**Mathematical modeling of diffuse flow in seafloor hydrothermal
systems: The potential extent of the subsurface biosphere at mid-ocean
ridges**

R.P. Lowell¹, Jen Houghton³, Aida Farough¹, Kathleen Craft^{1,4}, Ben Larson^{2,5}, and
Christof Meile²

¹Department of Geosciences, Virginia Tech, Blacksburg, VA

²Department of Marine Sciences, University of Georgia, Athens, GA

³Department of Earth and Planetary Sciences, Washington University, St. Louis MO

⁴Now at Applied Physics Laboratory, Johns Hopkins University, Baltimore, MD

⁵Now at JISAO/PMEL, Seattle, WA 98115

Submitted to *Earth and Planetary Science Letters*

August 4, 2014

Revised March 11, 2015

Corresponding author: R.P. Lowell, rlowell@vt.edu

Abstract

We describe a variety of one- and two-dimensional mathematical modeling approaches to characterizing diffuse flow circulation at mid-ocean ridge hydrothermal systems. The goal is to estimate the potential extent of the sub-seafloor microbial biosphere based on subsurface contours of the 120°C isotherm as determined from the various models. The models suggest that the sub-seafloor depth for microbial life may range from less than 1 m in some places to the thickness of crustal layer 2A of ~ 500 m in others. This depth depends primarily on how diffuse flow is driven. The 120°C isotherm tends to be much deeper if diffuse flow is induced as boundary layer flow near high-temperature plumes, than if it results from conductive cooling or mixing near the seafloor. Because the heat flow alone may not allow identification of the flow regime in the subsurface, we highlight the use of chemical tracers as an additional constraint that sheds light into the flow and reaction patterns associated with vents. We use thermodynamic modeling, which connects the temperature of the diffuse fluid to its chemical composition. As the temperature-composition relationships differ for mixing versus conductive heating and cooling, the fluid geochemistry can shed light on subsurface transport. Using methane as an example, the geochemical models indicate subsurface microbial methane production and consumption in different regions of the vent field near EPR 9°50'N.

1. Introduction

Diffuse flow at oceanic spreading centers is a highly complex phenomenon that exhibits wide variability both in style and properties. These slow flowing fluids are characterized by relatively low temperature (nominally less than $\sim 100^{\circ}\text{C}$) and exit the seafloor through porous patches and small cracks in bare basalt, as well as through mounds and walls and flanges of sulfide structures [e.g., *Bemis et al.*, 2012; *Barreyre et al.*, 2012]. They are generally a mixture between seawater and high-temperature hydrothermal fluid [e.g., *Von Damm and Lilley*, 2004; *Butterfield et al.*, 2004], though occasionally diffuse flow results in part from conductive heating of seawater [*Cooper et al.*, 2000]. Diffuse flow fluids can be detected as shimmering water [e.g., *Bemis et al.*, 2012], inferred from the presence of areas colonized by vent macrofauna [*Scheirer et al.*, 2006] or bacterial mats [*Barreyre et al.*, 2012], and by optical techniques [e.g., *Mittelstaedt et al.*, 2012; *Smart et al.*, 2013]. Quantitative estimates of fluid flow, heat, and chemical transfer at diffuse vents are limited [e.g., *Schultz et al.*, 1992; *Sarrazin et al.*, 2009; *Ramondenc et al.*, 2006; *Barreyre et al.*, 2012; *Von Damm and Lilley*, 2004], however; and mathematical modeling of diffuse flow at oceanic spreading centers has received relatively little attention compared to high-temperature black smoker discharge. Heat output data from a number of hydrothermal fields suggest that between 50% and 90% of the advective heat loss at oceanic spreading centers appears as low temperature diffuse flow [*Schultz et al.* 1992; *Rona and Trivett*, 1992; *Baker et al.*, 1993; *Veirs et al.* 2006; *Ramondenc et al.*, 2006; *Barreyre et al.*, 2012]. Modeling results coupled with limited geochemical data, however, indicate that most of the heat content of diffuse flow results from the admixture of a small fraction of high-temperature fluid into diffuse discharge.

61 Thus, most of the hydrothermal heat loss ultimately stems from high temperature fluids
62 that extract heat from a subaxial magma chamber rather than from conductively heated
63 low temperature seawater circulating in the shallow crust [Lowell *et al.*, 2013].

64 In an attempt to determine the potential extent of microbial life in the oceanic
65 lithosphere, Heberling *et al.* [2010] estimate the depth of the subsurface biosphere for
66 lithosphere older than ~ 1 Ma by calculating the depth to the 120°C isotherm using
67 lithospheric plate cooling models. They attempted to correct for the effects of
68 hydrothermal heat loss from lithosphere younger than 60 Ma by using one-dimensional
69 models for hydrothermal recharge and discharge; however, lack of constraining
70 temperature and fluid flow data prohibited meaningful quantitative estimates. Heberling
71 *et al.* [2010] specifically excluded lithosphere younger than ~1 Ma from their
72 calculations because they were making a “global scale” estimate; the effects of vigorous
73 high-temperature hydrothermal circulation on local scale thermal structure could not be
74 easily incorporated into such an estimate. Although there is considerable interest in
75 diffuse flow from biogeochemical perspectives in the young lithosphere, the data
76 compilation by Bemis *et al.* (2012; their Table 1) shows that measurements of fluid flow
77 rates and heat fluxes are limited.

78 The chemical composition of diffuse fluids emanating at the seafloor reflects the
79 activity of the subsurface biosphere. However, to date, despite the increasing number of
80 investigations of diffuse flow in hydrothermal vent systems, co-registered chemistry and
81 temperature data sets of diffuse fluids remain rare (see **Table 1** in Supplementary
82 Material for a summary of existing datasets from vents at 9°N East Pacific Rise, Juan de
83 Fuca Ridge, and Lucky Strike on the Mid-Atlantic Ridge). To connect the physical

constraints on microbial life in the mid-ocean ridge subsurface with its manifestation at the surface, we employ a number of modeling approaches to describe the thermal regime in the upper crust using the potential flow regimes described schematically in **Figure 1**. We first use scale analysis and a simple 1D advection-diffusion model to estimate the flow rate and subsurface temperature distribution in convectively-driven seawater circulation systems in the upper crust. We then discuss how mixing between high-temperature hydrothermal fluid and conductively heated seawater might affect the subsurface temperature distribution in these systems. Differences in the boundary conditions and the resulting subsurface temperature distributions between systems heated from below and from the side result in radically different estimates of subsurface volume that could harbor microbial life. Finally, we present two examples of numerical simulations that depict induced fluid circulation and the drawdown of seawater adjacent to high temperature plumes, suggesting that volume of the subsurface biosphere near high-temperature plumes may be large

We demonstrate how mixing between oxidized and reduced end-member fluids, essential for sustaining microbial activity, can be applied to a subset of the thermal models presented here. Observations of largely biogenic methane concentrations in diffuse fluids [Desbruyeres *et al.*, 2001; Von Damm and Lilley, 2004; Butterfield *et al.*, 2004; Seewald *et al.*, 2003; Wankel *et al.*, 2011] are used in combination with flux estimates from the various models presented here to illustrate the potential range of methane flux to the ocean resulting from subsurface microbial activity. Thus, the thermal model simulations, combined with empirical relationships between temperature and

solute concentrations, provide the foundation for rough, first order estimates of chemical fluxes from the subsurface to the water column.

2. Heat transport models

2.1 Scale analysis and analytical models

2.1.1. Seawater convection in a layer heated from below (Path A)

One approach to modeling diffuse flow is to assume that seawater in the shallow crust is heated by conduction from high-temperature hydrothermal fluid circulating deeper within the crust. The heated seawater may then convect, resulting in relatively low-temperature diffuse discharge. Analysis of diffuse flow discharge at Lucky Strike indicates that this mechanism (path A in **Figure 1**), coupled with a small degree of mixing with high-temperature fluid, best explains observed chemistry and temperature of diffuse flow fluid [Cooper *et al.*, 2000; Lowell *et al.*, 2013].

