fuca Ridge. *Deep-Sea Research Part I* 40:1,169–1,186, [http://dx.doi.org/10.1016/0967-0637\(93\)90132-M](http://dx.doi.org/10.1016/0967-0637(93)90132-M).
- Dick, G.J., and B.M. Tebo. 2010. Microbial diversity and biogeochemistry of the Guaymas Basin deep-sea hydrothermal plume. *Environmental Microbiology* 12:1,334–1,347, <http://dx.doi.org/10.1111/j.1462-2920.2010.02177.x>.
- Edwards, K.J., T.M. McCollom, H. Konishi, and P.R. Buseck. 2003. Seafloor bioalteration of sulfide minerals: Results from in situ incubation studies. *Geochimica et Cosmochimica Acta* 67:2,843–2,856, [http://dx.doi.org/10.1016/S0016-7037\(03\)00089-9](http://dx.doi.org/10.1016/S0016-7037(03)00089-9).
- Elderfield, H., and A. Schultz. 1996. Mid-ocean ridge hydrothermal fluxes and the chemical composition of the ocean. *Annual Review of Earth and Planetary Sciences* 24:191–224, <http://dx.doi.org/10.1146/annurev.earth.24.1.191>.
- Emerson, D., J.A. Rentz, T.G. Lilburn, R.E. Davis, H. Aldrich, C. Chan, and C.L. Moyer. 2007. A novel lineage of proteobacteria involved in formation of marine Fe-oxidizing microbial mat communities. *PLoS ONE* 2, e667, <http://dx.doi.org/10.1371/journal.pone.0000667>.
- Fisher, A.T., E.E. Davis, and K. Becker. 2008. Borehole-to-borehole hydrologic response across 2.4 km in the upper oceanic crust: Implications for crustal-scale properties. *Journal of Geophysical Research* 113, B07106, <http://dx.doi.org/10.1029/2007JB005447>.
- Flores, G.E., J.H. Campbell, J.D. Kirshtein, J. Meneghin, M. Podar, J.I. Steinberg, J.S. Seewald, M.K. Tivey, M.A. Voytek, Z.K. Yang, and A.L. Reysenbach. 2011. Microbial community structure of hydrothermal deposits from geochemically different vent fields along the Mid-Atlantic Ridge. *Environmental Biology* 13:2,158–2,171, <http://dx.doi.org/10.1111/j.1462-2920.2011.02463.x>.
- Foustoukos, D.I., J.L. Houghton, W.E. Seyfried Jr., S.M. Sievert, and G.D. Cody. 2011. Kinetics of H<sub>2</sub>-O<sub>2</sub>-H<sub>2</sub>O redox equilibria and formation of metastable H<sub>2</sub>O<sub>2</sub> under low temperature hydrothermal conditions. *Geochimica et Cosmochimica Acta* 75:1,594–1,607, <http://dx.doi.org/10.1016/j.gca.2010.12.020>.
- Gallant, R.M., and K.L. Von Damm. 2006. Geochemical controls on hydrothermal fluids from the Kairei and Edmond Vent Fields, 23°–25°S, Central Indian Ridge. *Geochemistry Geophysics Geosystems* 7, Q06018, <http://dx.doi.org/10.1029/2005GC001067>.
- Gamo, T., H. Chiba, T. Yamanaka, T. Okudaira, J. Hashimoto, S. Tsuchida, J. Ishibashi, S. Kataoka, U. Tsunogai, K. Okamura, and others. 2001. Chemical characteristics of newly discovered black smoker fluids and associated hydrothermal plumes at the Rodriguez Triple Junction, Central Indian Ridge. *Earth and Planetary Science Letters* 193:371–379, [http://dx.doi.org/10.1016/S0012-821X\(01\)00511-8](http://dx.doi.org/10.1016/S0012-821X(01)00511-8).