To quantify the subsurface temperature distribution for this mechanism, we consider a layer of thickness h of high-permeability crust in which thermal convection occurs. The Rayleigh number Ra describing convective vigor is given by

$$Ra = \frac{\alpha g k \Delta T h}{a^* \nu} \quad (1)$$

where α is the coefficient of thermal expansion of the fluid, g is the acceleration due to gravity, k is the permeability, ΔT is the temperature difference applied across the layer, a^* is the effective thermal diffusivity, and ν is the kinematic viscosity of the fluid, respectively. Assuming $\Delta T = 400^\circ\text{C}$, $h = 100$ m, $k = 10^{-12}$ m², and values of other parameters in **Table 1** we find that $Ra \approx 4000$, which is about 100 times the critical value $Ra_c = 40$ [Lapwood, 1948]. For such high Rayleigh number convection, heat transfer to

the seafloor occurs by thermal conduction across a thin boundary layer of thickness δ .

Using scale analysis, [e.g., *Bejan*, 1995; *Lowell and Germanovich*, 2004], δ varies with Ra according to the relation

$$\delta \approx h(Ra / Ra_c)^{-1}. \quad (2)$$

Equation (2) suggests that $\delta \approx 1$ m in this case. Scale analysis also indicates that the Darcian velocity of upflow u is related to Ra through the relationship

$$u \approx \frac{a^*}{h} \frac{Ra}{Ra_c} \approx \frac{a^*}{\delta} \approx 10^{-6} \text{ m/s} \quad (3)$$

where we have assumed that Ra_c represents the scaling factor in equations (2) and (3).

The value of h used to estimate Ra is at the lower limit of estimated layer 2A thicknesses, which typically ranges from approximately 200 to 600 m [e.g., *Harding et al.*, 1993;

Christeson et al., 1996; *Arnulf et al.*, 2011]. Equations (2) and (3), however, show that u

and δ are independent of the value of h , so the exact value used does not matter so long as

$Ra \gg Ra_c$. The value of ΔT assumed stems from an approximate estimate of

hydrothermal temperatures deeper in the crust and observed temperatures of black

smokers. The permeability of layer 2A may vary considerably, but a number of studies

yield values between 10^{-10} - 10^{-12} m² in young crust [e.g., *Wilcock and McNabb*, 1996;

Becker and Fisher, 2000; *Crone et al.*, 2011]. Equations (2) and (3) show that an increase

in k , or Ra by an order of magnitude would reduce δ and increase u by the same amount.

This result suggests that if diffuse flow occurs as a result of convection of a layer of

seawater heated from below, then the depth extent of life, which will be a fraction of the

boundary layer thickness δ , could be ~ 1 m or less.

2.1.2 Constant speed vertical upflow (Path B)

Another way to consider advective heat transfer in the shallow crust is to consider a fluid at a given temperature T_0 flowing upward from a depth h at a constant Darcian speed u . By considering a linear heat transfer boundary condition [Carslaw and Jaeger, 1986] at the surface, the discharging fluid will exit the seafloor as a warm spring at a surface temperature $T_s > 2^\circ\text{C}$. This scenario is denoted by path B in **Figure 1**. This simple approach is useful when temperature and heat flux are measured at the seafloor from a patch of diffuse flow. If the heat transfer coefficient is assumed to be a constant, an analytical steady-state solution may be found. With the z axis pointing positively downward, the problem can be formulated as:

$$\frac{d^2 T_{dif}}{dz^2} + \frac{u}{a^*} \frac{dT_{dif}}{dz} = 0 \quad (4)$$

where T_{dif} is the temperature of the fluid-rock mixture, and $a^* = \lambda_m / (\rho_f c_f)$ is the “effective” thermal diffusivity. In the expression for a^* , λ_m is the thermal conductivity of the water-rock medium, whereas ρ_f and c_f are the density and specific heat of the fluid, respectively.

With the boundary conditions

$$T_{dif}(h) = T_0 \quad (5)$$

$$\frac{dT_{dif}}{dz} - bT_{dif} \Big|_{z=0} = 0 \quad (6)$$

where b is a heat transfer coefficient. The mixed boundary condition at the seafloor given by equation (6) essentially expresses the effect of mixing between the deep ascending hydrothermal fluid and cold seawater just below the seafloor (path B in **Figure 1**), such that b is approximately inversely proportional to the mixing depth. As $b \rightarrow \infty$, the mixing layer thickness goes to 0, and the temperature drops rapidly within a short distance of the

171 seafloor, and the fluid exits the seafloor at $T_{dif}(0) \rightarrow 0$. As $b \rightarrow 0$, the fluid cooling is
 172 negligible and fluid exits the seafloor at $T \rightarrow T_0$. The solution to equation (4) with
 173 boundary conditions (5) and (6) is

$$174 \quad T_{dif}(z) = T_0 \frac{\exp(-Pe \frac{z}{h}) - (1 + \frac{Pe}{hb})}{\exp(-Pe) - (1 + \frac{Pe}{hb})} \quad (7)$$

175 where $Pe = uh/a^*$ is the Peclet number. In many cases, we do not have a good estimate of
 176 the depth h from which the discharge initiates, and if Pe is large, surface temperature is
 177 essentially independent of h . In this case, equation (7) can be written

$$178 \quad T_{dif}(z) = T_0 [1 - \frac{b}{b + u/a^*} \exp(-\frac{uz}{a^*})] \quad (8)$$

179 The heat transfer coefficient b and the velocity u are constrained by observed
 180 diffuse flow temperature and heat flux. For example, if advective heat flux H and diffuse
 181 flow temperature $T_{dif}(0)$ are measured from a patch of diffuse flow, then

$$182 \quad H = \rho_f c_f u T_{dif}(0) \quad (9)$$

183 But $T_{dif}(0)$ is related to subsurface conditions by setting $z = 0$ in equation (8). That is,

$$184 \quad T_{dif}(0) = T_0 [1 - \frac{b}{b + u/a^*}] \quad (10)$$

185 Eliminating the term u/a^* between equations (9) and (10) yields an expression for the heat
 186 transfer coefficient b :

$$187 \quad b = \frac{H}{\lambda T_{dif}(0)} \left(\frac{T_0}{T_{dif}(0)} - 1 \right) \quad (11)$$

Once b is determined for an assumed value T_0 in equation (11), the ratio u/a^* can be found from equation (10). Substituting values of b and u/a^* into equation (8) yields the subsurface temperature distribution.

We apply equations (8) through (11) to a number of diffuse flow patches from 9°50'N EPR, ASHES, MEF and Lucky Strike for which temperature and heat flow are available to determine the depth at which the temperature reaches 120°C. For these sites the heat flux varies more than four orders of magnitude. The results in **Table 2**, using a temperature at depth between 200°C and 300°C, show that the expected depth of the 120°C isotherm, corresponding to the limit of the subsurface biosphere, may range from less than a millimeter to approximately a meter. Thus, at diffuse flow sites at which the advective heat flux is greater than $\sim 10^5$ W/m², the potential depth of the subsurface biosphere may be exceptionally thin in some places.

Although this result seems counter-intuitive, temperatures of several tens of degrees have been measured within a few cm of the seafloor [e.g., *Rona et al.*, 1990; *Sohn*, 2007; *Barreyre et al.*, 2014]. *Rona et al.* [1990] measured a temperature of 94°C at a depth of 0.05 m into the crust beneath a patch of shimmering water with an area of $\sim 5 \times 10^3$ m² at the Sea Cliff hydrothermal field on the North Gorda Ridge. Using this measurement, *Lowell et al.* [1993] estimated an upflow velocity of 2×10^{-6} m/s and an advective heat flow of approximately 3500 W/m². Such rapid increases in temperature within centimeters of the seafloor suggest that the depth of the 120°C isotherm may be extremely shallow at localized sites where low-temperature diffuse discharge is associated with high heat flux; and this 1-D model, which represents Path B in **Figure 1**,

can be applied in circumstances in which mixing between high temperature end-member fluid and seawater takes place near the seafloor.

2.1.3. Seawater convection in a laterally heated region (Path C)

As a high-temperature plume rises toward the surface, it induces circulation near its edge as denoted by circulation path C in **Figure 1**. There, anhydrite precipitation results from conductive heating of sulfate-rich seawater or from mixing between high-temperature hydrothermal fluid ascending from depth (path E) and seawater circulation in layer 2A. Anhydrite precipitation can create a low permeability barrier (depicted in **Figure 1** in stipple pattern) that reduces the amount of direct mixing described above and results in relatively low-temperature circulation that occurs conceptually as a boundary layer flow along the low permeability wall [e.g., *Crowell et al.*, 2008; *Craft and Lowell*, 2009]. Although heat flow observations are not available to constrain models of low-temperature induced circulation, this concept represents another, perhaps more realistic, end-member manifestation of diffuse flow that can be approached using scale analysis.

In this model, the ascending high-temperature flow, depicted by a thick red line in **Figure 1** acts as a vertical hot boundary that induces circulation in the adjacent extrusive layer as shown schematically by path C. Mixing between the hot hydrothermal fluid and cold seawater results in the precipitation of anhydrite (stipple pattern) that is assumed to form an impermeable boundary between the high-temperature fluid and the induced circulation represented by path C [*Lowell et al.*, 2003]. For simplicity, we assume the wall is maintained at a constant temperature of 150°C, corresponding approximately to the temperature of anhydrite precipitation. Equations of conservation of mass, energy and momentum can be solved numerically to obtain steady-state boundary layer solutions (e.g.

Crowell et al. [2008] and *Craft and Lowell* [2009]). Key results of this method are that the boundary layer δ width scales as the local Rayleigh number $Ra_z^{-1/2}$. That is,

$$\delta \sim z Ra_z^{-1/2} \quad (12)$$

where z is the height of the layer and Ra_z is given by

$$Ra_z = \frac{\alpha_f g k (T_w - T_\infty) z}{a^* \nu} \quad (13)$$

where g is the acceleration due to gravity, k is the permeability, α_f is the thermal expansion coefficient of the fluid, ν is the kinematic viscosity, and T_w , T_∞ are the wall and far field temperatures, respectively. In the absence of mixing between the induced circulation in the boundary layer and high-temperature fluid from below, the habitable region defined by temperature would correspond to the region with temperatures below the 120°C isotherm. **Figure 2** shows the potential zone of life for three different boundary layer scenarios, and sketches the vent's area of influence on the subsurface temperature.

2.1.4 Laterally heated models with mixing (Path D)

The results of the simple side-heated boundary layer approach do not incorporate the effects of mixing some high-temperature fluid into the boundary layer flow as illustrated schematically in **Figure 1** as path D, representing mixing between vent fluid (path E) and shallow recharge in layer 2A as shown by the light blue line on the right hand side of **Figure 1**. To address this issue using analytical models we consider a few possible mixing scenarios.

Mixing between high-temperature hydrothermal fluid and low-temperature seawater in the shallow crust can most easily be discussed quantitatively using a two-

limb single pass model as shown in **Figure 3** and schematically in paths D and E of **Figure 1**. For example, *Lowell et al.* [2003] use this approach to determine whether anhydrite will be produced during mixing in the shallow crust. As discussed in *Lowell et al.* [2012, 2013], the model formulation shown in **Figure 3** can be used with temperature and heat output data from focused and diffuse flow at the vent field scale together with geochemical data from the venting fluids to estimate the amount of high-temperature fluid incorporated into the diffuse discharge. This batch mixing approach, however, does not incorporate details of the mixing process as a function of depth in the crust, and hence it does not provide an estimate of temperature-depth relationships. This issue is addressed, in part, by *Ramondenc et al.* [2008] who assumed that mixing occurred within a thin junction region at some nominal depth within the crust, assumed for simplicity to be ~ 100 m. In this case, mixing cools a portion of the black smoker discharge to ~ 100°C and the resulting fluid ascends essentially isothermally to the seafloor, where it cools to typical diffuse-flow temperatures in the boundary layer at the seafloor (at a single point along path D; **Figure 1**). The temperature distribution of the “diffuse flow” may be found from equation (8) with $T_0 = 100^\circ\text{C}$. Because the result of mixing in *Ramondenc et al.* [2008] yields a temperature less than 120°C, the subsurface biosphere could exist, in principle, within the entire zone above 100 m.

One can also modify the approach in *Ramondenc et al.* [2008] by assuming that mixing occurs uniformly from the junction to the surface (path D in **Figure 1**). In this case we use the heat flow [*Ramondenc et al.*, 2006] and chemical data [*Von Damm and Lilley*, 2004] from EPR 9°50' N to constrain the total mass fluxes for focused and diffuse flow and the amount of high-temperature fluid mixed into the diffuse discharge. For this

system, the high-temperature mass flow $Q_3 \sim 11$ kg/s, the diffuse flow discharge $Q_4 \sim 1236$ kg/s, and it contains 5.7% high-temperature fluid [Lowell *et al.*, 2013]. The results shown in **Figure 3 inset**, indicate that the depth to the 120°C isotherm lies at a depth of approximately 160 m below the seafloor. Note that this approach uses the total diffuse heat output at the EPR 9°50' N vent field. In order to apply this approach to an individual patch of diffuse flow, one would need to use temperature (or Mg) as a conservative tracer to determine the amount of high-temperature fluid incorporated into the diffuse flow patch. This is the approach taken in the geochemical calculations in section 4.

2.2 Numerical Simulations

Numerical solutions also provide insight into the mixing process as high-temperature plumes ascend toward the seafloor (represented by path E in **Figure 1**), as they are not subject to some of the simplifications underlying the analytical solutions [e.g., Lowell *et al.*, 2007]. As an example, consider convection of single-phase seawater simulated by solving the coupled equations of conservation of mass, momentum and energy, assuming Darcy flow in a two-dimensional rectangular box 2 km wide x 1.5 km deep with a high-permeability layer 2A imposed above (**Figure 4a**). The sides of the domain are insulated and impermeable, the top is open and maintained at a constant pressure of 25 MPa. To simulate hydrothermal venting, a flow-through condition is applied at the upper boundary so that fluid leaving the domain is assumed to have the temperature calculated at one node below the surface, whereas fluid entering the domain at the top has a seawater temperature of 5°C. The base of the model is impermeable with a fixed temperature distribution that decreases linearly from 400°C at the left hand node to 300°C at the right hand node, which results in the development of a single high-

temperature plume near the left hand boundary. As an example, we assume basal heating only, uniform seawater salinity, a layered permeability representative of a fast to intermediate spreading mid-ocean ridge. We impose a 400 m thick region as a mean layer 2A thickness perpendicular to the ridge axis [e.g., *Christeston et al.*, 1996] with a permeability of 10^{-12} m^2 [e.g., *Wilcock and McNabb*, 1996; *Lowell and Germanovich*, 2004] above the remaining region with permeability 10^{-13} m^2 [e.g., *Lowell et al.*, 2013]. For this simulation, the hydrothermal heat output is greater than 100 MW, which is similar to the East Pacific Rise hydrothermal system at $9^{\circ}50'N$ [*Ramondenc et al.*, 2006]. This simulation shows a single high-temperature plume near the left hand boundary of the domain and down-welling cold seawater being entrained into the plume near the base of layer 2A.

Alternatively, one may consider a model with a bottom temperature of 400°C extending for 1 km from the left-hand side of the domain, which then decreases to 300°C at the right hand side, and no high-permeability layer 2A. The larger region of uniform basal temperature allows for the development of multiple high-temperature plumes and thus simulates an along-axis circulation cell, as proposed in *Tolstoy et al.* (2008). The simulation shows deep recharge occurring near the right hand side of the simulation region and a number of plumes ascending above the zone of imposed high temperature at the base (**Figure 4b**). The 120°C isotherm shows that recharge between the plumes may extend to greater than 500 m. As in the numerical simulation in **Figure 4a**, the hydrothermal heat output is approximately 100 MW.