- Gamo, T., K. Okamura, J.L. Charlou, T. Urabe, J.M. Auzende, J. Ishibashi, K. Shitashima, and H. Chiba. 1997. Acidic and sulfate-rich hydrothermal fluids from the Manus back-arc basin, Papua New Guinea. *Geology* 25:139–142, [http://dx.doi.org/10.1130/0091-7613\(1997\)025<0139:AASRHF>2.3.CO;2](http://dx.doi.org/10.1130/0091-7613(1997)025<0139:AASRHF>2.3.CO;2).
- German, C.R., and K.L. Von Damm. 2004. Hydrothermal processes. Pp. 181–222 in *Treatise on Geochemistry, Volume 6: The Oceans and Marine Geochemistry*. H.D. Holland and K.K. Turekian, eds, Elsevier, London.
- German, C.R., A.M. Thurnherr, J. Knoery, J.L. Charlou, P. Jean-Baptiste, and H.N. Edmonds. 2010. Heat, volume and chemical fluxes from submarine venting: A synthesis of results from the Rainbow hydrothermal field, 36°N MAR. *Deep-Sea Research Part I* 57:518–527, <http://dx.doi.org/10.1016/j.dsr.2009.12.011>.
- Girguis, P.R., and J.F. Holden. 2012. On the potential for bioenergy and biofuels from hydrothermal vent microbes. *Oceanography* 25(1):213–217, <http://dx.doi.org/10.5670/oceanog.2012.20>.
- Haymon, R.M. 1983. Growth history of hydrothermal black smoker chimneys. *Nature* 301:695–698, <http://dx.doi.org/10.1038/301695a0>.
- Haymon, R.M., D.J. Fornari, K.L. Von Damm, M.D. Lilley, M.R. Perfit, J.M. Edmond, W.C. Shanks III, R.A. Lutz, J.M. Grebmeier, S. Carbotte, and others. 1993. Volcanic eruption of the mid-ocean ridge along the East Pacific Rise crest at 9°45'–52'N: Direct submersible observations of seafloor phenomena associated with an eruption event in April, 1991. *Earth and Planetary Science Letters* 119:85–101, [http://dx.doi.org/10.1016/0012-821X\(93\)90008-W](http://dx.doi.org/10.1016/0012-821X(93)90008-W).

- Heberling, C., R.P. Lowell, L. Liu, and M.R. Fisk. 2010. Extent of the microbial biosphere in the oceanic crust. *Geochemistry Geophysics Geosystems* 11, Q08003, <http://dx.doi.org/10.1029/2009GC002968>.
- Hoehler, T.M. 2004. Biological energy requirements as quantitative boundary conditions for life in the subsurface. *Geobiology* 2:205–215, <http://dx.doi.org/10.1111/j.1472-4677.2004.00033.x>.
- Holden, J.F., A. Lal Menon, and M.W.W. Adams. 2011. Hyperthermophile-metal interactions in hydrothermal environments. Pp. 39–63 in *Microbial Metal and Metalloid Metabolism: Advances and Applications*. J.F. Stolz and R.S. Oremland, eds, American Society for Microbiology, Washington, DC.
- Holden, J.F., M. Summit, and J.A. Baross. 1998. Thermophilic and hyperthermophilic microorganisms in 3–30°C hydrothermal fluids following a deep-sea volcanic eruption. *FEMS Microbiology Ecology* 25:33–41, <http://dx.doi.org/10.1111/j.1574-6941.1998.tb00458.x>.
- Houghton, J.L., and W.E. Seyfried Jr. 2010. An experimental and theoretical approach to determining linkages between geochemical variability and microbial biodiversity in seafloor hydrothermal chimneys. *Geobiology* 8:457–470, <http://dx.doi.org/10.1111/j.1472-4669.2010.00255.x>.
- Huber, J.A., D.B.M. Welch, H.G. Morrison, S.M. Huse, P.R. Neal, D.A. Butterfield, and M.L. Sogin. 2007. Microbial population structures in the deep marine biosphere. *Science* 318:97–100, <http://dx.doi.org/10.1126/science.1146689>.