3. Geochemical signatures

To assess the geochemical signatures associated with different flow regimes, resulting in fluid temperatures due to mixing or conductive heating or cooling, we used Geochemist's Workbench (GWB) [Bethke, 2008] to create a reaction path model of subsurface mixing between seawater and the end-member vent fluid from two vents measured at 9°N East Pacific Rise. All models used thermodynamic data generated with SUPCRT92 [Johnson *et al.*, 1992] using the recently updated 2007 database [Plyasunov and Shock, 2001; Shock *et al.*, 1997] at 250 bars, or seafloor pressure. Compositions of end-member seawater (T: 5°C; Cl_T: 540 mM; SO₄: 27.9 mM; H₂(aq): 10⁻¹⁵ μM; CH₄(aq): 0.003 μM), a vapor-poor vent fluid from Ty and Io vent measured in 1997 (T: 355°C; Cl_T: 403 mM; SO₄: 10⁻¹⁵ mM; H₂(aq): 390 μM; CH₄(aq): 50 μM), and a vapor-rich vent fluid from Bio9 measured in 1992 (T: 350°C; Cl_T: 75.5 mM; SO₄: 10⁻¹⁵ mM; H₂(aq): 2010 μM; CH₄(aq): 89 μM) were reported in Von Damm and Lilley [2004]. All minerals with the exception of anhydrite were prevented from precipitating during mixing. For comparison, we tested models of conductive heating of seawater and conductive cooling of vent fluid as well as mixing between the two end-member fluids. Using an energetically favorable electron donor in the vent fluid (dissolved H₂) and electron acceptor in seawater (sulfate) as examples to illustrate differences in these models, steep chemical gradients that can support microbial respiration are created during mixing that are not present during conductive heating or cooling (**Figure 5**).

The geochemical model we use in this study simulates simple mixing relationships and abiotic equilibration of fluid composition, but does not explicitly account for reaction kinetics and microbial catalysis within the zone of life. In this way, one can use predictions of geochemical transport in diffuse flow, and use deviations from

these predictions to identify subsurface microbial activity that acts as a source or sink for biogeochemically active constituents. These estimates are made at the vent field scale and differences between observed chemical signatures and modeled concentrations are interpreted as the imprint of microbial reactions. For this study, diffuse fluids sampled from bare basalt were used as the best indicators of subsurface processes to avoid any imprint of biological processes in macrofaunal assemblages on the fluid composition.

Of the chemical species routinely analyzed in diffuse fluids, methane concentrations were measured in many samples and predominantly indicates microbial activity, unlike dissolved H_2S , H_2 , CO_2 , or Fe that have multiple sources (volcanogenic) and sinks (mineral reactions) that make interpretation difficult. We therefore compare the offset of $\text{CH}_4(\text{aq})$ reported in the literature to the concentration predicted by the mixing model at the measured temperature of the diffuse flow (**Figure 6**). For this calculation, the predicted methane concentration at the corresponding temperature of the observation is computed using the slope of the mixing line between seawater (0 μM) and endmember vent fluid (Ty and Io 50 μM , Bio9 89 μM) (slope of 0.145 for the Ty and Io vent fluid and 0.258 for the Bio9 vent fluid). The computed value is then subtracted from the observed methane concentration. The majority of measurements from Bio9 suggest net subsurface methane consumption, which is consistent with the results of *Lowell et al.* [2013]. However, the measurements from near Ty and Io vents indicate net methane production in the subsurface.

4. Discussion

4.1 Estimating the location of the 120 °C isotherm

The thermal structure of the shallow crust in the neighborhood of high-temperature hydrothermal discharge provides insight into where microbial ecosystems may exist beneath the seafloor. Depending upon the mechanisms driving the low-temperature hydrothermal circulation, the apparent zone of life can range from less than 1 meter to depths of several hundred meters. For convection models driven by heating from below, thermal profiles tend to be nearly isothermal to very near the seafloor. The scale analysis for a convecting layer heated from below and steady-state 1-D calculations suggest that the zone of life may be within one meter of the seafloor or less. In each of these settings, we have assumed that the temperature at depth ranges between 200°C and 400°C in order for advection in the shallow crust to dominate the thermal regime. The data available to constrain the subsurface temperature in the shallow crust are sparse, however; and the high subsurface temperatures assumed in the models representing paths A and B in **Figure 1** may only occur in limited areas. If the temperature at the base of the conductively heated convecting layer is less than 120°C, or the ascending fluid in the 1-D model representing path B has already undergone mixing with high-temperature fluid [e.g., *Ramoncenc et al.*, 2008], the subsurface biosphere would extend more deeply than suggested by the results in sections 2.1.1 and 2.1.2.

On the other hand, models of hydrothermal circulation derived from side-wall heating suggest that the zone of life could extend to depths of several hundred meters below the seafloor. The boundary layer analyses shown in **Figure 2** suggest that the 120°C isotherm could be only a few meters from the edge of a high-temperature plume and predict a range of areas for the thermally favorable zone of life from ~1000-40,000 m² per unit length of ridge axis. This thermal regime would foster a relatively steep

thermal gradient nearly perpendicular to the plume edge and a lateral variation in microbial communities, with thermophiles living near the plume edge and lower-temperature species further away from the plume edge.

The results of boundary layer analysis, while providing a general guideline for the thermal regime, do not incorporate the effect of mixing between seawater and high-temperature black smoker fluid, however. Such mixing would tend to move the 120°C isotherm to shallower depths, depending on how mixing occurs. For example, if mixing occurs at a single narrow junction as assumed by *Ramondenc et al.* [2008] and the temperature in the diffuse flow limb is less than 120°C then the potential for subsurface microbial life would extend to the depth of the narrow region where mixing occurred. If seawater mixing is uniform, as shown in **Figure 3** where mixing occurs over a depth of 200 m, then the potential zone of life will occur at some depth above where mixing begins. In **Figure 3** the lateral extent of mixing is not defined, but examination of the regions with temperature below 120°C in the numerical model results shown in **Figures 4a** and **4b** predict suggest it could affect ~114,000-956,000 m² per unit length of ridge axis. The numerical models shown in **Figures 4a** and **4b** also suggest that relatively cold seawater is entrained to depths of several hundred meters near the edges of high-temperature plumes. Although the numerical simulations do not include anhydrite precipitation and mixing of induced circulation near a permeability barrier [e.g., *Lowell et al.*, 2007; *Singh et al.*, 2013}. these results tend to substantiate the results of scale analysis for the laterally heated systems. In order to better constrain the zone of potential life from expected thermal profiles in the shallow crust, additional, high-quality heat flow data are needed. Conventional conductive heat flow measurements cannot be made in

sediment free crust, but thermal blanket measurements [Johnson *et al.*, 2010] could provide useful information about conductive heat flow near high-temperature discharge sites. Better measurements of advective diffuse heat output are also needed.

4.2 Estimating methanogenesis in diffuse fluids

Fluid fluxes derived from the thermal models can be combined with predicted fluid composition to estimate biogeochemical fluxes. The fluid composition is mapped onto the temperature field using reaction path models that account for chemical speciation and phase separation (see also Larson *et al.*, 2015 in review). Importantly, conductive heating/cooling and mixing processes can both be responsible for changes in fluid temperature, but lead to different fluid composition at a given temperature. With the exception of a few samples from Lucky Strike [Cooper *et al.*, 2000], most diffuse fluids measured to date do not follow a trend consistent with conductive heating of seawater (the mechanism underlying the above 1D heat flow model representing path A in **Figure 1**). In addition, such a scenario suggests significant energy limitations for microbial metabolism, as heat conduction itself does induce steep redox gradients arising in the mixing of oxidized and reduced chemical species prevalent in seawater and vent fluid. Such conditions are thought to be required for formation of microbial flocs [Huber *et al.*, 2006; Von Damm and Lilley, 2004]. Thus, path A is not consistent with field observations in which microbial flocs are ejected into the water column by the hydraulics associated with volcanic eruptions [Haymon *et al.*, 1993; Huber *et al.*, 2003; Sievert *et al.*, 2008]. The heat flow models reviewed that incorporate mixing are described in **Figure 1** as paths B and D. Mixing via path B corresponds to the 1D thermal model described in section 2.1.2. It predicts a depth to the 120°C isotherm of <1 m but does not give

information on the lateral extent of this region. The 1D model that corresponds to mixing via path D predicts a depth to the 120°C isotherm of 160 m but also does not address the lateral extent of this region (**Figure 3**). The 2D models of **Figures 4a** and **4b** both represent variations of path D in **Figure 1**. Both models predict the 120°C isotherm could extend as deep as 500 m and although they lead to very different temperature fields just by changing permeability and the temperature at the base of the system, a particular fluid parcel that leaves the seafloor as diffuse fluid may follow a flow path that passes through a zone of biological methane consumption and production.

To assess the role of biotic processes in shaping these benthic fluxes, observational data on diffuse flow composition can then be compared to such model predictions. A data compilation indicates dissolved methane concentrations in diffuse fluids sometimes exceed the values predicted by an equilibrium-mixing model (**Figure 6**) consistent with subsurface methanogenesis [Von Damm and Lilley, 2004, Huber *et al.*, 2003, Lin *et al.*, 2012]. The observational data shows large scatter of methane concentration at any given temperature. Combining diffuse fluid flow rates (kg/s) from the thermal model shown in **Figure 3** and the difference between observed and predicted CH₄ concentration of diffuse fluids (μmol/kg) shown in **Figure 6**, the flux (μmol/s) of CH₄ microbially produced and/or consumed can be estimated. As the diffuse flow samples may reflect mixtures of different end-member vent fluids, a conservative interpretation would be that samples with methane concentrations lower than the Ty and Io mixing line represent subsurface methane consumption and samples with concentrations higher than the Bio9 mixing line represent methane production. Conservatively, then, the diffuse fluids measured near Ty and Io show methane

production whereas diffuse fluids measured near Bio9 show methane consumption. Multiplying the average deviation between observed and equilibrium methane concentrations as a function of the temperature of the diffuse fluid with the respective flow rate, one obtains a subsurface consumption rate of 4.2 mmol CH₄/s in the Bio9 diffuse fluids (using the Bio9 endmember vent fluid), while the deviation in the Ty&Io diffuse fluids (using the Ty&Io endmember fluid) gives a subsurface production rate of 11.6 mmol CH₄/s. The reality in the subsurface biosphere, however, is more likely that biomass has a patchy and localized distribution, such that methane cycling would not occur uniformly along a flow path. Without more field observations of both subsurface chemical conditions and microbial populations, it is not possible to extend this type of modeling further.

5. Conclusions

The models presented above highlight the uncertainty associated with determining the temperature distribution in the subsurface and the extent of the potential subsurface biosphere. If most of the mixing occurs near the seafloor as assumed in the 1-D models in section 2.1.2, the near-surface temperature gradient is extremely high and microbial activity may be limited to the upper few cm of the seafloor. This result assumed that the temperature of the convecting fluid in the shallow crust was between 200°C and 400°C, and thus may only apply to limited areas. On the other hand, 2-D (and potentially 3-D) models suggest that the biosphere may extend throughout much or all of layer 2A and even into the sheeted dikes (e.g., **Figures 2, 4a, 4b, 5**), with strong spatial heterogeneity associated with variations in permeability. Although estimates of the temperature distribution as a function of depth in the crust provides useful information on the

potential for microbial activity in the subsurface, coupling the temperature distribution with geochemical data or modeling is needed to better understand microbial processes. Unfortunately, the limited data on diffuse flow limits our understanding of subsurface temperatures and the extent of the subsurface biosphere in young oceanic crust. The heat flow models coupled to geochemical reaction path modeling constrain the spatial extent of a possible subsurface biosphere but do not explicitly address the rates of microbial activity, which may be patchy and dependent on other factors besides temperature and chemical gradient. Fully coupled models that account for fluid flow and geochemical and microbial reactions and interactions are required to address questions of subsurface microbial activity.

Acknowledgements. BL and CM would like to acknowledge support for BL through the Ridge 2000 Postdoctoral Fellowship Program, NSF-OCE 1039431. JH was supported by NSF Grant OCE-1155346. This work was also supported in part by NSF Grant OCE-0926418 to RPL.

References

- Arnulf, A.F., S.C. Singh, A.J. Harding, G.M. Kent, and W. Crawford (2011), Strong seismic heterogeneity in layer 2A near hydrothermal vents at the Mid-Atlantic Ridge, *Geophys. Res. Lett.*, **38**, L 13320, doi:10.1029/2011GL047753.
- Baker, E.T., G.J. Massoth, S. L. Walker, and R.W. Embley (1993), A method for quantitatively estimating diffuse and discrete hydrothermal discharge, *Earth Planet. Sci. Lett.*, **118**, 235-249.
- Barreyre, T., J. Escartín, R. Garcia, M. Cannat, E. Mittelstaedt, R. Prados (2012), Structure, temporal evolution, and heat flux estimates from the Lucky Strike deep-sea hydrothermal field derived from seafloor image mosaics, *Geochem. Geophys. Geosyst.*, **13**, Q04007, 29 PP., doi: 10.1029/2011GC003990.
- Barreyre, T., J. Escartin, R.A. Sohn, M. Cannat, V. Ballu, and W.C. Crawford (2014), Temporal variability and tidal modulation of hydrothermal exit-fluid temperatures at the Lucky Strike deep-sea vent field, Mid-Atlantic Ridge, *J. Geophys. Res.*, **119**, 254-2566, doi:10.1002/2013JB010478.
- Becker, K. and A. Fisher (2000), Permeability of upper oceanic basement on the eastern flank of the Endeavour Ridge determined with drill-string packer experiments, *J. Geophys. Res.*, **105**, 897–912.
- Bethke, C., (2008), *Geochemical and biogeochemical reaction modeling*. Cambridge University Press, Cambridge.
- Bejan, A. (1995), *Convection Heat Transfer*, 2nd ed., 639 p., Wiley, New York.
- Bemis, K., R.P. Lowell, and A. Farough (2012), Diffuse flow on and around hydrothermal vents at mid-oceanic ridges, *Oceanography*, **25**(1), 182-191, <http://dx.doi.org/10.5670/oceanog.2012.16>.
- 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, in *The Subseafloor Biosphere at Mid-Ocean Ridges*, *Geophys. Monogr. Ser.*, vol. **144**, edited by W. S. D. Wilcock, et al., pp. 269-289, AGU, Washington, DC.
- Carslaw, H.S. and J.C. Jaeger (1986), *Conduction of Heat in Solids*, 2nd ed., 510 p., Clarendon, Oxford, UK
- Christeson, G.L., G.M. Kent, G.M. Purdy, and R.S. Detrick (1996), Extrusive thickness variability at the East Pacific Rise 9°-10°N: Constraints from seismic techniques, *J. Geophys. Res.*, **101**, 2859-2873.