- Hügler, M., and S.M. Sievert. 2011. Beyond the Calvin Cycle: Autotrophic carbon fixation in the ocean. *Annual Review of Marine Science* 3:261–289, <http://dx.doi.org/10.1146/annurev-marine-120709-142712>.
- Jackson, B.E., and M.J. McInerney. 2002. Anaerobic microbial metabolism can proceed close to the thermodynamic limits. *Nature* 415:454–456, <http://dx.doi.org/10.1038/415454a>.
- Jakosky, B.M., and E.L. Shock. 1998. The biological potential of Mars, the early Earth, and Europa. *Journal of Geophysical Research* 103:19,359–19,364, <http://dx.doi.org/10.1029/98JE01892>.
- Kashefi, K., and D.R. Lovley. 2003. Extending the upper temperature limit for life. *Science* 301:934, <http://dx.doi.org/10.1126/science.1086823>.
- Khrifounoff, A., A. Vangriesheim, P. Crassous, M. Segonzac, V. Lafon, and A. Waren. 2008. Temporal variation of currents, particulate flux and organism supply at two deep-sea hydrothermal fields of the Azores Triple Junction. *Deep-Sea Research Part I* 55:532–551, <http://dx.doi.org/10.1016/j.dsr.2008.01.001>.
- Kristall, B., D.S. Kelley, M.D. Hannington, and J.R. Delaney. 2006. Growth history of a diffusely venting sulfide structure from the Juan de Fuca Ridge: A petrological and geochemical study. *Geochemistry Geophysics Geosystems* 7, Q07001, <http://dx.doi.org/10.1029/2005GC001166>.
- Lam, P., J.P. Cowen, B.N. Popp, and R.D. Jones. 2008. Microbial ammonia oxidation and enhanced nitrogen cycling in the Endeavour hydrothermal plume. *Geochimica et Cosmochimica Acta* 72:2,268–2,286, <http://dx.doi.org/10.1016/j.gca.2008.01.033>.
- Lang, S.Q., D.A. Butterfield, M. Schulte, D.S. Kelley, and M.D. Lilley. 2010. Elevated concentrations of formate, acetate and dissolved organic carbon found at the Lost City hydrothermal field. *Geochimica et Cosmochimica Acta* 74:941–952, <http://dx.doi.org/10.1016/j.gca.2009.10.045>.
- Lilley, M.D., D.A. Butterfield, J.E. Lupton, and E.J. Olson. 2003. Magmatic events can produce rapid changes in hydrothermal vent chemistry. *Nature* 422:878–881.
- Lipp, J.S., Y. Morono, F. Inagaki, and K.U. Hinrichs. 2008. Significant contribution of Archaea to extant biomass in marine subsurface sediments. *Nature* 454:991–994, <http://dx.doi.org/10.1038/nature07174>.
- Luther, G.W., B.T. Glazer, S. Ma, R.E. Trouwborst, T.S. Moore, E. Metzger, C. Kraiyya, 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>.
- McCollom, T.M. 1999. Methanogenesis as a potential source of chemical energy for primary biomass production by autotrophic organisms in hydrothermal systems on Europa. *Journal of Geophysical Research* 104:30,729–30,742, <http://dx.doi.org/10.1029/1999JE001126>.
- McCollom, T.M. 2000. Geochemical constraints on primary productivity in submarine hydrothermal vent plumes. *Deep-Sea Research Part I* 47:85–101, [http://dx.doi.org/10.1016/S0967-0637\(99\)00048-5](http://dx.doi.org/10.1016/S0967-0637(99)00048-5).
- McCollom, T.M., and J.P. Amend. 2005. A thermodynamic assessment of energy requirements for biomass synthesis by chemolithoautotrophic micro-organisms in oxic and anoxic environments. *Geobiology* 3:135–144, <http://dx.doi.org/10.1111/j.1472-4669.2005.00045.x>.