- Cooper, M. J., H. Elderfield, A. Schultz (2000), Diffuse hydrothermal fluids from Lucky Strike hydrothermal vent field: Evidence for a shallow conductively heated system, *J. Geophys. Res.*, *105*(B8), 19369–19375, doi: 10.1029/2000JB900138.
- Craft, K. and R.P. Lowell (2009), A boundary layer model for submarine hydrothermal flows at on-axis and near axis locations, *Geochem. Geophys. Geosyst.*, *10*(12) Q12012, doi:10.1029/2009GC002707.
- Crone, T.J., M. Tolstoy, and D.F. Stroup (2011), Permeability structure of young ocean crust from poroelastically triggered earthquakes, *Geophys. Res. Lett.*, *38*, L05305, doi:10.1029/2011GL046820.
- Crowell, B.W., R.P. Lowell, and K.L. Von Damm (2008), A model for the production of sulfur floc and “snowblower” events at mid-ocean ridges, *Geochem. Geophys. Geosyst.*, *9*, Q10T02, doi:10.1029/2008GC002103.
- Desbruyeres, D. et al. (2001), Variations in deep-sea hydrothermal vent communities on the Mid-Atlantic Ridge near the Azores plateau, *Deep-Sea Res. I*, *48*, 1325-1346.
- Farough, A., R.P. Lowell, K. Craft, L.N. Germanovich (2011), Some Approaches to Modeling Diffuse Flow at Mid-Ocean Ridges, American Geophysical Union, Fall Meeting 2011, abstract #OS11B-1479, <http://adsabs.harvard.edu/abs/2011AGUFMOS11B1479F>.
- Germanovich, L.N., R.P. Lowell, and P. Ramondenc (2011), Magmatic origin of hydrothermal response to earthquake swarms: Constraints from heat flow and geochemical data at 9°50' N, East Pacific Rise, *J. Geophys. Res.*, *116*, B05103, doi:10.1029/2009JB006588.
- Harding, A.J., G.M. Kent, and J.A. Orcutt (1993), A multichannel seismic investigation of the upper crustal structure at 9°N on the East Pacific Rise: Implications for crustal accretion, *J. Geophys. Res.*, *98*, 13,295-13,944, doi:10.1029/93JB00886.
- 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, D. Wright, E. McLaughlin, M. Smith, N. Beedle and E. Olson (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 Planet. Sci. Lett.*, *119*, 85-101.
- Heberling, C., R.P. Lowell, L. Liu, and M.R. Fisk (2010), The extent of the oceanic biosphere throughout geologic time, *Geochem. Geophys. Geosyst.*, *11*, Q08003, doi:10.1029/2009GC002968.
- Huber, J.A., D.A. Butterfield, and J.A. Baross (2003), Bacterial diversity in a subseafloor habitat following a deep-sea volcanic eruption. *FEMS Microbiol. Ecol.*, *43*, 393-409.
- Huber, J.A., D.A. Butterfield, and J.A. Baross (2006), Diversity and distribution of subseafloor Thermococcales populations in diffuse hydrothermal vents at an active deep-sea volcano in the northeast Pacific Ocean. *J. Geophys. Res.*, *111*, G04016.

- Johnson, J.W., E.H. Oelkers, and H.C. Helgeson (1992), SUPCRT92: A software package for calculating the standard molal thermodynamic properties of minerals, gases, aqueous species, and reactions from 1-5000 bars and 0-1000°C, *Comput. Geosci.*, 899-947.
- Johnson, H.P., M.A. Tivey, T.A. Bjorklund, and M.S. Salmi (2010), Hydrothermal circulation within the Endeavour Segment, Juan de Fuca Ridge, *Geochem. Geophys. Geosyst.*, 11, Q05002, doi:10.1029/2009GC002957.
- Lapwood, E.R. (1948), Convection of a fluid in a porous medium, *Proc. Cambridge Philos. Soc.*, 44, 508-521.
- Larson, B.I., J.L. Houghton, R.P. Lowell, A. Farough, and C.D. Meile (2015), Subsurface conditions in hydrothermal vents inferred from diffuse flow composition, and models of reaction and transport (submitted).
- Le Bris, N., P-M. Sarradin, D. Birot, A-M. Alayse-Danet (2000), A new chemical analyzer for in situ measurement of nitrate and total sulfide over hydrothermal vent biological communities, *Marine Chemistry*, 72, 1-15.
- Lin, H-T., J. P. Cowen, E.J. Olson, J.P. Amend, M.D. Lilley (2012), Inorganic chemistry, gas compositions and dissolved organic carbon in fluids from sedimented young basaltic crust on the Juan de Fuca Ridge flanks. *Geochim. Cosmochim. Acta*, 85. 213-227.
- Lowell, R.P., A. Farough, J. Hoover, and K.C. Cummings (2013), Characteristics of magma-driven hydrothermal systems at oceanic spreading centers, *Geochem. Geophys. Geosyst.*, 14, doi:10.1002/ggge.20109.
- Lowell, R.P. and L.N. Germanovich (2004), Seafloor hydrothermal processes: Results from scale analysis and single-pass models, in *Mid-Ocean Ridges: Hydrothermal Interactions Between the Lithosphere and Oceans*, *Geophys. Monogr. Ser.*, 148, ed. by C.R. German, J. Lin, and L.M. Parson, pp. 219-244, AGU, Washington, D. C.
- Lowell, R.P., S.R. Gosnell, and Y. Yang (2007), Numerical simulations of single-pass hydrothermal convection at mid-ocean ridges: Effects of the extrusive layer and temperature dependent permeability, *Geochem. Geophys. Geosyst.*, 8, Q10011, doi:10.1029/2007GC001653.
- Lowell, R.P., P. Van Cappellen, and L.N. Germanovich (1993), Silica precipitation in fractures and the evolution of permeability in hydrothermal upflow zones, *Science*, 260, 192-194.
- Lowell, R.P., Y. Yao, and L.N. Germanovich (2003), Anhydrite precipitation and the relationship between focused and diffuse flow in seafloor hydrothermal systems, *J. Geophys. Res.*, 108 (B9), 2424, doi: 10.1029/2002JB002371.
- McCollom, T.M. (2000), Geochemical constraints on primary productivity in submarine hydrothermal vent plumes. *Deep-Sea Res. Pt. I*, 47, 85-101.

- McCollom, T.M. and E.L. Shock (1997), Geochemical constraints on chemolithoautotrophic metabolism by microorganisms in seafloor hydrothermal systems, *Geochim. Cosmochim. Acta*, *61*, 4375-4391.
- Mittelstaedt, E., J. Escartin, N. Gracias, J-A. Olive, T. Barreyre, A. Davaille, M. Cannat, and R. Garcia (2012), Quantifying diffuse and discrete venting at the Tour Eiffel vent site, Lucky Strike hydrothermal field (2012), *Geochem. Geophys., Geosyst.*, *13*, Q04008, doi:10.1029/2011GC003991.
- 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 Res. II*, *56*, 1616-1621.
- Pascoe, A.R., and J.R. Cann (1995), Modeling diffuse hydrothermal flow in black smoker vent fields, in *Hydrothermal Vents and Processes, Geological Society Special Publication*, *87*, edited by L. M. Parson, et al., pp. 159-173, The Geological Society, London, UK.
- Plyasunov, A.V. and E.L. Shock (2001), Correlation strategy for determining the parameters of the revised Helgeson-Kirkham-Flowers model for aqueous nonelectrolytes, *Geochim. Cosmochim. Acta*, *65*, 3879-3900.
- Ramondenc, P., L.N. Germanovich, and R.P. Lowell (2008), Modeling the hydrothermal response to earthquakes with application to the 1995 event at 9°50' N, East Pacific Rise, in *Magma to Microbe: Modeling Hydrothermal Processes at Oceanic Spreading Centers, Geophys. Monogr. Ser.*, *178*, ed. by R.P. Lowell, J.S. Seewald, A. Metaxas, and M.R. Perfit, p. 97-122, American Geophys. Union, Washington, DC.
- Ramondenc, P., L.N. Germanovich, K.L. Von Damm, and R.P. Lowell (2006), The first measurements of hydrothermal heat output at 9°50' N, East Pacific Rise, *Earth Planet. Sci. Lett.*, *245*, 487-497, doi: 10.1016/j.epsl.2006.03.023.
- Rona, P.A., R.P. Denlinger, M.R. Fisk, K.J. Howard, G.L. Taghon, K.D. Klitgord, J.S. McClain, G.R. McMurray, and J.C. Wiltshire (1990), Major off-axis hydrothermal activity on the northern Gorda Ridge, *Geology*, *18*, 493-496.
- Rona, P.A. and D.A. Trivett (1992), Discrete and diffuse flow heat transfer at ASHES vent field, Axial Volcano, Juan de Fuca Ridge, *Earth Planet. Sci. Lett.*, *109*, 57-71.
- Sarrazin, J., P. Rodier, M.K. Tivey, H. Singh, A. Schultz, and P.M. Sarradin (2009), A dual sensor device to estimate fluid flow velocity at diffuse hydrothermal vents, *Deep Sea Res. I.*, *56*, 2065-2074.
- Scheirer, D.S., T.M. Shank, and D.J. Fornari (2006), Temperature variations at diffuse and focused flow hydrothermal vent sites along the northern East Pacific Rise, *Geochem. Geophys. Geosyst.*, *7*, doi:10.1029/2005GC001094.
- Schultz, A., J.M. Delaney, and R.E. McDuff (1992), On the partitioning of heat flux between diffuse and point source venting, *J. Geophys. Res.*, *97*, 12,229–12,314.