- McCollom, T.M., and W. Bach. 2009. Thermodynamic constraints on hydrogen generation during serpentinization of ultramafic rocks. *Geochimica et Cosmochimica Acta* 73:856–875, <http://dx.doi.org/10.1016/j.gca.2008.10.032>.
- McCollom, T.M., and E.L. Shock. 1997. Geochemical constraints on chemolithoautotrophic metabolism by microorganisms in seafloor hydrothermal systems. *Geochimica et Cosmochimica Acta* 61:4,375–4,391, [http://dx.doi.org/10.1016/S0016-7037\(97\)00241-X](http://dx.doi.org/10.1016/S0016-7037(97)00241-X).
- McEwen, A.S., L. Ojha, C.M. Dundas, S.S. Mattson, S. Byrne, J.J. Wray, S.C. Cull, S.L. Murchie, N. Thomas, and V.C. Gulick. 2011. Seasonal flows on warm Martian slopes. *Science* 333:740–743, <http://dx.doi.org/10.1126/science.1204816>.
- 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>.
- Mumma, M.J., G.L. Villanueva, R.E. Novak, T. Hewagama, B.P. Bonev, M.A. DiSanti, A.M. Mandell, and M.D. Smith. 2009. Strong release of methane on Mars in northern summer 2003. *Science* 323:1,041–1,045, <http://dx.doi.org/10.1126/science.1165243>.
- Ottesen, E.A., R. Marin III, C.M. Preston, C.R. Young, J.P. Ryan, C.A. Scholin, and E.F. DeLong. 2011. Metatranscriptomic analysis of autonomously collected and preserved marine bacterioplankton. *The ISME Journal* 5:1,881–1,895, <http://dx.doi.org/10.1038/ismej.2011.70>.
- Parkes, R.J., B.A. Cragg, S.J. Bale, J.M. Getliff, K. Goodman, P.A. Rochelle, J.C. Fry, A.J. Weightman, and S.M. Harvey. 1994. Deep bacterial biosphere in Pacific Ocean sediments. *Nature* 371:410–413, <http://dx.doi.org/10.1038/371410a0>.
- Preston, C.M., A. Harris, J.P. Ryan, B. Roman, R. Marin III, S. Jensen, C. Everlove, J. Birch, J.M. Dzenitis, D. Pargett, and others. 2011. Underwater application of quantitative PCR on an ocean mooring. *PLoS ONE* 6, e22522, <http://dx.doi.org/10.1371/journal.pone.0022522>.
- Price, P.B., and T. Sowers. 2004. Temperature dependence of metabolic rates for microbial growth, maintenance, and survival. *Proceedings of the National Academy of Sciences of the United States of America* 101:4,631–4,636, <http://dx.doi.org/10.1073/pnas.0400522101>.
- Reysenbach, A.L., Y. Liu, A.B. Banta, T.J. Beveridge, J.D. Kirshtein, S. Schouten, M.K. Tivey, K.L. Von Damm, and M.A. Voytek. 2006. A ubiquitous thermoacidophilic archaeon from deep-sea hydrothermal vents. *Nature* 442:444–447, <http://dx.doi.org/10.1038/nature04921>.
- Rogers, D.R., C.M. Santelli, and K.J. Edwards. 2003. Geomicrobiology of deep-sea deposits: Estimating community diversity from low-temperature seafloor rocks and minerals. *Geobiology* 1:109–117, <http://dx.doi.org/10.1046/j.1472-4669.2003.00009.x>.
- Sander, S.G., and A. Koschinsky. 2011. Metal flux from hydrothermal vents increased by organic complexation. *Nature Geosciences* 4:145–150, <http://dx.doi.org/10.1038/ngeo1088>.