- Seewald, J., A. Cruse, P. Saccocia (2003), Aqueous volatiles in hydrothermal fluids from the Main Endeavour Field, northern Juan de Fuca Ridge: temporal variability following earthquake activity. *Earth Planet. Sci. Lett.*, 216, 575-590.
- Sievert, S.M., M. Hugler, C.D. Taylor, and C.O. Wirsen (2008), Sulfur oxidation at deep-sea hydrothermal vents, in *Microbial Sulfur Metabolism* (eds. C. Dahl and C.G. Friedrich). pp 238-258.
- Shock, E.L., D.C. Sassani, M. Willis, and D.A. Sverjensky (1997), Inorganic species in geologic fluids: Correlations among standard molal thermodynamic properties of aqueous ions and hydroxide complexes: *Geochim. Cosmochim. Acta*, 61, 907-950.
- Singh, S., R.P. Lowell, and K.C. Lewis (2013), Numerical modeling of phase separation at the Main Endeavour Field, Juan de Fuca Ridge, *Geochem. Geophys. Geosyst.*, 14, doi:10.1002/ggge.20249.
- Smart, C.J., C. Roman, and S.N. Carey (2013), Detection of diffuse seafloor venting using structured light imaging, *Geochem. Geophys. Geosyst.*, 14, doi:10.1002/ggg2.20280.
- Sohn, R.A. (2007), Stochastic analysis of exit fluid temperature records from the active TAG hydrothermal mound (Mid-Atlantic Ridge, 26°N): I. Modes of variability and implications for subsurface flow, *J. Geophys. Res.*, 112, B07101, doi:10.1029/2006JB004435.
- Veirs, S.R., R.E. McDuff, and F.R. Stahr (2006), Magnitude and variance of near-bottom horizontal heat flux at the Main Endeavour hydrothermal vent field, *Geochem. Geophys. Geosyst.*, 7, Q02004, <http://dx.doi.org/10.1029/2005GC000952>.
- 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, in *The Subseafloor Biosphere at Mid-Ocean Ridges, Geophys. Monogr. Ser.*, 144, edited by W. S. D. Wilcock, et al., pp. 245-268, AGU, Washington, DC.
- 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, *Nat. Geosci.*, 4, 461-468.
- Wilcock, W.S.D. and A. McNabb (1996), Estimates of crustal permeability on the Endeavour segment Juan de Fuca mid-ocean ridge, *Earth Planet. Sci. Lett.*, 138, 83-91.

Figure Captions

Figure 1. Cartoon of subsurface hydrothermal upflow showing possible hydrothermal flow paths contributing to diffuse flow emanations, with red and blue representing high temperature chemically distinct vent fluid and low temperature seawater, respectively. Letters correspond to mechanisms of the fluid formation emanating in diffuse flow: A) shallow circulation of seawater with conductive heating, B) rapid cooling of vent fluid either by conduction or mixing near the boundary layer representing the seafloor, C) heating near the upflow zone associated with the anhydrite precipitation in the ‘hot wall’, E) deep circulation of seawater with subsequent conductive heating to create a chemically distinct vent fluid, D) mixing between cold seawater and rising vent fluid. The cartoon is not drawn to scale, with pathways A, B, C, D all confined to the top 100-500 m (within layer 2A of the upper crust) and the area below the diffusive boundary layer, including the base of pathway E, at a depth of 1-3 km.

Figure 2. Depiction of the 120°C isotherm and edge of the boundary layer from a 2D model, assuming that at some distance from the vent axis there is a hot wall at 150°C corresponding to the outer boundary of anhydrite precipitation [e.g., *Craft and Lowell, 2009*]. The inner curves mark the 120°C isotherm, to the left of which $T > 120^{\circ}\text{C}$; the outer curves (2°C) denote the outer edge of the zone of influence of the vent on the temperature regime. Note the differences in scale: case 1, bounded by the lines marked with squares, assumes a 100 m thick extrusive layer with $k = 10^{-11} \text{ m}^2$; case 2 (triangles) assumes a 500 m thick layer with $k = 10^{-11} \text{ m}^2$; and case 3 (circles) assumes a 500 m thick extrusive layer with $k = 10^{-12} \text{ m}^2$, respectively. These laterally heated convective regions correspond to path C in **Figure 1**.

Figure 3. Schematic of a “double-loop” single-pass model above a convecting, crystallizing, replenished AMC (not to scale). Heat transfer from the vigorously convecting, cooling, and replenished AMC across the conductive boundary layer δ drives the overlying hydrothermal system. The deep circulation represented by mass flux Q_1 (corresponding to path E in **Figure 1**) results in black smoker temperature T_3 and induces shallow circulation noted by Q_2 (corresponding to paths C or D in Figure 1). Some black smoker fluid mixes with seawater resulting in diffuse discharge Q_4 , T_4 , while the direct black smoker mass flux with temperature T_3 is reduced from Q_1 to Q_3 . Heat output, vent temperature, and geochemical data allow estimates of the various mass fluxes. [modified from *Lowell et al.*, 2013]. The inset shows the subsurface temperature distribution in the diffuse flow assuming that mixing between high-temperature vent fluid and seawater occurs uniformly between a depth of 200m and the seafloor. See text for details.

Figure 4. (a) A 2-D across-axis single-phase simulation with a 400 m thick layer 2A. Permeability of layer 2A is 10^{-12} m^2 , and rest of the simulation region is 10^{-13} m^2 . The basal temperature decreases linearly from 400°C at the left hand edge to 300°C at the right hand edge. (b) A 2-D along-axis simulation of single-phase hydrothermal convection in a homogeneous medium with $k = 10^{-13} \text{ m}^2$. The basal temperature of 400°C extends for 1 km from the left hand edge, and then decreases linearly to 300°C. Deep flow paths in both (a) and (b) correspond to path E in **Figure 1**, whereas zones of mixing between high-temperature fluid and seawater correspond to path D. The velocity vectors

are logarithmically scaled. Maximum velocities in high temperature flow are $\sim 10^{-5}$ m/s. whereas small recharge velocities are $\sim 10^{-8}$ m/s.

Figure 5. Comparison between GWB models of conductive heating of seawater (circles), conductive cooling of Bio9 vent fluid (squares), and mixing between vent fluid and seawater (triangles). Concentrations of a reduced component (dissolved H_2 , solid symbols) and an oxidized component (SO_4 , open symbols) show a lack of chemical gradients in conductive heating and cooling models. Indeed, thermal gradients produced without mixing produce fluids that remain generally as oxidized or reduced as the source fluid. The non-linear mixing line for SO_4 is a result of anhydrite precipitation that was allowed during the reaction path.

Figure 6: Comparison of GWB model results for predicted $CH_4(aq)$ and reported concentrations measured in diffuse flow fluids from basalt-hosted systems. The predicted concentrations from both vent fluid endmembers follow conservative mixing lines, consistent with the imposed lack of redox reactions and lack of mineral reactions involving methane. The observed Bio9 diffuse fluids indicate methane consumption taking place in the subsurface, whereas the Ty-Io diffuse fluids indicate subsurface methane production. The temperature dependence of methane in the Ty-Io mixing model has a slope of 0.145; the slope for the Bio9 mixing model is 0.258.