- Sander, S.G., A. Koschinsky, G. Massoth, M. Stott, and K.A. Hunter. 2007. Organic complexation of copper in deep-sea hydrothermal vent systems. *Environmental Chemistry* 4:81–89, <http://dx.doi.org/10.1071/EN06086>.
- Schidlowski, M. 1993. The initiation of biological processes on Earth: Summary of empirical evidence. Pp. 639–655 in *Organic Geochemistry*. M.H. Engel and S.A. Macko, eds, Plenum, New York.
- Schink, B. 1997. Energetics of syntrophic cooperation in methanogenic degradation. *Microbiology and Molecular Biology Reviews* 61:262–280.
- Schmidt, K., A. Koschinsky, D. Garge-Schönberg, L.M. de Carvalho, and R. Seifert. 2007. Geochemistry of hydrothermal fluids from the ultramafic-hosted Logatchev hydrothermal field, 15°N on the Mid-Atlantic Ridge: Temporal and spatial investigation. *Chemical Geology* 242:1–21, <http://dx.doi.org/10.1016/j.chemgeo.2007.01.023>.

- Scholin, C, G. Doucette, S. Jensen, B. Roman, D. Pargett, R. Marin III, C. Preston, W. Jones, J. Feldman, C. Everlove, and others. 2009. Remote detection of marine microbes, small invertebrates, harmful algae and biotoxins using the Environmental Sample Processor (ESP). *Oceanography* 22(2):158–167, <http://dx.doi.org/10.5670/oceanog.2009.46>.
- Schopf, J.W. 1993. Microfossils of the early Archean Apex chert: New evidence of the antiquity of life. *Science* 260:640–646, <http://dx.doi.org/10.1126/science.260.5108.640>.
- Seewald, J., A. Cruse, and P. Saccocia. 2003. Aqueous volatiles in hydrothermal fluids from the Main Endeavour Field, northern Juan de Fuca Ridge: Temporal variability following earthquake activity. *Earth and Planetary Science Letters* 216:575–590, [http://dx.doi.org/10.1016/S0012-821X\(03\)00543-0](http://dx.doi.org/10.1016/S0012-821X(03)00543-0).
- Shackelford, R., and J.P. Cowen. 2006. Transparent exopolymer particles (TEP) as a component of hydrothermal plume particle dynamics. *Deep-Sea Research Part I* 53:1,677–1,694, <http://dx.doi.org/10.1016/j.dsr.2006.08.001>.
- Shock, E.L., and M.D. Schulte. 1998. Organic synthesis during fluid mixing in hydrothermal systems. *Journal of Geophysical Research* 103:28,513–28,527, <http://dx.doi.org/10.1029/98JE02142>.
- Sievert, S.M., and C. Vetriani. 2012. Chemoautotrophy at deep-sea vents: Past, present, and future. *Oceanography* 25(1):218–233, <http://dx.doi.org/10.5670/oceanog.2012.21>.
- Sievert, S.M., E.B.A. Wleringa, C.O. Wirsens, and C.D. Taylor. 2007. Growth and mechanism of filamentous-sulfur formation by *Candidatus Arcobacter sulfidicus* in opposing oxygen-sulfide gradients. *Environmental Microbiology* 9:271–276, <http://dx.doi.org/10.1111/j.1462-2920.2006.01156.x>.
- Smith, J.N., and E.L. Shock. 2007. A thermodynamic analysis of microbial growth experiments. *Astrobiology* 7:891–904, <http://dx.doi.org/10.1089/ast.2006.0118>.
- Stein, C.A., and S. Stein. 1994. Constraints on hydrothermal heat flux through the oceanic lithosphere from global heat flow. *Journal of Geophysical Research* 99:3,081–3,095.
- Stroup, D.F., M. Tolstoy, T.J. Crone, A. Malinverno, D.R. Bohnenstiehl, and F. Waldhauser. 2009. Systematic along-axis tidal triggering of micro-earthquakes observed at 9°50'N East Pacific Rise. *Geophysical Research Letters* 36, L18302, <http://dx.doi.org/10.1029/2009GL039493>.