806
 807 **Figure 1.** Cartoon of subsurface hydrothermal upflow showing possible hydrothermal
 808 flow paths contributing to diffuse flow emanations, with red and blue representing high
 809 temperature chemically distinct vent fluid and low temperature seawater, respectively.
 810 Letters correspond to mechanisms of the fluid formation emanating in diffuse flow: A)
 811 shallow circulation of seawater with conductive heating, B) rapid cooling of vent fluid
 812 either by conduction or mixing near the boundary layer representing the seafloor, C)
 813 heating near the upflow zone associated with the anhydrite precipitation in the ‘hot wall’,
 814 E) deep circulation of seawater with subsequent conductive heating to create a chemically
 815 distinct vent fluid, D) mixing between cold seawater and rising vent fluid. The cartoon is
 816 not drawn to scale, with paths A, B, C, D all confined to the top 100-500 m (within layer
 817 2A of the upper crust) and the area below the diffusive boundary layer, including the base
 818 of pathway E, at a depth of 1-3 km.
 819

820

821

822

823 **Figure 2.** Depiction of the 120°C isotherm and edge of the boundary layer from a 2D
824 model, assuming that at some distance from the vent axis there is a hot wall at 150°C
825 corresponding to the outer boundary of anhydrite precipitation [e.g., *Craft and Lowell,*
826 2009] . The inner curves mark the 120°C isotherm, to the left of which $T > 120^{\circ}\text{C}$; the
827 outer curves (2°C) denote the outer edge of the zone of influence of the vent on the
828 temperature regime. Note the differences in scale: case 1, bounded by the lines marked
829 with squares, assumes a 100 m thick extrusive layer with $k = 10^{-11} \text{ m}^2$; case 2 (triangles)
830 assumes a 500 m thick layer with $k = 10^{-11} \text{ m}^2$; and case 3 (circles) assumes a 500 m thick
831 extrusive layer with $k = 10^{-12} \text{ m}^2$, respectively. These laterally heated convective regions
832 correspond to path C in Figure 1.
833

834
835

836
837
838
839
840
841
842
843
844
845
846
847
848
849
850
851
852

Figure 3. Schematic of a “double-loop” single-pass model above a convecting, crystallizing, replenished AMC (not to scale). Heat transfer from the vigorously convecting, cooling, and replenished AMC across the conductive boundary layer δ drives the overlying hydrothermal system. The deep circulation represented by mass flux Q_1 (corresponding to path E in **Figure 1**) results in black smoker temperature T_3 and induces shallow circulation noted by Q_2 (corresponding to paths C or D in **Figure 1**). Some black smoker fluid mixes with seawater resulting in diffuse discharge Q_4, T_4 , while the direct black smoker mass flux with temperature T_3 is reduced from Q_1 to Q_3 . Heat output, vent temperature, and geochemical data allow estimates of the various mass fluxes. [modified from *Lowell et al.*, 2013]. The inset shows the subsurface temperature distribution in the diffuse flow assuming that mixing between high-temperature vent fluid and seawater occurs uniformly between a depth of 200m and the seafloor. See text for details.

(a)

(b)

Figure 4. (a) A 2-D across-axis single-phase simulation with a 400 m thick layer 2A. Permeability of layer 2A is 10^{-12} m^2 , and rest of the simulation region is 10^{-13} m^2 . The basal temperature decreases linearly from 400°C at the left hand edge to 300°C at the right hand edge. (b) A 2-D along-axis simulation of single-phase hydrothermal convection in a homogeneous medium with $k = 10^{-13} \text{ m}^2$. The basal temperature of 400°C extends for 1 km from the left hand edge, and then decreases linearly to 300°C . Deep flow paths in both (a) and (b) correspond to path E in **Figure 1**, whereas zones of mixing between high-temperature fluid and seawater correspond to path D. The velocity vectors are logarithmically scaled. Maximum velocities in high temperature flow are $\sim 10^{-5} \text{ m/s}$, whereas small recharge velocities are $\sim 10^{-8} \text{ m/s}$.

Figure 5. Comparison between GWB models of conductive heating of seawater (circles), conductive cooling of Bio9 vent fluid (squares), and mixing between vent fluid and seawater (triangles). Concentrations of a reduced component (dissolved H_2 , solid symbols) and an oxidized component (SO_4 , open symbols) show a lack of chemical gradients in conductive heating and cooling models. Indeed, thermal gradients produced without mixing produce fluids that remain generally as oxidized or reduced as the source fluid. The non-linear mixing line for SO_4 is a result of anhydrite precipitation that was allowed during the reaction path.

Figure 6: Comparison of GWB model results for predicted CH₄(aq) and reported concentrations measured in diffuse flow fluids from basalt-hosted systems. The predicted concentrations from both vent fluid endmembers follow conservative mixing lines, consistent with the imposed lack of redox reactions and lack of mineral reactions involving methane. The observed Bio9 diffuse fluids indicate methane consumption taking place in the subsurface, whereas the Ty-Io diffuse fluids indicate subsurface methane production. The temperature dependence of methane in the Ty-Io mixing model has a slope of 0.145; the slope for the Bio9 mixing model is 0.258.

Table 1. System parameters used in the model

Symbol	Definition	Value: units
a^*	effective thermal diffusivity	$10^{-6} \text{ m}^2 \text{ s}^{-1}$
b	heat transfer coefficient	variable: m^{-1}
c_f	specific heat of fluid	$4 \times 10^3 \text{ J kg}^{-1} \text{ }^\circ\text{C}^{-1}$
g	gravitational acceleration	9.8 ms^{-2}
h	height of diffuse flow fluid layer	variable: m
H	heat flow from diffuse flow patch	observable: W m^{-2}
k	permeability	$10^{-12} - 10^{-13} \text{ m}^2$
Pe	Peclet number	variable: dimensionless
Ra	Rayleigh number	variable: dimensionless
Ra_c	critical Rayleigh number	40: dimensionless
T_{dif}	diffuse flow temperature	variable: $^\circ\text{C}$
T_0	basal temperature of diffuse flow fluid	
T_w	wall temperature in boundary layer model	
T_∞	far-field temperature in boundary layer model	
ΔT	temperature difference across convecting layer	
u	Darcian upflow velocity of diffuse flow	variable: ms^{-1}
z	vertical Cartesian coordinate	variable
α_f	thermal expansion coefficient of fluid	$10^{-4} \text{ }^\circ\text{C}^{-1}$
δ	boundary layer thickness	variable: m
λ	effective thermal conductivity of the medium	$2.0 \text{ W m}^{-1} \text{ }^\circ\text{C}^{-1}$
ν	kinematic viscosity of fluid	$10^{-6} \text{ m}^2 \text{ s}^{-1}$
ρ_f	fluid density	10^3 kg m^{-3}

Table 2. Estimated depth to 120°C from the 1-D thermal model for diffuse flow

Site	Style	$T_{dif}(0)$ °C	T_0 °C	u m/s	H MW/m ²	b m ⁻¹	Depth m	References
EPR 9°50'N	patches and cracks	10	300	0.04	1.6	2.3×10^6	1.2×10^{-5}	<i>Ramondenc et al</i> [2006]
ASHES	cracks	40	300	1×10^{-6}	2.6×10^{-4}	2.1×10^1	0.46	<i>Pruis and Johnson</i> [2004]
Lucky Strike	cracks and sulfide deposits	9.2	300	0.006	0.2	3.4×10^5	8.2×10^{-5}	<i>Cooper et al.</i> [2000] ¹
		10.7	200	0.01	0.5	4.1×10^5	8.9×10^{-5}	
MEF	sulfide structure	7-13	300	0.07- 0.13	2.9	4.2×10^6	4.9×10^{-6}	<i>Schultz et al.</i> [1992]

¹The upper value is from site F21M5; the lower value is from site F25M5.