- Takai, K., and K. Nakamura. 2010. Compositional, physiological and metabolic variability in microbial communities associated with geochemically diverse, deep-sea hydrothermal vent fluids. Pp. 251–283 in *Geomicrobiology: Molecular and Environmental Perspective*. A. Loy, M. Mandl, and L.L. Barton, eds, Springer, New York.
- Takai, K., K. Nakamura, T. Toki, U. Tsunogai, M. Miyazaki, J. Miyazaki, H. Hirayama, S. Nakagawa, T. Nunoura, and K. Horikoshi. 2008a. Cell proliferation at 122°C and isotopically heavy CH<sub>4</sub> production by a hyperthermophilic methanogen under high-pressure cultivation. *Proceedings of the National Academy of Sciences of the United States of America* 105:10,949–10,954, <http://dx.doi.org/10.1073/pnas.0712334105>.
- Takai, K., T. Nunoura, K. Horikoshi, T. Shibuya, K. Nakamura, Y. Suzuki, M. Stott, G.J. Massoth, B.W. Christenson, C.E.J. deRonde, and others. 2009. Variability in microbial communities in black smoker chimneys at the NW Caldera vent field, Brothers Volcano, Kermadec Arc. *Geomicrobiology Journal* 26:552–569, <http://dx.doi.org/10.1080/01490450903304949>.
- Takai, K., T. Nunoura, J. Ishibashi, J. Lupton, R. Suzuki, H. Hamasaki, Y. Ueno, S. Kawagucci, T. Gamo, Y. Suzuki, and others. 2008b. Variability in the microbial communities and hydrothermal fluid chemistry at the newly discovered Mariner hydrothermal field, southern Lau Basin. *Journal of Geophysical Research* 113, G02031, <http://dx.doi.org/10.1029/2007JG000636>.
- Tagliabue, A., L. Bopp, J.C. Dutay, A.R. Bowie, F. Chever, P. Jean-Baptiste, E. Bucciarelli, D. Lannuzel, T. Remenyi, G. Sarthou, and others. 2010. Hydrothermal contribution to the oceanic dissolved iron inventory. *Nature Geosciences* 3:252–256, <http://dx.doi.org/10.1038/ngeo818>.
- Taylor, C.D., K.D. Doherty, S.J. Molyneux, A.T. Morrison, J.D. Billings, I.B. Engstrom, D.W. Pfirsch, and S. Honjo. 2006. Autonomous Microbial Sampler (AMS), a device for the uncontaminated collection of multiple microbial samples from submarine hydrothermal vents and other aquatic environments. *Deep Sea Research Part I* 53:894–916, <http://dx.doi.org/10.1016/j.dsr.2006.01.009>.
- Tivey, M.K. 2004. Environmental conditions within active seafloor vent structures: Sensitivity to vent fluid composition and fluid flow. Pp. 137–152 in *The Seafloor Biosphere at Mid-Ocean Ridges*. W.S.D. Wilcock, E.F. DeLong, D.S. Kelley, J.A. Baross, and S.C. Cary, eds, Geophysical Monograph Series, vol. 144, American Geophysical Union, Washington, DC.
- Toner, B.M., S.C. Fakra, S.J. Manganini, C.M. Santelli, M.A. Marcus, J. Moffett, O. Rouxel, C.R. German, and K.J. Edwards. 2009a. Preservation of iron(II) by carbon-rich matrices in a hydrothermal plume. *Nature Geosciences* 2:197–201, <http://dx.doi.org/10.1038/ngeo433>.
- Toner, B.M., C.M. Santelli, M.A. Marcus, R. Wirth, C.S. Chan, T. McCollom, W. Bach, and K.J. Edwards. 2009b. Biogenic iron oxyhydroxide formation at mid-ocean ridge hydrothermal vents: Juan de Fuca Ridge. *Geochimica et Cosmochimica Acta* 73:388–403, <http://dx.doi.org/10.1016/j.gca.2008.09.035>.
- Toner, B.M., M.A. Marcus, K.J. Edwards, O. Rouxel, and C.R. German. 2012. Measuring the form of iron in hydrothermal plume particles. *Oceanography* 25(1):209–212, <http://dx.doi.org/10.5670/oceanog.2012.19>.
- Turekian, K.K. 1968. *Oceans*. Prentice-Hall, Englewood Cliffs, NJ, 149 pp.
- Varnes, E.S., B.M. Jakosky, and T.M. McCollom. 2003. Biological potential of Martian hydrothermal systems. *Astrobiology* 3:407–414, <http://dx.doi.org/10.1089/153110703769016479>.
- Ver Eecke, H.C., D.S. Kelley, and J.F. Holden. 2009. Abundances of hyperthermophilic autotrophic Fe(III) oxide reducers and heterotrophs in hydrothermal sulfide chimneys of the northeastern Pacific Ocean. *Applied and Environmental Microbiology* 75:242–245, <http://dx.doi.org/10.1128/AEM.01462-08>.
- Von Damm, K.L., and M.D. Lilley. 2004. Diffuse flow hydrothermal fluids from 9°50'N East Pacific Rise: Origin, evolution and biogeochemical controls. Pp. 245–268 in *The Seafloor Biosphere at Mid-Ocean Ridges*. W.S.D. Wilcock, E.F. DeLong, D.S. Kelley, J.A. Baross, and S.C. Cary, eds, Geophysical Monograph Series, vol. 144, American Geophysical Union, Washington, DC.
- Von Damm, K.L., A.M. Bray, L.G. Buttermore, and S.E. Oosting. 1998. The geochemical controls on vent fluids from the Lucky Strike vent field, Mid-Atlantic Ridge. *Earth and Planetary Science Letters* 160:521–536, [http://dx.doi.org/10.1016/S0012-821X\(98\)00108-3](http://dx.doi.org/10.1016/S0012-821X(98)00108-3).
- Wacey, D., M.R. Kilburn, M. Saunders, J. Cliff, and M.D. Brasier. 2011. Microfossils of sulphur-metabolizing cells in 3.4-billion-year-old rocks of Western Australia. *Nature Geoscience* 4:698–702, <http://dx.doi.org/10.1038/NNGEO1238>.
- Wakeham, S.G., J.P. Cowen, B.J. Burd, and R.E. Thomson. 2001. Lipid-rich ascending particles from the hydrothermal plume at Endeavour Segment, Juan de Fuca Ridge. *Geochimica et Cosmochimica Acta* 65:923–939, [http://dx.doi.org/10.1016/S0016-7037\(00\)00580-9](http://dx.doi.org/10.1016/S0016-7037(00)00580-9).
- Wankel, S.D., L.N. Germanovich, M.D. Lilley, G. Genc, C.J. DiPerna, A.S. Bradley, E.J. Olson, and P.R. Girguis. 2011. Influence of subsurface biosphere on geochemical fluxes from diffuse hydrothermal fluids. *Nature Geoscience* 4:461–468, <http://dx.doi.org/10.1038/ngeo1183>.
- Whitman, W.B., D.C. Coleman, and W.J. Wiebe. 1998. Prokaryotes: The unseen majority. *Proceedings of the National Academy of Sciences of the United States of America* 95:6,578–6,583.
- Woese, C.R. 1987. Bacterial evolution. *Microbiological Reviews* 51:221–271.
- Zolotov, M.Y., and E.L. Shock. 2003. Energy for biologic sulfate reduction in a hydrothermally formed ocean on Europa. *Journal of Geophysical Research* 108:5022, <http://dx.doi.org/10.1029/2002JE001966>.